AD NUMBER:	AD0132723

LIMITATION CHANGES

TO:

Approved for public release; distribution is unlimited.

FROM:

Distribution authorized to US Government Agencies only; Proprietary Information; 28 Sep 1956; All other requests shall be referred to Office of Naval Research, Arlington, VA 22217.

AUTHORITY

ONR ltr dtd 26 Oct 1977

132 723

[redacted]

NAVY DEPARTMENT
OFFICE OF NAVAL RESEARCH
WASHINGTON, D. C.

28 September 1956
Report No. 1162
(Final)
Copy No.________

FC

RESEARCH IN NITROPOLYMERS AND THEIR APPLICATION TO SOLID SMOKELESS PROPELLANTS

Contract N7onr-462, Task Order 1

Chemical Department

Aerojet-General CORPORATION
A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY
AZUSA, CALIFORNIA
THE GENERAL TIRE

[redacted]

United States Patent Office Secrecy Order

NOTICE

The Aerojet-General Corporation has filed patent applications in the U. S. Patent Office to cover inventions disclosed in this publication, and the Commissioner of Patents has issued a secrecy order thereon.

Compliance with the provisions of this secrecy order requires that those who receive a disclosure of the secret subject matter be informed of the existence of the secrecy order and of the penalties for the violation thereof.

The recipient of this report is accordingly advised that this publication includes information which is now under a secrecy order. It is requested that he notify all persons who will have access to this material of the secrecy order.

Each secrecy order provides that any person who has received a disclosure of the subject matter covered by the secrecy order is

> "in nowise to publish or disclose the invention or any material information with respect thereto, including hitherto unpublished details of the subject matter of said application, in any way to any person not cognizant of the invention prior to the date of the order, including any employee of the principals, but to keep the same secret except by written permission first obtained of the Commissioner of Patents."

Although the original secrecy order forbids disclosure of the material to persons not cognizant of the invention prior to the date of the order, a supplemental permit attached to each order does permit such disclosure to:

> "(a) Any officer or employee of any department, independent agency, or bureau of the Government of the United States.
>
> "(b) Any person designated specifically by the head of any department, independent agency or bureau of the Government of the United States, or by his duly authorized subordinate, as a proper individual to receive the disclosure of the above indicated application for use in the prosecution of the war.
>
> "The principals under the secrecy are further authorized to disclose the subject matter of this application to the minimum necessary number of persons of known loyalty and discretion, employed by or working with the principals or their licensees and whose duties involve cooperation in the development, manufacture or use of the subject matter by or for the Government of the United States, provided such persons are advised of the issuance of the secrecy order."

No other disclosures are authorized, without written permission from the Commissioner of Patents. Public Law No. 239, 77th Congress, provides that whoever shall "willfully publish or disclose or authorize or cause to be published or disclosed such invention, or any material information with respect thereto," which is under a secrecy order, "shall, upon conviction, be fined not more than $10,000 or imprisoned for not more than two years or both." In addition, Public Law No. 700, 76th Congress, provides that the invention in a patent may be held abandoned, if it be established that there has been a disclosure in violation of the secrecy order.

It must be understood that the requirements of the secrecy order of the Commissioner of Patents are in addition to the usual security regulations which are in force with respect to activities of the Aerojet-General Corporation. The usual security regulations must still be observed notwithstanding anything set forth in the secrecy order of the Commissioner of Patents.

CONFIDENTIAL

28 September 1956

Report No. 1162
(Final)

RESEARCH IN NITROPOLYMERS AND THEIR APPLICATION TO SOLID SMOKELESS PROPELLANTS

Contract N7onr-462, Task Order I

Written by:

J. R. Fischer
M. B. Frankel
R. D. Hamlin
J. P. Kispersky
G. B. Linden
C. R. Vanneman

No. of Pages: 370

Period Covered:

15 August 1947 through 31 July 1956

Approved by:

CK Vanneman
for G. B. Linden
Senior Chemist
Chemical Department

M. H. Gold
Associate Director
Chemical Department

NOTE 1: This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, USC, Sections 793 and 794. The transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

NOTE 2: This document contains proprietary information of Aerojet-General Corporation and is not to be transmitted, reproduced, used, or disclosed to anyone without the permission of Aerojet-General Corporation; except that the Government has the right to reproduce, use, and disclose for governmental purposes (including the right to give to foreign governments for their use as the national interest of the United States may demand) all or any part of this document as to which Aerojet-General Corporation is entitled to grant this right.

AEROJET-GENERAL CORPORATION
Azusa, California

CONFIDENTIAL

CONTENTS

CONTENTS (cont.)

CONTENTS (cont.)

CONTENTS (cont.)

CONTENTS (cont.)

CONTENTS (cont.)

CONTENTS (cont.)

CONTENTS (cont.)

CONTENTS (cont.)

CONTENTS (cont.)

CONTRACT FULFILLMENT STATEMENT

This summary report is submitted in partial fulfillment of Contract N7onr-462, Task Order I.

SUMMARY

The work performed under Contract N7onr-462 Task Order I, "Research in Nitropolymers and their Application to Solid Smokeless Propellants" has been compiled and summarized. This report covers a nine-year period: 15 August 1947 to 31 July 1956. All significant data covering synthesis, polymerization, formulation, process studies, and physical studies leading to nitropolymers and their applications have been included.

I. INTRODUCTION

A. HISTORY

The search for a smokeless propellant based on nitro-containing organic polymers had its inception at Aerojet-General Corporation in January 1946, and work was performed for 18 months under Contracts NOas 7968 and NOas 8446, T.O.2. The present contract, N7onr-462, Task Order I, was awarded Aerojet, and work was commenced, on 15 August 1947. This work was titled "Research in Nitropolymers and their Application to Solid Smokeless Propellants." This contract was extended and continued to 31 July 1956. During this almost-nine-year period, a continuing series of formal quarterly reports have been published. The only detailed summary report was an Annual Summary Report, No. 330, covering the first year's work. A number of special reports covering specific phases or literature reviews have also been published. An excellent review of the ONR Nitropolymer Program, which correlates this program with the propellant formulation programs and which indicates the potential applications of Nitropolymers, has been published: Aerojet Report No. 1078. It is the object of this Final Report to summarize all the work performed during this nine-year period.

The following tables list all formal reports published under this contract. Only the annual and quarterly progress reports are summarized in this Final Report. The Special Reports stand alone and are referred to throughout the body of the report where applicable.

TABLE 1

FORMAL PROGRESS REPORTS

Contract N7onr-462, Task Order I

Aerojet Report No.	Date Issued	Type of Report	Period Covered
971-1	17 March 1948	Quarterly Progress	15 Aug. 1947 - 15 Dec. 1947
301	17 May 1948	Semiannual Progress	15 Aug. 1947 - 15 Feb. 1948
971-2	19 May 1948	Bimonthly Progress	16 Feb. 1948 - 15 April 1948

TABLE 1 (cont.)

Aerojet Report No.	Date Issued	Type of Report	Period Covered
971-3	18 July 1948	Bimonthly Progress	16 April 1948 - 15 June 1948
330	3 Nov. 1948	Annual Summary	15 Aug. 1947 - 15 Aug. 1948
345	4 Jan. 1949	Quarterly Progress	16 Aug. 1948 - 15 Nov. 1948
371	15 April 1949	↓	16 Nov. 1948 - 15 Feb. 1949
386	18 July 1949	↓	16 Feb. 1949 - 15 May 1949
386A	18 July 1949	Supplement	16 Feb. 1949 - 15 May 1949
404	12 Sept. 1949	Quarterly Progress	16 May 1949 - 15 Aug. 1949
416	21 Nov. 1949	Annual Review	16 Aug. 1948 - 15 Aug. 1949
417	15 Dec. 1949	Quarterly Progress	16 Aug. 1949 - 15 Nov. 1949
417A	23 Dec. 1949	Supplement	16 May 1949 - 15 Nov. 1949
424	27 March 1950	Quarterly Progress	16 Nov. 1949 - 15 Feb. 1950
457	22 June 1950	↓	16 Feb. 1950 - 15 May 1950
468	15 Sept. 1950	↓	16 May 1950 - 15 Aug. 1950
482	15 Dec. 1950	↓	16 Aug. 1950 - 15 Nov. 1950
499	16 March 1951	↓	16 Nov. 1950 - 15 Feb. 1951
515	15 June 1951	↓	16 Feb. 1951 - 15 May 1951
540	19 Sept. 1951	↓	16 May 1951 - 15 Aug. 1951
552	4 Dec. 1951	Biennial Evaluation	12 Sept. 1949 - 1 Sept. 1951
563	31 Dec. 1951	Quarterly Progress	16 Aug. 1951 - 15 Nov. 1951
590	27 March 1952	↓	16 Nov. 1951 - 15 Feb. 1952
622	26 June 1952	↓	16 Feb. 1952 - 15 May 1952
638	7 Oct. 1952	↓	16 May 1952 - 15 Aug. 1952
663	23 Dec. 1952	↓	16 Aug. 1952 - 15 Nov. 1952
686	3 April 1953	↓	16 Nov. 1952 - 15 Feb. 1953
712	10 July 1953	↓	16 Feb. 1953 - 15 May 1953
740	15 Sept. 1953	↓	16 May 1953 - 15 Aug. 1953
772	30 Dec. 1953	↓	16 Aug. 1953 - 15 Nov. 1953
807	13 April 1954	↓	16 Nov. 1953 - 15 Feb. 1954
833	15 June 1954	↓	16 Feb. 1954 - 15 May 1954

TABLE 1 (Cont.)

Aerojet Report No.	Date Issued	Type of Report	Period Covered
868	17 Sept. 1954	Quarterly Progress	16 May 1954 - 15 Aug. 1954
907	15 Dec. 1954	↓	16 Aug. 1954 - 15 Nov. 1954
941	28 March 1955		16 Nov. 1954 - 11 Feb. 1955
967	20 June 1955		16 Feb. 1955 - 15 May 1955
1004	15 Sept. 1955		16 May 1955 - 15 Aug. 1955
1048	16 Dec. 1955		16 Aug. 1955 - 15 Nov. 1955
1083	19 March 1956		16 Nov. 1955 - 15 Feb. 1956
1119	20 June 1956		16 Feb. 1956 - 15 May 1956

TABLE 2

SPECIAL REPORTS

Contract N7onr-462, Task Order I

Aerojet Report No.	Date Issued	Title
461	20 July 1950	A Review of Dinitromethane and 2,2-Dinitroethanol
494	13 Feb. 1951	A Review of Nitroform and 2,2,2-Trinitroethanol
700	25 May 1953	Chain-Transfer of Nitro Compounds in Polymerization Reactions
1078	5 March 1956	Progress Review of the ONR Nitropolymer Program and Subsidiary Development

B. CONTRIBUTORS

During the first two years of this contract, work was supported, on a sub-contract basis, at Ohio State University and at Purdue University. During this period, the work performed at these Universities was reported, together with the Aerojet contributions. Thus, of the reports listed in Table 1, those up to and including No. 417 contain work performed at all three establishments. All reports published after December 1949 contain only the work performed at Aerojet. The groups at Ohio State and at Purdue continued their investigations under separate contracts, and their results were published independently.

In the Aerojet reports containing contributions from the Ohio State and Purdue groups, each section was clearly marked to indicate the separate contributions of each group. These two groups have made significant contributions to the Nitropolymer Program, and due credit is given in the original publications. However, in this report, no distinction has been made between the separate contributions reported up to and including No. 417 since this is a summary for the contract, not for Aerojet. Any products or processes developed by these two groups, after initiation of their independent contracts, which are mentioned in this report have been duly acknowledged in the same manner as other literature references.*

The research efforts on the nitropolymer program at Ohio State were directed by Dr. H. Shechter. At Purdue, the work was directed, at various times, by Drs. H. B. Hass, G. B. Bachman, and H. Feuer. At Aerojet, the work has been directed, at various times, by Dr. A. L. Antonio, Mr. R. D. Geckler, Drs. M. H. Gold, K. Klager, and G. B. Linden. For a short while, some work was performed at the General Tire & Rubber Company's Central Research Laboratories, Akron, under Mr. G. Swart.

C. ASSOCIATED CONTRACTS

Because the goal of the ONR-supported nitropolymer program has been to develop nitropolymers and examine their application to solid propellants, detailed formulation development and mechanical and ballistic studies have been

---

*All references to Aerojet reports published under this contract are given in the following manner: (Report No., Page No.), e.g., (371, 26). These references are always included in the text or in tables. All other references are given in footnotes.

carried out under separate contracts. Application of some of the monomers and polymers to high explosives has also been handled under a separate contract. These various contracts and their relationships are discussed.

1. Mechanical and Ballistics Evaluation

Contract NOas 52-359: Early rheological and ballistic studies on nitropolymers was supported under this BuAer, Aeroplex development contract. This contract covered the period May 1951 to September 1952. Most of the work is included in the ONR nitropolymer reports. The final report for the contract, Aerojet Report No. 649, summarizes all the work.

Contract NOas 53-618c: This BuAer-supported contract covered the period December 1952 to February 1954. The contract was let specifically for rheological and ballistic studies of nitropolymers. All the work is published in the ONR nitropolymer progress reports. A final report, Aerojet Report No. 817, was published which summarizes all the work. Some formulation work is also included under this contract.

2. Applications of Nitropolymers to Solid Rockets

Contract NOas 54-399c: This BuAer-supported contract covered the period May 1954 to March 1956. The work is summarized in Aerojet Report No. 1104. Until September 1955, all work under this contract was published, combined with the ONR nitropolymer work. Since that time, no associated contract work has been reported in the ONR reports. This contract dealt principally with screening of various systems developed under the ONR contract and development of two optimum systems - a compression-formed dinitropropyl acrylate-based propellant and a castable nitropolyurethane propellant. Cognizance of the contract was taken over by BuOrd, and the contract number was changed to NOrd 16584 in late 1955.

Contract NOrd 16878: This BuOrd contract was initiated in April 1956 and will run through March 1957. The task of this contract is in two phases, covering further developmental screening of nitropolymer candidates and the advancement of formulation studies to full-scale-rocket firings.

Contract AF33(616)-2519: This Air Force contract, for the period of 15 May 1954 to 31 August 1955, was directed toward the development of a high-performance rocket propellant. Under this contract, extruded linear nitropolyurethanes were examined and abandoned, and a castable dinitropropyl acrylate propellant was developed. Small motor firings were made with the latter propellant.

3. Thermal Stability

Contract AF18(600)-1215: This Air Force contract was initiated in September 1954 and was extended for another year in September 1955. A summary of the first year's work was published in Aerojet Technical Note 13. Under this contract, a fundamental study of the thermal stability of various aliphatic nitro-containing structures was undertaken. Some of the nitropolymers and compounds of related structure have been studied.

4. Applications to High Explosives

Contract N7onr-46208: This ONR program was initiated in 1951 to utilize the high-energy intermediates and nitromonomers for synthesis of high explosives. A large number of such materials were synthesized and tested. Nitropolymers were tested in RDX coatings and are presently being used in preparation of explosive cases containing glass fiber. This contract is still in force.

II. ORGANIC SYNTHESIS

A. UNSATURATED NITRO MONOMERS

1. Introduction

One of the methods of preparation of a nitropolymer is the vinyl-type polymerization of an unsaturated nitro monomer. At the beginning of the Nitropolymer Program, very few unsaturated nitro compounds were known in the open literature, and they possessed high carbon-to-oxygen ratios. Therefore, it became necessary to embark upon a synthetic program in order that unsaturated nitro monomers of sufficient energy would be available for propellant use. This section of the report records both the successful and attempted syntheses of all unsaturated nitro compounds prepared to date on this program.

Some of the unsaturated compounds, e.g., 2,2-dinitropropyl acrylate, have found utility in propellant compositions; others, such as 2-nitroallyl acetate, have been found to be more useful as synthetic intermediates.

2. Nitro Olefins

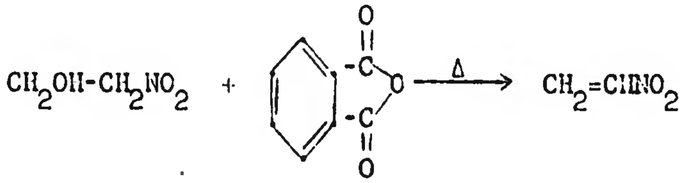
a. Introduction

Early efforts were devoted to the syntheses of polymerizable nitro olefins of high energy. An example of this line of thought was exemplified by the numerous attempts to prepare 1,1-dinitroethylene with a calculated specific impulse, for the polymer, of 260 lbf sec/lbm. After many unsuccessful attempts to prepare a high-energy nitro olefin which was suitable for polymerization, it became apparent that the greatest utility of this class of nitro compounds was as chemical intermediates in the preparation of other nitro compounds such as isocyanates, acids, and alcohols.

The two new nitro olefins that were prepared on this program were made by the sulfuric acid dehydration of the corresponding alcohol.

b. Nitroethylene

Nitroethylene was a known compound prior to the inception of this program. For use on this program, it was prepared by the phthalic anhydride dehydration of nitroethanol, using the procedure of Buckley and Scaife (386, 22).* Being a conjugated nitro olefin



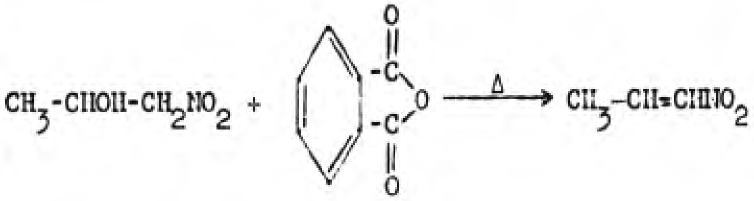
it is highly reactive and consequently its use lies in the preparation of more highly nitrated materials.

---

*Buckley and Scaife, J. Chem. Soc., 1947, 1472. (Numbers in parentheses refer to Aerojet reports and page(s) in the report.)

c. 1-Nitropropene

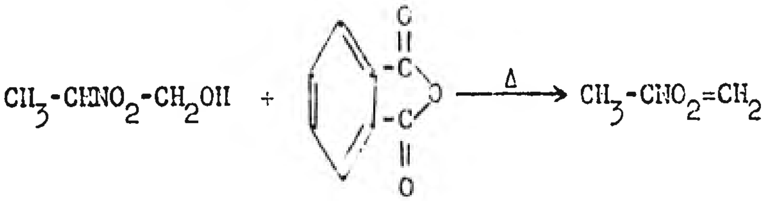
1-Nitropropene was also a known compound and was prepared in a similar manner, using the procedure of Buckley and Scaife (404, 55).*



It was also used as an intermediate in the attempted preparation of more highly nitrated compounds.

d. 2-Nitropropene

2-Nitropropene, likewise a prior known compound at the beginning of this program, was also prepared by the method of Buckley and Scaife (404, 55).*



It was useful only as a synthetic intermediate in the attempted preparation of more highly nitrated materials.

e. 5,5,5-Trinitro-2-pentene

The synthesis of 5,5,5-trinitro-2-pentene was accomplished by the sulfuric acid dehydration of 5,5,5-trinitro-2-pentanol (paragraph II,D,2,b) at 90 to 100°C (590, 60).

$$C(NO_2)_3\text{-}CH_2\text{-}CH_2\text{-}CHOH\text{-}CH_3 \xrightarrow{H_2SO_4} C(NO_2)_3\text{-}CH_2\text{-}CH{=}CH\text{-}CH_3$$

---

*Ibid.

The nitro olefin is a liquid with the following physical properties: b.p. 61 to 62°C/1.5 mm, n_D^{25} 1.4613, and $d^{25^\circ C}$ 1.3144 g/ml. The position of the double bond on the second carbon atom was established by analogy with 5,5-dinitro-2-hexene whose structure was proved unequivocally (paragraph II,C,2,c) (622, 71).

The influence of the nitro groups on the double bond was shown by the anomalous reactions observed with reagents which usually react with a double bond. For example, the olefin did not react with lead tetra-acetate, 2,4-dinitrobenzenesulfenyl chloride, nor did it give a color test with tetranitromethane. It is of interest to note that Shechter and Zelden also failed to obtain a positive test for unsaturation with this latter reagent on 3,3-dinitro-1-butene.* Absorption of bromine by the double bond in the trinitropentene is extremely slow. However, a dibromide was obtained which analyzed fairly well for the expected derivative. The olefin reacted readily with 2 mole of perbenzoic acid but did not give the desired epoxide. Finally, elemental analysis of the trinitropentene was in agreement with the expected values.

f. 5,5-Dinitro-2-hexene

5,5-Dinitro-2-hexene was prepared, in 66% yield, by the sulfuric acid dehydration of 5,5-dinitro-2-hexanol (paragraph II,D,2,b) (638, 77).

$$CH_3\text{-}C(NO_2)_2\text{-}CH_2\text{-}CH_2\text{-}CH_2OH\text{-}CH_3 \xrightarrow[\Delta]{H_2SO_4} CH_3\text{-}C(NO_2)_2\text{-}CH_2\text{-}CH{=}CH\text{-}CH_3$$

It is a liquid with the following physical properties: b.p. 59 to 60°C/1 to 2 mm, n_D^{25} 1.4557, $d^{25^\circ C}$ 1.4557, and $d^{25^\circ C}$ 1.167 g/ml. In order to establish the position of the double bond, the olefin was oxidized with potassium permanganate in acidic media. The product, 3,3-dinitrobutyric acid, proved that the olefin was principally the 2-hexene and not the 1-hexene (686, 76).

The anomalous reactions observed between the 5,5,5-trinitro-2-pentene with lead tetra-acetate and with tetranitromethane were likewise observed with the 5,5-dinitro-2-hexene. However, the hexene absorbed

---

*H. Shechter and L. Zelden, J. Am. Chem. Soc., 73, 1276 (1951).

bromine more readily than the pentene. This is expected inasmuch as the electronegative character of the carbon containing the double bond has decreased in the hexene.

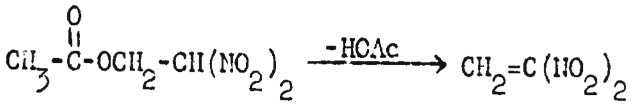
g. 3,3-Dinitro-1-butene

Early in the synthetic part of the program, many unsuccessful attempts were made to prepare 3,3-dinitro-1-butene (330, 69). Subsequently, its preparation was reported, on an associated contract, by a previously untried synthetic procedure.*

h. The Attempted Preparation of 1,1-Dinitroethylene

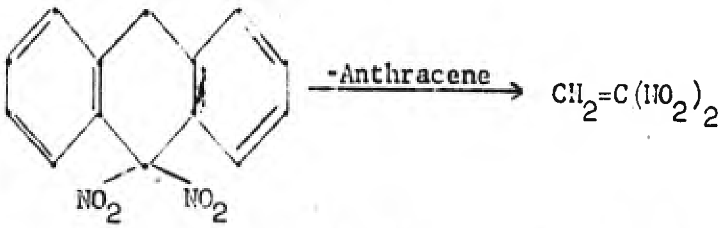
Very early in the nitropolymer program, the synthesis of 1,1-dinitroethylene was proposed. Had the synthesis and polymerization of this olefin been successful, a polymer with the very desirable calculated specific impulse of 260 lbf sec/lbm would have been obtained. The many repeated attempts to synthesize this compound can be summarized by the following general equations:

$$CH_2OH\text{-}CH(NO_2)_2 \xrightarrow{-H_2O} CH_2{=}C(NO_2)_2 \qquad (371,\ 40)$$



$$CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_2\text{-}CH(NO_2)_2 \xrightarrow{-HOAc} CH_2{=}C(NO_2)_2 \qquad (371,\ 50)$$

$$CH_3\text{-}C(NO_2)_3 \xrightarrow{-HNO_2} CH_2{=}C(NO_2)_2 \qquad (371,\ 9)$$



(468, 11)

Although dinitroethylene itself has never been isolated, it seems probable that it is at least capable of transitory existence in the condensation reactions of

---

*Ibid.

dinitroethanol (457, 16) (see paragraph II,F,2,e). Indeed, the derivatives supporting the erroneously reported synthesis of dinitroethylene can be obtained from 2,2-dinitroethanol itself (417A, 2).

i. Miscellaneous Attempts to Prepare Nitro Olefins

Several attempts to synthesize 4,4,4-trinitro-1-butene from the reaction of an allyl halide and silver nitroform were unsuccessful (330, 68).

An elaborate seven-step synthesis proposed for the preparation of 2,3-dinitro-1,3-butadiene failed in the fifth step (622, 64).

Bromination of the salt obtained from the reaction of potassium dinitromethane and glyoxal yielded 1,4-dibromo-1,1,4,4-tetranitro-2,3-butanediol (330, 127). It was proposed that acetylation of the diol, followed by the reaction with potassium iodide, would yield 1,1,4,4-tetranitro-1,3-butadiene (457, 6). However, only one hydroxyl group could be acetylated, and reaction with potassium iodide failed to yield the desired material (468, 37; 482, 12).

Attempts to obtain nitro olefins from the reaction of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene with an ether solution of nitrogen tetroxide failed to yield any useful materials (371, 38; 345, 22).

Recent attempts to prepare 4,4-dinitro-1-pentene by the pyrolysis of 4,4-dinitro-1-pentyl acetate have been unsuccessful (1119, 17). However, this compound has been previously prepared by others, using a different synthetic procedure.*

j. Summary and Evaluation

The many unsuccessful attempts to prepare a high-energy nitro olefin indicate that future work on this class of compounds, very likely, would not be fruitful in producing a nitro monomer suitable for vinyl-type polymerization. Their greatest utility appears to be as synthetic

---

*Rohm and Haas Report No. P-52-3, September 1952, p. 23; Ohio State University Report No. 9, March 1953, p. 6.

intermediates in the synthesis of bifunctional nitro monomers which are capable of condensation polymerization. The reactivity of conjugated nitro olefins is especially useful in this respect.

3. Nitroesters of Unsaturated Acids

a. Introduction

The most fruitful research effort with regard to the preparation of an unsaturated nitro monomer, capable of polymerization, has been the synthesis of nitroalkyl esters of unsaturated acids. The acrylates in particular have yielded several esters of continuing interest.

In all cases, the esters were prepared either by direct esterification of the alcohol and acid, or by the reaction between the alcohol and acid chloride. The physical properties of these monomers are compiled in Tables 3 and 4.

b. 2-Bromo-2,2-dinitroethyl Acrylate

2-Bromo-2,2-dinitroethyl acrylate was prepared by the reaction of 2-bromo-2,2-dinitroethanol (paragraph II,D,2,j) with acrylyl chloride (457, 75). It was prepared as an intermediate for the attempted synthesis of 2,2,4,4-tetranitrobutyl acrylate (paragraph II,A,3,q).

c. 2-Cyano-2,2-dinitroethyl Acrylate

Esterification of 2-cyano-2,2-dinitroethanol with acrylic acid in the presence of trifluoroacetic anhydride gave 2-cyano-2,2-dinitroethyl acrylate (712, 41). The ester was prepared for polymerization studies which were not carried out.

d. 2,2,2-Trinitroethyl Acrylate

Trinitroethyl acrylate was among the first of the unsaturated nitro monomers synthesized and has the highest specific impulse of all the acrylates prepared to date (663, App. B).

The monomer has been synthesized by esterification of trinitroethanol (paragraph II,D,2,a) with either acrylyl chloride or acrylic acid. When acrylyl chloride was used in the preparation, the ester was contaminated with chlorinated impurities which were difficult to remove (457, 3). Purification by distillation was not successful, because the halogenated impurities were not separated and trinitroethanol was found to co-distill with the monomer. Furthermore, the hazard in attempting to distill such a high-energy material would eliminate any such procedure on a large-scale preparation. An explosion resulted when the distillation of a small quantity of abnormal product was attempted (468, 66). The best method of preparation was found to be the direct esterification of acrylic acid and trinitroethanol, in benzene solution, with a catalytic amount of concentrated sulfuric acid (468, 8).

$$C(NO_2)_3\text{-}CH_2OH + CH_2\text{=}CH\text{-}CO_2H \xrightarrow{H+} CH_2\text{=}CH\text{-}CO_2CH_2\text{-}C(NO_2)_3$$

The water which formed in the reaction was removed by azeotropic distillation. Extraction of the crude product with hexane, in a Craig counter-current extraction apparatus, produced a monomer which, from a melting-curve determination, contained 2 mole % impurity. Distillation of the monomer resulted in reducing the amount of the impurity to 0.6 mole % (499, 6; 515, 3). The SPIA data sheet was prepared, using this material (515, App. A).

Trinitroethyl acrylate polymerizes readily; however, because it contains the trinitromethyl group, the resulting polymer has a very low molecular weight (540, 2). Due to this limitation, the monomer has not been useful in the development of a propellant.

e. 2,2-Dinitropropyl Acrylate

Without a doubt, the 2,2-dinitropropyl acrylate has found the greatest utility of all the unsaturated nitro monomers thus far prepared. The success of this monomer for application to propellant work is a result of the following facts: (1) the chain transfer constant of this monomer is low, hence the resulting polymers have a high molecular weight (868, 50); (2) its preparation is relatively easy; (3) it has the highest specific impulse of any monomer with equally desirable properties; (4) it is stable to temperatures normally encountered in propellant work; and (5) the mechanical properties of the polymer, while not ideal, are the best which have been encountered to date.

The first successful preparation of this monomer was achieved in these laboratories on another contract, by the direct esterification of 2,2-dinitropropanol and acrylic acid.*

$$CH_3\text{-}C(NO_2)_2\text{-}CH_2OH + CH_2{=}CO_2H \longrightarrow CH_2{=}CO_2CH_2\text{-}C(NO_2)_2CH_3$$

Early preparations yielded a monomer which was contaminated with a crosslinking agent that gave rise to gel formation and sometimes contained a retarder yielding a non-reproducible rate of polymerization (740, 4; 868, 5; 907, 5). Consequently, the purification of the monomer has received much attention. In order to determine the quality of the monomer, a simple test was devised. Monomer was considered to be of satisfactory quality if, at the end of 20 hr of bulk polymerization, using 0.2% azo bis-isobutyronitrile, at 50°C, the polymer was completely soluble in acetone and a 1% acetone solution had a relative viscosity of 1.8, or greater (868, 5). Using this quality-control test, satisfactory monomer has been produced by three methods of purification. Simple vacuum distillation of the crude reaction product, when carried out twice, seemed to yield a monomer of high quality. A sample prepared in this manner, for the determination of properties for the SPIA data sheet, had a purity of 99.8 mole % as determined from the melting curve (424, App. A). This method, while suitable for small quantities, could not be translated to large-scale use because of the hazard involved in distilling a high-energy material possessing a low vapor pressure. A second method of purification developed by the Los Alamos Scientific Laboratory was that of vacuum steam distillation of the crude monomer.** In these laboratories, it was observed that by using this process, some hydrolysis of the monomer occurred yielding initial fractions which contained a retarder; consequently, yields of acceptable monomer were low (868, 6; 1048, 18). It was also observed that under these conditions, the monomer was subjected to a high temperature in a nearly dry state. Thus the attendent hazards of a simple vacuum distillation of a high-energy material are also encountered. For these reasons,

---

*Aerojet Report No. 426, 15 February 1950.
**Los Alamos Scientific Laboratory Report No. 1974, 6 February 1956.

either of the foregoing methods is considered undesirable. The present method of purification, also developed by the Los Alamos Scientific Laboratory,* depends upon the removal of undesirable impurities by magnesium oxide absorbent. The crude monomer is prepared by esterification of dinitropropanol and acrylic acid in the presence of polyphosphoric acid, and then quenched with water and the residual oil taken up in benzene. The benzene solution is concentrated to a 50% solution, 8.5 to 9% of powdered magnesium oxide is added, and the mixture is stirred for 2 hr at room temperature. Filtration to remove the solid and stripping of the benzene at reduced pressure leave a monomer of acceptable quality. This process is relatively simple and avoids heating of the dinitropropyl acrylate. Attempts to substitute silica gel for the magnesium oxide were unsuccessful (1048, 21).

f. 2,2-Dinitro-1-butyl Acrylate

2,2-Dinitrobutyl acrylate is another monomer which has received attention for propellant formulation. However, because of its lower specific impulse, it has not been studied as thoroughly as the corresponding propyl ester.

The monomer was first prepared in these laboratories, under another contract, by the esterification of 2,2-dinitro-1-butanol (paragraph II,D,2,a) and acrylic acid. The crude monomer, similar to the corresponding propyl compound, was found to contain crosslinking impurities resulting in insoluble gels upon polymerization and retarding agents which slowed the rate or inhibited polymerization (590, 52; 622, 58). Inasmuch as the lower specific impulse of this monomer (663, App. B), as compared to the dinitropropyl acrylate, makes it a less desirable material, the purification of the crude product has not been as extensively studied. Purification has been achieved by hexane extraction of the crude material, followed by vacuum distillation of the extract residue after removal of the solvent (622, 58). Presumably, the purification

$$CH_3\text{-}CH_2\text{-}C(NO_2)_2\text{-}CH_2OH + CH_2\text{=}CH\text{-}CO_2H \longrightarrow CH_2\text{=}CH\text{-}CO_2CH_2\text{-}C(NO_2)_2\text{-}CH_2\text{-}CH_3$$

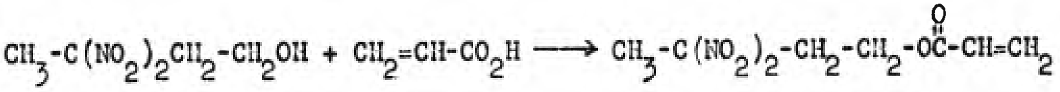
---

*Ibid.

procedure developed for dinitropropyl acrylate could be applied to dinitrobutyl acrylate if sufficient interest arose. An SPIA data sheet for this compound has been published (515, App. A).

g. 3,3-Dinitro-1-butyl Acrylate

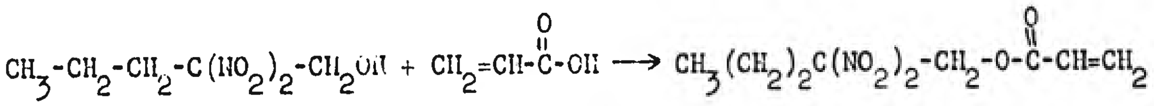
In order to study the effect of structure upon the mechanical properties of isomeric polymers, 3,3-dinitrobutyl acrylate was prepared since it is isomeric with 2,2-dinitrobutyl acrylate. The synthesis of this compound was carried out in a straightforward manner by the esterification of 3,3-dinitro-1-butanol (paragraph II,D,2,e) with acrylic acid (686, 54).



$$CH_3\text{-}C(NO_2)_2CH_2\text{-}CH_2OH + CH_2\text{=}CH\text{-}CO_2H \longrightarrow CH_3\text{-}C(NO_2)_2\text{-}CH_2\text{-}CH_2\text{-}O\overset{O}{\overset{\|}{C}}\text{-}CH\text{=}CH_2$$

h. 2,2-Dinitro-1-pentyl Acrylate

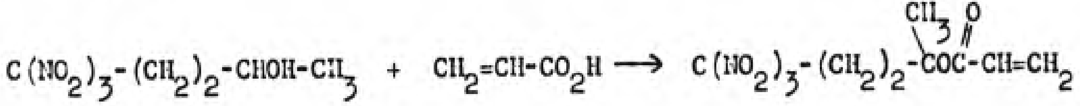
This compound was prepared by the acid-catalyzed esterification of 2,2-dinitro-1-pentanol (paragraph II,D,2,a) with acrylic acid in benzene solution (622, 60). The material polymerized readily, yielding an acetone-soluble polymer.



$$CH_3\text{-}CH_2\text{-}CH_2\text{-}C(NO_2)_2\text{-}CH_2OH + CH_2\text{=}CH\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH \longrightarrow CH_3(CH_2)_2C(NO_2)_2\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH\text{=}CH_2$$

i. 5,5,5-Trinitro-2-pentyl Acrylate

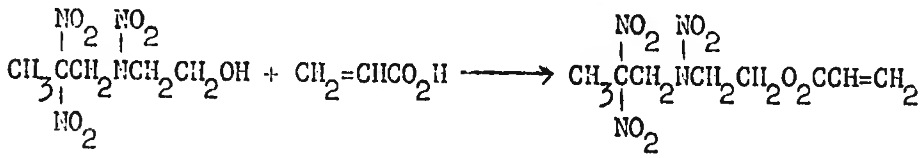
5,5,5-Trinitro-2-pentyl acrylate was prepared by the acid-catalyzed esterification of 5,5,5-trinitro-2-pentanol (paragraph II,D,2,b) with acrylic acid, in benzene solution (622, 70). The monomer has a reasonably high specific impulse (590, 45), and its preparation was carried out in order to determine the chain-transfer effect of the trinitromethyl group farther removed from the ester linkage than in trinitroethyl acrylate. The polymer had a low relative viscosity, indicating extensive chain transfer; therefore, further work was not warranted (622, 17).



$$C(NO_2)_3\text{-}(CH_2)_2\text{-}CHOH\text{-}CH_3 + CH_2\text{=}CH\text{-}CO_2H \longrightarrow C(NO_2)_3\text{-}(CH_2)_2\text{-}\overset{CH_3}{C}O\overset{O}{\overset{\|}{C}}\text{-}CH\text{=}CH_2$$

j. 3,5,5-Trinitro-3-aza-1-hexyl Acrylate

3,5,5-Trinitro-3-aza-1-hexyl acrylate was prepared in an effort to synthesize a high-energy monomer which contained groups that did not participate in chain transfer during polymerization. The synthesis was achieved by esterification of 3,5,5-trinitro-3-aza-1-hexanol (paragraph II,D,2,b) with acrylic acid (712, 41).



$$CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2CH_2OH + CH_2{=}CHCO_2H \longrightarrow CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2CH_2O_2CCH{=}CH_2$$

k. 2,2-Dinitrotrimethylene Diacrylate

This monomer, prepared for use as a crosslinking agent, was previously made by another method.* In these laboratories the preparation was carried out by the acid-catalyzed esterification of 2,2-dinitro-1,3-propanediol (paragraph II,D,2,a) with acrylic acid (468, 2).

$$HOCH_2\text{-}C(NO_2)_2\text{-}CH_2OH + 2\ CH_2{=}CHCO_2H \longrightarrow (CH_2{=}CHCO_2CH_2\text{-})_2C(NO_2)_2$$

l. 2-Methyl-2-nitrotrimethylene Diacrylate

The diacrylate of 2-methyl-2-nitro-1,3-propanediol was also prepared for use as a crosslinking agent. Acid-catalyzed esterification of the diol and acrylic acid, in benzene solution, was used (468, 3).

$$HOCH_2\text{-}C(NO_2)(CH_3)\text{-}CH_2OH + 2CH_2{=}CH\text{-}CO_2H \longrightarrow (CH_2{=}CH\text{-}CO_2CH_2\text{-})_2C(NO_2)(CH_3)$$

---

*General Tire and Rubber Co., Final Report, 15 December 1949.

TABLE 3

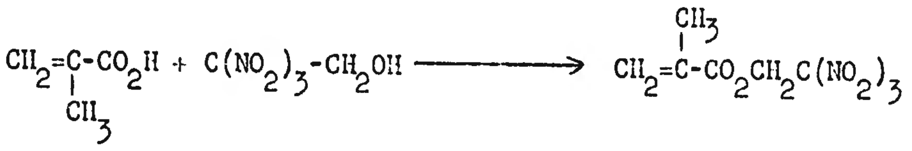
PHYSICAL PROPERTIES OF POLYNITROESTERS OF ACRYLIC ACID

Ester	b.p., °C	m.p., °C	n_D	Density, g/ml	Spec. Impulse, lbf sec/lbm	Reference
2-Bromo-2,2-dinitroethyl	93 to 97/2 mm	--	1.4930 (22°C)	--	--	457, 75
2-Cyano-2,2-dinitroethyl	70 to 80/1 μ	--	1.4580 (25°C)	--	175	712, 41
2,2,2-Trinitroethyl	45/5 μ	-4.9	1.4624 (25°C)	1.438 (25°C)	227	515, App. A; 663, App. B
2,2-Dinitropropyl	65/0.4 mm	-19	1.4609 (25°C)	1.303 (25°C)	171	552, 42; 663, App. B
2,2-Dinitrobutyl	64/0.25 mm	-2.5	1.4579 (25°C)	1.2572 (25°C)	150	552, 42; 663, App. B
3,3-Dinitrobutyl	78 to 80/2 μ	--	1.4660 (25°C)	--	150	686, 55; 663, App. B
2,2-Dinitropentyl	73 to 74/8 μ	--	1.4571 (25°C)	--	--	662, 61
5,5,5-Trinitro-2-pentyl	93 to 96/5 μ	--	1.4670 (25°C)	1.3273 (25°C)	187	590, 45; 622, 70
3,5,5-Trinitro-3-aza-1-hexyl	--	56 to 57	--	--	181	712, 41
2,2-Dinitrotrimethylene	91 to 93/3 μ	--	1.4724 (24°C)	--	--	468, 3
2-Methyl-2-nitrotrimethylene	93 to 94/1 μ	ca. 23	1.4735 (20°C)	--	--	468, 5

m. 2,2,2-Trinitroethyl Methacrylate

Trinitroethyl methacrylate was among the first of the high-energy, unsaturated nitro compounds prepared. It was hoped that this monomer, with the very desirable specific impulse of 220, would yield a high-energy polymer suitable for application as a propellant. However, subsequent work has shown that due to chain transfer of the trinitromethyl group, the polymer which was obtained was of low molecular weight, unsuited for propellant application (700, 24).

The initial synthesis of this compound was achieved, using methacrylyl chloride and trinitroethanol (371, 10). Later preparations were conveniently carried out by the acid-catalyzed esterification of trinitroethanol and acrylic acid in benzene solution, removing the water formed by azeotropic distillation (482, 5). The ester was readily purified, by recrystallization, from hexane. Data for the SPIA sheet were obtained on a sample of 99.1 mole % purity (482, App. A).



$$CH_2{=}\underset{CH_3}{C}{-}CO_2H + C(NO_2)_3{-}CH_2OH \longrightarrow CH_2{=}\overset{CH_3}{C}{-}CO_2CH_2C(NO_2)_3$$

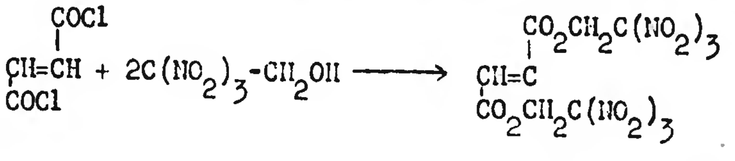
n. 2,2,2-Trinitroethyl Crotonate

This compound was prepared by the reaction of crotonyl chloride with trinitroethanol. No attempts were made to polymerize or copolymerize this monomer (386, 5; 416, 3).

$$CH_3{-}CH{=}CH{-}COCl + C(NO_2)_3CH_2OH \longrightarrow CH_3{-}CH{=}CH{-}CO_2CH_2{-}C(NO_2)_3$$

o. bis-2,2,2-Trinitroethyl Fumarate

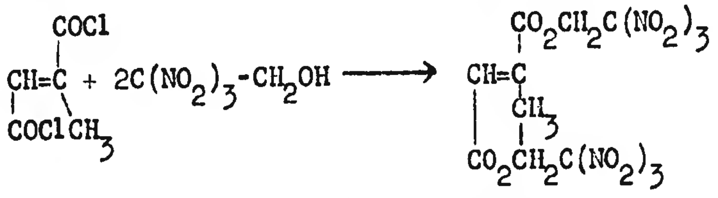
This compound was prepared by the reaction of fumaryl chloride with two molar equivalents of trinitroethanol (386, 5; 416, 3).



$$\underset{COCl}{\overset{COCl}{CH}}{=}CH + 2C(NO_2)_3{-}CH_2OH \longrightarrow \underset{CO_2CH_2C(NO_2)_3}{\overset{CO_2CH_2C(NO_2)_3}{CH}}{=}C$$

p. *bis*-2,2,2-Trinitroethyl Mesaconate

Attempts to prepare this compound by the reaction of mesaconyl chloride with trinitroethanol were unsuccessful when methylene chloride, chloroform, or xylene was used as a solvent for the reaction. When petroleum ether was employed as a solvent for the reaction, an oil was obtained which analyzed poorly for the desired ester (404, 6; 417, 4; 552, 17).



q. Miscellaneous Attempts to Prepare Nitroesters of Unsaturated Acids

Attempts to prepare 2-nitraminoethyl acrylate by esterification of nitraminoethanol with acrylyl chloride or acrylic acid in trifluoroacetic anhydride were unsuccessful. Severe degradation, with loss of the nitramino group, resulted (772, 67).

A number of unsuccessful attempts have been made to synthesize 2,2,4,4-tetranitro-1-butyl acrylate. It was hoped that 2-bromo-2,2-dinitroethyl acrylate, upon reaction with potassium iodide, would behave in a similar manner to 2-bromo-2,2-dinitroethyl acetate which produced the 2,2,4,4-tetranitrobutyl acetate (457, 13; 468, 36). Additional attempts to esterify 2,2,4,4-tetranitro-1-butanol with acrylyl chloride likewise failed (482, 6; 552, 20).

Two attempts to open the maleic anhydride ring to produce *bis*-2,2,2-trinitroethyl maleate yielded only recovered starting materials (386, 5).

One attempt to prepare *bis*-2,2,2-trinitroethyl muconate by ester interchange of diethyl muconate and trinitroethyl acetate was unsuccessful (386, 6).

TABLE 4

PHYSICAL PROPERTIES OF MISCELLANEOUS TRINITROETHYL ESTERS

Ester	b.p. °C	m.p. °C	Reference
2,2,2-Trinitroethyl Methacrylate	78/3 mm	28.3	371, 10; 386, 5; 482, 5
2,2,2-Trinitroethyl Crotonate	97/5 mm		386, 5
bis-2,2,2-Trinitro-ethyl Fumarate		150	386, 5
Pentaerythritol Acrylate Trinitrate		72 to 75	563, 53

r. Summary and Evaluation

As stated earlier in the report, this class of monomers has yielded the largest number of compounds with potential use in propellant compositions. The early preparation of the trinitroethyl esters gave materials of high, calculated specific impulse; however, their usefulness as nitropolymers was severely limited by their chain-transfer character upon polymerization. With this discovery, this class of monomers appeared less desirable because of the difficulty in synthesizing high-energy monomers without the use of the trinitroethyl group. Consequently, those materials which have found use in propellant formulation have a lower specific impulse and are formulated with added oxidizer to give composite solid propellants. If new high-energy groups become available which do not exhibit a correspondingly high chain transfer during polymerization, this class of compounds would again become a valuable source of new unsaturated nitromonomers.

4. Nitrato Esters of Unsaturated Acids

Pentaerythritol acrylate trinitrate, the only example of this class, was first prepared by the Allegany Ballistics Laboratory.* Inasmuch as the monomer has an estimated specific impulse of 214 lbf sec/lbm, a study of the

---

*ABL Abstract "Nitrate Monomers for Solution - Cast Propellants," Nitro Polymer Meeting (April 1951).

polymerization of this material was deemed worthwhile. The monomer was prepared in this laboratory by the same procedure developed by ABL. Pentaerythritol was nitrated to the trinitrate, and the remaining hydroxyl group was esterified with acrylyl chloride. The product after recrystallization was a white crystalline solid:

$$HOCH_2C(CH_2ONO_2)_3 + CH_2{=}CH{-}COCl \longrightarrow CH_2{=}CH{-}CO_2CH_2C(CH_2ONO_2)_3$$

m.p. 72.5 to 75°C. The impact stability was greater than 100 cm for a 2-kg weight (540, 32). An SPIA data sheet on this monomer was prepared (590, App. A).

Polymerization of this monomer in greater than 60% acetone solution gave rise to insoluble gels (638, 20).

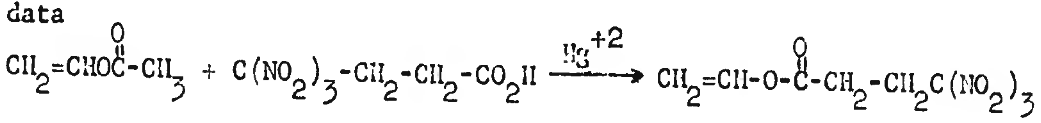
5. Unsaturated Esters of Nitroacids

a. Introduction

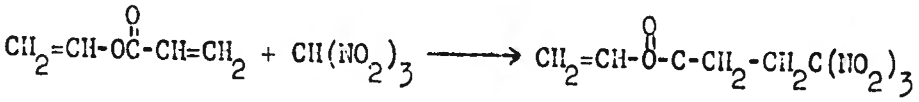
Another approach to the synthesis of unsaturated nitromonomers was through the preparation of unsaturated esters of nitroacids. Inasmuch as vinyl esters such as vinyl acetate polymerize readily and have found wide use, it was anticipated that the corresponding nitroacid derivatives would give useful materials. Although these materials were readily synthesized, their usefulness in propellant work was not realized because of the unpolymerizable nature of the monomers. The physical properties of these compounds are compiled in Table 5.

b. Vinyl 4,4,4-Trinitrobutyrate

This compound was originally prepared by the U.S. Rubber Co.* In this laboratory, it was also prepared by transvinylation and by the preferential addition of nitroform to vinyl acrylate (468, 5; 515, 3). An SPIA data



$$CH_2{=}CHO\overset{O}{C}{-}CH_3 + C(NO_2)_3{-}CH_2{-}CH_2{-}CO_2H \xrightarrow{Hg^{+2}} CH_2{=}CH{-}O{-}\overset{O}{C}{-}CH_2{-}CH_2C(NO_2)_3$$



$$CH_2{=}CH{-}O\overset{O}{C}{-}CH{=}CH_2 + CH(NO_2)_3 \longrightarrow CH_2{=}CH{-}\overset{O}{O}{-}C{-}CH_2{-}CH_2C(NO_2)_3$$

---

*U.S. Rubber Co., Report No. 9, p. 17.

sheet was prepared on a sample prepared by the latter method (515, App. A). The polymer, although never obtained, has an estimated specific impulse of 215 lbf sec/lbm.

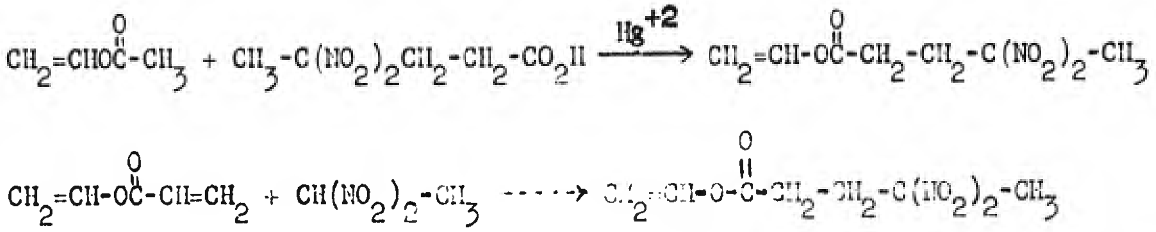
c. Allyl 4,4,4-Trinitrobutyrate

Allyl 4,4,4-trinitrobutyrate was prepared by the preferential addition of nitroform to allyl acrylate (563, 60).

$$\mathrm{CH_2{=}CH{-}CO_2CH_2{-}CH{=}CH_2 + CH(NO_2)_3 \longrightarrow C(NO_2)_3{-}CH_2{-}CH_2{-}CO_2CH_2{-}CH{=}CH_2}$$

d. Vinyl 4,4-Dinitropentanoate

Vinyl 4,4-dinitropentanoate has been prepared by the two methods outlined above. Transvinylation gave a material which, after two vacuum distillations, analyzed rather poorly. A product which analyzed correctly was obtained from the addition of 1,1-dinitroethane to vinyl acrylate (622, 63).



$$\mathrm{CH_2{=}CHO\overset{O}{\overset{\|}{C}}{-}CH_3 + CH_3{-}C(NO_2)_2CH_2{-}CH_2{-}CO_2H \xrightarrow{Hg^{+2}} CH_2{=}CH{-}O\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}C(NO_2)_2{-}CH_3}$$

$$\mathrm{CH_2{=}CH{-}O\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2 + CH(NO_2)_2{-}CH_3 \dashrightarrow CH_2{=}CH{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}CH_2{-}C(NO_2)_2{-}CH_3}$$

e. Allyl 4,4-Dinitro-1,7-heptanedioate

This compound was synthesized by the reaction of 4,4-dinitro-1,7-heptanedioic acid with allyl alcohol (457, 6). It was proposed to use this monomer as a crosslinking agent in vinyl polymerization.

$$\mathrm{2CH_2{=}CH{-}CH_2OH + C(NO_2)_2(CH_2{-}CH_2{-}CO_2H)_2 \xrightarrow{POCl_3} (CH_2{=}CH{-}CH_2OCOCH_2CH_2)_2C(NO_2)_2}$$

f. Summary and Evaluation

Early expectations for the application of the unsaturated esters of nitroacids toward the preparation of a nitropolymer propellant have not been realized. The reason for the failure of this class of compounds to live up to the expectations was the inability to polymerize these negatively substituted esters. A number of attempts to polymerize vinyl trinitrobutyrate, under a variety of conditions, met with failure. The ease with which these compounds have been produced may make them valuable when considered from the viewpoint of chemical intermediates.

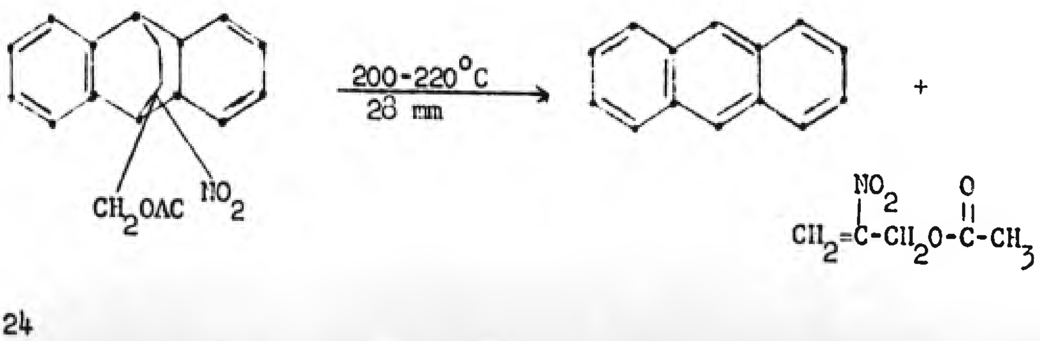
TABLE 5

PHYSICAL PROPERTIES OF UNSATURATED ESTERS OF NITROACIDS

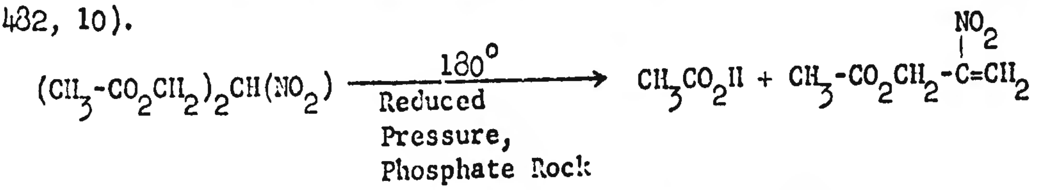
Ester	b.p., °C	n_D (°C)	Reference
Vinyl 4,4,4-trinitrobutyrate	75 to 78/1 μ	1.4723 (20)	468, 5
Allyl 4,4,4-trinitrobutyrate	35 to 41/35 μ	1.4658 (25)	563, 60
Vinyl 4,4-dinitropentanoate	80 to 90/0.5 μ	1.4664 (25)	622, 62
Allyl 4,4-dinitro-1,7-heptanedioate	138/1.4 μ	1.4780 (24)	457, 72

6. Unsaturated Nitroesters of Acids - 2-Nitroallyl Acetate

In an effort to utilize new reactions by which new nitro compounds could be synthesized, the thermal decomposition of the anthracene adduct with nitroethylene was studied (457, 5; 468, 11). The adduct with nitroethylene itself was found to be quite thermally stable and did not decompose to the original reactants under a wide range of conditions studied. The decomposition of the formaldehyde product of the nitroethylene adduct (*endo* -1-nitro-1-methylol anthracene) likewise did not yield an unsaturated nitro compound but, instead, split out formaldehyde. Attention was next turned to the acetate derivative of the methylol compound. It was observed that this compound did dissociate, giving 2-nitroallyl acetate as one of the products (482, 8).



Since the yield from the anthracene adduct decomposition was low, an alternate method of synthesis was sought. After some study, it was found possible to obtain a high yield of 2-nitroallyl acetate by splitting out acetic acid from 2-nitro-1,3-propanediol diacetate, in the vapor phase, over phosphate rock (482, 10).



$$(CH_3-CO_2CH_2)_2CH(NO_2) \xrightarrow[\text{Reduced Pressure, Phosphate Rock}]{180^\circ} CH_3CO_2H + CH_3-CO_2CH_2-\overset{NO_2}{\overset{|}{C}}=CH_2$$

Although this compound has such a low-energy content as to be of no utility in the preparation of a nitropolymer propellant composition, it was found to be a valuable intermediate for the preparation of several high-energy compounds (paragraph II,F,6,d). An SPIA data sheet was published (622, App.).

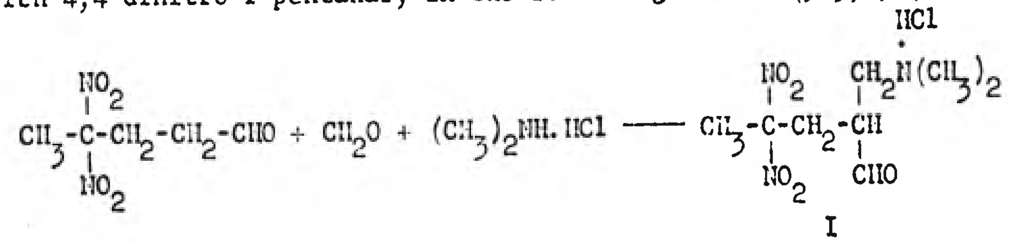
7. Esters of Unsaturated Nitroacids

a. Introduction

The successful application of nitroesters of unsaturated acids to propellant compositions showed them to be a valuable class of compounds. However, in all these esters the nitro groups were substituted in the alcohol moiety of the ester, and the acid portion was devoid of any oxygen donor. The relatively large acrylic acid portion, therefore, contributed nothing to improve the specific impulse of the polymer. Consequently, synthetic effort was devoted to the preparation of suitable unsaturated nitroacids in order to improve the specific impulse of these esters.

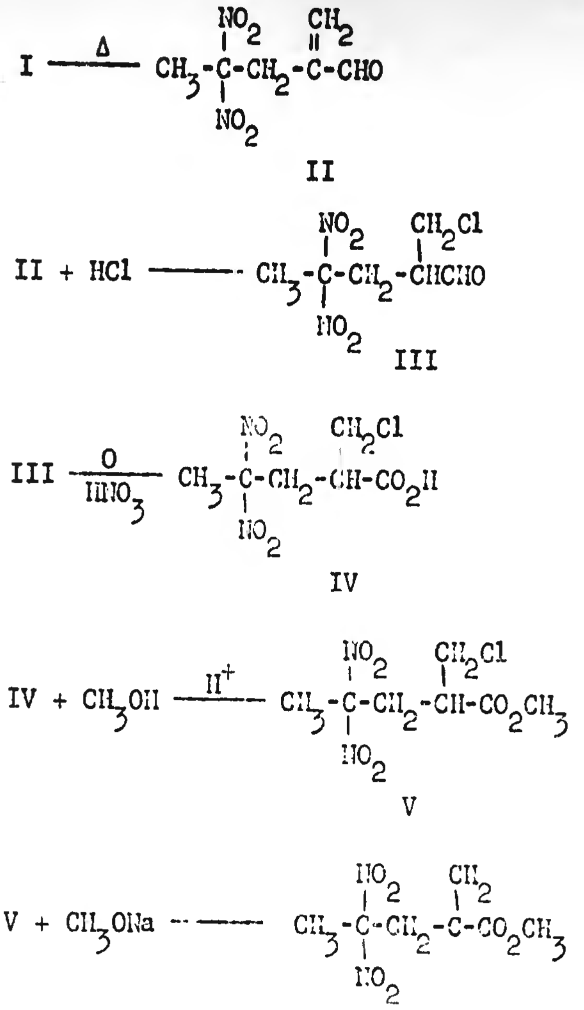
b. Methyl α-(2,2-Dinitropropyl)-acrylate

The synthesis of this ester was accomplished, starting with 4,4-dinitro-1-pentanal, in the following manner (563, 56):



$$CH_3-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-CHO + CH_2O + (CH_3)_2NH.HCl \;\text{——}\; CH_3-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-\underset{CHO}{\overset{CH_2N(CH_3)_2 \cdot HCl}{CH}}$$

I



$$\mathrm{I} \xrightarrow{\Delta} \mathrm{CH_3\text{-}\overset{NO_2}{\underset{NO_2}{C}}\text{-}CH_2\text{-}\overset{CH_2}{\overset{\|}{C}}\text{-}CHO}$$

II

$$\mathrm{II + HCl} \longrightarrow \mathrm{CH_3\text{-}\overset{NO_2}{\underset{NO_2}{C}}\text{-}CH_2\text{-}\overset{CH_2Cl}{CH}CHO}$$

III

$$\mathrm{III} \xrightarrow[\mathrm{HNO_3}]{\mathrm{O}} \mathrm{CH_3\text{-}\overset{NO_2}{\underset{NO_2}{C}}\text{-}CH_2\text{-}\overset{CH_2Cl}{CH}\text{-}CO_2H}$$

IV

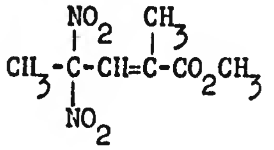
$$\mathrm{IV + CH_3OH} \xrightarrow{\mathrm{H^+}} \mathrm{CH_3\text{-}\overset{NO_2}{\underset{NO_2}{C}}\text{-}CH_2\text{-}\overset{CH_2Cl}{CH}\text{-}CO_2CH_3}$$

V

$$\mathrm{V + CH_3ONa} \longrightarrow \mathrm{CH_3\text{-}\overset{NO_2}{\underset{NO_2}{C}}\text{-}CH_2\text{-}\overset{CH_2}{C}\text{-}CO_2CH_3}$$

The product was a liquid b.p. 60 to 65°C/0.1 μ, $n_D^{25^\circ C}$ 1.4631. In a subsequent preparation of a larger quantity of the ester, it was observed that in the dehydrohalogenation step, some displacement of chlorine by the methoxyl group occurred. In order to avoid this side reaction, pyridine was used in the dehydrohalogenation reaction (590, 58).

It was observed that this monomer failed to form a homopolymer and also failed to copolymerize with other monomers. Two reasons for the failure of this compound to polymerize were suggested (622, 61). Duplicating the expected structure with Fisher-Hershfelder models suggests that the double bond is sterically hindered. The other suggested reason involves the chemical structure of the monomer. If a rearrangement of the double bond occurred to yield the following structure, polymerization would not be expected:

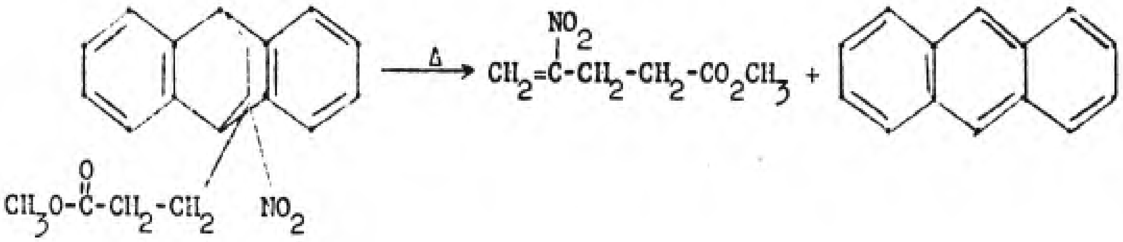


$$CH_3-\overset{NO_2}{\underset{NO_2}{C}}-CH=\overset{CH_3}{C}-CO_2CH_3$$

A rigorous proof of structure of the monomer has not been carried out, and the question as to which one it really is has not been answered.

c. Methyl 4-Nitro-4-pentenoate

It was observed that the anthracene-nitroethylene adduct would add across the conjugated double bond of methyl acrylate. Thermal dissociation of this compound gave methyl 4-nitro-4-pentenoate as a product (468, 12). The ester is a liquid b.p. 85 to 90°C/1 mm, n_D^{24} 1.4662.



An attempt to prepare the ester by an alternate method, by the addition of 1-chloronitroethane to methyl acrylate, followed by dehydrochlorination with quinoline, was unsuccessful (482, 11).

d. Miscellaneous Attempts to Prepare Esters of Unsaturated Nitroacids

Attempts to prepare methyl α-nitroacrylate by the condensation of formaldehyde with methyl nitroacetate, followed by dehydration, were unsuccessful (417, 4).

Numerous attempts to form ethyl α-trinitromethyl acrylate, by the reaction of nitroform with ethyl pyruvate and subsequent dehydration, were unsuccessful (499, 3; 515, 30).

An attempt to obtain diethyl 2-trinitromethylfumarate by the addition of nitroform to diethyl oxaloacetate also was unsuccessful (499, 5).

Attempts to prepare suitable derivatives of α-aminoacrylic acid for nitropolymer use were unsuccessful (638, 78; 663, 70).

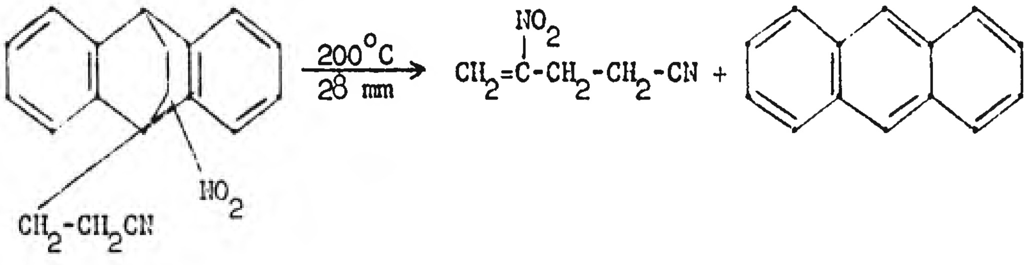
e. Summary and Evaluation

Of the many synthetic attempts to prepare compounds of this class, only a few have been successful. Those compounds that were made were of low-energy content, and they were suitable only as intermediates in the preparation of other materials.

8. Unsaturated Nitronitriles

a. 4-Nitro-4-pentenonitrile

Among the anthracene adducts whose dissociation was studied, was the addition product of the endo-nitroethylene anthracene and acrylonitrile. The thermal dissociation of this material proceeded smoothly, giving 4-nitro-4-pentenonitrile as product. The nitrile is a liquid, b.p. 120°C/5 mm, n_D^{22} 1.4735 (468, 32; 482, 7).



b. The Attempted Synthesis of α-Nitroacrylonitrile

An attempt to prepare α-nitroacrylonitrile by the reaction of 2-bromo-2-nitroethyl acetate with cuprous cyanide, followed by the splitting out of acetic acid, failed in the first step of the proposed synthesis (404, 6).

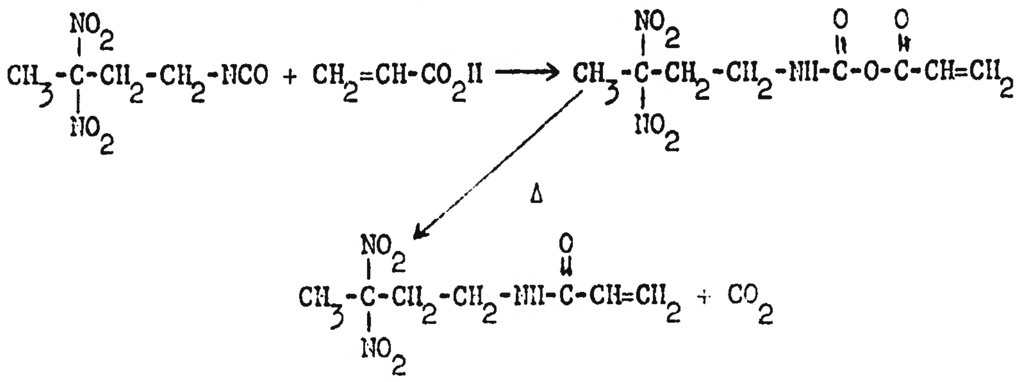
9. Unsaturated Nitroamides

a. Introduction

After it had been observed that nitromonomers containing the trinitromethyl group gave very low molecular weight polymers, the synthesis of high-energy monomers, devoid of such groups, was attempted. One approach to this problem was through the preparation of polynitroalkyl unsaturated amides whose specific impulse could be improved by nitration of the amide nitrogen.

b. N-3,3-Dinitrobutyl Acrylamide

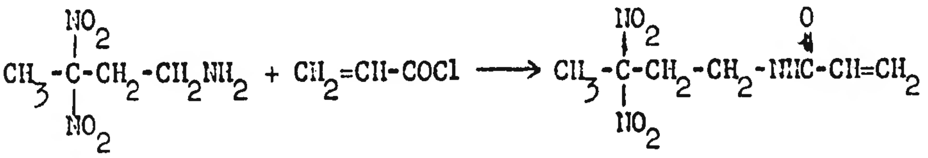
This compound was successfully prepared by two different methods. The reaction of 3,3-dinitro-1-butyl isocyanate (paragraph II,B,5) with glacial acrylic acid gave the acrylyl carbamate, which readily evolved carbon dioxide, upon heating, to yield N-3,3-dinitrobutyl acrylamide as the final product (638, 73).



$$CH_3\text{-}\underset{NO_2}{\overset{NO_2}{C}}\text{-}CH_2\text{-}CH_2\text{-}NCO + CH_2{=}CH\text{-}CO_2H \longrightarrow CH_3\text{-}\underset{NO_2}{\overset{NO_2}{C}}\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}CH_2$$

$$\xrightarrow{\Delta} CH_3\text{-}\underset{NO_2}{\overset{NO_2}{C}}\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH{=}CH_2 + CO_2$$

The second preparation was achieved by the reaction of acrylyl chloride with 3,3-dinitro-1-butylamine (paragraph II,B,5) (638, 73; 663, 70).



$$CH_3\text{-}\underset{NO_2}{\overset{NO_2}{C}}\text{-}CH_2\text{-}CH_2NH_2 + CH_2{=}CH\text{-}COCl \longrightarrow CH_3\text{-}\underset{NO_2}{\overset{NO_2}{C}}\text{-}CH_2\text{-}CH_2\text{-}NH\overset{O}{\overset{\|}{C}}\text{-}CH{=}CH_2$$

The yield obtained by either method was low. The N-3,3-dinitrobutyl acrylamide is a crystalline solid m.p. 38 to 39°C.

In order to increase the specific impulse of this monomer, nitration of the amide nitrogen was attempted. The use of nitric acid-acetic anhydride mixture, anhydrous nitric acid, or nitric acid-sulfuric acid mixture was unsuccessful in producing the desired product.

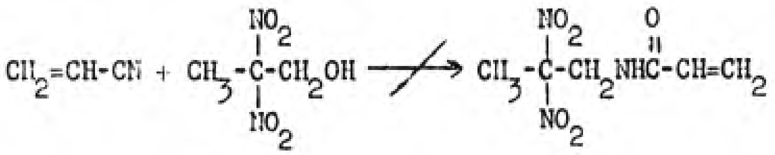
c. Miscellaneous Attempts to Prepare Unsaturated Nitroamides

Had the nitration of N-methyl acrylamide been successful, a monomer with an estimated specific impulse of 144 lbf sec/lbm would have resulted. However, nitration, when carried out at -30°C in a nitric acid-acetic anhydride mixture, gave a crystalline solid m.p. 120 to 121°C (dec), which had an empirical formula of $C_4H_6N_4O_7$. The structure of this material was not determined. Nitration with anhydrous nitric acid alone at 0, -20, and -30°C gave only water-soluble products (772, 68).

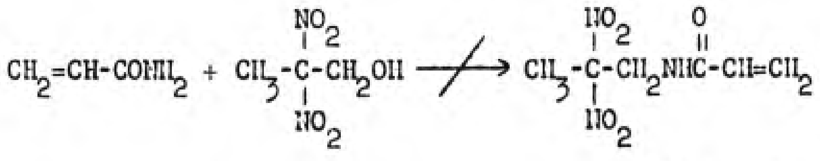
N-Nitro-N-nitratomethyl acrylamide has an estimated specific impulse of 229 lbf sec/lbm. An attempt to nitrate N-hydroxymethyl acrylamide, as the first step in the proposed synthesis, gave only water-soluble products. Extraction of the aqueous solution yielded nothing (663, 69).

The synthesis of N-nitro-N-nitratoethyl acrylamide was attempted, using two different methods of preparation. The first synthetic scheme, starting with acrylyl chloride and ethanolamine, gave only polymer instead of the expected β-hydroxyethyl acrylamide. Nitration of the polymer with 100% nitric acid gave a material which, from its heat of combustion, contained only one nitro group instead of the two expected (686, 59). Another attempt to prepare this compound was made by starting with the reaction of acrylyl chloride with 2-oxazolidone. The hydrolysis of the product was expected to yield β-hydroxyethyl acrylamide. The acrylation step yielded a high-boiling oil, which did not analyze for the expected product (740, 58).

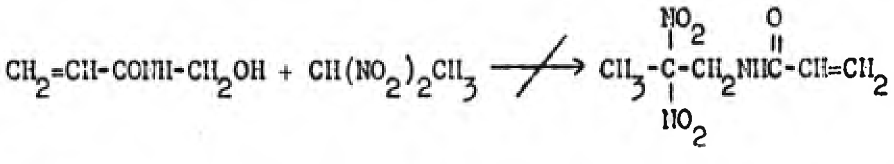
Many attempts were made to prepare N-2,2-dinitropropyl acrylamide, since nitration of this compound would have given a monomer with an estimated specific impulse of 210 lbf sec/lbm. The numerous attempts that failed can best be summarized by the following equations:

(1)  (590, 51)

$$CH_2{=}CH{-}CN + CH_3{-}\overset{NO_2}{\underset{NO_2}{C}}{-}CH_2OH \not\longrightarrow CH_3{-}\overset{NO_2}{\underset{NO_2}{C}}{-}CH_2NH\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2$$

(2)  (638, 75)

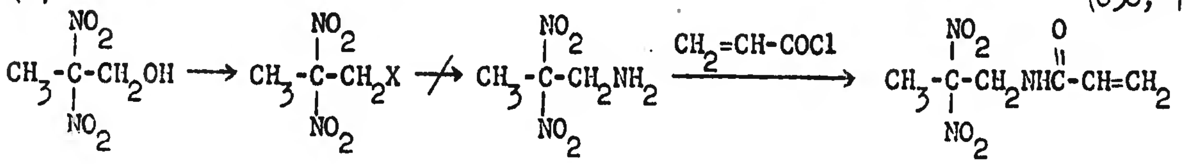
$$CH_2{=}CH{-}CONH_2 + CH_3{-}\overset{NO_2}{\underset{NO_2}{C}}{-}CH_2OH \not\longrightarrow CH_3{-}\overset{NO_2}{\underset{NO_2}{C}}{-}CH_2NH\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2$$

(3)  (638, 76)

$$CH_2{=}CH{-}CONH{-}CH_2OH + CH(NO_2)_2CH_3 \not\longrightarrow CH_3{-}\overset{NO_2}{\underset{NO_2}{C}}{-}CH_2NH\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2$$

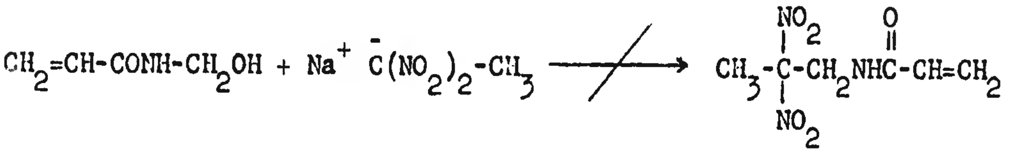
(4)

(638, 76)



$$CH_3\text{-}C(NO_2)_2\text{-}CH_2OH \longrightarrow CH_3\text{-}C(NO_2)_2\text{-}CH_2X \not\longrightarrow CH_3\text{-}C(NO_2)_2\text{-}CH_2NH_2 \xrightarrow{CH_2=CH\text{-}COCl} CH_3\text{-}C(NO_2)_2\text{-}CH_2NH\overset{O}{\overset{\|}{C}}\text{-}CH=CH_2$$

(5)

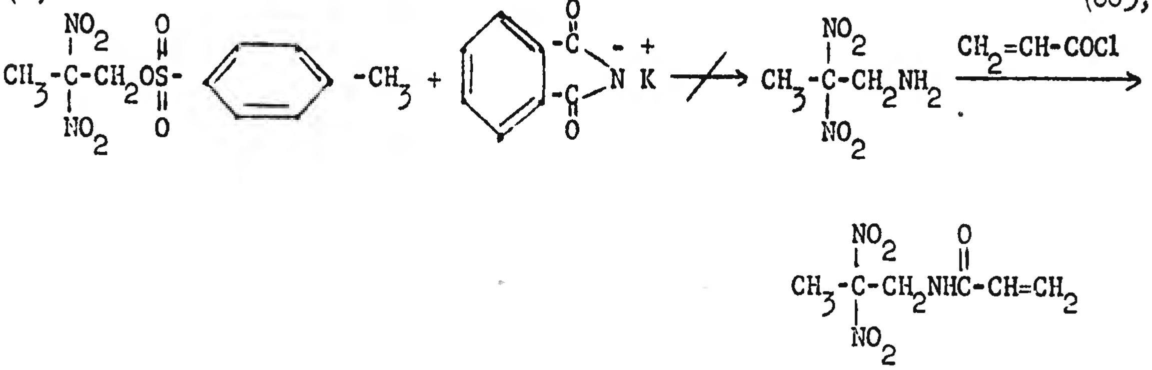


$$CH_2=CH\text{-}CONH\text{-}CH_2OH + Na^+\ \bar{C}(NO_2)_2\text{-}CH_3 \not\longrightarrow CH_3\text{-}C(NO_2)_2\text{-}CH_2NH\overset{O}{\overset{\|}{C}}\text{-}CH=CH_2$$

(663, 66)

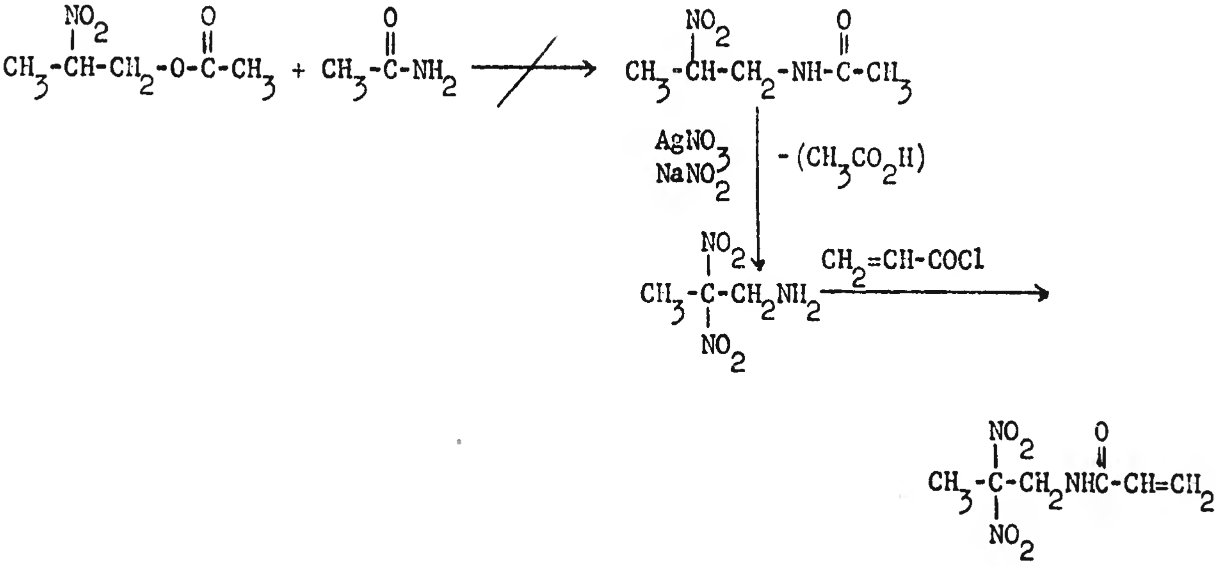
(6)

(663, 67)



(7)

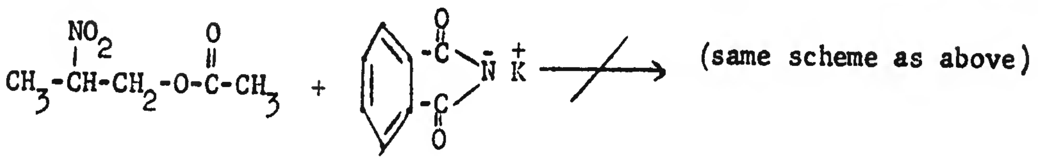
(663, 68)



$$CH_3\text{-}CH(NO_2)\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH_2 \not\longrightarrow CH_3\text{-}CH(NO_2)\text{-}CH_2\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \xrightarrow[-(CH_3CO_2H)]{AgNO_3,\ NaNO_2} CH_3\text{-}C(NO_2)_2\text{-}CH_2NH_2 \xrightarrow{CH_2=CH\text{-}COCl} CH_3\text{-}C(NO_2)_2\text{-}CH_2NH\overset{O}{\overset{\|}{C}}\text{-}CH=CH_2$$

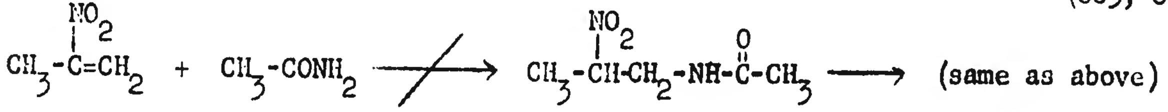
(8)

(663, 68)



(9)

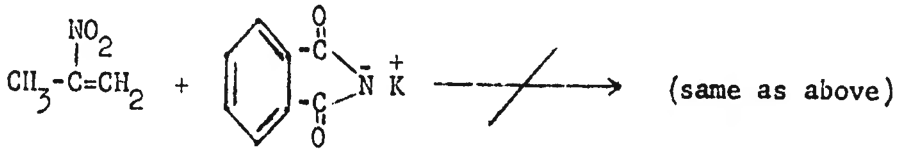
(663, 68)



$$CH_3\text{-}\overset{NO_2}{C}{=}CH_2 + CH_3\text{-}CONH_2 \not\longrightarrow CH_3\text{-}\overset{NO_2}{CH}\text{-}CH_2\text{-}NH\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 \longrightarrow \text{(same as above)}$$

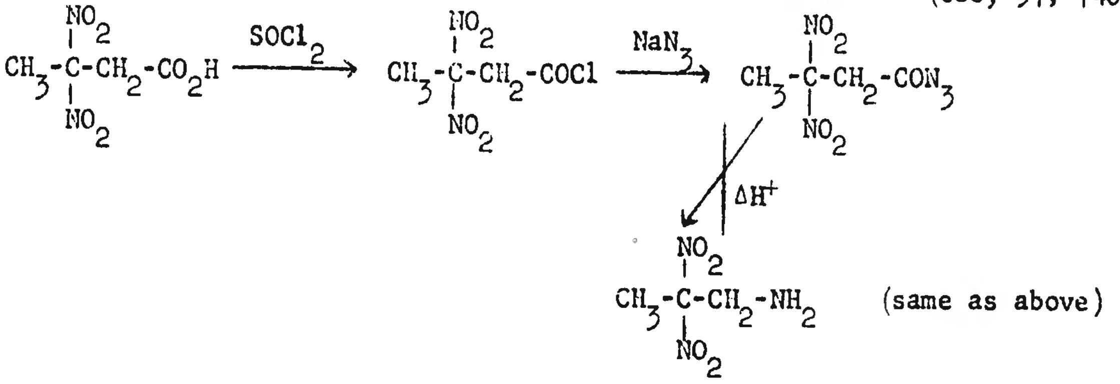
(10)

(663, 68)



(11)

(686, 57; 740, 57)



$$CH_3\text{-}\underset{NO_2}{\overset{NO_2}{C}}\text{-}CH_2\text{-}CO_2H \xrightarrow{SOCl_2} CH_3\text{-}\underset{NO_2}{\overset{NO_2}{C}}\text{-}CH_2\text{-}COCl \xrightarrow{NaN_3} CH_3\text{-}\underset{NO_2}{\overset{NO_2}{C}}\text{-}CH_2\text{-}CON_3 \xrightarrow[\Delta H^+]{} \!\!\!\!\!\!\!/\;\; CH_3\text{-}\underset{NO_2}{\overset{NO_2}{C}}\text{-}CH_2\text{-}NH_2 \quad \text{(same as above)}$$

d. Summary and Evaluation

Although the structures that can be proposed for this class of compounds appear desirable as nitromonomers, the difficulty experienced in synthesizing these materials is evidenced by the fact that only one polynitroalkyl unsaturated amide has been prepared thus far.

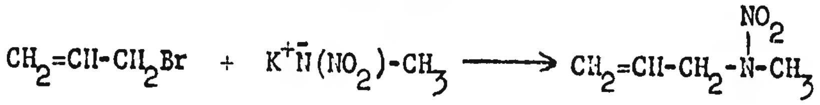
10. Unsaturated Nitramines

a. Introduction

Only two examples of this class of compounds have been prepared. They were made, for use as intermediates, for the preparation of other compounds and not for use as polymerizable monomers.

b. N-Methylallylnitramine

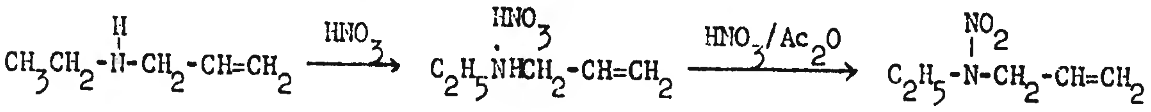
This compound was prepared by the reaction of potassium methylnitramine with allyl bromide. A 53% yield of N-methylallylnitramine, b.p. 91°C/13 mm, n_D^{25} 1.4750, was obtained (1083, 34; 1119, 15).



$$CH_2=CH\text{-}CH_2Br + K^+\bar{N}(NO_2)\text{-}CH_3 \longrightarrow CH_2=CH\text{-}CH_2\text{-}\overset{NO_2}{\overset{|}{N}}\text{-}CH_3$$

c. N-Ethylallylnitramine

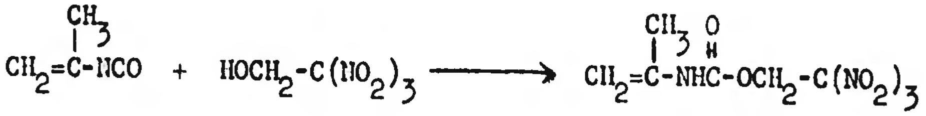
This compound was prepared by the nitration of ethylallylamine. The nitrate salt was first prepared and further nitrated in an acetic anhydride-nitric acid mixture containing chloride ion (1119, 13).



$$CH_3CH_2\text{-}\overset{H}{\overset{|}{N}}\text{-}CH_2\text{-}CH=CH_2 \xrightarrow{HNO_3} C_2H_5\overset{HNO_3}{\overset{\cdot}{N}}HCH_2\text{-}CH=CH_2 \xrightarrow{HNO_3/Ac_2O} C_2H_5\text{-}\overset{NO_2}{\overset{|}{N}}\text{-}CH_2\text{-}CH=CH_2$$

11. Unsaturated Nitrocarbamates; Isopropenyl 2,2,2-Trinitroethyl Carbamate

Isopropenyl 2,2,2-trinitroethyl carbamate was synthesized by the reaction of isopropenyl isocyanate with trinitroethanol; however, it was never characterized. Extraction of the crude product with hexane gave an oil which analyzed for the expected product (404, 36; 417, 34)



$$CH_2=\overset{CH_3}{\overset{|}{C}}\text{-}NCO + HOCH_2\text{-}C(NO_2)_3 \longrightarrow CH_2=\overset{CH_3}{\overset{|}{C}}\text{-}NH\overset{O}{\overset{\|}{C}}\text{-}OCH_2\text{-}C(NO_2)_3$$

12. The Attempted Preparation of an Unsaturated Nitroketone; Trinitromethyl Vinyl Ketone

This polymer, which would be obtained from trinitromethyl vinyl ketone if its synthesis were successful, has an estimated specific impulse of 250 lbf sec/lbm. Attempts to prepare this monomer from acrylyl chloride and silver or potassium nitroform gave either no isolable products or unstable oils which exploded upon attempted distillation (417, 2; 424, 3; 552, 19).

13. The Attempted Preparation of an Unsaturated Nitroalcohol; 2-Nitroallyl Alcohol

Thermal dissociation of endo(1-nitro-1-methylol) ethylene anthracene was expected to give, as products, 2-nitroallyl alcohol and anthracene. Instead, decomposition occurred yielding formaldehyde and endo-nitroethylene anthracene (468, 11; 552, 19).

14. The Attempted Preparation of an Unsaturated Nitroether; Vinyl 1,1,1-Trinitro-2-propyl Ether

The addition of nitroform to divinyl ether was expected to yield vinyl 1,1,1-trinitro-2-propyl ether. When methanol was used as solvent for the reaction, a product was isolated which analyzed correctly for methyl 1,1,1-trinitro-2-propyl ether. When diethyl ether was used as a solvent, the reactants were recovered and, with dioxan solvent, a high boiling product was obtained which fumed off upon attempted distillation (563, 54). Evidently the methanol solvent had participated in the reaction, yielding an undesired product.

15. Summary and Evaluation of the Work on Unsaturated Nitro Monomers

Of the various classes of nitromonomers whose synthesis has been investigated, the class of the nitroesters of unsaturated acids alone has been fruitful in producing nitromonomers of utility in propellant compositions. More specifically, the nitroesters of acrylic acid alone appear promising.

The observation that the trinitromethyl group is undesirable in an unsaturated nitromonomer was a severe blow to the goal of achieving a nitropolymer monopropellant. The greatest need, at the present time, is a new synthetic approach to the problem of finding a high-energy group to replace the trinitromethyl group. If this can be achieved, unsaturated monomers that are suitable for vinyl-type polymerization will again assume the importance they once held in the early stages of the program.

B. ISOCYANATES

1. Introduction

Because of their utilization in the preparation of nitropolyurethanes, isocyanates, the diisocyanates in particular, are one of the more important types of monomers developed on this program. Nitropolyurethanes are currently considered the more versatile of the polymers which were developed and/or studied.

Early work on the synthesis of isocyanates was concerned with the preparation of low-molecular-weight, un-nitrated diisocyanates, including dioxoisocyanogen, methylene diisocyanate, and ethylene diisocyanate. Theoretically, these materials could be polymerized with highly oxygenated diols and diamines, without appreciably lowering the specific impulse of the resulting polyurethane or polyurea from that of the oxygenated monomer. One of the main reasons for abandoning the preparation of these diisocyanates was the extreme shock sensitivity of the diazides from which the diisocyanates were obtained.

Concurrently, work was initiated on the attempted preparation of short-chain nitrodiisocyanates such as nitromethylene diisocyanate, trinitroethyl methylene diisocyanate, and trinitromethyl ethylene diisocyanate. The inability to obtain certain key intermediates in these syntheses was due to the inherent instability of nitro compounds in basic media, or the tendency for the short-chain, bifunctional intermediates to cyclize.

In subsequent work, considerably more success was achieved in the preparation of longer-chain nitro and nitraza diisocyanates. The preparation of the esters, acids, and acid chlorides which were intermediates in these syntheses are indicated in paragraph II,C. In addition to the prime objective of this program of preparing nitropolymers (paragraph IV,B), certain of these diisocyanates were utilized, on the explosives program (Contract N7onr-46208), in the preparation of new explosives in the form of highly nitrated urethanes and ureas. The amines obtained from these diisocyanates provided an even larger variety of explosive materials, such as nitrate salts, nitramines, nitramides, nitroureas, and nitrourethanes.

2. Un-nitrated Diisocyanates

a. Dioxoisocyanogen

Attempts were made to prepare dioxoisocyanogen, the lowest member of the series of aliphatic diisocyanates, by the conversion of diethyl oxalate to oxalyl dihydrazide, rearrangement of the dihydrazide to oxalyl diazide by treatment with nitrous acid, and subsequent thermal decomposition of the diazide to dioxoisocyanogen (345, 14; 371, 15). The actual existence of the latter material was never proved. The synthesis was abandoned because of two explosions involving oxalyl diazide.

b. Methylene Diisocyanate

Methylene diisocyanate was prepared by the following series of reactions (345, 16; 371, 13):

$$CH_2(CO_2CH_2CH_3)_2 + 2NH_2NH_2 \cdot H_2O \longrightarrow \underset{\text{I}}{CH_2(CO_2NHNH_2)_2} + 2H_2O + 2CH_3CH_2OH$$

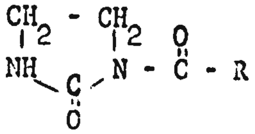
$$\text{I} + 2HCl + 2NaNO_2 \longrightarrow \underset{\text{II}}{CH_2(CON_3)_2} + 2NaCl + 4H_2O$$

$$\text{II} \xrightarrow{\Delta} \underset{\text{III}}{CH_2(NCO)_2}$$

Malonyl dihydrazide (I), m.p. 144-146°C, was obtained by the reaction of diethyl malonate and hydrazine hydrate. Malonyl diazide (II) was not isolated, but was immediately converted to methylene diisocyanate (III), b.p. 37-38°C/14 mm. Attempts to convert malonohydroxamic acid to methylene diisocyanate, thus avoiding the preparation of sensitive malonyl diazide, were unsuccessful (371, 14).

c. Ethylene Diisocyanate

Ethylene diisocyanate was prepared, by the method of Curtius and Hechtenburg,* from diethyl succinate by proceeding through the intermediate compounds, succinyl dihydrazide and succinyl diazide (330, 35; 515, 27). It was concluded that ethylene diisocyanate was not a satisfactory monomer for polymerization reactions because of the pronounced tendency of this material to form cyclic structures of the following general formula** (515, 27-30):



3. Nitro Diisocyanates

a. Discussion

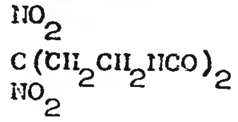
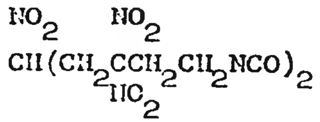
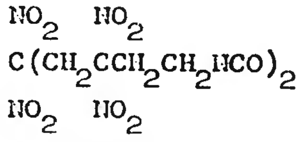
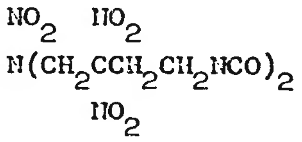
Table 6 lists those nitro and nitro-nitraza diisocyanates (and a single nitro triisocyanate) which were synthesized during the course of this program. All of these materials were obtained by the Curtius rearrangement of the appropriate azides. The latter compounds were prepared from the corresponding acid chlorides by reaction with sodium azide. Utilized to a greater extent than the other isocyanates in this table is 3,3-dinitro-1,5-pentane diisocyanate, which is discussed further in the following paragraph. Succeeding paragraphs (c, d, e, f) describe attempts to obtain a number of materials with which the research on nitro diisocyanates was concerned during the early phase of the program.

---

*Curtius and Hechtenburg, J. prakt. Chem. [2] 105, 289-318 (1923).
**Naegli and Lendorff, Helv. Chim. Acta 15, 49 (1932).

TABLE 6

NITRO DIISOCYANATES

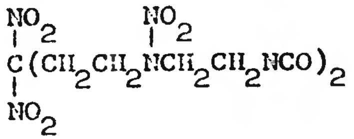
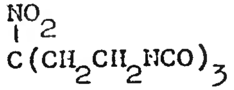
Name	Formula	m.p.	Urethane*	References
(1) 3,3-Dinitro-1,5-pentane Diisocyanate	 $\overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2NCO)_2$	37-38°	113-114°	See para B, 3, a
(2) 3,3,5,7,7-Pentanitro-1,9-nonane Diisocyanate	 $\overset{NO_2}{CH}(CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2NCO)_2$	oil	60-65°* and 107-108°	515, 10, 18, 22
(3) 3,3,5,5,7,7-Hexanitro-1,9-nonane Diisocyanate	 $\overset{NO_2}{\underset{NO_2}{C}}(CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2NCO)_2$	126-128°	--	540, 49; 563, 75
(4) 3,3,5,7,7-Pentanitro-5-aza-1,9-nonane Diisocyanate	 $\overset{NO_2}{N}(CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2NCO)_2$	106-108°	76-78° and 128-130°	621, 10; 712, 54; 740, 69

---

*The urethanes were the dimethyl urethanes, with the exception of 3,3,5,7,7-pentanitro-1,9-nonane diisocyanate, for which the diethyl derivative (exhibited a double melting point) was reported.

TABLE 6 (cont.)

NITRO DIISOCYANATES

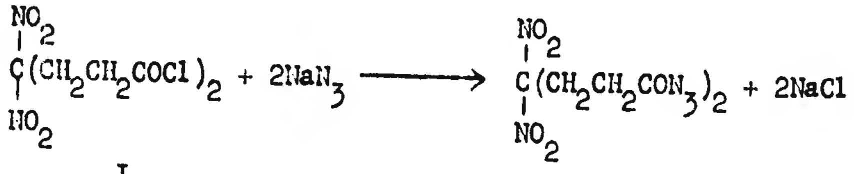
Name	Formula	m.p.	Urethane	References
(5) 3,6,6,9-Tetranitro-3,9-diaza-1,11-undecane Diisocyanate	 $\overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2\overset{NO_2}{N}CH_2CH_2NCO)_2$	88-90°	119.5-120°	638, 98; 663, 78
(6) Tri-(β-isocyanatoethyl)-nitromethane*	 $\overset{NO_2}{C}(CH_2CH_2NCO)_3$	--	--	712, 57

---

*Tri-(β-isocyanatoethyl)-nitromethane distilled at 160-165°/5 μ. The tris(diethylamine)-derivative melted at 121.5-122.5°C.

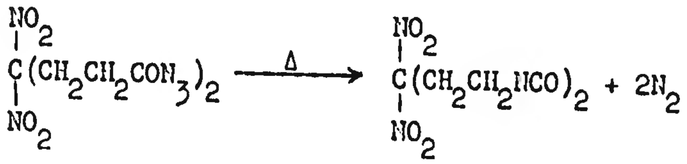
b. 3,3-Dinitro-1,5-pentane Diisocyanate

The preparation of 3,3-dinitro-1,5-pentane diisocyanate (386, 11) marked the first synthesis of a diisocyanate containing geminal dinitro groups.* The 3,3-dinitro-1,5-pentane diisocyanate proved to be one of the more desirable diisocyanates for polyurethane formation, and its preparation on a larger scale in the chemical pilot plant is described elsewhere (Section V). The synthesis was carried out according to the following equations:



$$\underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}(\mathrm{CH_2CH_2COCl})_2 + 2\mathrm{NaN_3} \longrightarrow \underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}(\mathrm{CH_2CH_2CON_3})_2 + 2\mathrm{NaCl}$$

I II



$$\underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}(\mathrm{CH_2CH_2CON_3})_2 \xrightarrow{\Delta} \underset{\mathrm{NO_2}}{\overset{\mathrm{NO_2}}{\mathrm{C}}}(\mathrm{CH_2CH_2NCO})_2 + 2\mathrm{N_2}$$

II III

4,4-Dinitro-1,7-heptanedioyl chloride (I) (see paragraph II,C,3,c) was converted to 4,4-dinitro-1,7-heptanedioyl azide (II) by reaction with sodium azide while employing a heterogeneous reaction medium (386, 11; 404, 7; 417, 5; 686, 69). An early laboratory procedure (468, App. B) for the preparation of 3,3-dinitro-1,5-pentane diisocyanate (III) was based on experiments in which the diazide (m.p. 68-69°C, dec.; impact stability 20-30 cm/2 kg) was isolated in crystalline form (417, 5). A safer and more satisfactory procedure (686, 69) involved the isolation of the diazide in chloroform solution with subsequent thermal rearrangement to the diisocyanate.

---

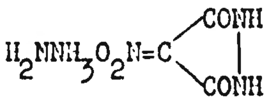
*Herzog, Gold, and Geckler, J. Am. Chem. Soc. 73, 749 (1951).

A comparison of distillation with recrystallization techniques for the purification of 3,3-dinitro-1,5-pentane diisocyanate indicated the latter to be more satisfactory (404, 7). Failure to obtain 4,4-dinitro-1,7-heptanedioyl hydrazide (371, 12; 317, 5; 941, 36) prevented the formation of 3,3-dinitro-1,5-pentane diisocyanate by a second method involving the intermediate dihydrazide and diazide. The diisocyanate, m.p. 37-38°C, gave [illegible] thyl 5,5-dinitro-2,8-diaza-1,9-nonanedioate, m.p. 113-114°C, on treatment with methanol (404, 7). The aniline derivative, N,N'-diphenyl 5,5-dinitro-2,8-diaza-1,9-nonanediamide, melted at 186-187°C (386, 11).

Hydrolysis of the dimethyl urethane using hydrochloric acid yielded 3,3-dinitro-1,5-pentanediamine dihydrochloride, m.p. 225-230°C (dec), and the latter gave the free amine, m.p. 73-74°C, on treatment with alcoholic sodium hydroxide (417, 39; 468, App. B). The diacetyl and dibenzoyl derivatives of 3,3-dinitro-1,5-pentanediamine melted at 155-157°C and 144-145°C, respectively (417, 39). The 3,3-dinitro-1,5-pentane diamine was used in the preparation of 4,7,7,10-tetranitro-4,10-diaza-1,13-tridecanedioic acid (II,C,3,g). SPIA data sheets were prepared for 3,3-dinitro-1,5-pentane diisocyanate (424) and 3,3-dinitro-1,5-pentanediamine (468).

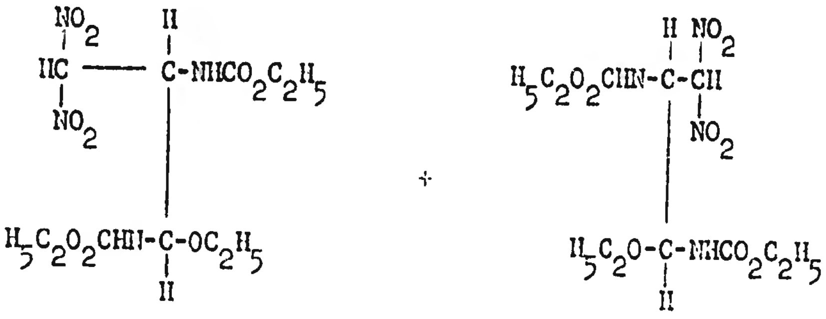
c. Nitromethylene Diisocyanate, Attempted Preparation

An early report (345, 18) proposed the preparation of nitromethylene diisocyanate from diethyl nitromalonate via the intermediate dihydrazide and diazide. This work was abandoned when attempts to obtain nitromalonyl dihydrazide (371, 12; 386, 7) gave low yields of a product for which the analytical data corresponded to the following structure:

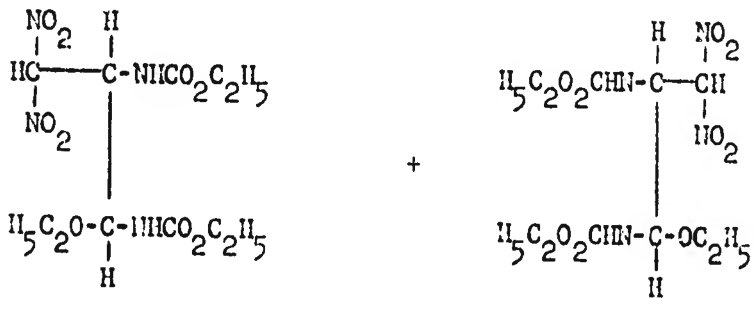


d. Trinitromethyl Ethylene Diisocyanate, Attempted Preparation

Initial work on the proposed synthesis of trinitromethyl ethylene diisocyanate involved unsuccessful attempts to add nitroform to diethyl maleate (371, 11), diethyl fumarate, and fumaric acid (386, 7; 404, 8). In an alternative approach, trans-1,2-ethene diisocyanate was prepared from diethyl fumarate via the dihydrazide and diazide (404, 9), but attempts to add nitroform to the unsaturated diisocyanate were also unsuccessful. The reactive isocyanate groups were blocked by conversion to trans-1,2-ethene di(ethylcarbamate), m.p. 220°C (404, 10), which reacted with nitroform in ethanol solution to yield two products, m.p. 173° and m.p. 127°C (417, 6). A thorough investigation of these products (417, 7; 424, 4) indicated that the addition of nitroform to the diethyl carbamate was accompanied by the elimination of nitrous acid and the addition of ethanol. The isolated products were postulated as two racemic mixtures of the following structures:



and



e. 2,2,2-Trinitroethyl Methylene Diisocyanate, Attempted Preparation

The preparation of 2,2,2-trinitroethyl methylene diisocyanate, isomeric with trinitromethyl ethylene diisocyanate (paragraph II,B,3,d), was never accomplished. Attempts to convert diethyl 2,2,2-trinitroethylmalonate* to the corresponding dihydrazide resulted in the reduction of the starting material to diethyl 2,2-dinitroethyl malonate, as shown by the bromination of the latter material (417, 5). When diisopropylidene malonyl dihydrazide was condensed with formaldehyde and nitroform in an effort to produce the diisopropylidene trinitroethyl malonyl dihydrazide, no pure product could be isolated (424, 7).

f. 2,2,2-Trinitroethyl Ethylene Diisocyanate, Attempted Preparation

In preparing intermediates for the proposed synthesis of 2,2,2-trinitroethyl ethylene diisocyanate, the addition of nitroform to dimethyl itaconate yielded dimethyl (2,2,2-trinitroethyl)-succinate (b.p. 137-140°C/3 mm, n_D^{20} 1.4648), but attempts to convert the latter material to the corresponding dihydrazide were unsuccessful (404, 11). The (2,2,2-trinitroethyl)-succinic acid, m.p. 176-177°C, obtained by the hydrolysis of the methyl ester or by the addition of nitroform to itaconic acid, gave only the anhydride, m.p. 86-88°C, in attempts to prepare the acid chloride (417, 13), thus preventing the desired preparation of the dihydrazide or diazide from this material.

4. Nitraza Diisocyanates

a. Discussion

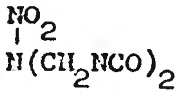
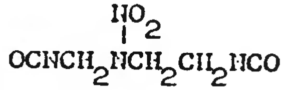
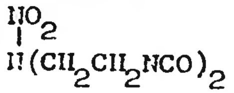
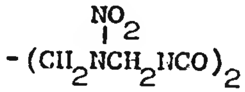
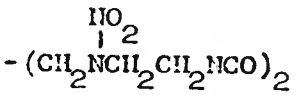
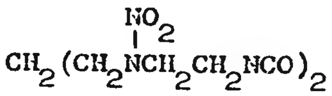
The nitraza diisocyanates listed in Table 7, were obtained by the general procedure utilized for the preparation of nitro diisocyanates (paragraph II,B,3, above) involving the conversion of a diacid chloride to the diisocyanate via the intermediate diazide. 3-Nitraza-1,5-pentane diisocyanate, which is described in some detail below (paragraph II,B,4,b), was also prepared from the dihydrazide.

---

*U. S. Rubber Co., Report No. 5, p. 22.

TABLE 7

NITRAZA DIISOCYANATES

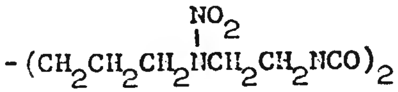
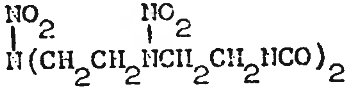
Name	Formula	m.p.	Dimethyl Urethane, m.p.	Reference
(1) 2-Nitraza-1,3-propane Diisocyanate	 $\overset{\overset{\displaystyle NO_2}{\mid}}{N}(CH_2NCO)_2$	(liquid)	--	920, 17-18
(2) 2-Nitraza-1,4-butane Diisocyanate*,**	 $OCNCH_2\overset{\overset{\displaystyle NO_2}{\mid}}{N}CH_2CH_2NCO$	(liquid)	133-134°	772, 76-78; 807, 68-69
(3) 3-Nitraza-1,5-pentane Diisocyanate*,**	 $\overset{\overset{\displaystyle NO_2}{\mid}}{N}(CH_2CH_2NCO)_2$	35.5°	150-152°	712, 52-54
(4) 2,5-Dinitraza-1,6-hexane Diisocyanate	 $-(CH_2\overset{\overset{\displaystyle NO_2}{\mid}}{N}CH_2NCO)_2$	98-100°	169-171°	833, 45-47
(5) 3,6-Dinitraza-1,8-octane Diisocyanate*	 $-(CH_2\overset{\overset{\displaystyle NO_2}{\mid}}{N}CH_2CH_2NCO)_2$	91.5-93°	182.5-184°	638, 96-97
(6) 3,7-Dinitraza-1,9-nonane Diisocyanate	 $CH_2(CH_2\overset{\overset{\displaystyle NO_2}{\mid}}{N}CH_2CH_2NCO)_2$	--	139.5-140°	807, 71-73

---

*3-Nitraza-1,5-pentane diisocyanate and 3,6-dinitraza-1,8-octane diisocyanate were converted to the corresponding diamine dihydrochlorides (740, 72-74). An unsuccessful attempt was made to prepare 2-nitraza-1,4-butanediamine dihydrochloride (807, 73).

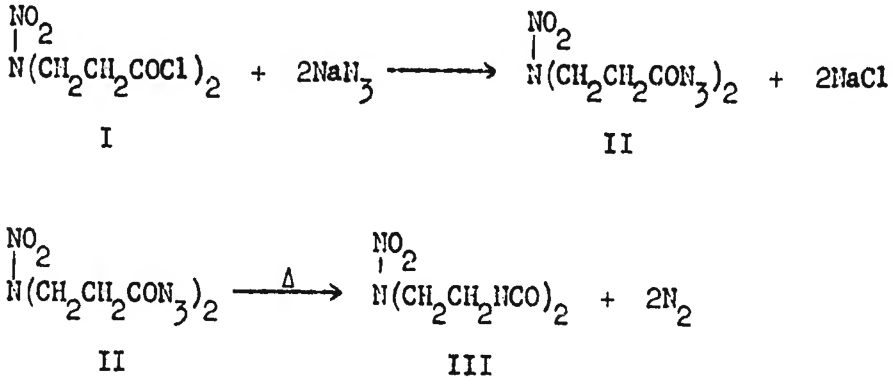
**SPIA data sheets were prepared for 3-nitraza-1,5-pentane diisocyanate (807) and 2-nitraza-1,4-butane diisocyanate (833).

TABLE 7 (cont.)

Name	Formula	m.p.	Dimethyl Urethane, m.p.	Reference
(7) 3,10-Dinitraza-1,12-dodecane Diisocyanate	 $-(CH_2CH_2CH_2\overset{NO_2}{N}CH_2CH_2NCO)_2$	75-76°	164.5-166	833, 48-49
(8) 3,6,9-Trinitraza-1,11-undecane Diisocyanate	 $\overset{NO_2}{N}(CH_2CH_2\overset{NO_2}{N}CH_2CH_2NCO)_2$	90-95°	186-189°	807, 69-71

b. 3-Nitraza-1,5-pentane Diisocyanate

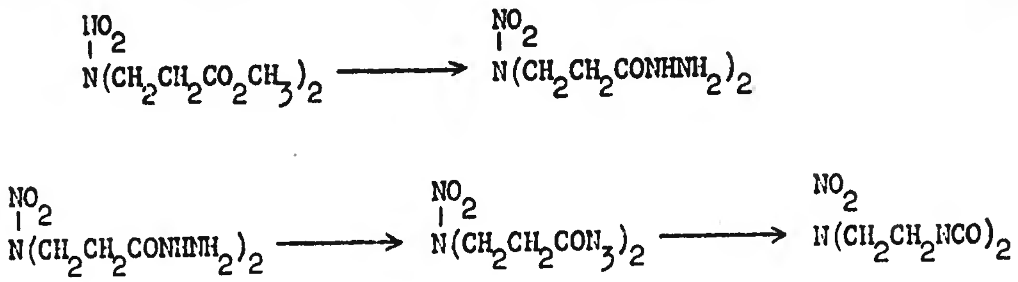
From the standpoint of availability, as well as utility, 3-nitraza-1,5-pentane diisocyanate was possibly the most promising diisocyanate derived from this program, although a number of other diisocyanates of higher specific impulse were obtained. The feasibility of large-scale preparation of 3-nitraza-1,5-pentane diisocyanate and the various intermediates was demonstrated in the pilot plant production of this monomer (Section V). Currently, 3-nitraza-1,5-pentane diisocyanate (III) is obtained by the following reactions:



$$\underset{\text{I}}{\overset{NO_2}{\overset{|}{N}}(CH_2CH_2COCl)_2} + 2NaN_3 \longrightarrow \underset{\text{II}}{\overset{NO_2}{\overset{|}{N}}(CH_2CH_2CON_3)_2} + 2NaCl$$

$$\underset{\text{II}}{\overset{NO_2}{\overset{|}{N}}(CH_2CH_2CON_3)_2} \xrightarrow{\Delta} \underset{\text{III}}{\overset{NO_2}{\overset{|}{N}}(CH_2CH_2NCO)_2} + 2N_2$$

4-Nitraza-1,7-heptanedioyl chloride (I) (II,C,4,d) was converted to the corresponding diazide (II) by treatment of a chloroform solution of the acid chloride with aqueous sodium azide at 5°C. Because of the solubility of the diazide in the chloroform layer, it was possible to avoid the actual isolation of this product. The chloroform solution was dried, and the diazide was rearranged to 3-nitraza-1,5-pentane diisocyanate on heating this solution (712, 53). In this original synthesis of the diisocyanate, the low-melting product (m.p. 35.5°C; SPIA Data Sheet, 807 App.) was characterized by conversion to the dimethyl urethane, methyl 5-nitro-2,5,8-triaza-1,9-nonanedioate. The treatment of the diisocyanate with hydrochloric acid yielded 3-nitraza-1,5-pentanediamine dihydrochloride, m.p. 258.5°-261.5°C (dec), and the latter gave the free amine as a viscous oil on neutralization with sodium methoxide (740, 74). An alternative method which was used for the preparation of 3-nitraza-1,5-pentane diisocyanate is shown in the following diagram (941, 35):



$$\overset{NO_2}{\overset{|}{N}}(CH_2CH_2CO_2CH_3)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2CONHNH_2)_2$$

$$\overset{NO_2}{\overset{|}{N}}(CH_2CH_2CONHNH_2)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2CON_3)_2 \longrightarrow \overset{NO_2}{N}(CH_2CH_2NCO)_2$$

4-Nitraza-1,7-heptanedioyl hydrazide, m.p. 114-115°C, was obtained by treatment of methyl 4-nitraza-1,7-heptanedioate with hydrazine, and the reaction of this product with nitrous acid yielded the diazide. Thus far, this alternate route to 3-nitraza-1,5-pentane diisocyanate has not been investigated on a large scale but it does offer the advantages of eliminating the use or presence of poisonous or hazardous materials, such as sodium azide, hydrazoic acid, and thionyl chloride.

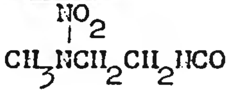
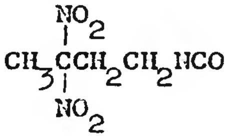
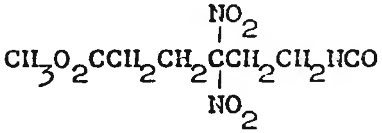
5. Monoisocyanates

The utilization of nitro and nitraza monoisocyanates has been restricted to the formation of polyurethanes by the reaction of these materials with hydroxyl-containing polymers such as cellulose and polyvinyl alcohol. However, these isocyanates were also used extensively on the explosives program, in the preparation of new explosive derivatives.

The monoisocyanates (Table 8) were all prepared by rearrangement of acyl azides, which were obtained from the corresponding acyl chlorides.

TABLE 8

MONOISOCYANATES

Name	Formula	b.p.	n_D^t	Urethane*	Reference
(1) 3-Nitrazabutyl Isocyanate**	 $CH_3\overset{NO_2}{N}CH_2CH_2NCO$	m.p., 25-26°	--	88.5°	907, 56; 941, 37
(2) 3,3-Dinitrobutyl Isocyanate**	 $CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2NCO$	106-110°/1 µ	n_D^{25} 1.4708	48-49°	638, 99
(3) 3,3,3-Trinitropropyl Isocyanate**, ***	$(NO_2)_3CCH_2CH_2NCO$	73-75°/1 µ	n_D^{25} 1.4805	65.5-66°*	563, 76; 538, 5
(4) 5-Carbomethoxy-3,3-dinitropentyl**, *** Isocyanate	 $CH_3O_2CCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2NCO$	140-150°/1 µ	n_D^{24} 1.4793	75°	686, 70; 622, 80

---

*The methyl urethanes were prepared with the exception of 3,3,3-trinitropropyl isocyanate for which the ethyl derivative was reported.

**3-Nitrazabutylamine hydrochloride (904, 13), 3,3-dinitrobutylamine hydrochloride (638, 101; 663, 81), and 3,3,3-trinitropropylamine hydrochloride (660, 2) were obtained from the corresponding isocyanates. The hydrolysis of the methyl urethane of 5-carbomethoxy-3,3-dinitropentyl isocyanate in hydrochloric acid yielded 6-amino-4,4-dinitrohexanoic acid hydrochloride (622, 81).

***Treatment of 3,3,3-trinitropropyl isocyanate and 5-carbomethoxy-3,3-dinitropentyl isocyanate with water yielded N,N'-<u>bis</u>-(3,3,3-trinitropropyl)-urea (589, 10; 1048, 3) and N,N'-di-(5-carbomethoxy-3,3-dinitropentyl)-urea (686, 67).

C. ACIDS

1. Introduction

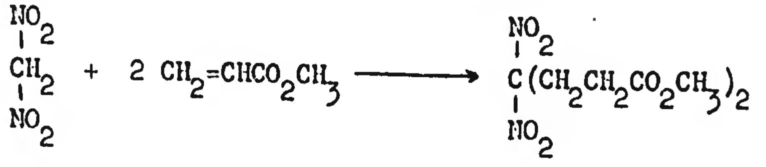
Although nitro dicarboxylic acids were used in polyester formulations during the early phase of the nitropolymer program, the current importance of nitro- and nitramino-containing acids is based on their wide utilization as intermediates in the preparation of diisocyanates, alcohols and diols, and esters. The diisocyanates (paragraph II,B) and diols (paragraph II,D) are extensively used in the preparation of nitropolyurethanes (paragraph III,B). The nitroesters (the esters of monocarboxylic acids in particular) have been tested and used extensively as plasticizers, for both nitropolyurethanes and nitroalkyl polyacrylates, on this program and in associated work (Contracts NOrd 16584 and NOas 54-399-c). Certain of the acids prepared were also adapted to the synthesis of new explosive compounds on Contract N7onr-46208.

2. Methods of Preparation

a. Michael Reaction

Probably the most productive method for the preparation of aliphatic nitro acids has been the Michael-type reaction involving the addition of nitroalkanes (containing one or more active hydrogen atoms attached to carbon) to negatively substituted olefins such as α, β-unsaturated acids, esters, and nitriles. This alkylation reaction provided a ready means of obtaining monofunctional and bifunctional derivatives (and trifunctional adducts, in the case of nitromethane) in fair to high yields. The use of this reaction in the preparation of 4,4,4-trinitrobutyric acid (468, 23), methyl 4,4-dinitro-1,7-heptanedioate (371, 12), and tri-(β-cyanoethyl)-nitromethane (712, 49) is illustrated in the following equations:

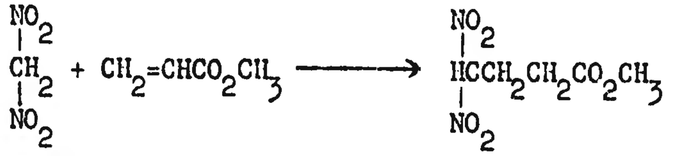
$$(O_2N)_3CH + CH_2{=}CHCO_2H \longrightarrow (O_2N)_3CCH_2CH_2CO_2H \qquad (1)$$



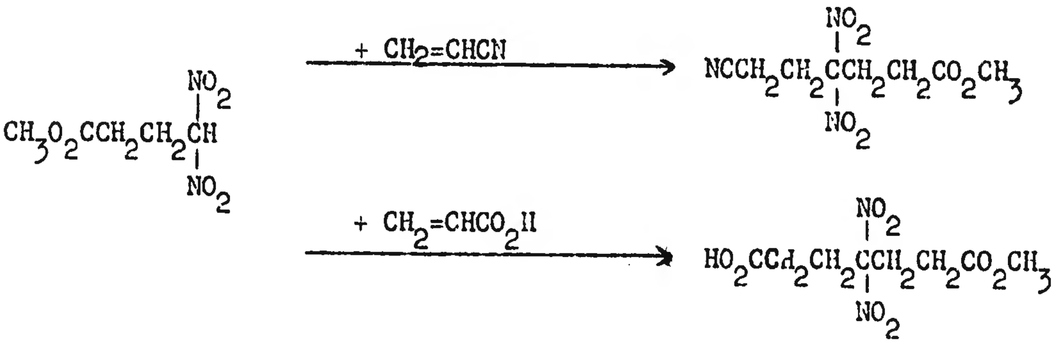
$$O_2N{-}CH_2{-}NO_2 + 2\ CH_2{=}CHCO_2CH_3 \longrightarrow (O_2N)_2C(CH_2CH_2CO_2CH_3)_2 \qquad (2)$$

$$CH_3NO_2 + 3\ CH_2{=}CHCN \longrightarrow O_2NC(CH_2CH_2CN)_3 \qquad (3)$$

The reaction proceeds in step-wise fashion, permitting the isolation of 1:1 adducts in high yields through the proper choice of reaction conditions. For example, the above reaction of dinitromethane and methyl acrylate (Equation (2)) was stopped at methyl 4,4-dinitrobutyrate (404, 49), and the latter material was utilized in the preparation of methyl 6-cyano-4,4-dinitrohexanoate (457, 11) and methyl 6-carboxy-4,4-dinitrohexanoate (622, 80) by reaction with acrylonitrile and acrylic acid, as indicated below.



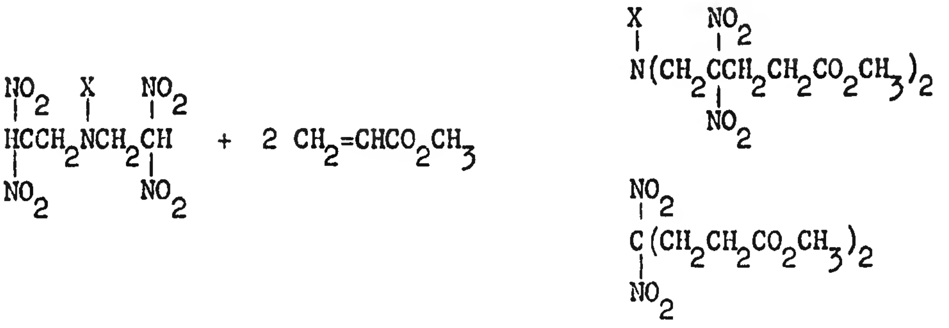
$$\underset{NO_2}{\overset{NO_2}{CH_2}} + CH_2{=}CHCO_2CH_3 \longrightarrow \underset{NO_2}{\overset{NO_2}{HC}}CH_2CH_2CO_2CH_3 \qquad (4)$$



$$CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2}{CH}} \xrightarrow{+\ CH_2{=}CHCN} NCCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3 \qquad (5)$$

$$CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2}{CH}} \xrightarrow{+\ CH_2{=}CHCO_2H} HO_2CCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3$$

Despite the utility of the Michael reaction, a number of nitro compounds containing replaceable hydrogen atoms do not undergo this reaction. For example, 2,2,2',2'-tetranitrodiethylamine (417, 14) and the N-nitro (424, 21) and N-cyano (424, 23) derivatives did not give the expected Michael adducts on reaction with methyl acrylate (424, 21-25). Instead, methyl 4,4-dinitro-1,7-heptanedioate, the 2:1 adduct of methyl acrylate and dinitromethane (Equation (2)), was formed, apparently due to the disproportionation of the original nitro compounds under the basic or mildly alkaline conditions of the Michael reaction.



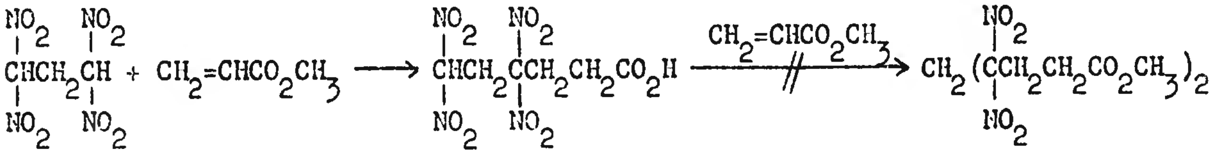
$$\underset{NO_2}{\overset{NO_2}{HC}}CH_2\overset{X}{N}CH_2\underset{NO_2}{\overset{NO_2}{CH}} + 2\ CH_2{=}CHCO_2CH_3 \qquad \overset{X}{N}(CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3)_2 \qquad \underset{NO_2}{\overset{NO_2}{C}}(CH_2CH_2CO_2CH_3)_2$$

(6)

where X = H, NO_2, CN

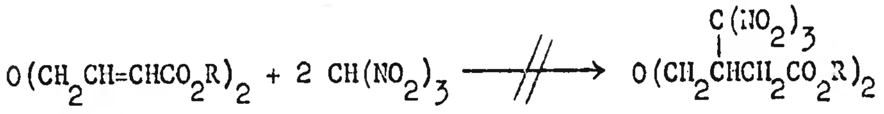
A similar polynitroalkane, 1,1,3,3-tetranitropropane, reacted with 1 mole of methyl acrylate to yield methyl 4,4,6,6-tetranitrohexanoate (424, 23), but the latter would not react further to give methyl 4,4,6,6-tetranitro-1,9-nonanedioate (424, 23-25).

(7)



$$\underset{NO_2}{\overset{NO_2}{CH}}CH_2\underset{NO_2}{\overset{NO_2}{CH}} + CH_2{=}CHCO_2CH_3 \longrightarrow \underset{NO_2}{\overset{NO_2}{CH}}CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2H \xrightarrow[\quad /\!/ \quad]{CH_2{=}CHCO_2CH_3} CH_2(\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3)_2$$

The Michael reaction is further limited by the fact that all negatively substituted olefins do not undergo this reaction with nitroalkanes. Previous summary reports (461, 494), which were compiled following much of the basic work with the Michael reaction, described the variety of successful and unsuccessful additions of dinitromethane and nitroform to negatively substituted olefins. On the basis of these summaries, it was not too surprising that the attempted addition of nitroform to ω,ω'-dicarboxydiallyl ether (468, 25) or the corresponding dimethyl ester (482, 18) was unsuccessful.

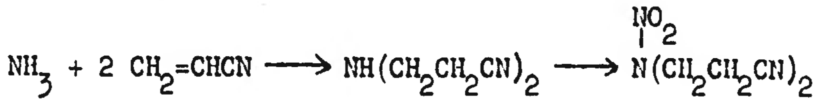


$$O(CH_2CH{=}CHCO_2R)_2 + 2\ CH(NO_2)_3 \xrightarrow{\ /\!/\ } O(CH_2\overset{C(NO_2)_3}{CH}CH_2CO_2R)_2$$

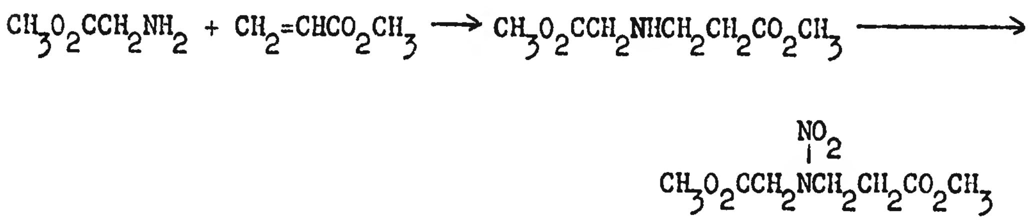
(8)

where R = H, CH_3

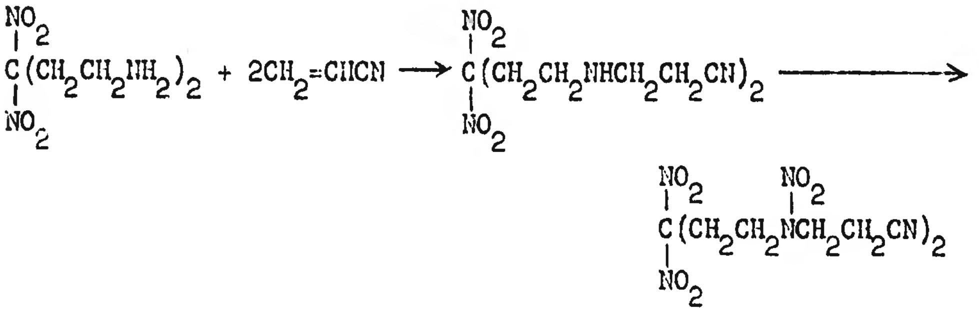
A second variation of the Michael reaction involving the addition of primary amines to α, β-conjugated carbonyls provides a ready means for the preparation of secondary amines. The latter materials were extensively used, on this program, as a source of nitraza nitriles, esters, and acids as shown in the syntheses of di-(β-cyanoethyl)-nitramine (686, 73; 712, 50), methyl 3-nitraza-1,6-hexanedioate (807, 60), and 4,7,7,10-tetranitro-4,10-diaza-1,13-tridecane dinitrile (638, 92).



$$NH_3 + 2\ CH_2{=}CHCN \longrightarrow NH(CH_2CH_2CN)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2CN)_2 \tag{9}$$



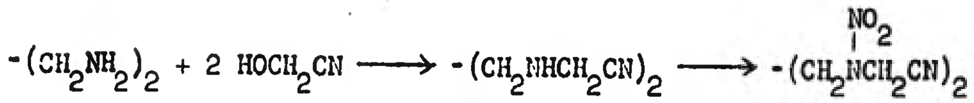
$$CH_3O_2CCH_2NH_2 + CH_2{=}CHCO_2CH_3 \longrightarrow CH_3O_2CCH_2NHCH_2CH_2CO_2CH_3 \xrightarrow{\qquad\quad} CH_3O_2CCH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2CO_2CH_3 \tag{10}$$



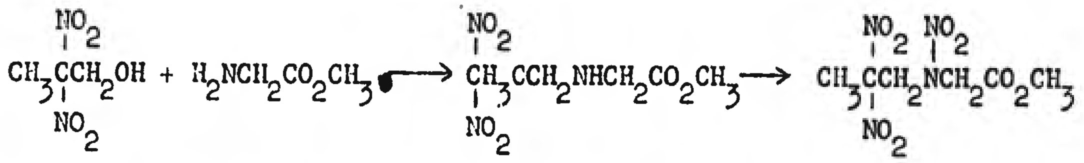
$$\underset{NO_2}{\underset{|}{\overset{NO_2}{\overset{|}{C}}}}(CH_2CH_2NH_2)_2 + 2CH_2{=}CHCN \longrightarrow \underset{NO_2}{\underset{|}{\overset{NO_2}{\overset{|}{C}}}}(CH_2CH_2NHCH_2CH_2CN)_2 \xrightarrow{\qquad\quad} \underset{NO_2}{\underset{|}{\overset{NO_2}{\overset{|}{C}}}}(CH_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2CN)_2 \tag{11}$$

b. Mannich Reaction

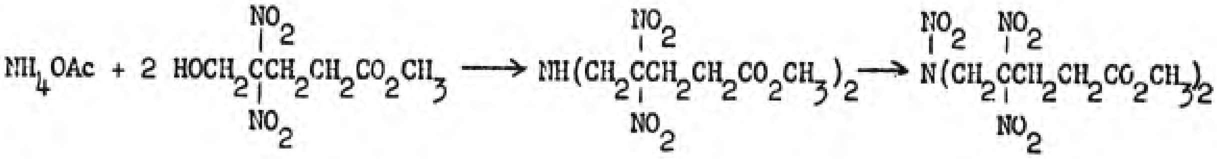
The Mannich condensation of ammonia or a primary or secondary amine, formaldehyde, and a compound containing at least one labile hydrogen atom results in the formation of materials containing an aminomethyl group (when ammonia is used) or an N-substituted aminomethyl group (when amines are used). β-Nitroalcohols, prepared by the addition of formaldehyde to nitroalkanes containing a labile hydrogen atom, undergo the Mannich condensation directly with amines. This is also true of such materials as glycolonitrile. The utilization of the Mannich reaction in the formation of nitraza acids, esters, and nitriles is exemplified in the preparation of 3,6-dinitraza-1,8-octane dinitrile (833, 41), methyl 3,5,5-trinitro-3-azahexanoate (663, 77), and methyl 4,4,6,8,8-pentanitro-6-aza-1,11-undecanedioate (622, 76).



$$-(CH_2NH_2)_2 + 2\ HOCH_2CN \longrightarrow -(CH_2NHCH_2CN)_2 \longrightarrow -(CH_2N(NO_2)CH_2CN)_2$$



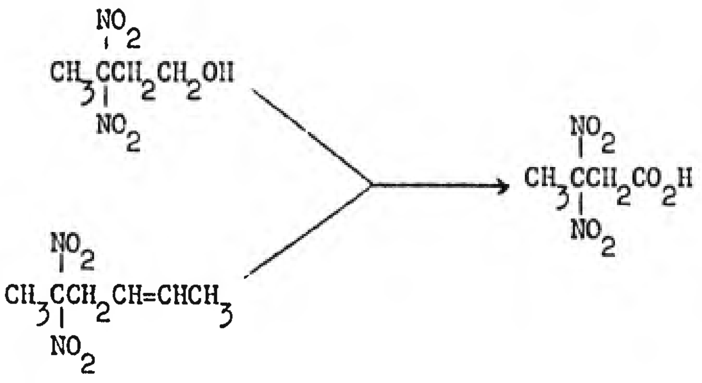
$$CH_3C(NO_2)_2CH_2OH + H_2NCH_2CO_2CH_3 \longrightarrow CH_3C(NO_2)_2CH_2NHCH_2CO_2CH_3 \longrightarrow CH_3C(NO_2)_2CH_2N(NO_2)CH_2CO_2CH_3$$



$$NH_4OAc + 2\ HOCH_2C(NO_2)_2CH_2CH_2CO_2CH_3 \longrightarrow NH(CH_2C(NO_2)_2CH_2CH_2CO_2CH_3)_2 \longrightarrow N(CH_2C(NO_2)_2CH_2CH_2CO_2CH_3)_2$$

c. Miscellaneous Reactions

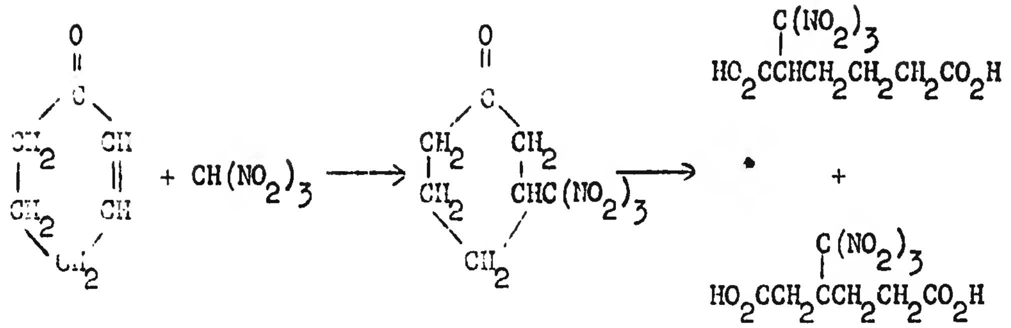
Despite numerous attempts to utilize methods other than the Michael or Mannich reaction for the preparation of nitro and nitraza acids or intermediates on this program, success along these lines was quite limited. 3,3-Dinitrobutyric acid was obtained by the oxidation of 3,3-dinitro-1-butanol or 5,5-dinitro-2-hexene, by means of permanganate in aqueous sulfuric acid solution (686, 56).



$$CH_3C(NO_2)_2CH_2CH_2OH \text{ or } CH_3C(NO_2)_2CH_2CH{=}CHCH_3 \longrightarrow CH_3C(NO_2)_2CH_2CO_2H$$

Similar attempts to oxidize 3,3-dinitro-1-butylamine and 1,3,3-trinitrobutane were unsuccessful (686, 55).

The following preparation of trinitromethyladipic acid met with limited success.



3-Trinitromethylcyclohexanone was obtained by the Michael addition of nitroform to 2-cyclohexene-1-one (590, 78), and subsequent oxidation of this material, using 70% nitric acid, gave a mixture of 2-trinitromethyl and 3-trinitromethyl-1,6-hexanedioic acids (622, 86).

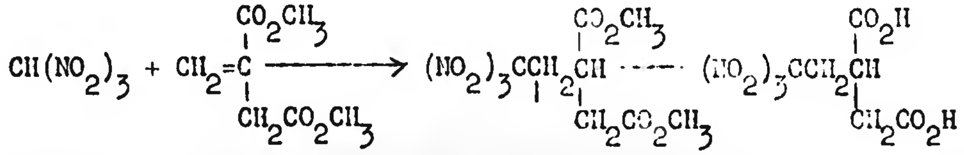
3. Nitro Dicarboxylic Acids

a. Discussion

Table 9 lists those nitro and nitro-nitraza dicarboxylic acids (and one nitro tricarboxylic acid) which were prepared on this program. Reference is made to the corresponding dimethyl ester, dinitrile, and diacid chloride where these materials were prepared. Subsequent paragraphs describe the method of preparation for each compound. The attempted preparation of a variety of compounds are also described, although this is not intended to be a complete compilation of the large number of unsuccessful experiments which were made.

b. (2,2,2-Trinitroethyl)-succinic Acid

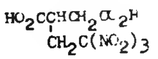
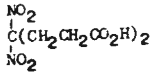
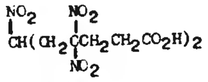
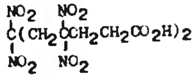
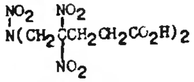
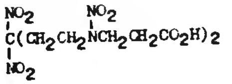
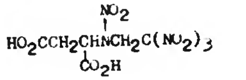
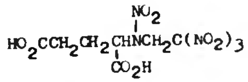
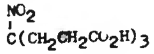
Dimethyl (2,2,2-trinitroethyl)-succinate was obtained by the Michael addition of nitroform to methyl itaconate in methanol solution (404, 11, 43) and the acid hydrolysis of the methyl ester yielded (2,2,2-trinitroethyl)-succinic acid (417, 13).



$$CH(NO_2)_3 + CH_2{=}C(CO_2CH_3)CH_2CO_2CH_3 \longrightarrow (NO_2)_3CCH_2CH(CO_2CH_3)CH_2CO_2CH_3 \cdots\cdots (NO_2)_3CCH_2CH(CO_2H)CH_2CO_2H$$

TABLE 9

NITRO DICARBOXYLIC ACIDS

Name	Formula	m.p.	Reference	Methyl Ester		Dinitrile			
				m.p.	Reference	m.p.	Reference	m.p.	Reference
(1) (2,2,2-Trinitroethyl)-succinic Acid	 $HO_2C\underset{CH_2C(NO_2)_3}{C}HCH_2CO_2H$	177°	417, 13, 38	b.p 137-140° /3mm; n_D^{20} 1.4648	404, 11, 43	--	--	86-88°*	417, 13, 38
(2) 4,4-Dinitro-1,7-heptanedioic Acid**	 $\overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2CO_2H)_2$	137°	371, 21, 62; 424, App. B; 632(I), 119	45°	371, 12, 54; 386, 18, 39; 404, 50; 424, App. B; 468, 27, App. B; 482, 32	79°	371, 21, 63	47-49°	371, 21; 386, 11, 35
(3) 4,4,6,8,8-Pentanitro-1,11-undecanedioic Acid**	 $\overset{NO_2}{C}H(CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2H)_2$	147° (dec)	499, 14; 515, 9	62-63°	499, 14; 515, 9	--	--	137°	499, 17
(4) 4,4,6,6,8,8-Hexanitro-1,11-undecanedioic Acid**	 $\overset{NO_2}{\underset{NO_2}{C}}(CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2H)_2$	154-155°(dec)	540, 43, 48; 563, 72, App. B	74°	515, 12; 540, 46	--	--	120-121°	540, 46
(5) 4,4,6,8,8-Pentanitro-6-aza-1,11-undecanedioic Acid	 $\overset{NO_2}{N}(CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2H)_2$	202-205°(dec)	621, 8	93°	621, 8; 622, 76	--	--	169-171°	621, 9; 712, 56
(6) 4,7,7,10-Tetranitro-4,10-diaza-1,13-tridecanedioic Acid	 $\overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2\overset{NO_2}{N}CH_2CH_2CO_2H)_2$	155-156°	638. 91, 92	79-80°	638, 93	118.5-119°	638, 92	103.5-105°	638, 93
(7) N-Nitro-N-(2,2,2-trinitroethyl)-aspartic Acid**	 $HO_2CCH_2\underset{CO_2H}{C}H\overset{NO_2}{N}CH_2C(NO_2)_3$	171.5-173.5°	515, 15	172-174°***	515, 15	--	--	68-69°	499, 10; 515, 13
(8) N-Nitro-N-(2,2,2-trinitroethyl)-glutamic Acid	 $HO_2CCH_2CH_2\underset{CO_2H}{C}H\overset{NO_2}{N}CH_2C(NO_2)_3$	133-134°	540, 50	117-118°	515, 17	--	--	65-66.5°	499, 10; 540, 51
(9) Tri-(β-carboxyethyl)-nitromethane	 $\overset{NO_2}{C}(CH_2CH_2CO_2H)_3$	186.5-188°	712, 48, 49	--	--	111-112°	712, 49	76-77.5°	712, 49

---

*The reported melting point is for 2,2,2-trinitroethylsuccinic anhydride which was obtained in all attempts to prepare the acid chloride.

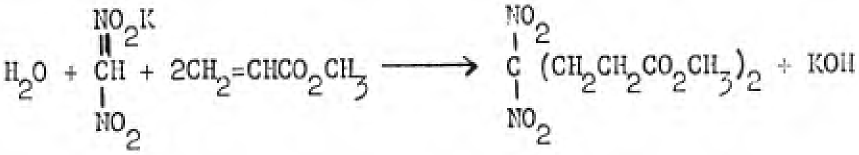
**SPIA data sheets were prepared for 4,4-dinitro-1,7-heptanedioic acid (386), 4,4,6,8,8-pentanitro-1,11-undecanedioic acid (563), 4,4,6,6,8,8-hexanitro-1,11-undecanedioic acid (563), and N-nitro-N-(2,2,2-trinitroethyl)-aspartic acid (563).

***The reported melting point is for the diethyl ester of N-nitro-N-(2,2,2-trinitroethyl)-aspartic acid.

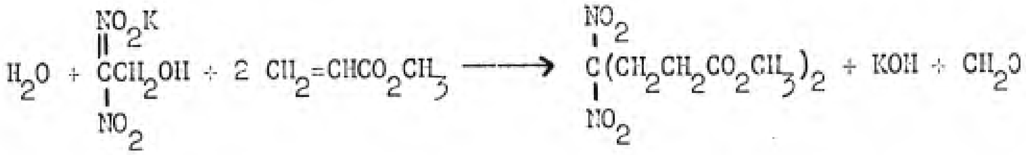
The latter material was also obtained directly by the addition of nitroform to itaconic acid in methyl ethyl ketone or nitromethane (417, 13, 38). The usual product melted at 177°, but a lower-melting isomer, m.p. 147°, was obtained in a few cases, which could be converted to the higher-melting material, by recrystallization from water. Attempts to convert the acid to the acid chloride using either thionyl chloride or phosphorous pentachloride in carbon tetrachloride, or phosphorous oxychloride solution, or by the use of a large excess of thionyl chloride, yielded only the anhydride (<u>loc. cit.</u>). Under more vigorous conditions, degradation occurred.

c. 4,4-Dinitro-1,7-heptanedioic Acid*

Methyl 4,4-dinitro-1,7-heptanedioate was obtained by the Michael reaction of potassium dinitromethane and two moles of methyl acrylate (371, 12, 54) or by reacting methyl acrylate directly with potassium dinitroethanol (<u>loc. cit.</u>; 424, App. B), thus eliminating the intermediate formation of dinitromethane.



$$H_2O + \overset{NO_2K}{\underset{NO_2}{CH}} + 2CH_2{=}CHCO_2CH_3 \longrightarrow \overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2CO_2CH_3)_2 + KOH$$



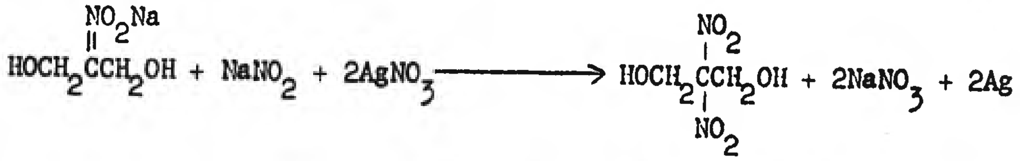
$$H_2O + \overset{NO_2K}{\underset{NO_2}{C}}CH_2OH + 2\,CH_2{=}CHCO_2CH_3 \longrightarrow \overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2CO_2CH_3)_2 + KOH + CH_2O$$

Comparable yields were obtained when potassium dinitromethane was prepared <u>in situ</u> by the alkaline deformylation of 2,2-dinitro-1,3-propanediol (386, 18, 39), although subsequent work (482, 32) indicated that the utilization of 2,2-dinitro-1,3-propanediol in this Michael reaction required only catalytic amounts of base. Utilizing the oxidative nitration reaction, the current procedure (468, 27; App. B) is based on the following series of reactions, which are carried out essentially as a one-step process without isolation of intermediates.

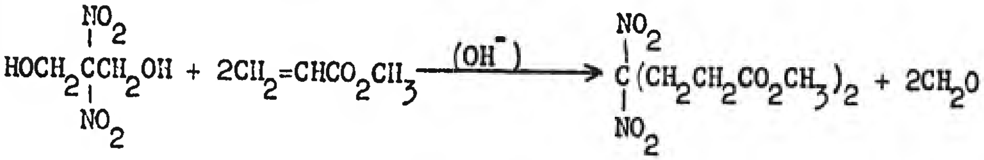
---

*Herzog, Gold, and Geckler, <u>J. Am. Chem. Soc.</u> <u>73</u>, 749 (1951).

$$CH_3NO_2 + 2CH_2O + NaOH \longrightarrow HOCH_2\overset{NO_2Na}{\overset{\|}{C}}CH_2OH + H_2O$$



$$HOCH_2\overset{NO_2Na}{\overset{\|}{C}}CH_2OH + NaNO_2 + 2AgNO_3 \longrightarrow HOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OH + 2NaNO_3 + 2Ag$$

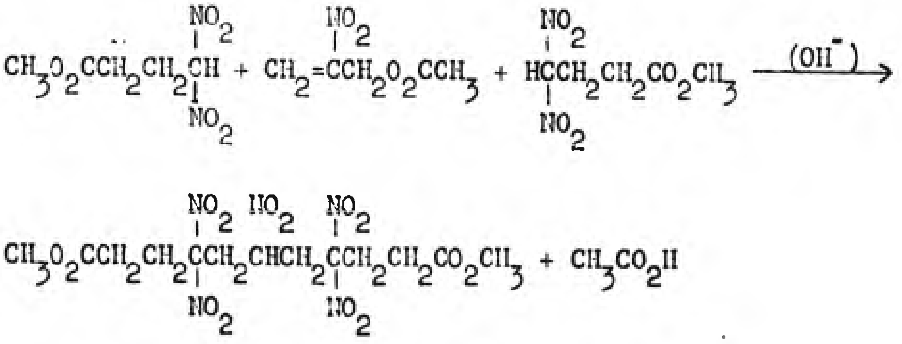


$$HOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OH + 2CH_2{=}CHCO_2CH_3 \xrightarrow{(OH^-)} \underset{NO_2}{\overset{NO_2}{C}}(CH_2CH_2CO_2CH_3)_2 + 2CH_2O$$

The hydrolysis of methyl 4,4-dinitro-1,7-heptanedioate to 4,4-dinitro-1,7-heptanedioic acid was originally carried out in hydrochloric acid (371, 21, 62; 424, App. B), but an alkaline hydrolysis was later adapted to this process.* Initial attempts to obtain 4,4-dinitro-1,7-heptanedioyl chloride by treatment of the acid with thionyl chloride in benzene (371, 21), ether, or chloroform (386, 36) were unsuccessful, necessitating the use of a large excess of thionyl chloride (386, 35; 457, App.). More recently, the use of thionyl chloride in chloroform was successfully employed for this conversion by catalysis with pyridine (941, 26). The large-scale preparation of these compounds, which are intermediates in the synthesis of 3,3-dinitro-1,5-pentane diisocyanate, is described in Section V.

d. 4,4,6,8,8-Pentanitro-1,11-undecanedioic Acid

Methyl 4,4,6,8,8-pentanitro-1,11-undecanedioate was prepared by the condensation of 2-nitroallyl acetate (482, 8), with 2 moles of sodium methyl 4,4-dinitrobutyrate (404, 49), according to the following equation (494, 14-16).



$$CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}H + CH_2{=}\overset{NO_2}{C}CH_2O_2CCH_3 + H\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3 \xrightarrow{(OH^-)}$$

$$CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{C}HCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3 + CH_3CO_2H$$

---

*Aerojet Report No. 632, Volume I, p. 119, 7 October 1952; Contract NOas 52-359.

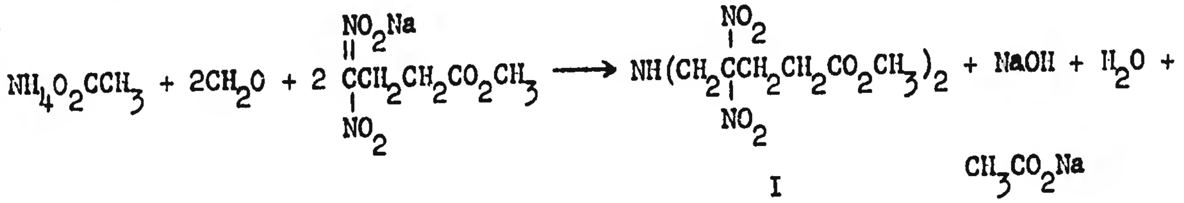
It was found that comparable results were obtained by the use of the precursor of 2-nitroallyl acetate, 1,3-diacetoxy-2-nitropropane, in the reaction with sodium methyl 4,4-dinitrobutyrate (515, 9). 4,4,6,8,8-Pentanitro-1,11-undecanedioic acid was prepared by the hydrolysis of the dimethyl ester in hydrochloric acid (499, 14), and the acid was converted to 4,4,6,8,8-pentanitro-1,11-undecanedioyl chloride by means of phosphorous pentachloride in phosphorous oxychloride solution (499, 17). Compounds in this series were quite sensitive to basic treatment, the dicarboxylic acid being readily degraded to succinic acid and the acid chloride forming the corresponding anilide, m.p. 170°(dec), in good yield only with aniline acetate in acetic acid solution (515, 22).

e. 4,4,6,6,8,8-Hexanitro-1,11-undecanedioic Acid

When it was found that the purification of 4,4,6,8,8-pentanitro-1,11-undecanedioic acid (paragraph d, above) was facilitated by recrystallization of the crude material from 70% nitric acid, the latter reagent was adapted to both the hydrolysis of the dimethyl ester and the purification of the dicarboxylic acid. However, a second dicarboxylic acid, which was shown to be 4,4,6,6,8,8-hexanitro-1,11-undecanedioic acid (540, 43-47, was also isolated from such experiments. The corresponding acid chloride was prepared and subsequently converted to 3,3,5,5,7,7-hexanitro-1,9-nonane diisocyanate (Table 6). Because of the pronounced difference in the solubility of the pentanitro and hexanitro diacid chlorides in benzene, this fact provided the basis for a more facile separation of the two acids (563, 72, App. B). The pentanitro and hexanitro derivatives were obtained in approximately a 2:1 ratio, limiting the large-scale preparation of pure materials in either series. Attempts to obtain methyl 4,4,6,6,8,8-hexanitro-1,11-undecanedioate by the oxidative nitration of the corresponding pentanitro ester (515, 12), or by direct nitration (540, 48), were unsuccessful.

f. 4,4,6,8,8-Pentanitro-6-aza-1,11-undecanedioic Acid

The preparation of methyl 4,4,6,8,8-pentanitro-6-aza-1,11-undecanedioate (II) was effected according to the following equations, involving the initial formation of methyl 4,4,8,8-tetranitro-6-aza-1,11-undecanedioate (I), m.p. 78-80°, by means of a Mannich reaction and by subsequent nitration of this material, using mixed acid or acetic anhydride-anhydrous nitric acid* (622, 76).



$$NH_4O_2CCH_3 + 2CH_2O + 2\,\underset{NO_2}{\overset{NO_2Na}{\overset{\|}{C}}}CH_2CH_2CO_2CH_3 \longrightarrow \underset{I}{NH(CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3)_2} + NaOH + H_2O + CH_3CO_2Na$$

$$NH(CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3)_2 \longrightarrow \overset{NO_2}{N}(CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3)_2$$

I II

A prior attempt to obtain methyl 4,4,8,8-tetranitro-6-aza-1,11-undecandioate (I) by the Michael reaction of dipotassium 2,2,2',2'-tetranitrodiethylamine with 2 moles of methyl acrylate gave only methyl 4,4-dinitro-1,7-heptanedioate (417, 14). A similar attempt to utilize N-nitro-2,2,2',2'-tetranitrodiethylamine in the formation of methyl 4,4,6,8,8-pentanitro-6-aza-1,11-undecanedioate (II) gave identical results (424, 21). Methyl 4,4,6,8,8-pentanitro-6-aza-1,11-undecanedioate was readily hydrolyzed to 4,4,6,8,8-pentanitro-6-aza-1,11-undecanedioic acid (621, 8), and the latter gave the corresponding acid chloride on treatment with phosphorous pentachloride (621, 9).

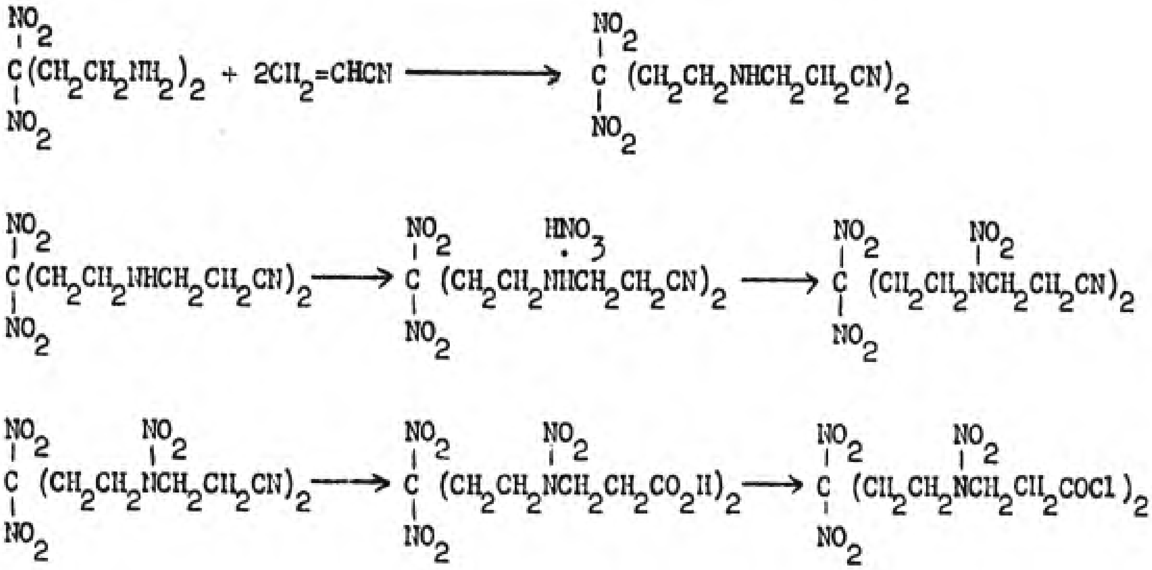
g. 4,7,7,10-Tetranitro-4,10-diaza-1,13-tridecanedioic Acid

By the utilization of 3,3-dinitro-1,5-pentanediamine (417, 15, 39; 468, App. B) in a Michael reaction with acrylonitrile, 7,7-dinitro-4,10-diaza-1,13-tridecane dinitrile was obtained. This material was converted to a bis-nitric acid salt, and the chloride-catalyzed nitration of the nitrate in acetic anhydride-anhydrous nitric acid yielded 4,7,7,10-tetranitro-4,10-diaza-1,13-tridecane dinitrile. The latter compound was hydrolyzed to 4,7,7,10-tetranitro-4,10-diaza-1,13-tridecanedioic acid in hydrochloric acid solution, and the corresponding acid chloride was obtained by treatment

---

*Aerojet Report No. 621, p. 7; Contract N7onr 46208.

of the dicarboxylic acid with a mixture of phosphorous pentachloride and phosphorous oxychloride. High conversions were obtained in each step of the synthesis (638, 91-93), which is illustrated in the following scheme.



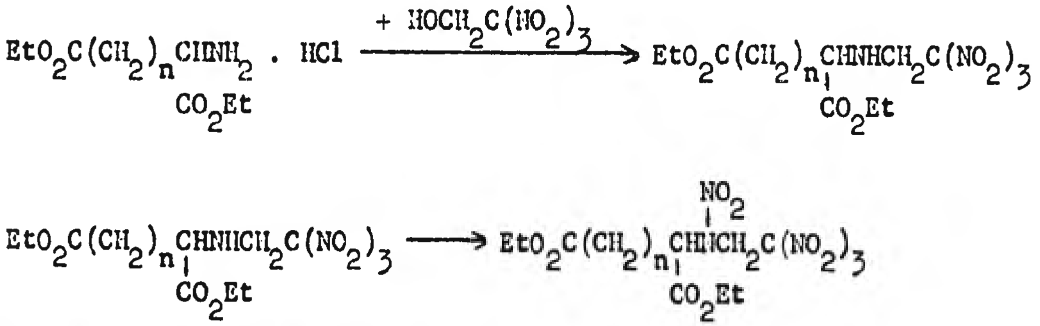
$$\overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2NH_2)_2 + 2CH_2{=}CHCN \longrightarrow \overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2NHCH_2CH_2CN)_2$$

$$\overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2NHCH_2CH_2CN)_2 \longrightarrow \overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2\overset{HNO_3}{\overset{\cdot}{N}}HCH_2CH_2CN)_2 \longrightarrow \overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2\overset{NO_2}{N}CH_2CH_2CN)_2$$

$$\overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2\overset{NO_2}{N}CH_2CH_2CN)_2 \longrightarrow \overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2\overset{NO_2}{N}CH_2CH_2CO_2H)_2 \longrightarrow \overset{NO_2}{\underset{NO_2}{C}}(CH_2CH_2\overset{NO_2}{N}CH_2CH_2COCl)_2$$

h. N-Nitro-N-trinitroethylaspartic Acid and N-Nitro-N-trinitroethyl-glutamic Acid

The preparation of N-nitro-N-trinitroethylaspartyl chloride* and N-nitro-N-trinitroethylglutamyl chloride** was repeated to obtain sufficient quantities of these materials for evaluation in polyester formation. The reaction sequence used in the synthesis is indicated below. Minor improvement in the preparation of certain intermediates was achieved (499, 10; 515, 13; 540, 50).



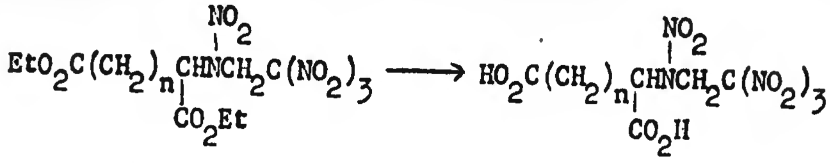
$$EtO_2C(CH_2)_n\underset{CO_2Et}{CH}NH_2 \cdot HCl \xrightarrow{+\ HOCH_2C(NO_2)_3} EtO_2C(CH_2)_n\underset{CO_2Et}{CH}NHCH_2C(NO_2)_3$$

$$EtO_2C(CH_2)_n\underset{CO_2Et}{CH}NHCH_2C(NO_2)_3 \longrightarrow EtO_2C(CH_2)_n\underset{CO_2Et}{CH}\overset{NO_2}{N}CH_2C(NO_2)_3$$

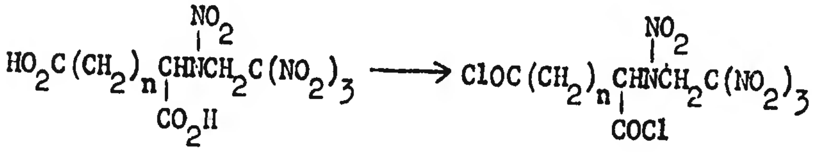
---

*Koller, PhD. Thesis, Purdue University.

**Purdue University Report No. 2, p. 26 (25 May 1950); No. 3, p. 23 (31 July 1950).



$$\mathrm{EtO_2C(CH_2)_n\underset{CO_2Et}{CH}\overset{NO_2}{N}CH_2C(NO_2)_3 \longrightarrow HO_2C(CH_2)_n\underset{CO_2H}{CH}\overset{NO_2}{N}CH_2C(NO_2)_3}$$



$$\mathrm{HO_2C(CH_2)_n\underset{CO_2H}{CH}\overset{NO_2}{N}CH_2C(NO_2)_3 \longrightarrow ClOC(CH_2)_n\underset{COCl}{CH}\overset{NO_2}{N}CH_2C(NO_2)_3}$$

where n = 1, aspartic acid derivatives;

where n = 2, glutamic acid derivatives.

i. Tri-(β-carboxyethyl)-nitromethane

Tri-(β-carboxyethyl)-nitromethane (712, 48) was obtained by the hydrolysis of tri-(β-cyanoethyl)-nitromethane,* and the tricarboxylic acid was converted to the acid chloride by treatment with thionyl chloride or phosphorous pentachloride in phosphorous oxychloride solution (712, 49).

$$\mathrm{O_2NC(CH_2CH_2CN)_3 \longrightarrow O_2NC(CH_2CH_2CO_2H)_3 \longrightarrow O_2NC(CH_2CH_2COCl)_3}$$

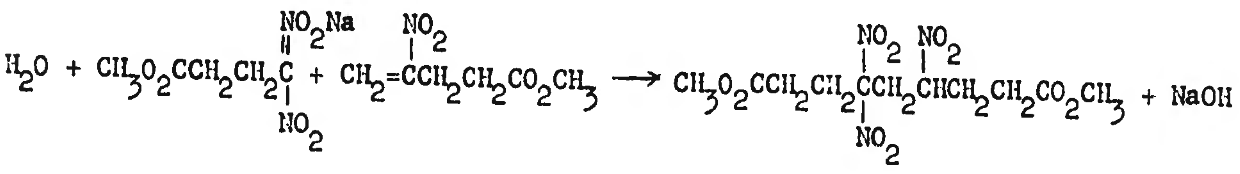
Tri-(β-chlorocarboxyethyl)-nitromethane was characterized by preparation of the tris-anilide, m.p. 192-193°.

j. Trinitromethyladipic Acid

For the preparation of this material, see paragraph II,C,2,c.

k. Methyl 4,4,6-Trinitro-1,9-nonanedioate

The formation of methyl 4,4,6-trinitro-1,9-nonanedioate was carried out by the Michael addition of the sodium salt of methyl 4,4-dinitrobutyrate (404, 49) to methyl 4-nitro-4-pentenoate (468, 12), according to the following equation (482, 16).



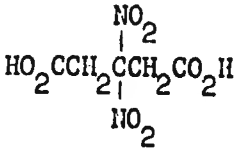
$$\mathrm{H_2O + CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2Na}{\overset{\|}{C}}} + CH_2{=}\overset{NO_2}{C}CH_2CH_2CO_2CH_3 \longrightarrow CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{C}HCH_2CH_2CO_2CH_3 + NaOH}$$

---

*Bruson and Riener, J. Am. Chem. Soc. 65, 23 (1943).

The identity of the crude product was proved by bromination to yield methyl 6-bromo-4,4,6-trinitro-1,9-nonanedioate, m.p. 105° (482, 17). However, the attempted hydrolysis of methyl 4,4,6-trinitro-1,9-nonanedioate gave a small amount of an unidentified crystalline material, m.p. 202-203°, which was not the desired 4,4,6-trinitro-1,9-nonanedioic acid as shown by analysis.

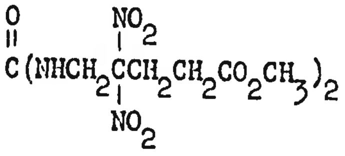
l. 3,3-Dinitro-1,5-pentanedioic Acid, Attempted Preparation



$$HO_2CCH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CO_2H$$

Considerable effort was applied to the attempted preparation of 3,3-dinitro-1,5-pentanedioic acid during the early stages of the program, because it offered possible routes to high-impulse propellants. Despite the many classical and ingenious methods investigated (371, 22; 386, 18; 417, 12; 424, 12; 457, 7; 468, 24), this compound was never synthesized.

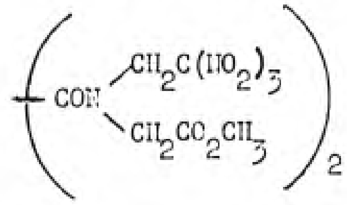
m. Methyl 4,4,10,10-Tetranitro-6,8-diaza-7-keto-1,13-tridecanedioate, Attempted Preparation



$$\overset{\overset{O}{\|}}{C}(NHCH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2CH_3)_2$$

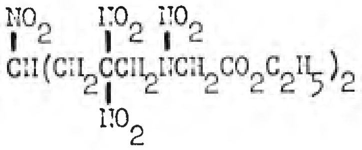
The preparation of this material by the Michael addition of N,N'-bis-(2,2-dinitroethyl)-urea and 2 moles of methyl acrylate was proposed, but the formation of the urea derivative by the reduction of N,N'-bis-(2,2,2-trinitroethyl)-urea (482, 31; 499, 23) and by Mannich reactions (499, 24) were unsuccessful. The direct formation of the desired ester by Mannich condensations of urea with methyl 5-hydroxy-4,4-dinitropentanoate and dimethylol urea with sodium methyl 4,4-dinitrobutyrate were also unsuccessful (499, 25).

n. N,N'-bis-(2,2,2-Trinitroethyl)-N,N'-bis-(carbomethoxymethyl)-oxamide, Attempted Preparation



The attempted formation of the above material (404, 20) by the Mannich reaction of the secondary amide, N,N'-bis-(carbomethoxymethyl)-oxamide (404, 44), and 2,2,2-trinitroethanol was unsuccessful. An alternate Mannich reaction of nitroform with N,N'-bis-(carbomethoxymethyl)-N,N'-bis-(methylol)-oxamide was not possible because of the inability to obtain the latter compound (417, 14).

o. Ethyl 3,5,5,7,9,9,11-Heptanitro-3,11-diaza-1,13-tridecanedioate, Attempted Preparation



$\overset{NO_2}{CH}(CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2CO_2C_2H_5)_2$

The reaction of ethyl 3,5,5,-trinitro-3-azapentanoate* with 2-nitroallyl acetate, in an attempted preparation of the highly nitrated ester, ethyl 3,5,5,7,9,9,11-heptanitro-3,11-diaza-1,13-tridecanedioate, yielded an intractable oil from which no pure product could be isolated (515, 11).

4. Nitraza Dicarboxylic Acids

a. Discussion

The nitraza dicarboxylic acids listed in Table 10 were prepared as intermediates in the synthesis of new nitraza diisocyanates (Table 7). In succeeding paragraphs, brief descriptions of the preparation of these acids and the corresponding acid chlorides are presented.

b. 3-Nitraza-1,5-pentanedioic Acid

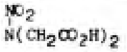
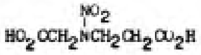
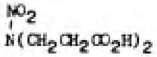
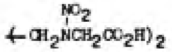
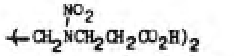
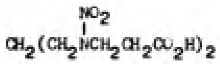
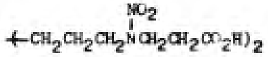
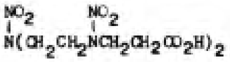
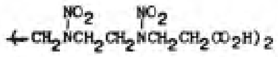
The following reaction sequence was used in the preparation of 3-nitraza-1,5-pentanedioic acid (868, 52):

---

*May, PhD. Thesis, Purdue University.

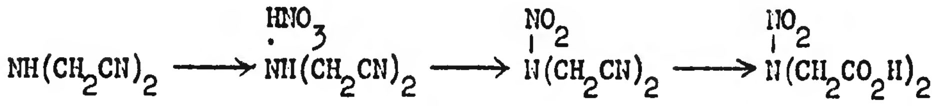
TABLE 10

NITRAZA DICARBOXYLIC ACIDS

Name	Formula	m.p.	Reference	Dinitrile		Acid Chloride		Methyl Ester	
				m.p.	Reference	m.p.	Reference	m.p.	Reference
(1) 3-Nitraza-1,5-pentanedioic Acid	 $\overset{NO_2}{N}(CH_2CO_2H)_2$	145-150°(dec)	868, 52; 920, 15	95.5-96.5°	868, 54	77-78°	920, 17	--	—
(2) 3-Nitraza-1,6-hexanedioic Acid	 $HO_2CCH_2\overset{NO_2}{N}CH_2CH_2CO_2H$	156.5-158°	740, 75; 772, 73-76; 807, 60	—	—	46-47°	772, 77	b.p. 110°/3 μ	772, 73-76; 807, 61
(3) Di-(β-carboxyethyl)-nitramine	 $\overset{NO_2}{N}(CH_2CH_2CO_2H)_2$	163-166°	712, 51	54-55°	686, 73,82; 712, 51,60	60-61.5°	712, 52	62-62.5°	712, 52
(4) 3,6-Dinitraza-1,8-octanedioic Acid	 $-(CH_2\overset{NO_2}{N}CH_2CO_2H)_2$	207-209°(dec)	833, 40	Indeterminate*	833, 41	105-106.5°	833, 46	84-85°	833, 47
(5) 4,7-Dinitraza-1,10-decanedioic Acid	 $-(CH_2\overset{NO_2}{N}CH_2CH_2CO_2H)_2$	141.5-142.5°	638, 87	130-131°	638, 89; 686, 85	94-94.5°	638, 90	124.5-125.5°	638, 90
(6) 4,8-Dinitraza-1,11-undecanedioic Acid	 $CH_2(CH_2\overset{NO_2}{N}CH_2CH_2CO_2H)_2$	147.5-149°	807, 66	81-82°	807, 67	60-61°	807, 72	56-57°	807, 72
(7) 4,11-Dinitraza-1,14-tetradecanedioic Acid	 $-(CH_2CH_2CH_2\overset{NO_2}{N}CH_2CH_2CO_2H)_2$	138.5-140°	833, 42	89.5-90.5°	833, 43	66.5-68.5°	833, 48	47-47.5°	833, 48
(8) 4,7,10-Trinitraza-1,13-tridecanedioic Acid	 $\overset{NO_2}{N}(CH_2CH_2\overset{NO_2}{N}CH_2CH_2CO_2H)_2$	176-178° and 186-189°	663, 77; 807, 61	149-151°	663, 76; 868, 71,82; 740, 66-68; 807, 63	100-108°	686, 68; 807, 70	112.5-114°	807, 64, 70
(9) 4,7,10,13-Tetranitraza-1,16-hexadecanedioic Acid	 $-(CH_2\overset{NO_2}{N}CH_2CH_2\overset{NO_2}{N}CH_2CH_2CO_2H)_2$	203.5-205.5°	833, 44	138.5-139.5°	740, 63; 833, 44	—	—	--	-

---

*3,6-Dinitraza-1,8-octane dinitrile decomposed in the range from 176 to 195°, depending upon the rate of heating.

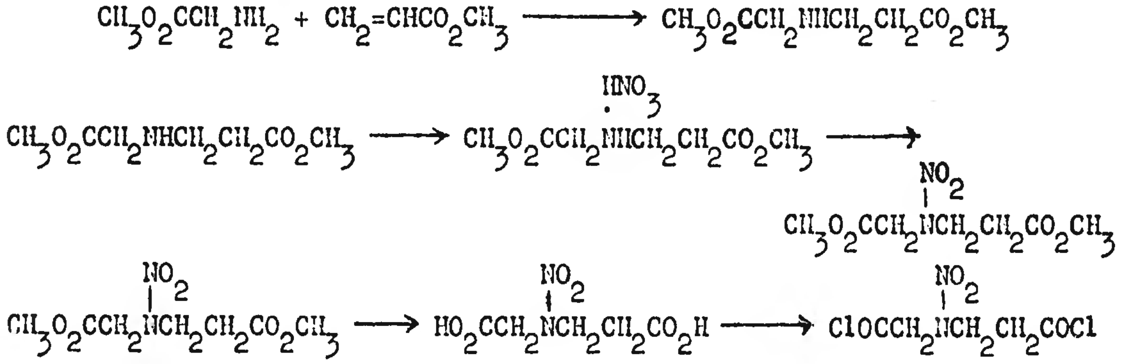


$$NH(CH_2CN)_2 \longrightarrow \overset{HNO_3}{\overset{\cdot}{N}}H(CH_2CN)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CN)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CO_2H)_2$$

Iminodiacetonitrile* was converted to the corresponding nitric acid salt, m.p. 128-132°, and a chloride-catalyzed nitration of the latter material gave nitriminodiacetonitrile.** The dinitrile was hydrolyzed to 3-nitraza-1,5-pentanedioic acid, and the latter was converted to the corresponding acid chloride by means of phosphorous pentachloride in phosphorous oxychloride (920, 17). Starting material was recovered from attempted oxidations of 4-nitromorpholine to 3-nitraza-1,5-pentanedioic acid (868, 52).

c. 3-Nitraza-1,6-hexanedioic Acid

The following procedure was the preferred method for obtaining 3-nitraza-1,6-hexanedioic acid (807, 60).



$$CH_3O_2CCH_2NH_2 + CH_2{=}CHCO_2CH_3 \longrightarrow CH_3O_2CCH_2NHCH_2CH_2CO_2CH_3$$

$$CH_3O_2CCH_2NHCH_2CH_2CO_2CH_3 \longrightarrow CH_3O_2CCH_2\overset{HNO_3}{\overset{\cdot}{N}}HCH_2CH_2CO_2CH_3 \longrightarrow CH_3O_2CCH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2CO_2CH_3$$

$$CH_3O_2CCH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2CO_2CH_3 \longrightarrow HO_2CCH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2CO_2H \longrightarrow ClOCCH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2COCl$$

Slight variations in the above procedure, involving the use of acrylonitrile in place of methyl acrylate in the Mannich reaction, were less satisfactory (740, 75; 772, 73). In such cases, difficulty was encountered in separating 3-nitraza-1,6-hexanedioic acid and ammonium chloride, the latter resulting from the hydrolysis of the cyano-group.

d. Di-(β-carboxyethyl)-nitramine

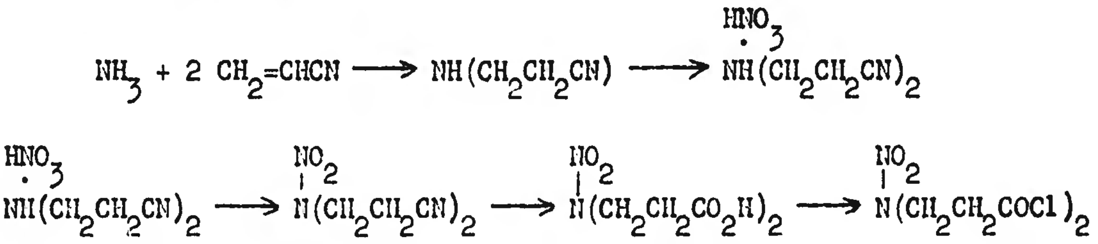
The synthesis of di-(β-carboxyethyl)-nitramine has been investigated more fully and has been carried out on a larger scale (Section V) than other nitraza dicarboxylic acids, because of its importance as an intermediate in the preparation of 3-nitraza-1,5-pentane diisocyanate.

---

*Dubsky, Ber. 54, 2659 (1921).

**Franchimont and Dubsky, Chem. Zentr. 1912 II, 1428; Wright et al, Can. J. Research 26B, 124 (1948).

Di-(β-carboxyethyl)-nitramine has the decided advantage over many dicarboxylic acids, such as 4,4-dinitro-1,7-heptanedioic acid, of being available from economical, commercial starting materials. The synthesis is indicated by the following equations (712, 50):



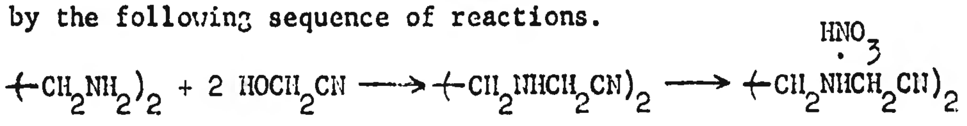
$$NH_3 + 2\ CH_2{=}CHCN \longrightarrow NH(CH_2CH_2CN) \longrightarrow \overset{HNO_3\ \cdot}{NH(CH_2CH_2CN)_2}$$

$$\overset{HNO_3\ \cdot}{NH(CH_2CH_2CN)_2} \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2CN)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2CO_2H)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2COCl)_2$$

Considerable difficulty was encountered in attempts to convert di-(β-cyanoethyl)-amine* to di-(β-cyanoethyl)-nitramine until the method of Wright,** involving the chloride-catalyzed nitration of di-(β-cyanoethyl)-ammonium nitrate using a mixture of acetic anhydride and anhydrous nitric acid, was utilized. These prior experiments included attempts to obtain di-(β-cyanoethyl)-nitramine by the nitration of di-(β-cyanoethyl)-amine (686, 74), N,N-di(β-cyanoethyl)-benzenesulfonamide (712, 60), and N,N-di(β-cyanoethyl)-urea (712, 62), and the attempted oxidation of di-(β-cyanoethyl)-nitrosamine (686, 82-87). The attempted nitration of di-(β-carboxyethyl)-amine hydrochloride was also unsuccessful (686, 74). The subsequent steps in the synthesis, the hydrochloric acid hydrolysis of di-(β-cyanoethyl)-nitramine to di-(β-carboxyethyl)-nitramine and the conversion of the latter to 4-nitraza-1,7-heptanedioyl chloride by means of thionyl chloride in chloroform solution, produced no difficulties.

e. 3,6-Dinitraza-1,8-octanedioic Acid

3,6-Dinitraza-1,8-octanedioic acid (833, 40) was prepared by the following sequence of reactions.



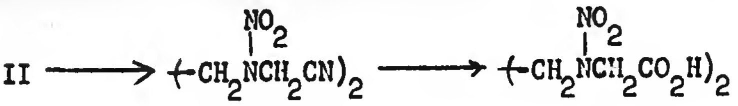
$$(-CH_2NH_2)_2 + 2\ HOCH_2CN \longrightarrow (-CH_2NHCH_2CN)_2 \longrightarrow \overset{HNO_3\ \cdot}{(-CH_2NHCH_2CN)_2}$$

I II

---

*Buc, Ford and Wise, J. Am. Chem. Soc. 67, 92 (1945); Wiedemann and Montgomery, ibid., 67, 1994 (1945).

**Wright et al., Can. J. Research 26, 126 (1948).



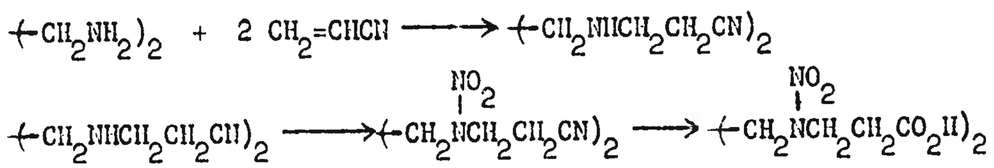
$$\text{II} \longrightarrow (\!-CH_2\overset{\overset{NO_2}{|}}{N}CH_2CN)_2 \longrightarrow (\!-CH_2\overset{\overset{NO_2}{|}}{N}CH_2CO_2H)_2$$

III IV

3,6-Diaza-1,8-octane dinitrile (I) was previously obtained by a Mannich condensation of ethylene diamine, hydrogen cyanide, and aqueous formaldehyde in the presence of an alkaline-earth cyanide.* Employing the commercially available aqueous glycolonitrile, the condensation with ethylene diamine was effected without inorganic catalysts. The reaction solution was treated with nitric acid to yield the bis-nitric acid salt of 3,6-diaza-1,8-octane dinitrile (II) directly. The latter was converted to 3,6-dinitraza-1,8-octane dinitrile (III) by means of a chloride-catalyzed nitration, and the dinitrile was hydrolyzed to 3,6-dinitraza-1,8-octanedioic acid (IV) using hydrochloric acid. The conversion of the acid to the acid chloride (833, 46) was best effected by means of phosphorous pentachloride.

f. 4,7-Dinitraza-1,10-decanedioic Acid

4,7-Dinitraza-1,10-decanedioic acid (638, 87) was prepared according to the following reaction sequence.



$$(\!-CH_2NH_2)_2 + 2\ CH_2{=}CHCN \longrightarrow (\!-CH_2NHCH_2CH_2CN)_2$$

$$(\!-CH_2NHCH_2CH_2CN)_2 \longrightarrow (\!-CH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2CN)_2 \longrightarrow (\!-CH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2CO_2H)_2$$

4,7-Diaza-1,10-decane dinitrile was obtained by the Michael reaction of ethylene diamine and acrylonitrile, and it was characterized by preparation of a bis-benzenesulfonamide (638, 88) and by conversion to 4,7-dinitroso-4,7-diaza-1,10-decane dinitrile (638, 89). 4,7-Dinitraza-1,10-decanedinitrile was obtained by a chloride-catalyzed nitration of 4,7-diaza-1,10-decanedinitrile (638, 89), but attempts to obtain this material by the oxidation of the corresponding dinitroso compound were unsuccessful (686, 85). Subsequent work (740, 68) showed that the use of the pre-formed bis-nitric

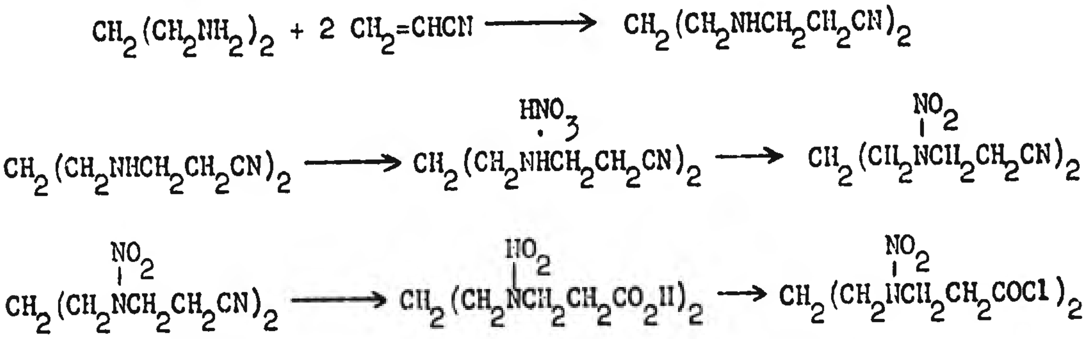
---

*Fick and Ulrich, German Pat. 638, 071, November 9, 1936.

acid salt of 4,7-diaza-1,10-decane dinitrile was preferred for the preparation of 4,7-dinitraza-1,10-decane dinitrile. 4,7-Dinitraza-1,10-decanedioic acid resulted from the hydrochloric acid hydrolysis of 4,7-dinitraza-1,10-decanedinitrile, and the diacid chloride was obtained by the action of either thionyl chloride or phosphorous pentachloride on the acid (638, 90).

g. 4,8-Dinitraza-1,11-undecanedioic Acid

4,8-Dinitraza-1,11-undecanedioic acid (807, 66) and 4,8-dinitraza-1,11-undecanedioyl chloride (807, 72) were prepared by the following series of reactions, which preparation directly parallels that of 4,7-dinitraza-1,10-decanedioic acid (paragraph f, above).



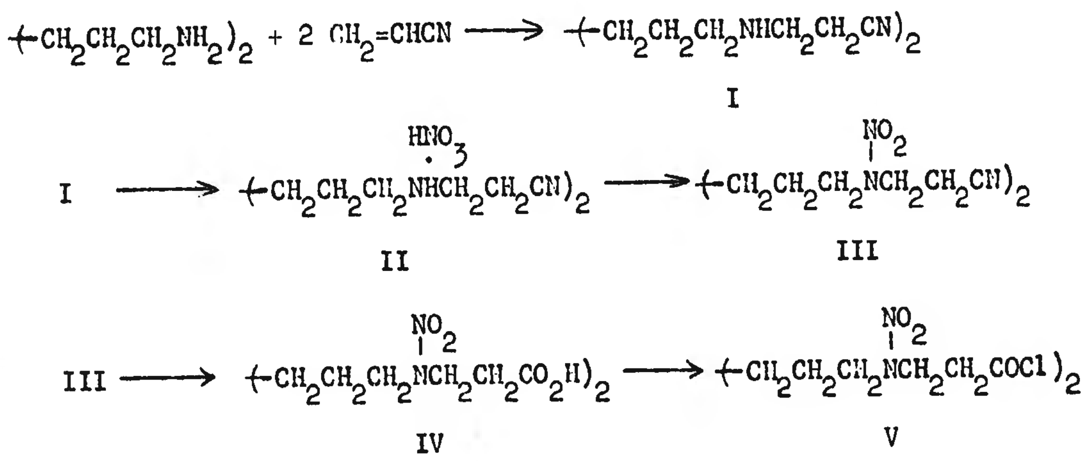
$$CH_2(CH_2NH_2)_2 + 2\ CH_2{=}CHCN \longrightarrow CH_2(CH_2NHCH_2CH_2CN)_2$$

$$CH_2(CH_2NHCH_2CH_2CN)_2 \longrightarrow CH_2(CH_2\overset{\overset{HNO_3}{\cdot}}{N}HCH_2CH_2CN)_2 \longrightarrow CH_2(CH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2CN)_2$$

$$CH_2(CH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2CN)_2 \longrightarrow CH_2(CH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2CO_2H)_2 \longrightarrow CH_2(CH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2COCl)_2$$

h. 4,11-Dinitraza-1,14-tetradecanedioic Acid

The utilization of a Michael reaction of a diamine and 2 moles of acrylonitrile as the basic or initial reaction in the synthesis of a dinitraza dicarboxylic acid was again illustrated in the following formation of 4,11-dinitraza-1,14-tetradecanedioic acid (IV) (833, 42, 48).



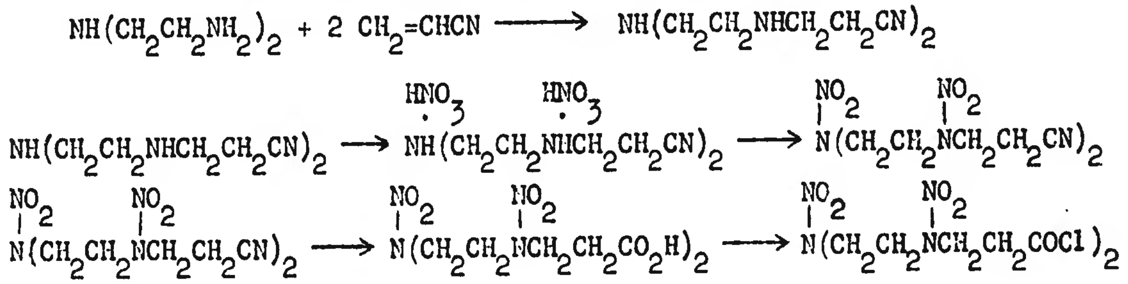
$$-(CH_2CH_2CH_2NH_2)_2 + 2\ CH_2{=}CHCN \longrightarrow \underset{I}{-(CH_2CH_2CH_2NHCH_2CH_2CN)_2}$$

$$I \longrightarrow \underset{II}{-(CH_2CH_2CH_2\overset{\overset{HNO_3}{\cdot}}{N}HCH_2CH_2CN)_2} \longrightarrow \underset{III}{-(CH_2CH_2CH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2CN)_2}$$

$$III \longrightarrow \underset{IV}{-(CH_2CH_2CH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2CO_2H)_2} \longrightarrow \underset{V}{-(CH_2CH_2CH_2\overset{\overset{NO_2}{|}}{N}CH_2CH_2COCl)_2}$$

i. 4,7,10-Trinitraza-1,13-tridecanedioic Acid

4,7,10-Trinitraza-1,13-tridecanedioic acid was originally prepared by the following scheme (663, 75; 686, 68,71,82), but the overall yield was extremely low, due to the low conversion of the tris-nitric acid salt of 4,7,10-triaza-1,13-tridecane dinitrile to 4,7,10-trinitraza-1,13-tridecane dinitrile by a chloride-catalyzed nitration:

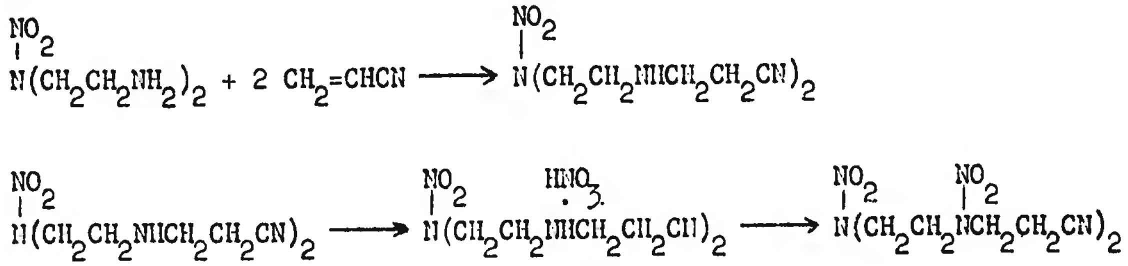


$$NH(CH_2CH_2NH_2)_2 + 2\ CH_2{=}CHCN \longrightarrow NH(CH_2CH_2NHCH_2CH_2CN)_2$$

$$NH(CH_2CH_2NHCH_2CH_2CN)_2 \longrightarrow \overset{HNO_3}{\overset{\cdot}{NH}}(CH_2CH_2\overset{HNO_3}{\overset{\cdot}{N}}HCH_2CH_2CN)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2CN)_2$$

$$\overset{NO_2}{\overset{|}{N}}(CH_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2CN)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2CO_2H)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2COCl)_2$$

An alternative method of obtaining the intermediate, 4,7,10-trinitraza-1,13-tridecane dinitrile, was developed which utilized a Michael reaction of 3-nitraza-1,5-pentanediamine with acrylonitrile for the formation of the starting material, 7-nitro-4,7,10-triaza-1,13-tridecane dinitrile (740, 66). The nitration of the corresponding nitric acid salt gave high yields of 4,7,10-trinitraza-1,13-tridecane dinitrile (740, 67). A particular disadvantage of this procedure for the preparation of large quantities of 4,7,10-trinitraza-1,13-tridecane dinitrile was the limited availability of 3-nitraza-1,5-pentanediamine (740, 74), which was obtained from 3-nitraza-1,5-pentane diisocyanate.



$$\overset{NO_2}{\overset{|}{N}}(CH_2CH_2NH_2)_2 + 2\ CH_2{=}CHCN \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2NHCH_2CH_2CN)_2$$

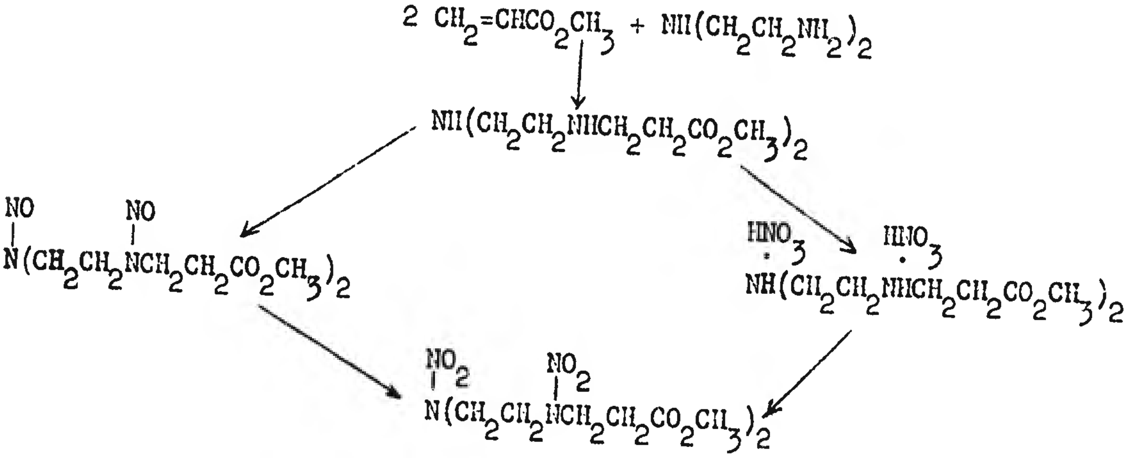
$$\overset{NO_2}{\overset{|}{N}}(CH_2CH_2NHCH_2CH_2CN)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2\overset{HNO_3}{\overset{\cdot}{N}}HCH_2CH_2CN)_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2\overset{NO_2}{\overset{|}{N}}CH_2CH_2CN)_2$$

Two additional procedures (807, 61-65) were developed for the preparation of 4,7,10-trinitraza-1,13-tridecanedioic acid. One of these procedures involved the use of the Emmons method* of oxidizing nitrosamines to nitramines by means of peroxytrifluoroacetic acid for the conversion of methyl 4,7,10-trinitroso-4,7,10-triaza-1,13-tridecanedioate to methyl 4,7,10-trinitraza-1,13-tridecanedioate followed by

---

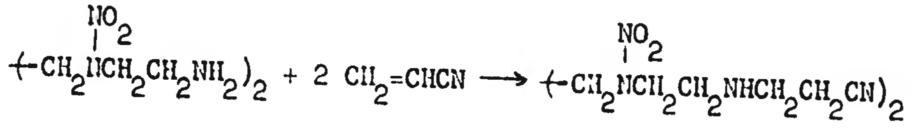
*Emmons and Ferris, J. Am. Chem. Soc. 75, 4623 (1953).

hydrolysis of the latter material. The key reaction of the second method was the preparation of this same dimethyl ester by the nitration of the tris-nitric acid salt of methyl 4,7,10-triaza-1,13-tridecanedioate. Although both methods were satisfactory, the latter was particularly interesting because of the success in obtaining the dimethyl ester by direct nitration, whereas the corresponding dinitrile was obtained in negligible yields by direct nitration. The alternative methods are indicated in the following diagram.



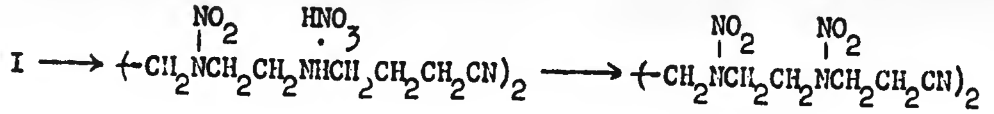
j. 4,7,10,13-Tetranitraza-1,16-hexadecanedioic Acid

The Michael reaction of 3,6-dinitraza-1,8-octanediamine (740, 72) with acrylonitrile yielded 7,10-dinitro-4,7,10,13-tetraza-1,16-hexadecane dinitrile (I) (740, 63), and the nitration of the corresponding bis nitric acid salt (II) gave 4,7,10,13-tetranitraza-1,16-hexadecane dinitrile (III) in low yield (833, 44). The hydrolysis of the dinitrile to the dicarboxylic acid (IV) was carried out in concentrated hydrochloric acid (833, 45). On the basis of previous experience in the 4,7,10-triaza-1,13-tridecane series (paragraph i, above), the use of the bis-nitric acid salt of methyl 7,10-dinitro-4,7,10,13-tetraza-1,16-hexadecanedioate would probably give a higher conversion in the nitration step.



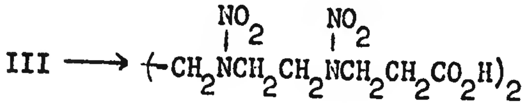
$$\left(-CH_2\overset{NO_2}{N}CH_2CH_2NH_2\right)_2 + 2\ CH_2{=}CHCN \longrightarrow \left(-CH_2\overset{NO_2}{N}CH_2CH_2NHCH_2CH_2CN\right)_2$$

I



$\text{I} \longrightarrow (-CH_2\overset{NO_2}{N}CH_2CH_2\overset{HNO_3}{NH}CH_2CH_2CH_2CN)_2 \longrightarrow (-CH_2\overset{NO_2}{N}CH_2CH_2\overset{NO_2}{N}CH_2CH_2CN)_2$

II III



$\text{III} \longrightarrow (-CH_2\overset{NO_2}{N}CH_2CH_2\overset{NO_2}{N}CH_2CH_2CO_2H)_2$

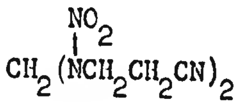
IV

k. Methyl 3,6-Dinitraza-4,5-diketo-1,8-octanedioate

Methyl 3,6-dinitraza-4,5-diketo-1,8-octanedioate was prepared as a precursor of 3,6-dinitraza-4,5-diketo-1,8-octanedioic acid, but the attempted hydrolysis of the dimethyl ester in acid solution resulted in degradation (638, 94). Attempts to prepare the dicarboxylic acid by the nitration of N,N'-di-(carboxymethyl)-oxamide (404, 44; 622, 78; 638, 94) were also unsuccessful (622, 78). Methyl 3,6-dinitraza-4,5-diketo-1,8-octanedioate, m.p. 130.5-131°, was obtained (417, 14,38; 638, 94) by the nitration of N,N'-<u>bis</u>-(carbomethoxymethyl)-oxamide (417, 44; 622, 78; 638, 94), using a mixture of acetic anhydride and nitric acid.

$(-CONHCH_2CO_2CH_3)_2 \longrightarrow (-CO\overset{NO_2}{N}CH_2CO_2CH_3)_2$

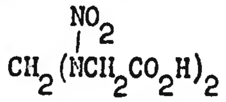
l. 4,6-Dinitraza-1,9-nonane Dinitrile, Attempted Preparation



$CH_2(\overset{NO_2}{N}CH_2CH_2CN)_2$

4,6-Dinitraza-1,9-nonane dinitrile and the corresponding dicarboxylic acid were desired as intermediates in the proposed preparation of 3,5-dinitraza-1,7-heptane diisocyanate. However, the key reaction in this synthesis, the Michael reaction of methylenediamine and acrylonitrile, gave the ammonia-acrylonitrile adduct, di-(β-cyanoethyl)-amine, instead of the desired 4,6-diaza-1,9-nonane dinitrile (686, 75).

m. 3,5-Dinitraza-1,7-heptanedioic Acid, Attempted Preparation



$$\mathrm{CH_2(\overset{NO_2}{\overset{|}{N}}CH_2CO_2H)_2}$$

The literature contains a single reference to the preparation of 3,5-diaza-1,7-heptanedioic acid (as the *bis* hydrochloride) by the Mannich condensation of formaldehyde with two moles of glycine in hydrochloric acid solution.[*] An attempt to repeat this reaction gave an apparent mixture which failed to yield a water-insoluble product on nitration (833, 49). When the condensation was attempted in the presence of nitric acid, the sole product was the nitric acid salt of glycine. When the methyl ester of glycine was utilized in the Mannich condensation, a viscous, water-soluble oil was obtained which yielded a viscous, water-insoluble oil on nitration. Neither of these products was characterized. This synthesis merits further investigation, inasmuch as the desired product offers a route to 3,5-dinitraza-1,7-heptanedioic acid and 2,4-dinitraza-1,5-pentane diisocyanate.

5. Monocarboxylic Acids

a. Discussion

The contribution and/or importance of the monocarboxylic acids (Table 11) to the nitropolymer program varied considerably among compounds. For example, 4,4-dinitrobutyric acid was used primarily in the synthesis of bifunctional derivatives, and 4,4-dinitropentanoic acid, 4-nitrazapentanoic acid, and 4,4,4-trinitrobutyric acid were utilized extensively in the formation of nitroplasticizers. A number of the acids provided a means of obtaining the appropriate monoisocyanates, and in the case of certain acids, particularly those of cyclic structure, the main contribution has been one of further elucidating the behavior of nitro compounds.

b. 3,3-Dinitrobutyric Acid

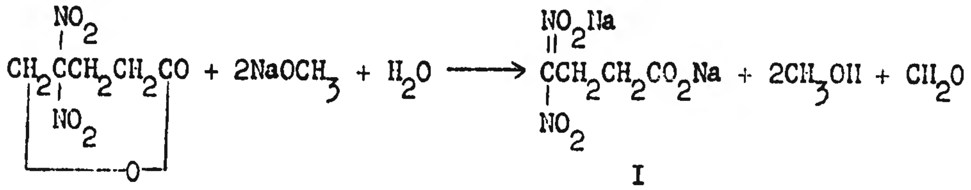
The preparation of 3,3-dinitrobutyric acid was described in paragraph II,C,2,c.

---

[*] N. Löb, *Biochem. Z.* *51*, 122 (1913).

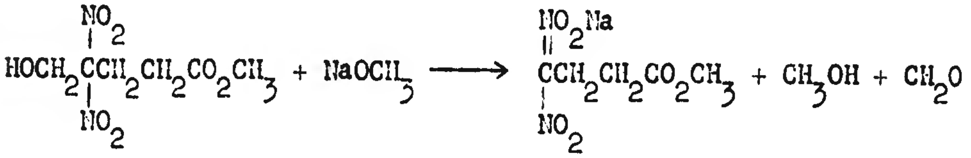
c. 4,4-Dinitrobutyric Acid*

The preparation of 4,4-dinitrobutyric acid (404, 50) and methyl 4,4-dinitrobutyrate (404, 31,49), as the aci-nitro sodium salts, was effected by treatment of 4,4-dinitro-5-pentanolactone (see paragraph d, below) and methyl 4,4-dinitro-5-hydroxypentanoate (paragraph d) with sodium methoxide according to the following equations.



$$CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO + 2NaOCH_3 + H_2O \longrightarrow \overset{NO_2Na}{\overset{\|}{\underset{NO_2}{C}}}CH_2CH_2CO_2Na + 2CH_3OH + CH_2O$$

I



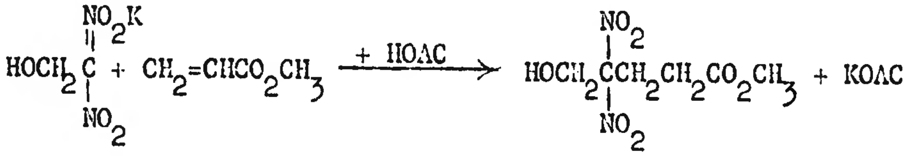
$$HOCH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2CH_3 + NaOCH_3 \longrightarrow \overset{NO_2Na}{\overset{\|}{\underset{NO_2}{C}}}CH_2CH_2CO_2CH_3 + CH_3OH + CH_2O$$

II

The identity of the disodium salt of 4,4-dinitrobutyric acid (I) was proved by bromination to yield 4-bromo-4,4-dinitrobutyric acid, m.p. 88-89° (404, 33,50). Sodium methyl 4,4-dinitrobutyrate (II) was also characterized by the formation of a bromo-derivative, methyl 4-bromo-4,4-dinitrobutyrate, m.p. 17-18°C (loc. cit.). 4,4-Dinitrobutyric acid and the methyl ester were not characterized in the free state. In the subsequent utilization of these materials in synthesis, the alkali metal salts were employed.

d. 4,4-Dinitro-5-hydroxypentanoic Acid*

Methyl 4,4-dinitro-5-hydroxypentanoate was prepared by the Michael reaction of potassium 2,2-dinitroethanol and methyl acrylate (404, 31,49).

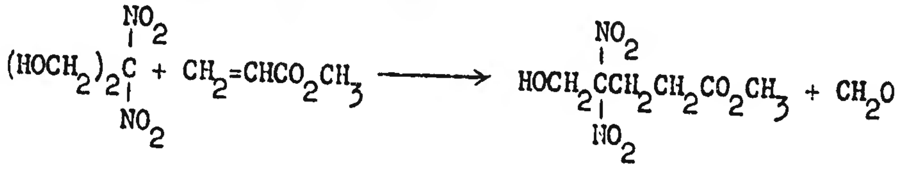


$$HOCH_2\overset{NO_2K}{\overset{\|}{\underset{NO_2}{C}}} + CH_2{=}CHCO_2CH_3 \xrightarrow{+\ HOAC} HOCH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2CH_3 + KOAC$$

---

*Klager, J. Org. Chem. 16, 161 (1951).

In order to stop the reaction at this stage, avoiding the formation of methyl 4,4-dinitro-1,7-heptanedioate (II,C,3,c), it was necessary to use equivalent quantities of the two reactants and to carry out the reaction, at pH 5-6, by means of a buffer such as sodium acetate. Methyl 4,4-dinitro-5-hydroxypentanoate was also prepared from 2,2-dinitro-1,3-propanediol and methyl acrylate in the presence of catalytic amounts of base (515, 26).



$$(HOCH_2)_2\underset{NO_2}{\overset{NO_2}{C}} + CH_2{=}CHCO_2CH_3 \longrightarrow HOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3 + CH_2O$$

The methyl ester cyclized to 4,4-dinitro-5-pentanolactone on hydrolysis with hydrochloric acid and subsequent vacuum distillation (404, 31,49). The modification of this procedure, by treatment of the crude mixture of lactone and acid obtained from the hydrolysis reaction with thionyl chloride, gave the lactone in increased yield and eliminated the necessity of vacuum distillation (868, 55).

e. 4,4,4-Trinitrobutyric Acid

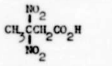
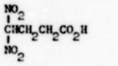
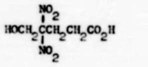
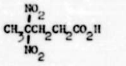
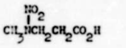
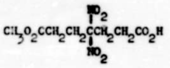
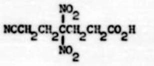
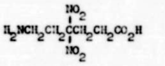
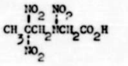
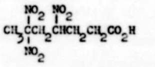
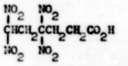
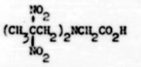
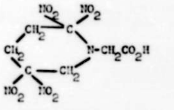
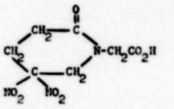
4,4,4-Trinitrobutyric acid, previously obtained by the addition of nitroform to acrylamide, followed by acid hydrolysis,* was prepared by the addition of nitroform to acrylic acid in aqueous solution (468, 23). Treatment of the acid with thionyl chloride for a 4-hr period gave low yields of 4,4,4-trinitrobutyric anhydride, whereas prolonged treatment gave 4,4,4-trinitrobutyryl chloride in good yield (540, 51). An improved method of obtaining the anhydride involved the reaction of 4,4,4-trinitrobutyric acid with half an equivalent of thionyl chloride, using benzene as a solvent (563, 74). The "falling film" molecular still** was employed for the distillation of large quantities of the sensitive 4,4,4-trinitrobutyryl chloride (590, 68).

---

*U. S. Rubber Co., Quarterly Report No. 5.
**Gold, Anal. Chem. 21, 636 (1949).

TABLE 11

MONOCARBOXYLIC ACIDS AND DERIVATIVES

Name	Formula	mp	Reference	Methyl Ester		Acid Chloride	
				mp	Reference	bp	Reference
(1) 3,3-Dinitrobutyric Acid	 $CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2CO_2H$	88-89°	663, 68; 686, 55	--	--	60-80°/1 mm, n_D^{25} 1.4731	686, 58
(2) 4,4-Dinitrobutyric Acid	 $\overset{NO_2}{\underset{NO_2}{C}}HCH_2CH_2CO_2H$	88-89°[1]	404, 50	17-18°[1]	404, 49	--	--
(3) 5-Hydroxy-4,4-dinitro-pentanoic Acid[2]	 $HOCH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2H$	--	--	oil, n_D^{25} 1.4738	404, 49	--	--
(4) 4,4,4-Trinitrobutyric Acid[3]	$(O_2N)_3CCH_2CH_2CO_2H$	61°	330, 68; 468, 23	24.5-26°	499, 24; 622, 89	65-66°/0.5 μ, n_D^{25} 1.4835	540, 51; 590, 68
(5) 4,4-Dinitropentanoic Acid[6]	 $CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2H$	97-99°	Ohio State Report No. 1, p. 10,15 May 1950	bp 146-147°/8 mm, n_D^{20} 1.4557	336, 32; 417, 28,42	--	--
(6) 4-Nitrazapentanoic Acid	 $CH_3\overset{NO_2}{N}CH_2CH_2CO_2H$	53-54°	801, 13	bp 107°/1 mm, n_D^{25} 1.4694	907, 42	100-107°/10 μ, n_D^{25} 1.4997	801, 13
(7) 6-Carbomethoxy-4,4-dinitrohexanoic Acid	 $CH_3O_2CCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2H$	92-93°	622, 80	45°	See methyl 4,4-dinitro-1,7-heptanedioate Table 9	oil	622, 80; 686, 71
(8) 6-Cyano-4,4-dinitrohexanoic Acid	 $NCCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2H$	--	--	50°	457, 11	--	--
(9) 6-Amino-4,4-dinitrohexanoic Acid[4]	 $H_2NCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2H$	190° (dec)	638, 96	127° (dec)[5]	638, 95	--	--
(10) 3,5,5-Trinitro-3-azahexanoic Acid	 $CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2CO_2H$	139-140°	711, 16	78-80°	663, 77	mp 87-88°	711, 16
(11) 4,6,6-Trinitroheptanoic Acid	 $CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2\overset{NO_2}{C}HCH_2CH_2CO_2H$	--	--	56°	499, 12	--	--
(12) 4,4,6,6-Tetranitrohexanoic Acid[6]	 $\overset{NO_2}{\underset{NO_2}{C}}HCH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2H$	--	--	36-37°	424, 37; 457, 79	--	--
(13) N,N-bis-(2,2-Dinitropropyl)-glycine	 $(CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2)_2NCH_2CO_2H$	121-122°	622, 83	94-95°	622, 84	--	--
(14) 1-Carboxymethyl-3,3,5,5-tetranitropiperidine		147° (dec)	499, 9	129-130°	417, 13; 499, 10	--	--
(15) 5,5-Dinitro-2-piperidone-N-acetic Acid		128-130°	622, 81	126-127°	622, 83	--	--

NOTES:

[1] The reported melting points are of the 4-bromo derivatives. 4,4-Dinitrobutyric acid and the methyl ester were not characterized in the free state. In syntheses, the alkali metal salts were utilized.

[2] 4,4-Dinitro-5-pentanolactone (404, 49; 868, 55) melted at 78.5-79.5°.

[3] 4,4,4-Trinitrobutyric anhydride (540, 51; 563, 73) melted at 109-110°.

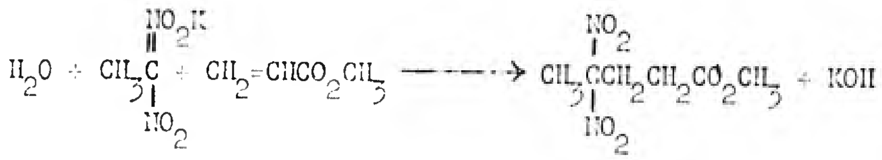
[4] 4,4-Dinitro-6-hexanolactam (638, 96) melted at 184-185°.

[5] The melting point of the hydrochloride is reported.

[6] SPIA data sheets were prepared for methyl 4,4,6,6-tetranitrohexanoate (468) and methyl 4,4-dinitropentanoate (941).

f. 4,4-Dinitropentanoic Acid

Methyl 4,4-dinitropentanoate was prepared by the Michael reaction of potassium 1,1-dinitroethane and methyl acrylate (417, 28,44).

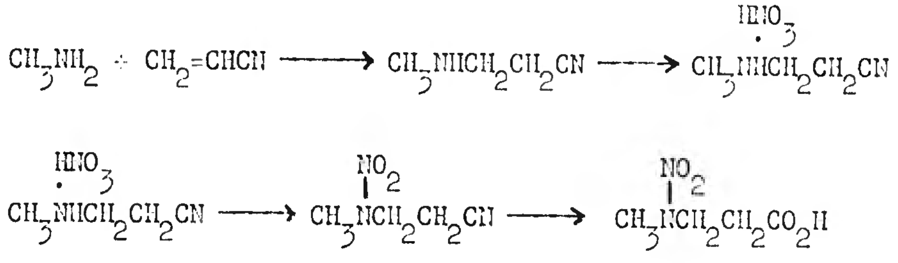


$$\mathrm{H_2O + CH_3\overset{NO_2K}{\overset{\|}{\underset{\underset{NO_2}{|}}{C}}} + CH_2{=}CHCO_2CH_3 \longrightarrow CH_3\overset{NO_2}{\overset{|}{\underset{\underset{NO_2}{|}}{C}}}CH_2CH_2CO_2CH_3 + KOH}$$

Hydrolysis of the methyl ester using dilute hydrochloric acid gave 4,4-dinitropentanoic acid,* and treatment of the latter with thionyl chloride yielded 4,4-dinitropentanoyl chloride, bp 111°/2 mm.**

g. 4-Nitrazapentanoic Acid

4-Nitrazapentanoic acid*** was prepared in the following manner, utilizing 4-azapentanonitrile,**** the 1:1 Michael-adduct of methylamine and acrylonitrile, as starting material.



$$\mathrm{CH_3NH_2 + CH_2{=}CHCN \longrightarrow CH_3NHCH_2CH_2CN \longrightarrow CH_3\overset{HNO_3}{\overset{\cdot}{N}}HCH_2CH_2CN}$$

$$\mathrm{CH_3\overset{HNO_3}{\overset{\cdot}{N}}HCH_2CH_2CN \longrightarrow CH_3\overset{NO_2}{\overset{|}{N}}CH_2CH_2CN \longrightarrow CH_3\overset{NO_2}{\overset{|}{N}}CH_2CH_2CO_2H}$$

The acid was converted to the corresponding acid chloride by means of thionyl chloride.*** Improvements in both yield and procedure were effected on converting the synthesis of 4-nitrazapentanoic acid to pilot plant scale (Section V). Methyl 4-nitrazapentanoate was prepared by the methanolysis of 4-nitrazapentanonitrile in the presence of sulfuric acid (907, 42).

h. 6-Carbomethoxy-4,4-dinitrohexanoic Acid

6-Carbomethoxy-4,4-dinitrohexanoic acid was prepared by the Michael reaction of the sodium salt of methyl 4,4-dinitrobutyrate with excess acrylic acid (622, 80) according to the following equation.

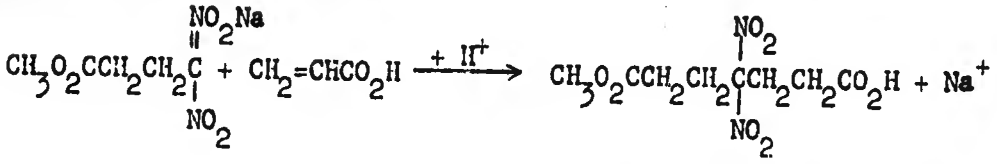
---

*Ohio State University Report No. 1, p. 10, 15 May 1950; Contract N6onr-22524.

**Aerojet-General Corp (unpublished work).

***Aerojet Report No. 801, p. 12, 16 March 1954; Contract N7onr-46208.

****Tarbell et al., J. Am. Chem. Soc. 68, 1217 (1946); Cook and Reed, J. Chem. Soc. 1945, 399.

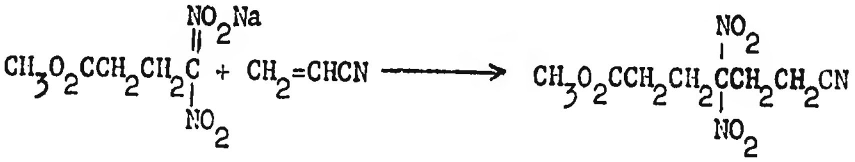


$$CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2Na}{\overset{\|}{C}}} + CH_2{=}CHCO_2H \xrightarrow{+H^+} CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2H + Na^+$$

6-Carbomethoxy-4,4-dinitrohexanoyl chloride was obtained as a honey-like oil, upon treatment of the acid with thionyl chloride (622, 80).

i. Methyl 6-cyano-4,4-dinitrohexanoate

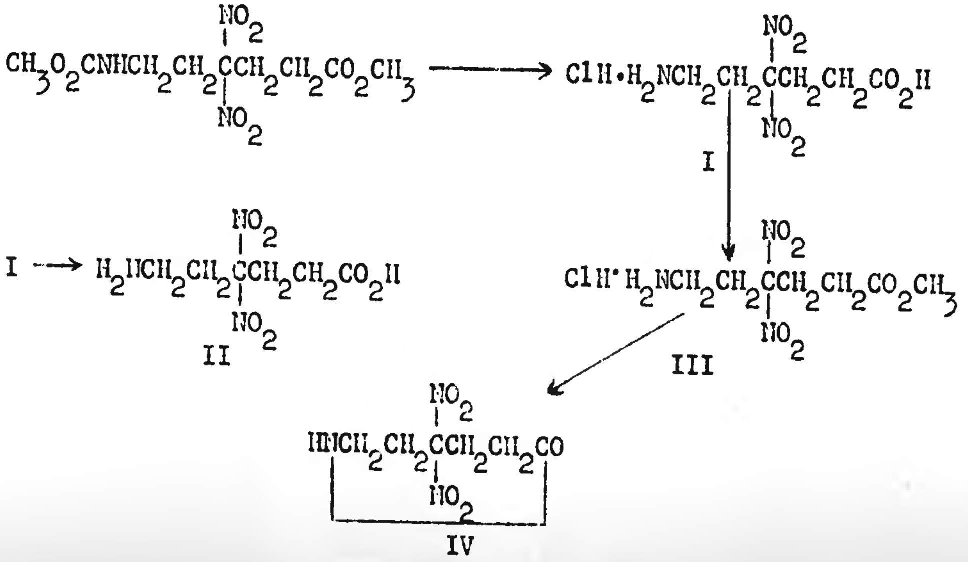
Methyl 6-cyano-4,4-dinitrohexanoate was prepared by the Michael addition of aci-sodium methyl 4,4-dinitrobutyrate with acrylonitrile (457, 11).



$$CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2Na}{\overset{\|}{C}}} + CH_2{=}CHCN \longrightarrow CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CN$$

j. 6-Amino-4,4-dinitrohexanoic Acid

6-Amino-4,4-dinitrohexanoic acid was obtained as the hydrochloride (I) by the hydrolysis of the methyl urethane of 5-carbomethoxy-3,3-dinitropentyl isocyanate, methyl 5,5-dinitro-2-aza-1,8-octanedioate, in hydrochloric acid (622, 80). Neutralization of the hydrochloride with aqueous sodium bicarbonate gave the free 6-amino-4,4-dinitrohexanoic acid (II) (638, 96). The hydrochloride of methyl 6-amino-4,4-dinitrohexanoate (III) was obtained by refluxing 6-amino-4,4-dinitrohexanoic acid hydrochloride with anhydrous methanolic hydrogen chloride (ibid., 95). 4,4-Dinitro-6-hexanolactam (IV) resulted from the treatment of methyl 6-amino-4,4-dinitrohexanoate hydrochloride with aqueous sodium carbonate (loc. cit.). The various reactions are illustrated below.



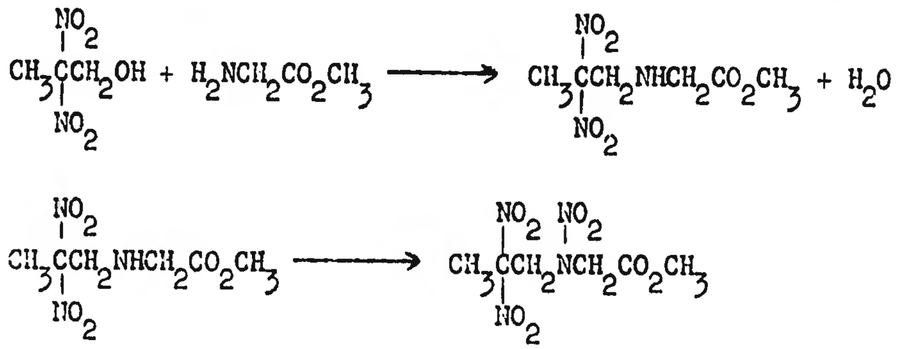
$$CH_3O_2CNHCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3 \longrightarrow \underset{I}{ClH\cdot H_2NCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2H}$$

$$I \longrightarrow \underset{II}{H_2NCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2H}$$

$$I \longrightarrow \underset{III}{ClH\cdot H_2NCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_3} \longrightarrow \underset{IV}{\underbrace{HNCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CO}}$$

k. 3,5,5-Trinitro-3-azahexanoic Acid

Methyl 5,5-dinitro-3-azahexanoate was obtained by a Mannich condensation of 2,2-dinitro-1-propanol with the methyl ester of glycine at a pH of 7. Nitration of the product using a mixture of acetic anhydride and anhydrous nitric acid gave methyl 3,5,5-trinitro-3-azahexanoate (663, 77).



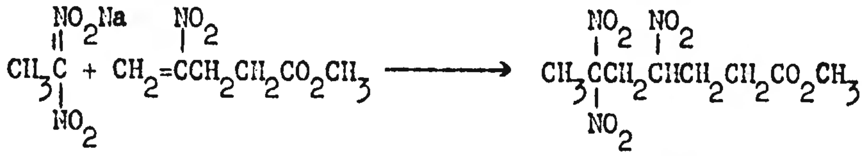
$$CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2OH + H_2NCH_2CO_2CH_3 \longrightarrow CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2NHCH_2CO_2CH_3 + H_2O$$

$$CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2NHCH_2CO_2CH_3 \longrightarrow CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2CO_2CH_3$$

The methyl ester was subsequently hydrolyzed to 3,5,5-trinitro-3-azahexanoic acid in concentrated hydrochloric acid, and the acid yielded the corresponding acid chloride on treatment with thionyl chloride.*

l. Methyl 4,6,6-Trinitroheptanoate

Methyl 4,6,6-trinitroheptanoate (499, 12) was obtained by the Michael reaction of sodium 1,1-dinitroethane and methyl 4-nitro-4-pentenoate (468, 12).



$$CH_3\underset{NO_2}{\overset{NO_2Na}{\overset{\|}{C}}} + CH_2{=}\overset{NO_2}{C}CH_2CH_2CO_2CH_3 \longrightarrow CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{C}HCH_2CH_2CO_2CH_3$$

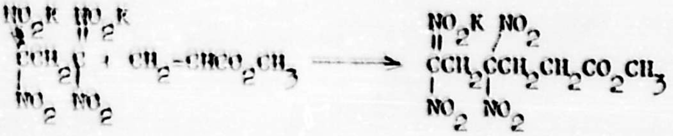
The identity of the product was confirmed by bromination of the sodium salt to yield methyl 4-bromo-4,6,6-trinitroheptanoate, mp 78-79° (499, 13). An attempt to add methyl acrylate at the 4-position of methyl 4,6,6-trinitroheptanoate was unsuccessful, resulting in near-quantitative recovery of the starting material (<u>loc. cit</u>).

---

*Aerojet Report No. 711, p. 16, 19 June 1953; Contract N7onr-46208.

m. Methyl 4,4,6,6-Tetranitrohexanoate

The Michael reaction of dipotassium 1,1,3,3-tetranitropropane with methyl acrylate yielded the potassium salt of methyl 4,4,6,6-tetranitrohexanoate (424, 23,37).

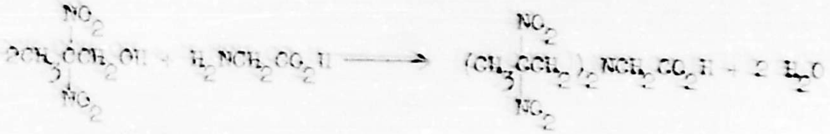


$$\overset{NO_2K}{\underset{NO_2}{C}}CH_2\overset{NO_2K}{\underset{NO_2}{C}} + CH_2{-}CHCO_2CH_3 \longrightarrow \overset{NO_2K}{\underset{NO_2}{C}}CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2CH_3$$

The potassium salt yielded methyl 6-bromo-4,4,6,6-tetranitrohexanoate, mp 65-66°, on bromination (*ibid*, 24,38). Acidification of an aqueous solution of the potassium salt with sulfuric acid yielded methyl 4,4,6,6-tetranitrohexanoate; impact stability 40 cm/2 kg (457, 18,79). The degradation of methyl 4,4,6,6-tetranitrohexanoate in alkaline media was exhibited by heating the potassium salt of methyl 4,4,6,6-tetranitrohexanoate in aqueous alkali with subsequent acidification to yield succinic acid (*ibid*, 19,30). Numerous attempts to utilize methyl 4,4,6,6-tetranitrohexanoate in the preparation of bifunctional derivatives by reaction with methyl acrylate and acrylonitrile (424, 24; 457, 10; 468, 24) or formaldehyde (499, 12) were unsuccessful. A number of other attempts to utilize this material in synthesis also failed (457, 19; 468, 41-42).

n. N,N-*bis*-(2,2-Dinitropropyl)-glycine

N,N-*bis*-(2,2-Dinitropropyl)-glycine was obtained by a Mannich reaction of 2,2-dinitropropanol and glycine at a pH of 9 (522, 85). This material was obtained in an original attempt to prepare 5,5-dinitro-3-azahexanoic acid (paragraph k, above).



$$2CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2OH + H_2NCH_2CO_2H \longrightarrow (CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2)_2NCH_2CO_2H + 2\,H_2O$$

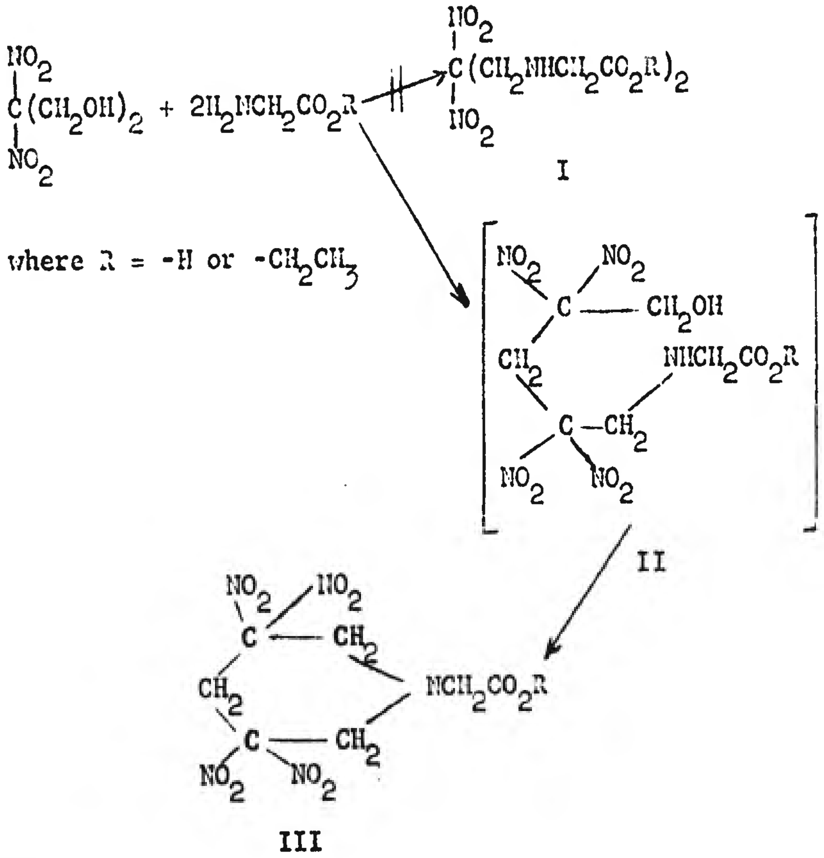
The methyl ester was prepared by the sulfuric acid-catalyzed esterification of N,N-*bis*-(2,2-dinitropropyl)-glycine with methanol (*ibid*, 84,85). Treatment of either the acid or methyl ester with a mixture of nitric and sulfuric acids yielded *bis*-(2,2-dinitropropyl)-nitramine, mp 169° (*loc. cit.*).

$$(CH_3C(NO_2)_2CH_2)_2NCH_2CO_2H \longrightarrow (CH_3C(NO_2)_2CH_2)_2NNO_2$$

Similarly, the action of acetic anhydride-anhydrous nitric acid on N,N-bis-(2,2-dinitropropyl)-glycine yielded bis-(2,2-dinitropropyl)-nitrosamine, m.p. 130-131° (loc. cit.). The latter material also gave the corresponding nitramine on treatment with mixed acid.

o. 1-Carboxymethyl-3,3,5,5-tetranitropiperidine

The attempted formation of ethyl 5,5-dinitro-3,7-diaza-1,9-nonanedioate (I) by the Mannich condensation of 2,2-dinitro-1,3-propanediol and the ethyl ester of glycine gave an unidentified product, m.p. 126° (417, 13,37), which was later shown to be 1-carbethoxymethyl-3,3,5,5-tetranitropiperidine* (III). The corresponding acid was obtained by the use of glycine.* The cyclization was presumed to occur by an internal condensation of ethyl 3-aza-8-hydroxy-5,5,7,7-tetranitro-1-octanoate (II).*

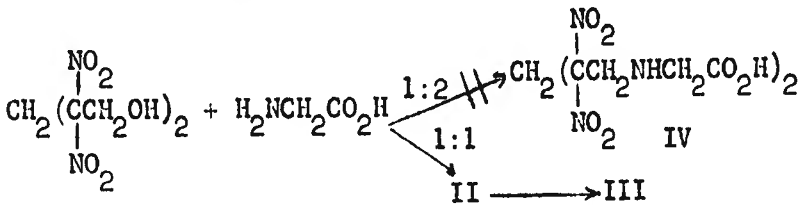


where $R = -H$ or $-CH_2CH_3$

---

*May, PhD Thesis, Purdue University.

In a similar Mannich condensation, the reaction of 2,2,4,4-tetranitro-1,5-pentanediol (paragraph II,D) with glycine also yielded 1-carboxymethyl-3,3,5,5-tetranitropiperidine instead of the desired 3,9-diaza-5,5,7,7-tetranitro-1,11-undecanedioic acid (IV) (499, 8). In this case, the intermediate, II, and the postulated 1:1 Michael condensation product of 2,2,4,4-tetranitro-1,5-pentanediol and glycine are identical structures. Consequently, the formation of the cyclic compound was not unexpected.

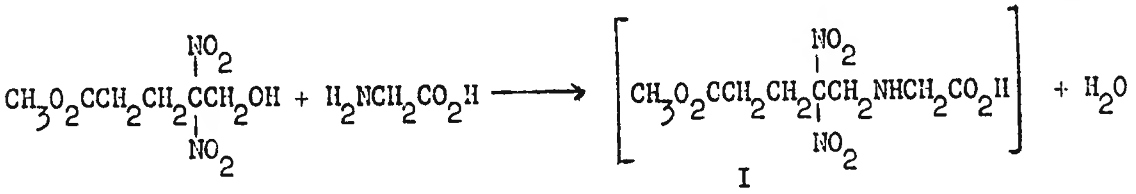


$$CH_2(\underset{NO_2}{\overset{NO_2}{C}}CH_2OH)_2 + H_2NCH_2CO_2H \xrightarrow{1:2} CH_2(\underset{NO_2}{\overset{NO_2}{C}}CH_2NHCH_2CO_2H)_2 \quad IV$$

$$\xrightarrow{1:1} II \longrightarrow III$$

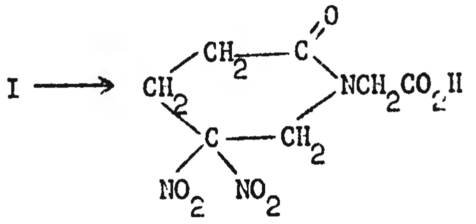
p. 5,5-Dinitro-2-piperidone-N-acetic Acid

5,5-Dinitro-2-piperidone-N-acetic acid (II) was formed by a Mannich reaction of methyl 5-hydroxy-4,4-dinitropentanoate (paragraph d, above) with glycine during an attempted formation of the monomethyl ester of 3-aza-5,5-dinitro-1,8-octanedioic acid (I) (622, 81). The latter material was apparently formed but immediately cyclized to (II) by an internal condensation.



$$CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OH + H_2NCH_2CO_2H \longrightarrow \left[CH_3O_2CCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2NHCH_2CO_2H\right] + H_2O$$

I



II

The structure of the product was verified by analysis, by determination of the equivalent weight, and by conversion to a monomethyl ester (loc. cit.).

D. NITRO ALCOHOLS

1. Introduction

Nitro alcohols constitute one of the most important classes of nitro monomers, and considerable effort has been devoted to their synthesis. Nitro monoalcohols may be converted to acrylate esters and, in this way, produce useful vinyl polymers. Nitro diols may be condensed with diacids and diisocyanates to give polyesters and polyurethanes, respectively. In addition, the nitro alcohols are valuable intermediates for the preparation of nitro olefins and other polynitro compounds. The different methods that were used in preparing the nitro alcohols are discussed, together with the individual nitro alcohols that were synthesized. The synthesis of nitro epoxides, which are intermediates for the preparation of long-chain diols, is also described.

2. Methods of Preparation of Nitro Alcohols

The different methods that were used in preparing nitro alcohols are summarized below.

a. The Henry Reaction

b. Selective Reduction of Polynitro Acid Chlorides, Aldehydes, and Ketones with Sodium Borohydride

c. Addition of Acidic Polynitro Alkanes to Hydroxymethyl Vinyl Ketone

d. The Michael Reaction

e. Diazotization of Polynitro Alkyl Amines

f. The Hunsdiecker Reaction

g. Hydrolysis of 3-Nitro-2-oxazolidone and Derivatives

h. Conversion of Iminoalcohols to Nitriminoalcohols

i. Addition of Ethylene Oxide to Primary Nitramines

j. The ter Meer Reaction

k. Miscellaneous Attempted Preparations

A discussion of each of these methods follows, including the compounds prepared by each method. The pertinent data on all of the nitro alcohols prepared are summarized in Table 12.

a. The Henry Reaction

(1) Discussion

All of the nitro alcohols commercially available in the United States (mononitro alcohols) are prepared by the condensation of a nitroparaffin and an aldehyde in the presence of a basic catalyst (Henry reaction). This reaction may be illustrated by the condensation of nitromethane and formaldehyde:

$$CH_3NO_2 + CH_2O \xrightleftharpoons{OH^-} O_2NCH_2CH_2OH$$

$$O_2NCH_2CH_2OH + CH_2O \rightleftharpoons O_2NCH(CH_2OH)_2$$

$$O_2NCH(CH_2OH)_2 + CH_2O \rightleftharpoons O_2NC(CH_2OH)_2$$

These condensations are equilibrium reactions, and the position of equilibrium depends upon the structure of the aldehyde and of the nitroparaffin. Formaldehyde is the most reactive aldehyde and nitromethane is the most reactive nitroparaffin, and the reactivities of both classes decrease as the series are ascended. After completion of the reaction, care must be taken to make the reaction mixture acidic, to prevent reversal of the reaction during isolation of the nitro alcohol. The Henry reaction, with the use of formaldehyde and acidic polynitro alkanes, has been the most useful general reaction for the preparation of polynitro alcohols on this program. It should be pointed out, however, that the Henry reaction is limited by the availability of the corresponding polynitro compounds and, moreover, that only α, β-nitroalcohols can be prepared by this method.

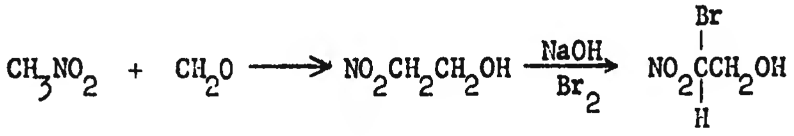
TABLE 12

NITRO ALCOHOLS

Nitro Alcohol	Method of Prep.	Yield %	b.p. °C	n_D^{25}	m.p. °C	References	Derivatives
A. Mononitro Alcohols							
(1) 2-Nitro-1-ethanol	a	31.8-50	84/5mm			417, App.	2-Bromo-2-nitro-1-ethanol, b.p. 83°/2mm, n_D^{25} 1.5000 (404, 40; 417 App.)
(2) 4-Methyl-4-nitro-1-pentanol	b	70	111-115/3 mm	1.4439		712,44	
B. Polynitro Alcohols							
(1) Potassium 2,2-Dinitro-1-ethanol	j	31-34			174 d	417, App.	2,2-Dinitro-1-ethanol, m.p. 2-3 (417A, 15); 2-Bromo-2,2-dinitro-1-ethanol, 84-91°/3 mm (371, 43)
(2) 2,2,2-Trinitroethanol	a	80-95			72	494, App.; 1033,39	
(3) 2,2-Dinitropropanol	a	35			88-92	426,58	
(4) 2,2-Dinitro-1-butanol	a	66.7	59-61/2 μ	1.4589		499,56	
(5) 3,3-Dinitro-1-butanol	c	43	70-80/μ	1.4660		663,32	
(6) 4,4,4-Trinitro-1-butanol	b	50	80-100/0.5 μ	1.4720		540,34	p-Nitrobenzoate, m.p. 113-114 (540, 37)
(7) 2,2,4,4-Tetranitro-1-butanol	d				35-36	457,78	
(8) 2,2-Dinitro-1-pentanol	a					622,60	
(9) 4,4-Dinitro-1-pentanol	b	63	114-118/1.2mm	1.4641		712,43	
(10) 2,2,4,4-Tetranitro-1-pentanol	a				66-67	436,16	
(11) 5,5,5-Trinitro-2-pentanol	b	78	70-80/0.5 μ	1.4633	36-37	563,70; 712,47	
(12) 5,5,5-Trinitro-2-keto-1-pentanol	c	35				515,4	Acetate, m.p. 52.5-53.5 (590,75)
(13) 5,5-Dinitro-2-hexanol	b	80	100-105/2 μ	1.4627		638,77	
(14) 5,5-Dinitro-2-keto-1-hexanol	c	37.8	126-130/1 μ		26-27	515,6	
C. Nitraza Alcohols							
(1) 2-Nitramino-1-ethanol	g	94			35	772,80	
D. Polynitronitraza Alcohols							
(1) 3,5,5-Trinitro-3-aza-1-hexanol	b	82			59-60	712,43	Acetate, m.p. 55-56 (740,61; 941,42)
E. Nitro Diols							
(1) 2-Nitro-1,3-propanediol	a				58	432,22; 907,54	2-Chloro, m.p. 115-117 (907,54); 2-Bromo, m.p. 133-134.5 (868,51)
F. Polynitro Diols							
(1) 2,2-Dinitro-1,3-propanediol	a	66-76			146	461,26	
(2) 1,4-Dinitro-2,3-butanediol	a					330,125	Dibromo, m.p. 134 (330,125)
(3) 1,1,4,4-Tetranitro-2,3-butanediol	a				182-183	330,126; 457,77	Dibromo, m.p. 182-183 (457,77)
(4) 3,3-Dinitro-1,5-pentanediol	f				72-73	424,8	Diacetate, m.p. 34-34.5 (424,8)
(5) 2,2,4,4-Tetranitro-1,5-pentanediol	a	27-36			97-99	515,8	
(6) 5,5,5-Trinitro-1,2-pentanediol	b	90.3		1.4886	54-55	563,61; 868,52	
(7) 5,5-Dinitro-1,2-hexanediol	b	94	125-135/0.5 μ	1.4831		638,85	bis-Phenyl Urethane, m.p. 113-114 (638,87)
(8) 2,5-Dinitro-3,4-hexanediol	a				149-150	330,126	
(9) 2,2,5,5-Tetranitro-1,6-hexanediol	a	32			127-128	404,42	
(10) 4,4-Dinitro-1,7-heptanediol	b	49.5			73-74	563,64	
(11) 4,4,6,8,8-Pentanitro-1,11-undecanediol	b	70			108-109	563,64	Diacetate, m.p. 94-95 (563,67)
(12) 4,4,6,6,8,8-Hexanitro-1,11-undecanediol	b	35			125-125.5	563,67	Diacetate, m.p. 77.5-78.5 (563,69)
G. Nitraza Diols							
(1) 3-Nitraza-1,5-pentanediol	h		150-160/3 μ		23-24	772,71; 807,57	Dibenzoate, m.p. 125.5-127 (772,73)
(2) 4-Nitraza-1,2-pentanediol	h			1.4444		807,57	Dibenzoate, m.p. 105-105.5 (807,57)
(3) 3,6-Dinitraza-1,8-octanediol	i	29			94-95	807,74; 941,32	
H. Polynitronitraza Diols							
(1) 4,4,6,8,8-Pentanitro-6-aza-1,11-undecanediol	b	90			106-108	638,79	Diacetate, m.p. 93-94 (638,79)

(2) Mononitro Alcohols and Derivatives; 2-Nitroethanol (SPIA Data Sheet; 371, App.)

2-Nitro-1-ethanol was prepared from nitromethane and formaldehyde, and was converted to 2-nitro-2-bromo-1-ethanol (417, App.).



$$CH_3NO_2 + CH_2O \longrightarrow NO_2CH_2CH_2OH \xrightarrow[Br_2]{NaOH} NO_2\overset{Br}{\underset{H}{C}}CH_2OH$$

Large-scale preparation and purification of these compounds are described in paragraph V,B,1.

(3) Polynitro Alcohols

(a) 2,2,2-Trinitroethanol (SPIA Data Sheet; 424, App.)

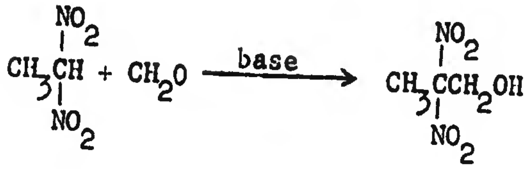
Because of the importance of 2,2,2-trinitroethanol for the synthesis of high-energy compounds, a special report has been written covering its preparation, properties, and reactions (494). 2,2,2-Trinitroethanol was prepared from potassium nitroform, formaldehyde, and acid:

$$\overset{NO_2K}{\overset{\|}{C}}(NO_2)_2 + CH_2O \xrightarrow{H^+} (NO_2)_3CCH_2OH$$

Originally, potassium nitroform was isolated from the reaction of tetranitromethane, potassium hydroxide, and hydrogen peroxide (494, App.). The salt was then acidified and treated with formaldehyde. More recently, it has been found that the hazardous operation of isolating potassium nitroform can be eliminated by acidifying the salt in situ with a mixture of sulfuric and sulfamic acids, which destroys the nitrous acid as it is formed (1083, 31).

(b) 2,2-Dinitropropanol

A great deal of work has been done on the preparation of 2,2-dinitropropanol, because of its importance in the synthesis of 2,2-dinitropropyl acrylate (Section II,A,3,e) and nitroplasticizers (Section II,E,2,b). Principally, 2,2-dinitropropanol has been prepared by the condensation of 1,1-dinitroethane and formaldehyde (426, 58).

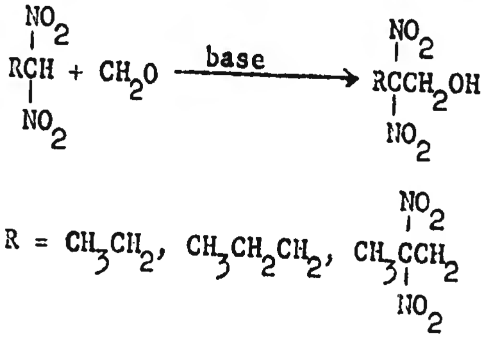


$$CH_3\overset{NO_2}{\underset{NO_2}{C}}H + CH_2O \xrightarrow{\text{base}} CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2OH$$

2,2-Dinitropropanol has also been prepared by the oxidative nitration of 2-nitro-1-propanol (907, 40) and 2-nitro-2-methyl-1,3-propanediol (468, 33). For a discussion of the oxidative nitration reaction, see paragraph II,F,3,a. The large-scale preparation of 2,2-dinitropropanol is described in paragraph V,B,6,b.

(c) 2,2-Dinitro-1-butanol, 2,2-Dinitro-1-pentanol and 2,2,4,4-Tetranitro-1-pentanol

2,2-Dinitro-1-butanol, (499, 56; SPIA Data Sheet; 499, App.) 2,2-dinitro-1-pentanol (622, 60), and 2,2,4,4-tetranitro-1-pentanol (486, 16) were prepared by the Henry reaction from the corresponding polynitro alkane, formaldehyde, and a basic catalyst:



$$R\overset{NO_2}{\underset{NO_2}{C}}H + CH_2O \xrightarrow{\text{base}} R\overset{NO_2}{\underset{NO_2}{C}}CH_2OH$$

$$R = CH_3CH_2,\ CH_3CH_2CH_2,\ CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2$$

(4) Nitro Diols and Derivatives; 2-Nitro-1,3-propanediol

2-Nitro-1,3-propanediol was prepared from nitromethane and formaldehyde* (482, 22; 907, 54). This diol is very hygroscopic and thus difficult to isolate in the pure state, but it has proved useful in the preparation of derivatives such as 2-nitro-2-chloro-1,3-propanediol** (907, 54), 2-nitro-2-bromo-1,3-propanediol* (868, 51), and 2,2-dinitro-1,3-propanediol.

$$CH_3NO_2 + 2\ CH_2O \longrightarrow NO_2CH(CH_2OH)_2 \xrightarrow[X_2]{NaOH} NO_2CX(CH_2OH)_2$$

X = Cl, Br

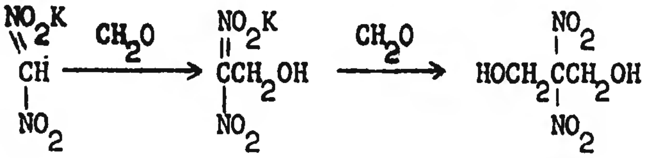
---

*Schmidt and Wilkendorf, Ber. 52, 389 (1919).
**Schmidt and Wilkendorf, Ber. 55, 317 (1922).

(5) Polynitro Diols

(a) 2,2-Dinitro-1,3-propanediol (SPIA Data Sheet; 371, App.)

2,2-Dinitro-1,3-propanediol is one of the most important and widely used polynitro diols that was prepared on the nitropolymer program. It was first prepared by the Henry reaction from potassium dinitromethane or potassium 2,2-dinitro-1-ethanol (461, 26).

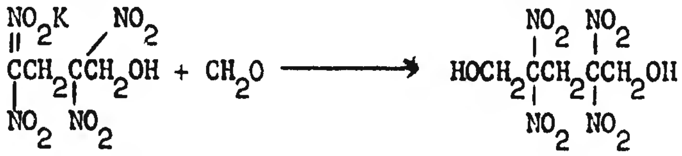


$$\underset{NO_2}{\overset{NO_2K}{CH}} \xrightarrow{CH_2O} \underset{NO_2}{\overset{NO_2K}{C}}CH_2OH \xrightarrow{CH_2O} HOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OH$$

Large-scale preparations of this highly desirable diol have been carried out in the pilot plant by the oxidative nitration of sodium 2-nitro-1,3-propanediol and sodium 2,2-dimethyl-5-nitro-1,3-dioxane (see paragraph V,B,3 for a complete discussion of these reactions).

(b) 2,2,4,4-Tetranitro-1,5-pentanediol (SPIA Data Sheet; 499, App.)

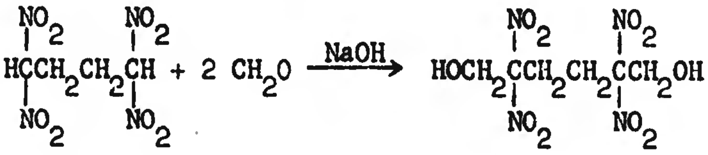
2,2,4,4-Tetranitro-1,5-pentanediol was prepared from potassium 2,2,4,4-tetranitro-1-butanol and formaldehyde (515, 8).



$$\underset{NO_2}{\overset{NO_2K}{C}}CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OH + CH_2O \longrightarrow HOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OH$$

(c) 2,2,5,5-Tetranitro-1,6-hexanediol

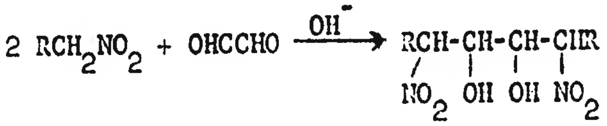
The condensation of 1,1,4,4-tetranitrobutane and formaldehyde gave 2,2,5,5-tetranitro-1,6-hexanediol (404, 42).



$$H\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}H + 2\ CH_2O \xrightarrow{NaOH} HOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OH$$

(d) 1,4-Dinitro-2,3-butanediol (SPIA Data Sheet; 371, App.), 2,5-Dinitro-3,4-hexanediol, and 1,1,4,4-Tetranitro-2,3-butanediol

Polynitro diols were also prepared by extending the Henry reaction to the condensation of acidic nitroalkanes and dialdehydes. The condensation of nitromethane, nitroethane, and dinitromethane with glyoxal gave 1,4-dinitro-2,3-butanediol (330, 125), 2,5-dinitro-3,4-hexanediol (330, 126), and 1,1,4,4-tetranitro-2,3-butanediol (330, 126; 457, 77), respectively:



$$2\,RCH_2NO_2 + OHCCHO \xrightarrow{OH^-} \underset{NO_2}{RCH}-\underset{OH}{CH}-\underset{OH}{CH}-\underset{NO_2}{CHR}$$

$R = H, CH_3, NO_2$

The yields in these reactions are low, and the products have found little application.

b. Selective Reduction of Polynitro Acid Chlorides, Aldehydes, and Ketones with Sodium Borohydride

(1) Discussion

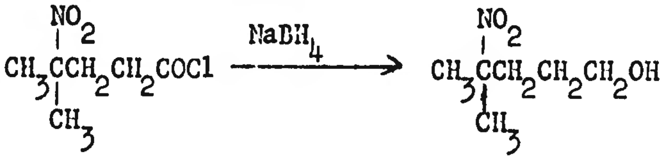
It has been demonstrated that nitro-containing carbonyl compounds are readily reduced to the corresponding alcohols with sodium borohydride.* This new method has been applied to the synthesis of polynitro alcohols from the corresponding acid chlorides, aldehydes, and ketones. Whereas only α, β-nitroalcohols can be prepared by the Henry reaction, many types of nitro alcohols can be prepared in good yield using the selective reduction technique, the only limitation being the availability of the starting materials. At present, sodium borohydride is an expensive chemical, but increased demand will undoubtedly reduce the price to a reasonable level.

---

*Chaikin and Brown, *J. Am. Chem. Soc.* *71*, 122 (1949).
Shechter, Ley and Zeldin, *ibid*, *74*, 3664 (1952).

(2) Mononitro Alcohols; 4-Methyl-4-nitro-1-pentanol

4-Methyl-4-nitro-1-pentanol was prepared from 4-methyl-4-nitro-1-pentanoyl chloride by reduction with sodium borohydride (712, 44).



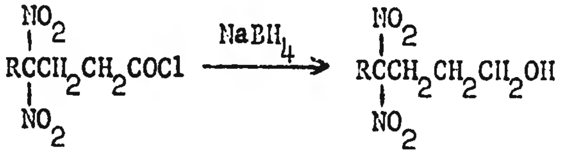
$$CH_3\underset{CH_3}{\overset{NO_2}{C}}CH_2CH_2COCl \xrightarrow{NaBH_4} CH_3\underset{CH_3}{\overset{NO_2}{C}}CH_2CH_2CH_2OH$$

This alcohol has been prepared previously by reduction of methyl 4-methyl-4-nitropentanoate using lithium borohydride.*

(3) Polynitro Alcohols

(a) 4,4,4-Trinitro-1-butanol and 4,4-Dinitro-1-pentanol

4,4,4-Trinitro-1-butanol and 4,4-dinitro-1-pentanol were prepared by the reduction of the corresponding acid chlorides with sodium borohydride.



$$R\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2COCl \xrightarrow{NaBH_4} R\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CH_2OH$$

$R = NO_2, CH_3$

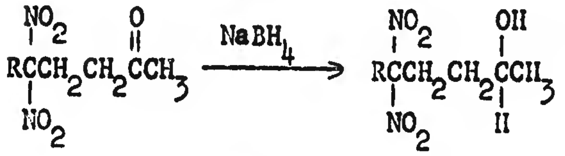
4,4-Dinitro-1-pentanol has previously been prepared by the sodium borohydride reduction of 4,4-dinitro-1-pentanal and the lithium borohydride reduction of methyl 4,4-dinitropentanoate.* 4,4,4-Trinitro-1-butanol was also prepared by the sodium borohydride reduction of 4,4,4-trinitro-1-butanal (590, 62).

(b) 5,5,5-Trinitro-2-pentanol and 5,5-Dinitro-2-hexanol

Reduction of 5,5,5-trinitro-2-pentanone and 5,5-dinitro-2-hexanone with sodium borohydride gave 5,5,5-trinitro-2-pentanol (563, 70; 712, 47) and 5,5-dinitro-2-hexanol (638, 77).

---

*Ohio State Report No. 7, 15 February 1952.



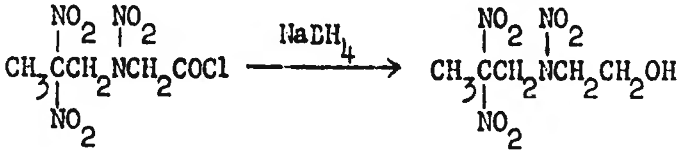
$$\mathrm{R\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{NaBH_4} R\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\underset{H}{\overset{OH}{C}}CH_3}$$

$R = NO_2, CH_3$

These compounds were first prepared at Ohio State* and then made on a larger scale in these laboratories. Conversion of these nitro alcohols to nitro olefins is described in paragraph II,A,2.

(4) Polynitronitraza Alcohols; 3,5,5-Trinitro-3-aza-1-hexanol

3,5,5-Trinitro-3-aza-1-hexanoyl chloride was reduced to the corresponding alcohol (712, 43).



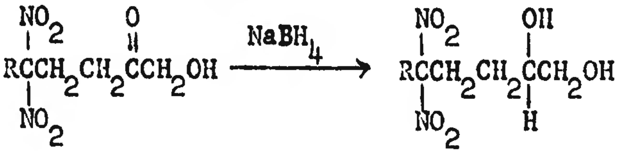
$$\mathrm{CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2COCl \xrightarrow{NaBH_4} CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2CH_2OH}$$

This alcohol was also prepared by the Mannich condensation of 2,2-dinitropropanol and ethanolamine followed by nitration (paragraph II,D,3,d).

(5) Polynitro Diols

(a) 5,5,5-Trinitro-1,2-pentanediol (SPIA Data Sheet; 638, App.) and 5,5-Dinitro-1,2-hexanediol

5,5,5-Trinitro-1,2-pentanediol (563, 61; 868, 52) and 5,5-dinitro-1,2-hexanediol (638, 85) were prepared by the reduction of 5,5,5-trinitro-2-keto-1-pentanol and 5,5-dinitro-2-keto-1-hexanol.



$$\mathrm{R\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2OH \xrightarrow{NaBH_4} R\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\underset{H}{\overset{OH}{C}}CH_2OH}$$

$R = NO_2, CH_3$

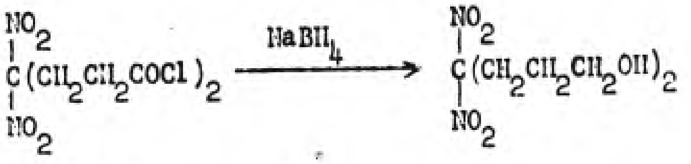
Pilot-plant preparations of 5,5,5-trinitro-1,2-pentanediol have been carried out (paragraph V,B,5).

---

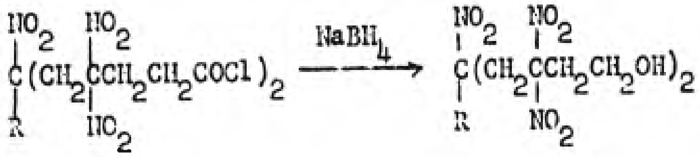
*Ohio State Report No. 7, 15 February 1952.

(b) 4,4-Dinitro-1,7-heptanediol, 4,4,6,8,8-Pentanitro-1,11-undecanediol (SPIA Data Sheet; 590, App.), and 4,4,6,6,8,8-Hexanitro-1,11-undecanediol (SPIA Data Sheet; 590, App.)

4,4-Dinitro-1,7-heptanediol (563, 64) 4,4,6,8,8-pentanitro-1,11-undecanediol (563, 64), and 4,4,6,6,8,8-hexanitro-1,11-undecanediol (563, 67) were prepared by the reduction of the corresponding acid chlorides:



$$\underset{NO_2}{\overset{NO_2}{C}}(CH_2CH_2COCl)_2 \xrightarrow{NaBH_4} \underset{NO_2}{\overset{NO_2}{C}}(CH_2CH_2CH_2OH)_2$$



$$\underset{R}{\overset{NO_2}{C}}(CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2COCl)_2 \xrightarrow{NaBH_4} \underset{R}{\overset{NO_2}{C}}(CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2OH)_2$$

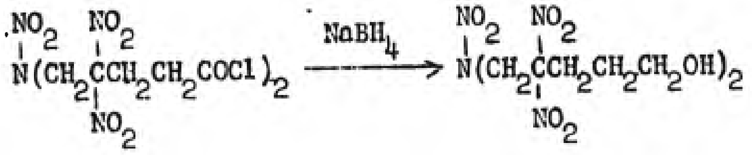
$R = H, NO_2$

(6) Nitraza Diols; 4,7-Dinitraza-1,10-decanediol, Attempted Preparation

Reduction of 4,7-dinitraza-1,10-decanedioyl chloride with sodium borohydride gave an uncrystallizable oil. All attempts to purify this oil or to prepare crystalline derivatives were unsuccessful (663, 74).

(7) Polynitronitraza Diols; 4,4,6,8,8-Pentanitro-6-aza-1,11-undecanediol

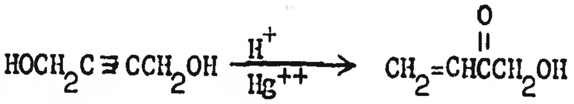
4,4,6,8,8-Pentanitro-6-aza-1,11-undecanediol was prepared by reduction of the corresponding acid chloride (638, 79).



$$\overset{NO_2}{N}(CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2COCl)_2 \xrightarrow{NaBH_4} \overset{NO_2}{N}(CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CH_2OH)_2$$

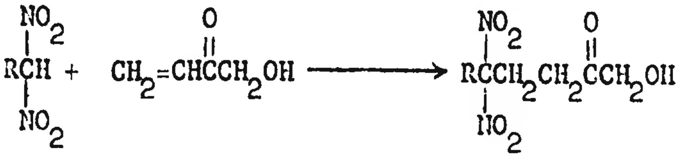
c. Addition of Polynitro Alkanes to Hydroxymethyl Vinyl Ketone; 5,5,5-Trinitro-2-keto-1-pentanol and 5,5-Dinitro-2-keto-1-hexanol

Hydroxymethyl vinyl ketone was prepared <u>in situ</u> from 1,4-butynediol, mercuric sulfate, and sulfuric acid by a Meyer-Schuster rearrangement:*



$$HOCH_2C\equiv CCH_2OH \xrightarrow[Hg^{++}]{H^+} CH_2{=}CH\overset{\overset{O}{\|}}{C}CH_2OH$$

Addition of nitroform and 1,1-dinitroethane to hydroxymethyl vinyl ketone gave 5,5,5-trinitro-2-keto-1-pentanol and 5,5-dinitro-2-keto-1-hexanol (515, 4).



$$R\underset{NO_2}{\overset{NO_2}{C}}H + CH_2{=}CH\overset{\overset{O}{\|}}{C}CH_2OH \longrightarrow R\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2\overset{\overset{O}{\|}}{C}CH_2OH$$

$R = NO_2, CH_3$

This method is unique for the preparation of polynitro keto alcohols.

d. The Michael Reaction; Potassium 2,2,4,4-Tetranitro-1-butanol

Partial acidification of potassium 2,2-dinitroethanol gave potassium 2,2,4,4-tetranitro-1-butanol. It is postulated that 1,1-dinitroethylene is the intermediate in this reaction, and that the Michael addition of potassium 2,2-dinitroethanol to 1,1-dinitroethylene gives the product (see II,F,6,e,(3) for discussion of this reaction).

e. Diazotization of Nitro Alkyl Amines; 3,3-Dinitro-1-butanol

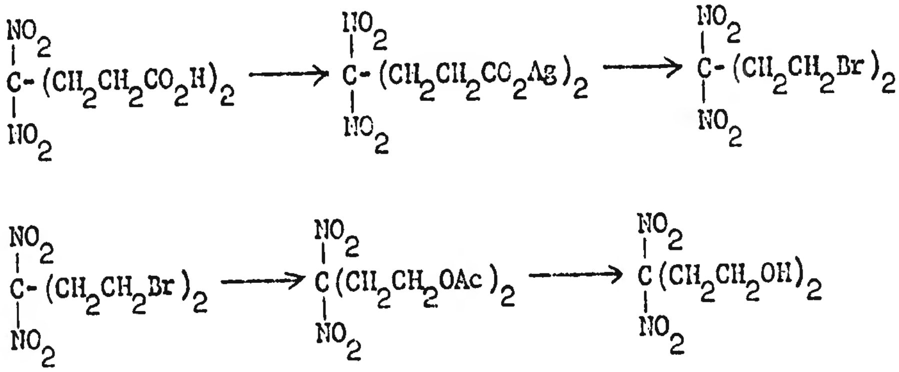
This method is of little preparative value because of the difficulty in preparing polynitro alkyl amines and the low yields encountered in the diazotization reaction. 3,3-Dinitro-1-butanol was prepared from the corresponding amine by this method (663, 82). Oxidation of the alcohol to 3,3-dinitrobutyric acid is described in paragraph II,C,2c.

---

*Ber. 55, 819 (1922); cf Bigelow and Copenhaver, Acetylene and Carbon Monoxide Chemistry, p. 135, Reinhold Publishing Corp., New York, N.Y.

f. The Hunsdiecker Reaction; 3,3-Dinitro-1,5-pentanediol

The Hunsdiecker Reaction* has very little application because of its inherent difficulties. An example of this reaction is the preparation of 3,3-dinitro-1,5-pentanediol from 4,4-dinitro-1,7-heptanedioic acid (424, 8).



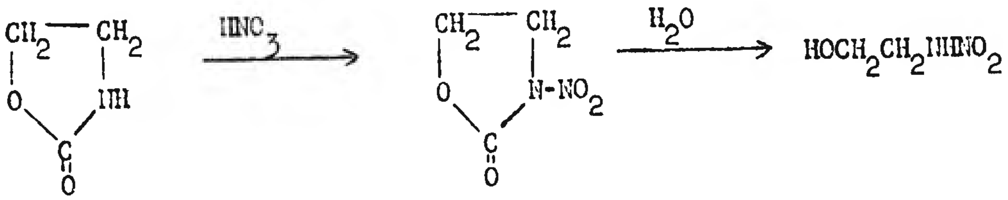
$$C(NO_2)_2(CH_2CH_2CO_2H)_2 \longrightarrow C(NO_2)_2(CH_2CH_2CO_2Ag)_2 \longrightarrow C(NO_2)_2(CH_2CH_2Br)_2$$

$$C(NO_2)_2(CH_2CH_2Br)_2 \longrightarrow C(NO_2)_2(CH_2CH_2OAc)_2 \longrightarrow C(NO_2)_2(CH_2CH_2OH)_2$$

g. Hydrolysis of 3-Nitro-2-oxazolidone and Derivatives

(1) 2-Nitramino-1-ethanol

2-Nitramino-1-ethanol was prepared following the procedure of Franchimont and Lubin.** 2-Oxazolidone was nitrated to give 3-nitro-2-oxazolidone, which was hydrolyzed to 2-nitramino-1-ethanol (772, 80).



(2) 3-Nitramino-1,2-propanediol, Attempted Preparation

Attempts to convert 5-chloromethyl-2-oxazolidone to 3-nitramino-1,2-propanediol by the same reactions as those used in the preparation of 2-nitramino-1-ethanol were unsuccessful (772, 70).

---

*Ber. 75 B, 291 (1942).
**Rec. trav. chim. 21, 45 (1902).

h. Conversion of Iminoalcohols to Nitriminoalcohols

(1) Discussion

Two general methods for converting aliphatic secondary amines to the corresponding nitramines are the catalyzed nitration procedure of Wright*

$$\mathrm{R_2NH + HNO_3 \longrightarrow R_2NH\cdot HNO_3 \xrightarrow[Cl^-]{Ac_2O} R_2NNO_2}$$

and the nitrosoamine oxidation procedure of Emmons.**

$$\mathrm{R_2NH \xrightarrow{HONO} R_2NNO \xrightarrow{CF_3CO_3H} R_2NNO_2}$$

These methods have been applied to the conversion of iminoalcohols to nitriminoalcohols.

(2) 3-Nitraza-1,5-pentanediol

The Wright procedure was used first by Carmack*** and, later in these laboratories, it was used for the preparation of 3-nitraza-1,5-pentanediol from diethanolamine (772, 71; 807, 57).

$$\mathrm{(HOCH_2CH_2)_2NH \xrightarrow{HNO_3} (O_2NOCH_2CH_2)_2NH\cdot HNO_3 \xrightarrow[Ac_2O]{AcCl}}$$

$$\mathrm{(O_2NOCH_2CH_2)_2NNO_2 \xrightarrow{H_2O} (HOCH_2CH_2)_2NNO_2}$$

This method is capable of giving high yields of the crude diol, but a convenient procedure for preparing the pure material has not yet been worked out. In addition, this procedure is beleaguered by the serious disadvantage of working with the intermediate dinitrate, which is a high explosive.

The second path to the 3-nitraza-1,5-pentanediol is via the oxidation of 3-aza-3-nitroso-1,5-pentanediol (772, 71; 805, 57).

$$\mathrm{(HOCH_2CH_2)_2NH \xrightarrow{HNO_2} (HOCH_2CH_2)_2NNO \xrightarrow[CF_3CO_2H]{H_2O_2} (HOCH_2CH_2)_2NNO_2}$$

---

*Wright *et al.*, *Can. J. Res. B*, *26*, 89-137.

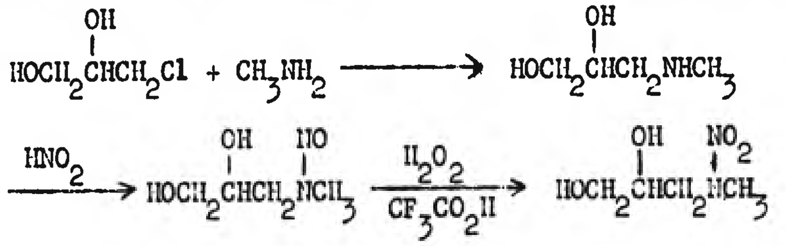
**Emmons and Ferris, *J. Am. Chem. Soc.* *75*, 4623 (1953).

***OSRD Report No. 5157, June 19, 1945.

The 3-nitraza-1,5-pentanediol prepared by this method was contaminated with the bis-trifluoroacetate and was thus difficult to purify. Another disadvantage of this procedure lies in the use of the expensive trifluoroacetic acid.

(3) 4-Nitraza-1,2-pentanediol

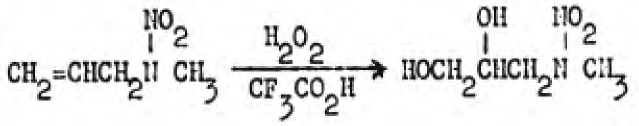
4-Nitraza-1,2-pentanediol was prepared from 4-aza-1,2-pentanediol via the oxidation of the corresponding nitroso compound (807, 57).



$$HOCH_2\overset{OH}{C}HCH_2Cl + CH_3NH_2 \longrightarrow HOCH_2\overset{OH}{C}HCH_2NHCH_3$$

$$\xrightarrow{HNO_2} HOCH_2\overset{OH}{C}HCH_2\overset{NO}{N}CH_3 \xrightarrow[CF_3CO_2H]{H_2O_2} HOCH_2\overset{OH}{C}HCH_2\overset{NO_2}{N}CH_3$$

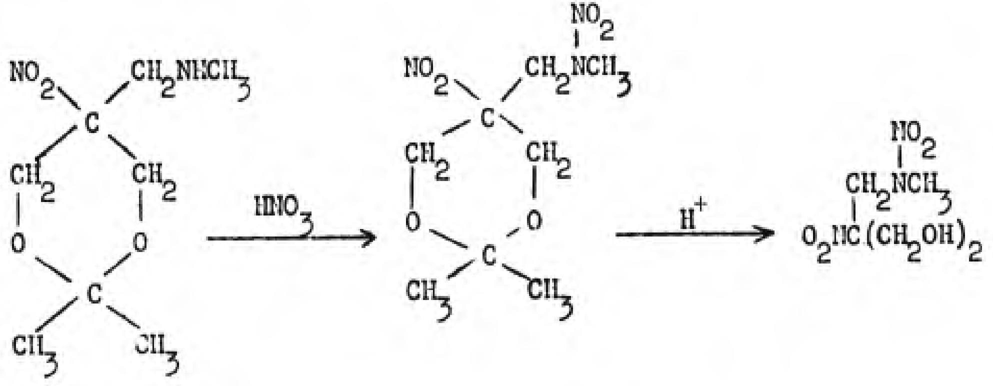
The adaptation of the olefin hydroxylation procedure of Emmons* to the preparation of 4-nitraza-1,2-pentanediol from N-methyl-allylnitramine is currently being studied **



$$CH_2{=}CHCH_2\overset{NO_2}{N}CH_3 \xrightarrow[CF_3CO_2H]{H_2O_2} HOCH_2\overset{OH}{C}HCH_2\overset{NO_2}{N}CH_3$$

(4) 2-Nitro-2-(methylnitraminomethyl)-1,3-propanediol, Attempted Preparation

Attempts to prepare 2-nitro-2-(methylnitraminomethyl)-1,3-propanediol from 2,2-dimethyl-5-nitro-5-methylaminomethyl-1,3-dioxan were unsuccessful (740, 58)

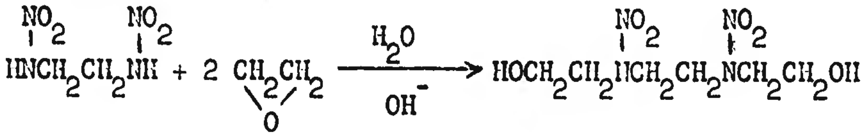


---

*Emmons et al., J. Am. Chem. Soc., 76, 3472 (1954).
**Aerojet Report No. L831-91.

i. Addition of Ethylene Oxide to Primary Nitramines; 3,6-Dinitraza-1,8-octanediol

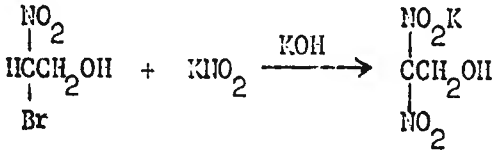
3,6-Dinitraza-1,8-octanediol was prepared first by Bloomquist* and later in these laboratories by the addition of ethylene oxide to ethylene dinitramine (807, 74; 941, 32).



The yields in this reaction are low, and it is necessary to handle the highly explosive ethylene dinitramine. Attempts to prepare 3,5-dinitraza-1,7-heptanediol from methylene dinitramine and ethylene oxide were unsuccessful.

j. The ter Meer Reaction; 2,2-Dinitroethanol

Potassium 2,2-dinitroethanol was prepared from 2-nitro-2-bromoethanol by the ter Meer reaction (417, App. C).**



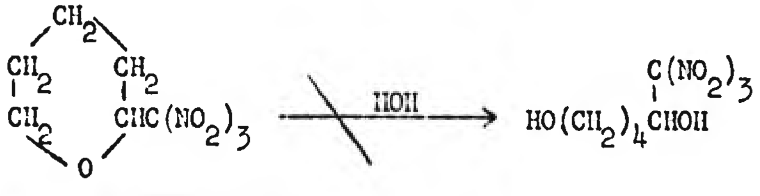
$$\mathrm{H\overset{NO_2}{\underset{Br}{C}}CH_2OH} + \mathrm{KNO_2} \xrightarrow{\mathrm{KOH}} \mathrm{\overset{NO_2K}{\underset{NO_2}{C}}CH_2OH}$$

This reaction is discussed in detail in paragraph V,B,1. Acidification of the salt with sulfuric acid gave 2,2-dinitroethanol (417A, 15). Bromination of the salt gave 2-bromo-2,2-dinitroethanol which was converted to 2-bromo-2,2-dinitroethyl acetate (371, 47). A review of the chemistry of dinitromethane and 2,2-dinitroethanol has been compiled (461).

k. Miscellaneous Attempted Preparations

(1) 1-Trinitromethyl-1,5-pentanediol

Attempts to hydrolyze 2-trinitromethyl-tetrahydropyran to yield 1-trinitromethyl-1,5-pentanediol were unsuccessful (482, 14)



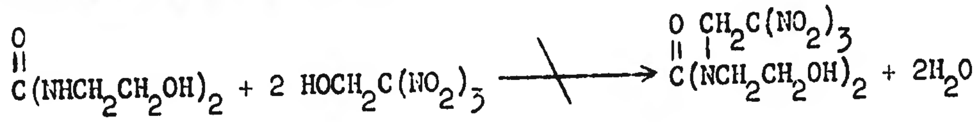
---

*Bloomquist et al., OSRD 5155, 9 June 1945.

**Ann. 181, 4 (1876).

(2) N,N'-bis-(2,2,2-Trinitroethyl)-N,N'-bis-(2-hydroxyethyl)-urea

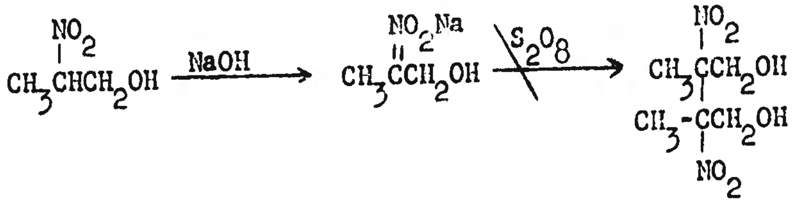
Attempts to prepare N,N'-bis-(2,2,2-trinitroethyl)-N,N'-bis-(2-hydroxyethyl)-urea from N,N'-bis-(β-hydroxyethyl)-urea and 2,2,2-trinitroethanol were unsuccessful (482, 13).



$$\overset{\overset{O}{\|}}{C}(NHCH_2CH_2OH)_2 + 2\ HOCH_2C(NO_2)_3 \cancel{\longrightarrow} \overset{\overset{O}{\|}}{C}(\overset{\overset{CH_2C(NO_2)_3}{|}}{N}CH_2CH_2OH)_2 + 2H_2O$$

(3) 2,3-Dinitro-2,3-dimethyl-1,4-butanediol

An attempt to prepare 2,3-dinitro-2,3-dimethyl-1,4-butanediol by the oxidative coupling of 2-nitro-1-propanol was unsuccessful (638, 83)



$$CH_3\overset{\overset{NO_2}{|}}{C}HCH_2OH \xrightarrow{NaOH} CH_3\overset{\overset{NO_2Na}{\|}}{C}CH_2OH \cancel{\xrightarrow{S_2O_8}} \begin{array}{c} NO_2 \\ | \\ CH_3CCH_2OH \\ | \\ CH_3-CCH_2OH \\ | \\ NO_2 \end{array}$$

3. Reactions

An extensive survey of the reactions of potassium 2,2-dinitroethanol and 2,2,2-trinitroethanol has been compiled in Aerojet Reports No. 461 and 494, respectively. The general reactions of nitro alcohols which have been studied are summarized below:

a. Esterification

The esters prepared from nitro alcohols have proved to be of great value, in many instances, as plasticizers for nitropolymers (paragraph II,E,b). The unsaturated esters are discussed under nitro monomers (paragraph II,A,3).

b. Urethane Formation

The prime purpose for preparing nitro diols was to treat them with diisocyanates in order to prepare polynitrourethanes. These reactions are discussed in the polymer section (paragraph III,B).

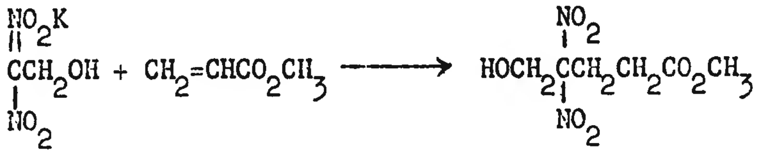
c. Michael Addition

(1) Discussion

The salts of nitro alcohols have been found to readily undergo a Michael reaction with α, β-unsaturated compounds.

(2) Methyl 5-Hydroxy-4,4-dinitropentanoate

Methyl 5-hydroxy-4,4-dinitropentanoate was prepared by the addition of potassium 2,2-dinitroethanol to methyl acrylate (404, 49).



$$\overset{NO_2K}{\underset{NO_2}{C}}CH_2OH + CH_2{=}CHCO_2CH_3 \longrightarrow HOCH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2CH_3$$

(3) Potassium 2,2,4,4-Tetranitro-1-butanol

The preparation of this alcohol is described in paragraph II,D,2,d.

d. Mannich Condensation

(1) Discussion

One of the most fruitful reactions of nitro alcohols is the Mannich condensation of α, β-nitro alcohols, formed by the Henry reaction, with ammonia, amines, and amino acids. This reaction is carried out easily and in good yield to give many interesting and useful compounds. Many high explosives have been prepared in this manner.*

(2) Dipotassium 1,1,5,5-Tetranitro-3-azapentane

Potassium 2,2-dinitro-1-ethanol condensed readily with ammonia to give dipotassium 1,1,5,5-tetranitro-3-azapentane (417, 24).

$$2\,\overset{NO_2K}{\underset{NO_2}{C}}CH_2OH + NH_3 \longrightarrow \overset{H}{N}-\left[CH_2C\begin{matrix}NO_2K\\NO_2\end{matrix}\right]_2$$

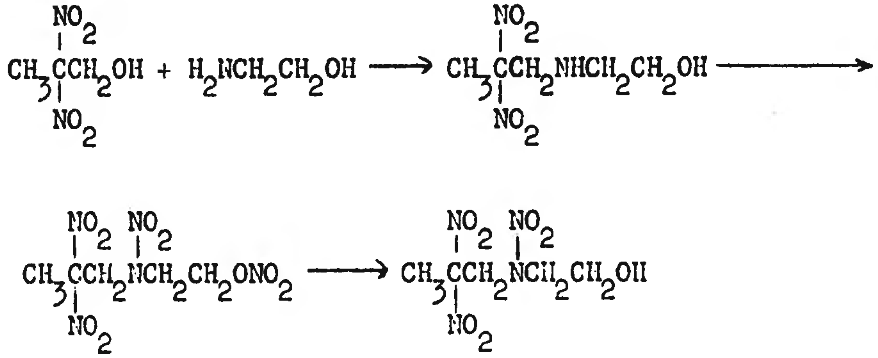
---

*Aerojet Reports No. 660, 682, and 711; Contract N7onr-46208.

The chemistry of this compound was studied extensively and is described in Report No. 461, 13.

(3) 3,5,5,-Trinitro-3-aza-1-hexanol

The condensation product of 2,2-dinitropropanol and ethanolamine was nitrated and hydrolyzed to give 3,5,5-trinitro-3-aza-1-hexanol (740, 61).



$$\mathrm{CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2OH + H_2NCH_2CH_2OH \longrightarrow CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2NHCH_2CH_2OH \longrightarrow}$$

$$\mathrm{CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2CH_2ONO_2 \longrightarrow CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2CH_2OH}$$

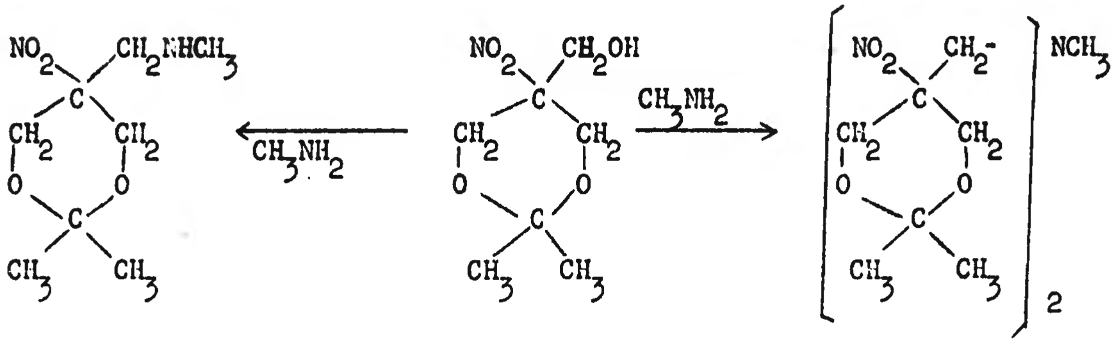
This method has the disadvantage that it involves the preparation of the intermediate nitrate ester, which is a high explosive. This alcohol was also prepared by the reduction of 3,5,5-trinitro-3-aza-1-hexanoyl chloride (paragraph II,D,2,b).

(4) Condensation of Nitro Alcohols with Glycine

The condensations of 2,2-dinitropropanol, 2,2,4,4-tetranitro-1,5-pentanediol, and methyl 5-hydroxy-4,4-dinitropentanoate with glycine have been studied (paragraph II,C,5).

(5) 2,2-Dimethyl-5-nitro-5-methylaminomethyl-1,3-dioxan and N,N'-bis-(1-Nitro-4,4-dimethyl-3,5-dioxa-cyclohexylmethyl) methylamine

The condensation of 2,2-dimethyl-5-nitro-5-hydroxymethyl-1,3-dioxan and methylamine gave both 2,2-dimethyl-5-nitro-5-methylaminomethyl-1,3-dioxan (I) and N,N-bis-(1-nitro-4,4-dimethyl-3,5-dioxacyclohexylmethyl)-methylamine (II) (686, 65).

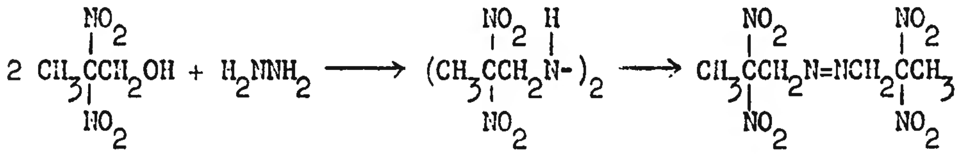


I

II

(6) N,N'-*bis*-(2,2-Dinitropropyl)-hydrazine

The condensation of 2,2-dinitropropanol and hydrazine gave N,N'-*bis*-(2,2-dinitropropyl)-hydrazine, which was oxidized to azo-*bis*-(2,2-dinitropropane) (622, 94).

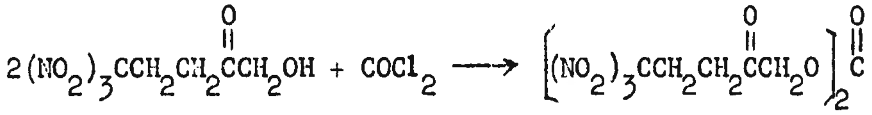


$$2\ CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2OH + H_2NNH_2 \longrightarrow (CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2\overset{H}{N}-)_2 \longrightarrow CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2N{=}NCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_3$$

e. Condensation with Phosgene

(1) *bis*-(5,5,5-Trinitro-2-keto-1-pentyl) Carbonate

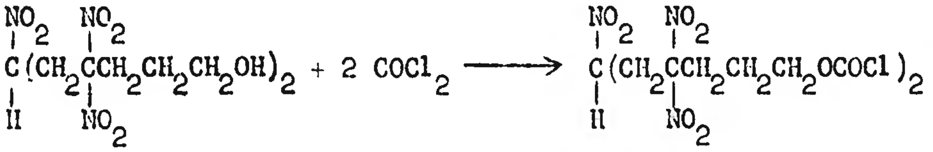
Treatment of 5,5,5-trinitro-2-keto-1-pentanol with phosgene gave *bis*-(5,5,5-trinitro-2-keto-1-pentyl) carbonate (590, 66).



$$2(NO_2)_3CCH_2CH_2\overset{\overset{O}{\|}}{C}CH_2OH + COCl_2 \longrightarrow \left[(NO_2)_3CCH_2CH_2\overset{\overset{O}{\|}}{C}CH_2O\right]_2\overset{\overset{O}{\|}}{C}$$

(2) *bis*-Chloroformate of 4,4,6,8,8-Pentanitro-1,11-undecanediol

The reaction of phosgene and 4,4,6,8,8-pentanitro-1,11-undecanediol yielded a *bis*-chloroformate (590, 67).



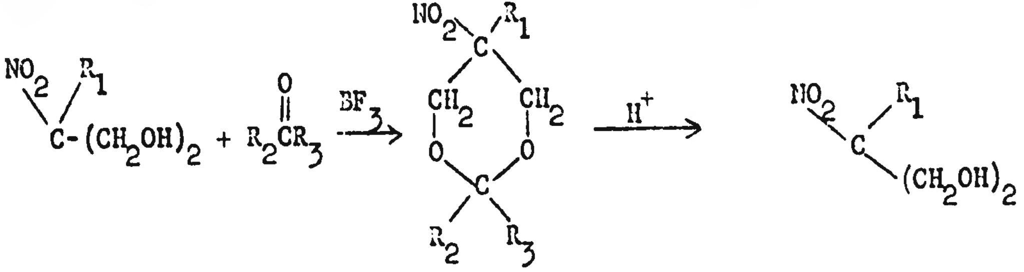
$$\underset{H}{\overset{NO_2}{C}}(CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CH_2OH)_2 + 2\ COCl_2 \longrightarrow \underset{H}{\overset{NO_2}{C}}(CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2CH_2OCOCl)_2$$

f. Dehydration

The conversion of nitro alcohols to nitro olefins is described in paragraph II,A,2.

4. Purification of Substituted 2-Nitro-1,3-propanediols

A new method has been developed for the preparation of cyclic ketals and acetals of variously substituted 2-nitro-1,3-propanediols. This method involves the condensation of the diols and the carbonyl reagent in the presence of boron trifluoride. The crystalline cyclic compounds are easily purified and then readily hydrolyzed to give pure diols. The following diols were purified by this method (638, 80; 663, 71; 686, 60; 712, 59):



R_1	R_2	R_3
CH_3	CH_3	CH_3
CH_2OH	CH_3	CH_3
NO_2	CH_3	CH_3
C_2H_5	CH_3	C_2H_5
CH_3	H	H
H	CH_3	CH_3
C_2H_5	CH_3	CH_3
CH_2OH	CH_3	$(NO_2)_3CCH_2CH_2$
CH_2OH	H	$CH_3C(NO_2)_2CH_2CH_2$
CH_2OH	CH_3	$CH_3C(NO_2)_2CH_2CH_2$

Thus, this method offers a ready means of purifying technical products that are difficult to obtain free from small amounts of impurities of related structure.

5. Preparation of Nitro Epoxides

a. Introduction

The nitro epoxides were prepared by the two general methods listed below and are summarized in Table 13.

(1) Epoxidation of the Corresponding Olefins

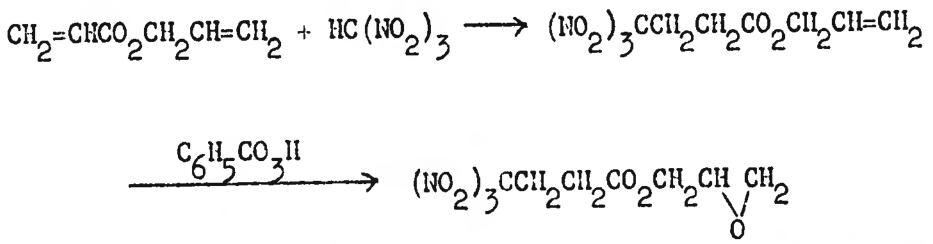
The epoxidation of the olefins was carried out with peracids such as perbenzoic and peroxytrifluoroacetic acids. Emmons and Pagano* recently reported that the epoxidation of negatively substituted olefins could be more conveniently accomplished by the use of a properly buffered peroxytrifluoroacetic acid solution.

(2) Dehydrohalogenation of Halohydrin

Epoxy compounds are readily formed by treating a halohydrin with base.

b. Glycidyl 4,4,4-Trinitrobutyrate

The preparation of glycidyl 4,4,4-trinitrobutyrate started from allyl acrylate, which gave allyl 4,4,4-trinitrobutyrate in a Michael reaction with nitroform. The conversion of allyl 4,4,4-trinitrobutyrate to glycidyl 4,4,4-trinitrobutyrate was conducted by oxidation with perbenzoic acid (563, 80).



$$CH_2{=}CHCO_2CH_2CH{=}CH_2 + HC(NO_2)_3 \longrightarrow (NO_2)_3CCH_2CH_2CO_2CH_2CH{=}CH_2$$

$$\xrightarrow{C_6H_5CO_3H} (NO_2)_3CCH_2CH_2CO_2CH_2\underset{\backslash O /}{CH\ CH_2}$$

Glycidyl butyrate was prepared as a model compound in a similar manner (590, 84).

c. 5,5-Dinitro-1,2-epoxyhexane

5,5-Dinitro-1,2-hexanediol was converted to 5,5-dinitro-2-bromo-1-hexanol, which was dehydrohalogenated to give 5,5-dinitro-1,2-epoxyhexane (L831-91).

---

*Emmons and Pagano, J. Am. Chem. Soc. 77, 89 (1955).

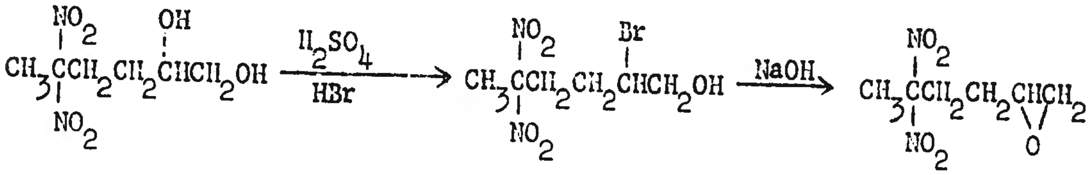
TABLE 13

NITRO EPOXIDES

Epoxides	b.p. °C	n_D^t	m.p. °C	References
(1) Glycidyl 4,4,4-Trinitrobutyrate			39-40*	563, 80
(2) 5,5-Dinitro-1,2-epoxyhexane	110/4 μ	n_D^{28} 1.4623		L831-91
(3) 5,5-Dinitro-2,3-epoxyhexane	77/0.3 μ	n_D^{25} 1.4584		1119, 20
(4) 4-Nitraza-1,2-epoxypentane	55-56/6 μ	n_D^{25} 1.4827		1119, 22; L831-92
(5) Glycidyl Nitrate	46-50/1 mm	n_D^{25} 1.4349		941, 33

---

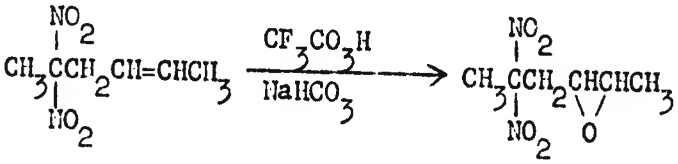
*Benzene Solvate



$$CH_3C(NO_2)_2CH_2CH_2CH(OH)CH_2OH \xrightarrow[HBr]{H_2SO_4} CH_3C(NO_2)_2CH_2CH_2CHBrCH_2OH \xrightarrow{NaOH} CH_3C(NO_2)_2CH_2CH_2\underset{O}{CHCH_2}$$

d. 5,5-Dinitro-2,3-epoxyhexane

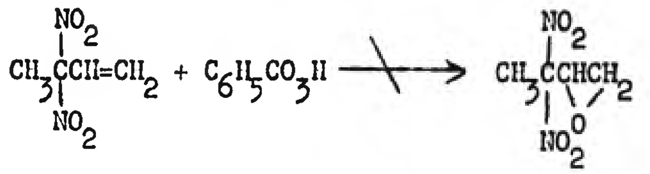
5,5-Dinitro-2-hexene was converted to 5,5-dinitro-2,3-epoxyhexane, using peroxytrifluoroacetic acid buffered with sodium acid carbonate (1119, 20).



$$CH_3C(NO_2)_2CH_2CH{=}CHCH_3 \xrightarrow[NaHCO_3]{CF_3CO_3H} CH_3C(NO_2)_2CH_2\underset{O}{CHCH}CH_3$$

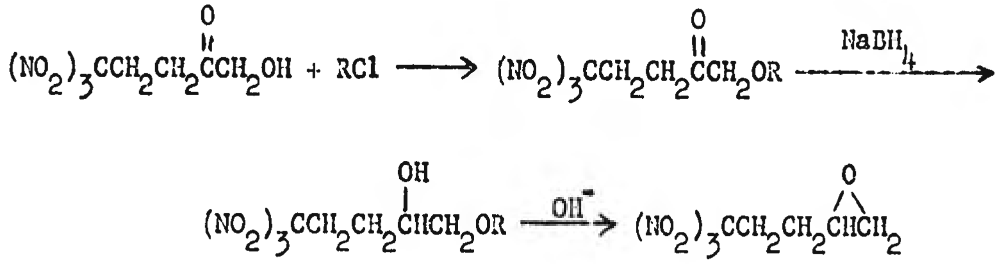
e. 3,3-Dinitro-1,2-epoxybutane, Attempted Preparation

Attempts to epoxidize 3,3-dinitro-1-butene with perbenzoic acid were unsuccessful, as the nitro olefin was unreactive (590, 69).



f. 5,5,5-Trinitro-1,2-epoxypentane, Attempted Preparation

It was planned to prepare 5,5,5-trinitro-1,2-epoxypentane from 5,5,5-trinitro-2-keto-1-pentanol in the following manner (590, 70).

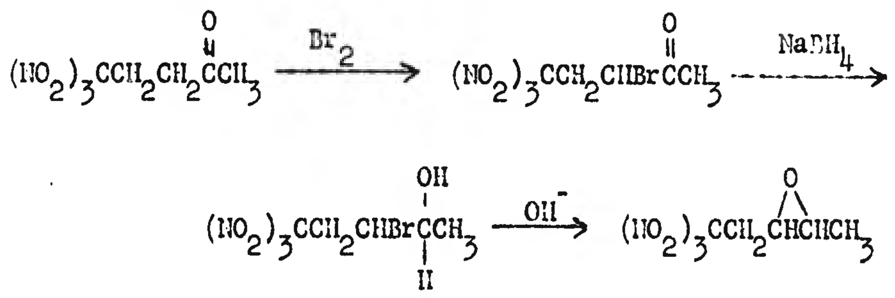


R = p-$CH_3C_6H_4SO_2$-

5,5,5-Trinitro-2-keto-1-pentyl p-toluenesulfonate was prepared but in poor yield, and no further work was done.

g. 5,5,5-Trinitro-2,3-epoxypentane, Attempted Preparation

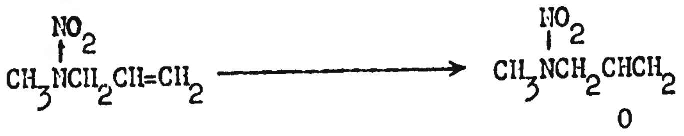
The preparation of 5,5,5-trinitro-2,3-epoxypentane was initiated, starting with 5,5,5-trinitro-2-pentanone (590, 70).



The synthesis was carried as far as the preparation of 5,5,5-trinitro-3-bromo-2-pentanone.

h. 4-Nitraza-1,2-epoxypentane

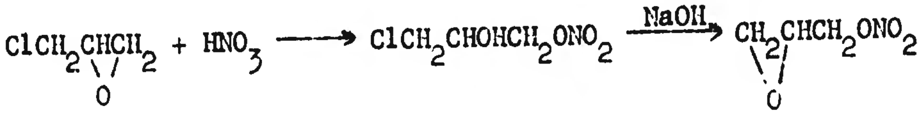
4-Nitraza-1,2-epoxypentane was prepared by the epoxidation of 4-nitraza-1-pentene, using both perbenzoic acid and buffered peroxytrifluoroacetic acid (1119, 22; L831-92).



$$CH_3\overset{NO_2}{\overset{\uparrow}{N}}CH_2CH{=}CH_2 \longrightarrow CH_3\overset{NO_2}{\overset{|}{N}}CH_2\underset{O}{CHCH_2}$$

i. Glycidyl Nitrate

Following the NOTS procedure,* glycidyl nitrate was prepared by treatment of epichlorohydrin with nitric acid and subsequent treatment with sodium hydroxide (941, 33).



$$ClCH_2\underset{\diagdown O \diagup}{CHCH_2} + HNO_3 \longrightarrow ClCH_2CHOHCH_2ONO_2 \xrightarrow{NaOH} \underset{\diagdown O \diagup}{CH_2CH}CH_2ONO_2$$

j. Summary and Evaluation

The epoxidation of nitro and nitramino olefins takes place more readily with peroxytrifluoroacetic acid than with any of the other peracids tried. It would be worthwhile repeating some of the earlier work, such as the attempted epoxidation of 3,3-dinitro-1-butene with perbenzoic acid, with peroxytrifluoroacetic acid. The disadvantages with this method are the difficulty in the preparation of the olefins and the high cost of peroxytrifluoroacetic acid. The preparation of epoxides by the dehydrohalogenation of halohydrins appears to be an attractive approach from the standpoint of ease of preparation and cost, and more work should be done along these lines.

E. NITRO PLASTICIZERS

1. Introduction

The nitropolymers prepared on this program are, for the most part, hard, brittle materials. These properties prohibit their use on the roller mill and the extrusion press, except at high temperatures and pressures,

---

*NAVORD Report No. 2028, Parts I and II (NOTS 685, 686).

and these conditions cause extensive degradation of nitropolymers. It is apparent that a plasticizer will be necessary to permit the fabrication of nitropolymers with the usual plastics-processing equipment. The ideal additive must possess the properties of low volatility, low melting point, and mutual solubility with the polymer, as well as the ability to plasticize the polymer. In addition, both a high energy content and a high density are desirable in order to maintain the specific impulse of the final propellant at a high level. Moreover, as would be expected, high thermal and impact stabilities are a primary requirement. The work described herein deals with the preparation of such compounds, in an attempt to meet the above requirements. The classes of compounds, containing the plosophoric nitro, nitramino, and/or nitrato groups, that were synthesized included carbamates, esters, ketones, ketoesters, lactones, and nitriles. The compounds synthesized and their properties are summarized in Table 14.

2. Preparation

a. Carbamates

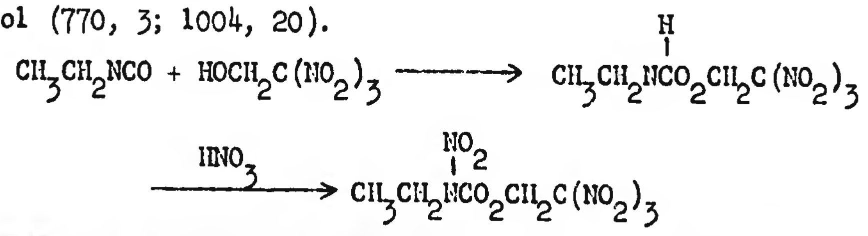
(1) Methyl 2-Nitrazapropionate

Methyl 2-nitrazapropionate has previously been prepared by nitration of methyl N-methylcarbamate.* The methyl N-methylcarbamate was prepared from methyl chloroformate and methyl amine (941, 43).

$$CH_3NH_2 + ClCO_2CH_3 \longrightarrow CH_3NHCO_2CH_3 \xrightarrow{HNO_3} CH_3\overset{NO_2}{N}CO_2CH_3$$

(2) 2,2,2-Trinitroethyl 2-Nitrazabutyrate

2,2,2-Trinitroethyl 2-nitrazabutyrate was prepared by the nitration of the adduct from ethyl isocyanate and 2,2,2-trinitroethanol (770, 3; 1004, 20).



$$CH_3CH_2NCO + HOCH_2C(NO_2)_3 \longrightarrow CH_3CH_2\overset{H}{N}CO_2CH_2C(NO_2)_3$$

$$\xrightarrow{HNO_3} CH_3CH_2\overset{NO_2}{N}CO_2CH_2C(NO_2)_3$$

---

*Franchimont and Klobbie, Rec. trav. chim. I, 354 (1888).

TABLE 14

NITRO PLASTICIZERS

Nitro Plasticizer	b.p. °C	n_D^{25}	m.p. °C	Density 25°	Reference
A. Carbamates					
(1) Methyl 2-nitrazapropionate	64-65/2 mm	1.4535	9-10		941, 43
(2) 2,2,2-Trinitroethyl-2-nitrazabutyrate			52-53		770, 3; 1004, 20
(3) Methyl 2,5-dinitrazahexanoate			57-57.5		941, 37
B. Esters					
(1) Methyl 4,4,4-trinitrobutyrate	86/0.5 mm	1.4590	24.5-26		622, 88
(2) 2-Methoxyethyl 4,4,4-trinitrobutyrate		1.4610	3.5	1.380	622, 88
(3) 2,2-Dinitropropyl 4,4,4-trinitrobutyrate			91.5-93		622, 90
(4) 2,2-Dinitrobutyl 4,4,4-trinitrobutyrate			82-83		622, 90
(5) 5,5,5-Trinitro-2-pentyl 4,4,4-trinitrobutyrate			61-62		622, 91
(6) 2,2-Dinitropropyl 4-nitro-4-methylpentanoate			73.5-74		1119, 25
(7) 2,2,2-Trinitroethyl 4-nitro-4-methylpentanoate			68.5-69		1119, 25
(8) Methyl 4,4-dinitropentanoate	115/1 mm		23	1.300	417, 28

TABLE 14 (cont.)

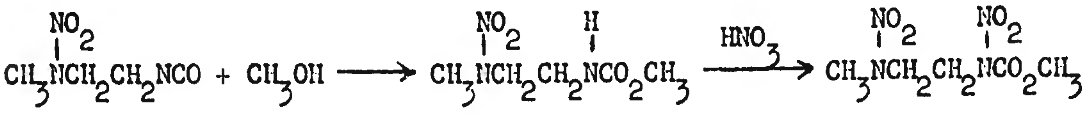
Nitro Plasticizer	b.p. °C	n_D^{25}	m.p. °C	Density 25°	Reference
(9) 2,2-Dinitropropyl 4,4-dinitropentanoate			101-101.5		967, 33; 1004, 21
(10) 2,2,2-Trinitroethyl 4,4-dinitropentanoate			93.5-94.5		1004, 21
(11) Ethylene bis(4,4-dinitropentanoate)			39-40	1.448	941, 40
(12) bis(2,2,2-Trinitroethyl) azelate		1.4739	18-20		622, 93
(13) 1,2-bis(4,4,4-Trinitrobutyroxy)-ethane			94-95		563, 83
(14) 1,2-bis(4,4,4-Trinitrobutyroxy)-propane			63.5-64.5		590, 74
(15) 1,2,3-tris(4,4,4-Trinitrobutyroxy)-propane			90-92		590, 74
(16) 1,5-bis(4,4,4-Trinitrobutyroxy)-3-oxapentane			34.5-35.5		590, 75
(17) 2,2-Dinitropropyl 4,4-dinitro-1,7-heptanedioate			127-129		622, 92
(18) 2,2-Dinitrobutyl 4,4-dinitro-1,7-heptanedioate			118-120		622, 92
(19) Methyl 4-nitrazapentanoate	107/1 mm	1.4694		1.232	801, 12; 907, 41
(20) 2,2-Dinitropropyl 4-nitrazapentanoate			39-40	1.488	1004, 21; 1083, 30
(21) 2,2,2-Trinitroethyl 4-nitrazapentanoate			58-59	1.545	1048, 24; 1083, 31
(22) Ethylene bis(4-nitrazapentanoate)			60-62	1.399	1083, 32

TABLE 14 (cont.)

Nitro Plasticizer	b.p. °C	n_D^{25}	m.p. °C	Density 25°	Reference
(23) Nitroisobutyl glyceryl *tris*-(4-nitrazapentanoate)			81-82		907, 55
(24) 3,5,5-Trinitro-3-aza-1-hexyl acetate			55-56		740, 61; 941, 42
(25) Methyl 3,5,5-trinitro-3-aza-1-hexanoate			78-80		663, 77
C. Ketones					
(1) 5,5,5-Trinitro-2-pentanone			43-44	1.454	563, 70
(2) 5,5-Dinitro-2-hexanone	110/1 mm			1.245	417, 28
D. Ketoesters					
(1) 5,5,5-Trinitro-2-keto-1-pentyl acetate			52.5-53.5		590, 75
E. Lactones					
(1) 4,4-Dinitrovalerolactone			78.5-79.5		868, 55
F. Nitrates					
(1) 1,4-Dinitratobutane	57-59/4 μ	1.4488		1.321	907, 54
(2) 1,2,6-Trinitratohexane	115-120/0.5 μ	1.4685		1.390	941, 41
G. Nitriles					
(1) 4,4-Dinitropentanonitrile	125-130/2 mm	1.4688		1.318	941, 40
(2) 4-Nitrazapentanonitrile	120/1 mm	1.4863		1.225	801, 12; 907, 41

(3) Methyl 2,5-Dinitrazahexanoate

Methyl 2,5-dinitrazahexanoate was prepared by the nitration of the adduct from 3-nitrazabutyl isocyanate and methanol (941, 37).



$$CH_3\overset{NO_2}{N}CH_2CH_2NCO + CH_3OH \longrightarrow CH_3\overset{NO_2}{N}CH_2CH_2\overset{H}{N}CO_2CH_3 \xrightarrow{HNO_3} CH_3\overset{NO_2}{N}CH_2CH_2\overset{NO_2}{N}CO_2CH_3$$

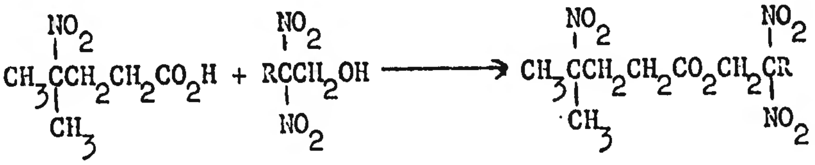
b. Esters

(1) Esters of 4,4,4-Trinitrobutyric Acid

The following esters of 4,4,4-trinitrobutyric acid were prepared either by the addition of nitroform to the corresponding acrylic ester or the esterification of 4,4,4-trinitrobutyric acid with the appropriate alcohol: methyl 4,4,4-trinitrobutyrate (622, 88), 2-methoxyethyl 4,4,4-trinitrobutyrate (622, 88; SPIA Data Sheet - 622, App.), 2,2-dinitropropyl 4,4,4-trinitrobutyrate (622, 90), 2,2-dinitrobutyl 4,4,4-trinitrobutyrate (622, 90), 5,5,5-trinitro-2-pentyl 4,4,4-trinitrobutyrate (622, 91), *bis*-(2,2,2-trinitroethyl) azelate (622, 93), 1,2-*bis*-(4,4,4-trinitrobutyroxy)-ethane (563, 83; SPIA Data Sheet - 590, App.), 1,2-*bis*-(4,4,4-trinitrobutyroxy)-propane (590, 74; SPIA Data Sheet - 622, App.), 1,2,3-*tris*-(4,4,4-trinitrobutyroxy-propane (590, 74; SPIA Data Sheet - 622, App.), and 1,5-*bis*-(4,4,4-trinitrobutyroxy)-3-oxapentane (590, 75; SPIA Data Sheet - 622, App.).

(2) Esters of 4-Nitro-4-methylpentanoic Acid

2,2-Dinitropropyl 4-nitro-4-methylpentanoate and 2,2,2-trinitroethyl 4-nitro-4-methylpentanoate were prepared from 4-nitro-4-methylpentanoic acid and the corresponding alcohol, using polyphosphoric acid as the catalyst (1119, 25).



$$CH_3\underset{CH_3}{\overset{NO_2}{C}}CH_2CH_2CO_2H + R\underset{NO_2}{\overset{NO_2}{C}}CH_2OH \longrightarrow CH_3\underset{CH_3}{\overset{NO_2}{C}}CH_2CH_2CO_2CH_2\underset{NO_2}{\overset{NO_2}{C}}R$$

$R = CH_3, NO_2$

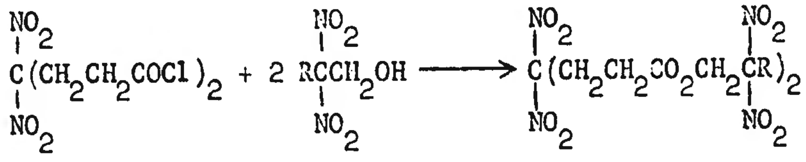
These esters had been prepared previously from the acid chloride and alcohol, using aluminum chloride as catalyst.*

(3) Esters of 4,4-Dinitropentanoic Acid

Methyl 4,4-dinitropentanoate (417, 28; SPIA Data Sheet - 941, App.), 2,2-dinitropropyl 4,4-dinitropentanoate (967, 33; 1004, 21), 2,2,2-trinitroethyl 4,4-dinitropentanoate (1004, 21), and ethylene bis-(4,4-dinitropentanoate) (941, 40) were prepared from 4,4-dinitropentanoic acid and the corresponding alcohol in the presence of polyphosphoric acid or from the acid chloride and the alcohol.

(4) Esters of 4,4-Dinitro-1,7-heptanedioic Acid

2,2-Dinitropropyl 4,4-dinitro-1,7-heptanedioate and 2,2-dinitrobutyl 4,4-dinitro-1,7-heptanedioate were prepared from 4,4-dinitro-1,7-heptanedioyl chloride and the corresponding alcohol (622, 92).

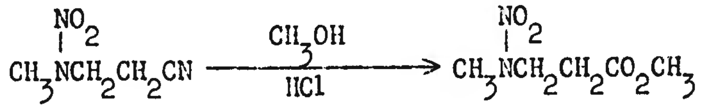


$$\underset{NO_2}{\overset{NO_2}{C}}(CH_2CH_2COCl)_2 + 2\ R\underset{NO_2}{\overset{NO_2}{C}}CH_2OH \longrightarrow \underset{NO_2}{\overset{NO_2}{C}}(CH_2CH_2CO_2CH_2\underset{NO_2}{\overset{NO_2}{C}}R)_2$$

$R = CH_3,\ CH_3CH_2$

(5) Esters of 4-Nitrazapentanoic Acid

Methyl 4-nitrazapentanoate was prepared by the alcoholysis of 4-nitrazapentanonitrile (801, 12; 907, 41).



$$CH_3\overset{NO_2}{N}CH_2CH_2CN \xrightarrow[HCl]{CH_3OH} CH_3\overset{NO_2}{N}CH_2CH_2CO_2CH_3$$

2,2-Dinitropropyl 4-nitrazapentanoate (1004, 21; 1083, 30), 2,2,2-trinitroethyl 4-nitrazapentanoate (1048, 24; 1083, 31), ethylene bis-(4-nitrazapentanoate) (1083, 32), and tris-(4-nitrazapentanoxy-methyl)-nitromethane (907, 55), were prepared from 4-nitrazapentanoic acid

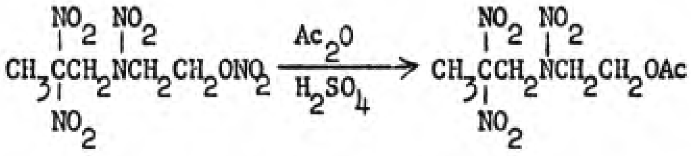
---

*Hercules Powder Co., Navy Contract NOrd-11280, Task A, 18 August 1955.

and the corresponding alcohol in the presence of polyphosphoric acid or from the acid chloride and the alcohol. The large-scale preparation of the esters of 4-nitrazapentanoic acid is described in paragraph V,C.

(6) 3,5,5-Trinitro-3-aza-1-hexyl Acetate

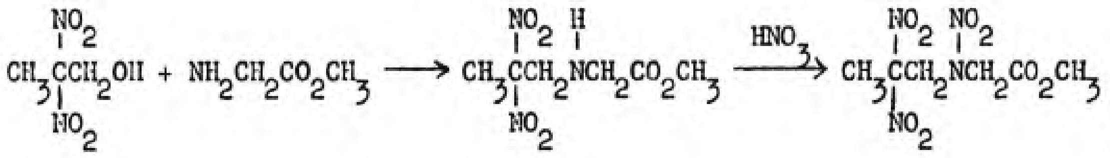
3,5,5-Trinitro-3-aza-1-hexyl acetate was prepared by acetolysis of 3,5,5-trinitro-3-aza-1-hexyl nitrate (740, 61; 941, 42).



$$CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2CH_2ONO_2 \xrightarrow[H_2SO_4]{Ac_2O} CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2CH_2OAc$$

(7) Methyl 3,5,5-Trinitro-3-aza-1-hexanoate

Methyl 3,5,5-trinitro-3-aza-1-hexanoate was prepared by nitration of the condensation product of methyl glycine and 2,2-dinitropropanol (663, 77).

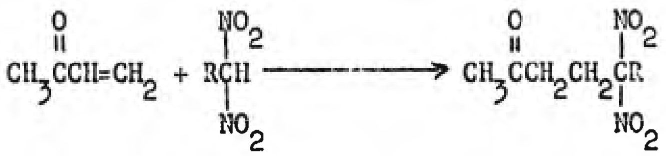


$$CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2OH + NH_2CH_2CO_2CH_3 \longrightarrow CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2\overset{H}{N}CH_2CO_2CH_3 \xrightarrow{HNO_3} CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2\overset{NO_2}{N}CH_2CO_2CH_3$$

c. Ketones

(1) 5,5,5-Trinitro-2-pentanone and 5,5-Dinitro-2-hexanone

5,5,5-Trinitro-2-pentanone* (563, 70), and 5,5-dinitro-2-hexanone (417, 28) were prepared by the addition of nitroform and 1,1-dinitroethane to methyl vinyl ketone.



$$CH_3\overset{O}{\overset{\|}{C}}CH{=}CH_2 + R\overset{NO_2}{\underset{NO_2}{C}}H \longrightarrow CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}R$$

$R = NO_2, CH_3$

---

*U.S. Rubber Co., Quarterly Report No. 4.

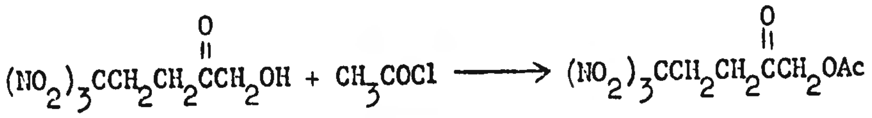
(2) 5-Nitraza-2-hexanone, Attempted Preparation

The nitration of 1-methylamino-3-butanone was considered the most feasible method of synthesizing 5-nitraza-2-hexanone. However, the preparation of this β-aminoketone by the addition of methyl amine to methyl vinyl ketone was unsuccessful (868, 56).

d. Ketoesters

(1) 5,5,5-Trinitro-2-keto-1-pentyl Acetate

5,5,5-Trinitro-2-keto-1-pentyl acetate was prepared from the corresponding alcohol and acetyl chloride (590, 75).

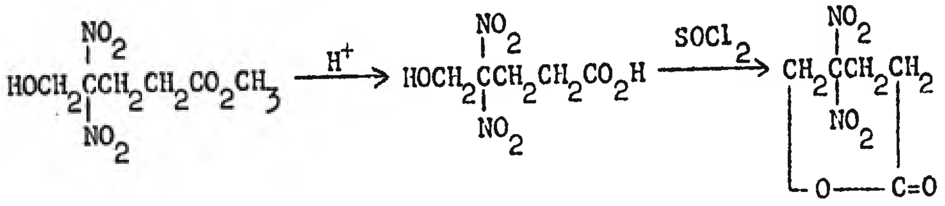


$$(NO_2)_3CCH_2CH_2\overset{O}{\overset{\|}{C}}CH_2OH + CH_3COCl \longrightarrow (NO_2)_3CCH_2CH_2\overset{O}{\overset{\|}{C}}CH_2OAc$$

e. Lactones

(1) 4,4-Dinitro-5-pentanolactone

Methyl 5-hydroxy-4,4-dinitropentanoate was hydrolyzed to the corresponding acid, which was dehydrated with thionyl chloride to give 4,4-dinitro-5-pentanolactone (868, 55).



f. Nitrates

Treatment of 1,4-butanediol and 1,2,6-hexanetriol with nitric acid gave 1,4-dinitratobutane (907, 54) and 1,2,6-trinitratohexane (941, 41), respectively.

g. Nitriles

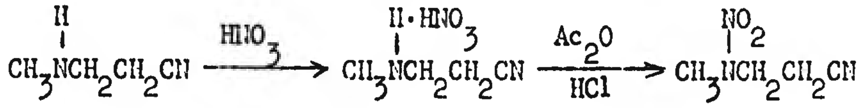
(1) 4,4-Dinitropentanonitrile

4,4-Dinitropentanonitrile was prepared by the addition of 1,1-dinitroethane to acrylonitrile (941, 40).

$$CH_3CH(NO_2)_2 + CH_2{=}CHCN \longrightarrow CH_3C(NO_2)_2CH_2CH_2CN$$

(2) 4-Nitrazapentanonitrile

4-Azapentanonitrile was converted to the corresponding nitraza compound via the nitric acid salt (801, 12; 907, 41).



$$CH_3N(H)CH_2CH_2CN \xrightarrow{HNO_3} CH_3N(H\cdot HNO_3)CH_2CH_2CN \xrightarrow[HCl]{Ac_2O} CH_3N(NO_2)CH_2CH_2CN$$

3. Summary and Evaluation

In studying the properties of the plasticizers that have been prepared, it has been found that a marked transition in properties appears around a molecular weight of 280. For the compounds having a molecular weight greater than 280, there was found to be a very low volatility, and frequently melting points are above room temperature, densities are higher, and thermal stabilities are significantly improved. For formulation purposes, the desirable melting point range of the plasticizers appears to be below 60°. Solids containing the trinitromethyl group and melting below 40° exhibit poor thermal stability, whereas above 60° the ability to plasticize the nitropolymer is diminished. As far as classes of compounds are concerned, nitrate esters are not useful because of their poor thermal stability, but the organic esters have found the widest application. In particular, the esters of 4-nitrazapentanoic acid have shown the most promise. The esters of 4,4-dinitropentanoic acids and 4,4,4-trinitrobutyric acid were not as satisfactory, because of their higher melting points. The best method for the preparation of these esters has been from the acid, alcohol, and polyphosphoric acid catalyst. The use of mixed plasticizers, such as 4-nitrazapentanonitrile and 2,2,2-trinitroethyl 4-nitrazapentanoate, has been found to have considerable merit.

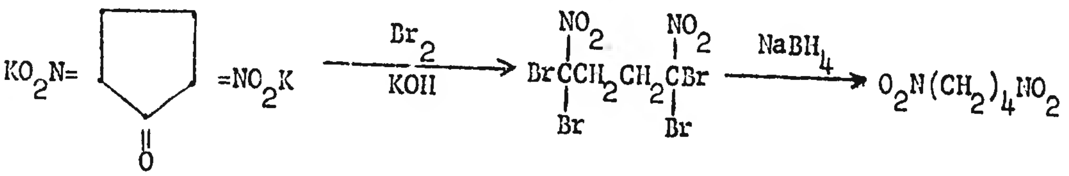
F. INTERMEDIATES

1. Introduction

The first objective of the nitropolymer program was the synthesis of polynitro aliphatic compounds and their derivatives. Examination of the literature indicated a sparsity of such compounds. Vapor-phase nitration of hydrocarbons has been shown to produce mononitroalkanes only and not to lead to polynitroalkanes. Liquid-phase nitration at elevated temperatures and pressures gives gem-dinitroalkanes, but it is only practical for introducing the two nitro groups on secondary carbon atoms and for compounds which can stand the vigorous conditions employed. Thus, it was evident that there was a great need for new and convenient methods for the introduction of nitro groups, particularly α,ω-dinitro, gem-dinitro, and trinitromethyl groups into aliphatic compounds. These new methods and applications are described in the following sections.

2. α,ω-Dinitro Compounds

α,ω-Dinitro alkanes have been prepared in fair yield from α,ω-dihaloalkanes and silver nitrite,* but the method is expensive. A new method for the preparation of α,ω-dinitro compounds from cyclic ketones has been developed** and is shown in the following equations:



Nitration of cyclopentanone with ethyl nitrate in the presence of potassium ethoxide gave dipotassium 2,5-dinitrocyclopentanone, which was brominated to yield 1,1,4,4-tetrabromo-1,4-dinitrobutane. The tetrabromo compound was

---

*H. Feuer and G. Leston, Organic Synthesis, Vol. 34, J. Wiley and Sons, New York, N.Y.

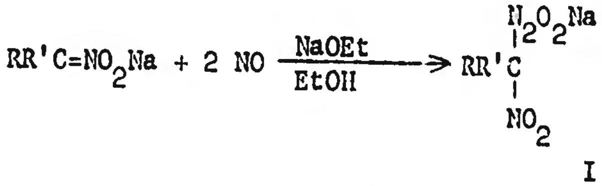
**K. Klager, J. Org. Chem. 20, 646 (1955); 468, 38; 482, 20; 563, 85.

readily reduced with sodium borohydride to give 1,4-dinitrobutane. This new method of opening cyclic ketones was also successfully applied in the case of dipotassium 2,6-dinitrocyclohexanone to give 1,1,5,5-tetrabromo-1,5-dinitropentane.

3. gem-Dinitro Compounds

a. By Oxidative Nitration

Traube,* in his studies of the reaction of nitric oxide with molecules containing an active methylene group, reported that the 2-nitrosohydroxylamino-2-nitroalkanes (by acidification of the sodium salts prepared from nitric oxide on the sodium-1-nitroalkanes) decomposed rapidly to the corresponding nitrolic acids, and that the silver salts of those nitric oxide reaction products deposited silver. The course of the silver salt decomposition was not investigated by Traube. In an attempt to find a general method for the introduction of the nitro group into nitroalkanes, the reaction of nitric oxide with salts of secondary nitroalkanes was investigated (404, 30). The sodium salts of 2-nitropropane, 2-nitrobutane, and nitrocyclohexane were treated with nitric oxide to give salts which were assumed to have the Traube structure (I):



$$RR'C{=}NO_2Na + 2\ NO \xrightarrow[EtOH]{NaOEt} RR'\overset{\overset{\displaystyle N_2O_2Na}{|}}{\underset{\underset{\displaystyle NO_2}{|}}{C}}$$

I

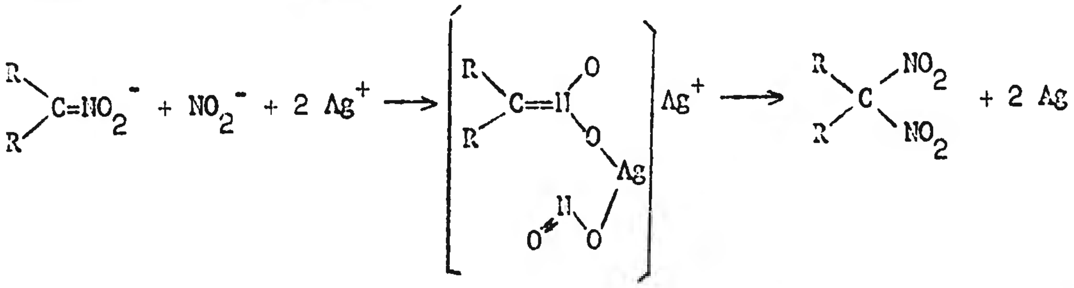
Treatment of these salts (I) with silver ion gave 2,2-dinitropropane, 2,2-dinitrobutane, and 1,1-dinitrocyclohexane in yields of 50 to 70%. The preparation of gem-dinitro compounds in this manner constitutes a new and important method for the preparation of such compounds.

Further study (417, 29) showed that in no experiment did the yield of salt (I), the desired intermediate, exceed 50%; furthermore, analysis of the salt obtained from nitric oxide and sodium 2-nitrobutane

---

*Ann. 300, 81-104 (1898).

indicated that the product has an empirical formula of $C_4H_8O_4N_2Na_2$ rather than $C_4H_8O_4N_3Na$ (I). These results suggested that the secondary salts are double or complex salts consisting of sodium secondary nitroalkane and sodium nitrite (1:1). These observations have led to a new preparative method for gem-dinitro compounds. When an aqueous solution containing nitroalkane and nitrite ion (1:1) was treated with two equivalents of silver ion, a gem-dinitroalkane was formed. 2,2-Dinitropropane, 2,2-dinitrobutane, 1,1-dinitrocyclohexane, and 2,2-dinitro-1,3-propanediol have been prepared by this reaction in yields of 70-92%. The reaction was also found to be applicable for the preparation of 1,1-dinitro compounds as 1,1-dinitroethane was obtained in 40% yield from nitroethane. This new reaction has been called an oxidative nitration reaction and it appears likely that the introduction of the second nitro group may depend on an intermediate complex:



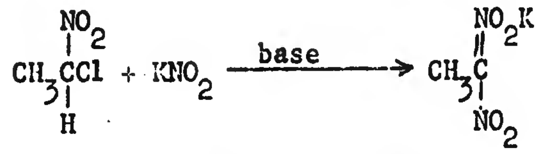
The decomposition of the complex to products is sterically favored, because of the six-membered ring formation in the transition state. Oxidizing agents such as hypobromite, permanganate, persulfate, ferric, and mercuric ions do not effect this transformation. The choice of oxidizing agents is dependent on the requirement that the reaction proceeds only in alkaline or neutral media; under acidic conditions, the formation of pseudonitrole occurs rapidly.

b. By the ter Meer Reaction

The ter Meer reaction* has been used for the preparation of terminal gem-dinitro compounds from the corresponding chloronitro compounds. The reaction consists in treating a chloronitro compound such as 1-chloro-1-nitroethane with potassium nitrite and base to give potassium 1,1-dinitroethane:

---

*Ann. 181, 4 (1876).

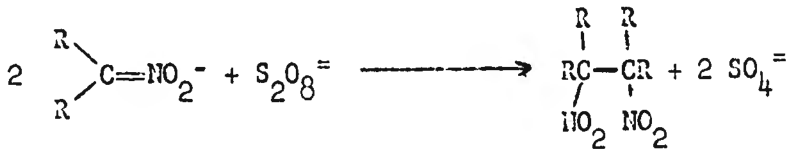


$$CH_3\overset{NO_2}{\underset{H}{C}}Cl + KNO_2 \xrightarrow{base} CH_3\overset{NO_2K}{\underset{NO_2}{C}}$$

Potassium 1,1-dinitroethane was prepared by the ter Meer reaction, using the improved procedure of the Naval Ordnance Laboratory,* and converted directly to 2,2-dinitropropanol (1119, 26). The conversion of 2-bromo-2-nitroethanol to potassium 2,2-dinitroethanol has been described (paragraph II,D,2,j).

4. vic-Dinitro Compounds

It was found that salts of nitroalkanes are converted by oxidizing agents such as persulfate ion, ferricyanide ion, or hydrogen peroxide, in aqueous medium, into dimeric dinitro compounds (417, 31). The best yields (30-55%) were obtained with persulfate ion:



$$2\ R_2C{=}NO_2^- + S_2O_8^{=} \longrightarrow \overset{R}{\underset{NO_2}{RC}}-\overset{R}{\underset{NO_2}{CR}} + 2\ SO_4^{=}$$

Ketones are side-products. Dinitro compounds which have been prepared conveniently by this method are 2,3-dimethyl-2,3-dinitrobutane, 3,4-dimethyl-3,4-dinitrohexane, and 1,1′-dinitro-bicyclohexyl.

5. Pseudo Nitroles

Treatment of the sodium salts of 2-nitropropane, 2-nitrobutane, and nitrocyclohexane with nitric oxide gave salts which were postulated as being complex salts consisting of sodium secondary nitroalkane and sodium nitrite (1:1) (paragraph II,F,3,a). Acidification of these complex salts gave propyl, butyl, and cyclohexyl pseudo nitroles in yields of 50 to 75% (404, 30).

6. Adducts of Acidic Nitro Compounds and Nitro Olefins

a. Introduction

One of the best methods for the introduction of nitro groups into an organic molecule is the Michael addition of acidic nitro

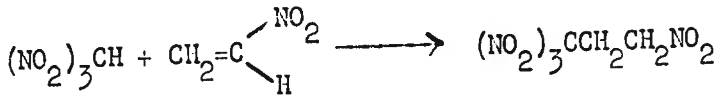
---

*NAVORD Report No. 3777, 20 October 1954.

compounds to negatively substituted olefins. The preparation of aliphatic nitro acids by the addition of acidic nitro compounds to α, β-unsaturated acids, esters, and nitriles has been described (paragraph II,C,2,a). The addition of acidic nitro compounds to nitro olefins is described in the following section and summarized in Table 15.

b. Nitroethylene

1,1,1,3-Tetranitropropane was prepared by the addition of nitroform to nitroethylene (371, 20; 386A, 4; 417A, 5).

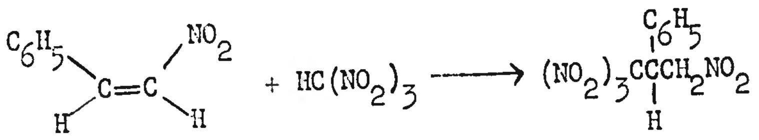


$$(NO_2)_3CH + CH_2{=}C\begin{matrix}NO_2\\H\end{matrix} \longrightarrow (NO_2)_3CCH_2CH_2NO_2$$

The original procedure has been improved by running the reaction in aqueous methanol with a catalytic amount of base.* The two possible modes of addition could give either 1,1,1,2 or 1,1,1,3-tetranitropropane. The latter structure was established by reduction of the adduct with tin and hydrochloric acid to 1,3-diaminopropane (417A, 19). Attempted reactions of 1,1,1,3-tetranitropropane with aldehydes were unsuccessful (371, 20; 386A, 5; 417A, 5). The properties of 1,1,1,3 are recorded in a SPIA Data Sheet (417A, 7).

c. β-Nitrostyrene

2-Phenyl-1,1,1,3-tetranitropropane was prepared by the addition of nitroform to β-nitrostyrene (417A, 20).



$$\begin{matrix}C_6H_5\\H\end{matrix}C{=}C\begin{matrix}NO_2\\H\end{matrix} + HC(NO_2)_3 \longrightarrow (NO_2)_3C\overset{C_6H_5}{\underset{H}{C}}CH_2NO_2$$

Attempted reactions of this nitro compound with aldehydes were also unsuccessful (417A, 6).

d. 2-Nitroallyl Acetate

A new and fruitful reaction was discovered in studying the addition of acidic nitro compounds to 2-nitroallyl acetate. The path of the reaction has been postulated as follows. The acidic nitro compound (I)

---

*Aerojet Report No. 530, 3, Contract N7onr-46208.

TABLE 15

ADDUCTS OF ACIDIC NITRO COMPOUNDS AND NITRO OLEFINS

Acidic Nitro Compound	Nitro Olefin	Adduct	m.p. °C	Reference
(1) Nitroform	Nitroethylene	1,1,1,3-Tetranitropropane	50-51	371, 20; 386A, 4; 417A, 5; 538, 3
(2) Nitroform	β-Nitrostyrene	2-Phenyl-1,1,1,3-tetranitropropane	86-87	417A, 20
(3) 2-Nitropropane	2-Nitroallyl Acetate	2,4,6-Trinitro-2,6-dimethylheptane	124-126	499, 21
(4) 1,1-Dinitroethane	2-Nitroallyl Acetate	2,2,4,6,6-Pentanitroheptane*	82-83	499, 18
(5) 1,1-Dinitropropane	2-Nitroallyl Acetate	3,3,5,7,7-Pentanitrononane	91-92	638, 102
(6) 1,1-Dinitrobutane	2-Nitroallyl Acetate	4,4,6,8,8-Pentanitroundecane	81-82	638, 102
(7) 2,2-Dimethyl-5-nitro-1,3-dioxane	2-Nitroallyl Acetate	2-Nitro-1,3-propylene-bis-(1-nitro-4,4-dimethyl-3,5-dioxan)	240	638, 103
(8) Potassium 2,2-Dinitroethyl Acetate**	1,1-Dinitroethylene**	Potassium 2,2,4,4-Tetranitrobutyl Acetate	174	424, 26
(9) Sodium 1,1-Dinitroethane	1,1-Dinitroethylene**	Sodium 1,1,3,3-Tetranitrobutane	***	468, 34
(10) Sodium Phthalimide	1,1-Dinitroethylene**	Sodium 1,1-Dinitro-2-phthalimido ethane	238	432, 27
(11) Potassium 2,2-Dinitro-1-ethanol	1,1-Dinitroethylene**	Potassium 2,2,4,4-Tetranitrobutanol	****	457, 13

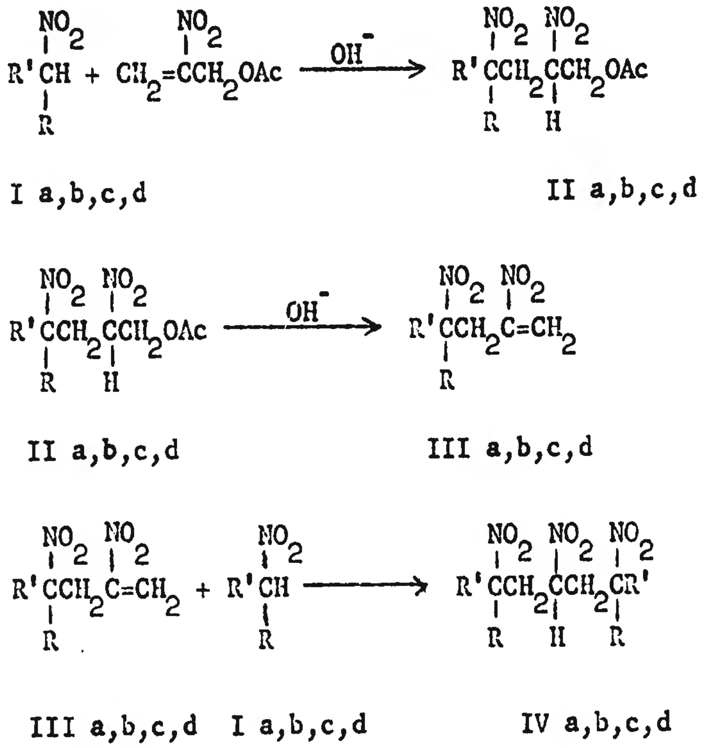
* Converted to potassium 2,2,4,6,6-pentanitroheptane, m.p. 110° d (499, 20); 2,2,4,6,6-pentanitro-4-bromoheptane, m.p. 137-138° (499, 20).

** Compound never isolated but postulated as the transitory intermediate.

*** Converted to the more easily purified potassium 1,1,3,3-tetranitrobutane, m.p. 137-138° (468, 35).

**** Converted to 2,2,4,4-tetranitro-1-butanol, m.p. 35-36° (457, 17) and to 2,2,4,4-tetranitro-1,5-pentanediol, m.p. 97-99° (482, 14).

added readily, in the presence of a basic catalyst, to 2-nitroallyl acetate to give a 1:1 adduct (II). Acetic acid was split out from II to give a nitroolefin (III) again. A second mole of I was then added to III to give the product (IV). It was not possible to isolate the intermediates II or III. The polynitroalkanes prepared by this method were 2,4,6-trinitro-2,6-dimethylheptane (IVa) (499, 21), 2,2,4,6,6-pentanitroheptane (IVb) (499, 18), 3,3,5,7,7-pentanitrononane (IVc) (638, 102), and 4,4,6,8,8-pentanitroundecane (IVd) (638, 102).



$$\underset{R}{\overset{NO_2}{R'CH}} + CH_2{=}\overset{NO_2}{C}CH_2OAc \xrightarrow{OH^-} R'\underset{R}{\overset{NO_2}{C}}CH_2\underset{H}{\overset{NO_2}{C}}CH_2OAc$$

I a,b,c,d II a,b,c,d

$$R'\underset{R}{\overset{NO_2}{C}}CH_2\underset{H}{\overset{NO_2}{C}}CH_2OAc \xrightarrow{OH^-} R'\underset{R}{\overset{NO_2}{C}}CH_2\overset{NO_2}{C}{=}CH_2$$

II a,b,c,d III a,b,c,d

$$R'\underset{R}{\overset{NO_2}{C}}CH_2\overset{NO_2}{C}{=}CH_2 + \underset{R}{\overset{NO_2}{R'CH}} \longrightarrow R'\underset{R}{\overset{NO_2}{C}}CH_2\underset{H}{\overset{NO_2}{C}}CH_2\underset{R}{\overset{NO_2}{C}}R'$$

III a,b,c,d I a,b,c,d IV a,b,c,d

a: $R{=}R'{=}CH_3$

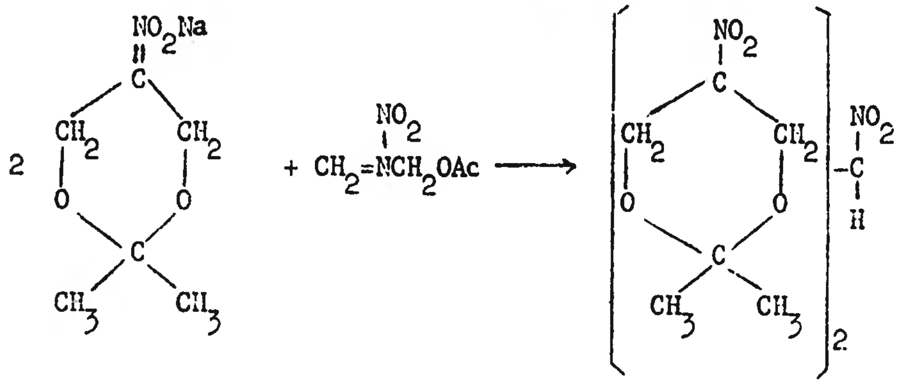
b: $R{=}NO_2$, $R'{=}CH_3$

c: $R{=}NO_2$, $R'{=}CH_3CH_2$

d: $R{=}NO_2$, $R'{=}CH_3CH_2CH_2$

The potassium salt of IVb was prepared, as well as 2,2,4,6,6-pentanitro-4-bromoheptane (499, 20); IV did not undergo the Henry or Michael reactions (499, 18). It was also found that comparable results were obtained in the preparation of 2,2,4,6,6-pentanitroheptane (IVb) through the use of the precursor of 2-nitroallyl acetate, i.e., 1,3-diacetoxy-2-nitropropane (515, 24).

2-Nitro-1,3-propylene-bis-(1-nitro-4,4-dimethyl-3,5-dioxane) was prepared by the condensation of the sodium salt of 2,2-dimethyl-5-nitro-1,3-dioxane and 2-nitroallyl acetate (638, 103).



The preparation of dimethyl 4,4,6,8,8-pentanitro-1,11-undecanedioate from the sodium salt of methyl 4,4-dinitrobutyrate and 2-nitroallyl acetate is described in paragraph II,C,3,d.

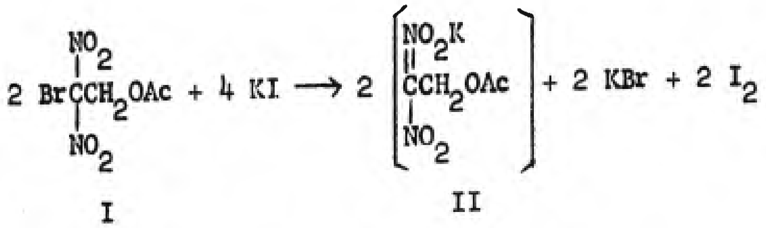
e. 1,1-Dinitroethylene

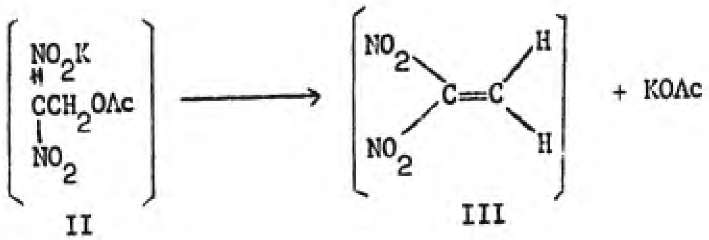
(1) Introduction

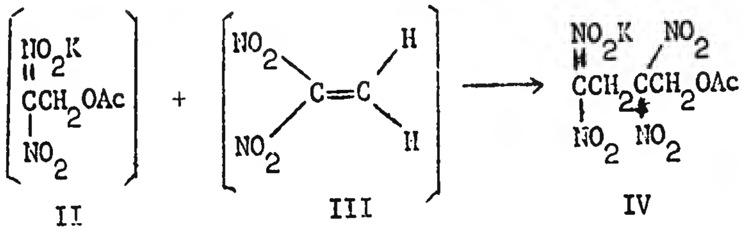
The many attempts to prepare 1,1-dinitroethylene are discussed in paragraph II,A,2,h. Although it has never been possible to isolate 1,1-dinitroethylene, its existence as a reactive intermediate capable of transitory existence has been demonstrated in the studies on the reactions of 2-bromo-2,2-dinitroethyl acetate and potassium 2,2-dinitroethanol, which are described below.

(2) Reactions of 2-Bromo-2,2-dinitroethyl Acetate

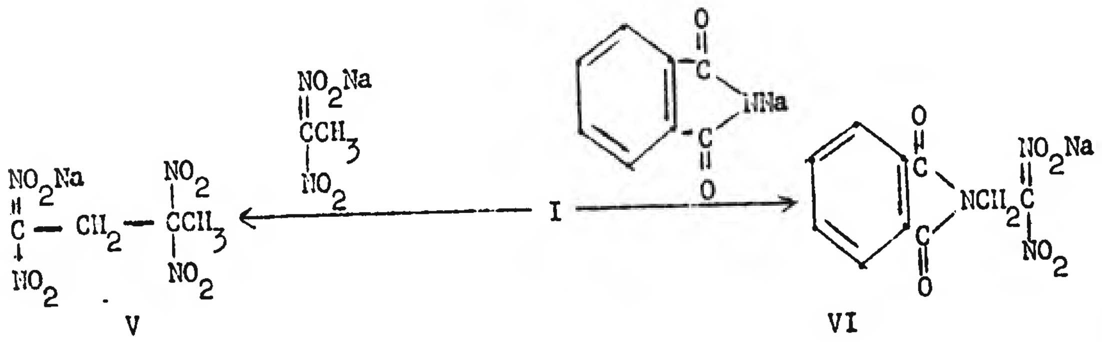
Treatment of 2-bromo-2,2-dinitroethyl acetate (I) with potassium iodide gave a salt which was identified as potassium 2,2,4,4-tetranitrobutyl acetate (IV) (424, 26). The formation of IV was explained by the mechanism shown in the following equations:







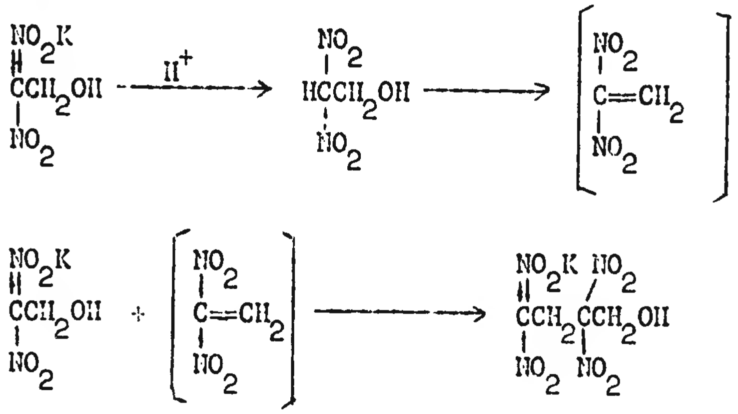
Acidification of IV gave 2,2,4,4-tetranitrobutyl acetate (427, 26; SPIA Data Sheet - 468, App.). The structure of IV was confirmed by its basic hydrolysis to dipotassium 1,1,3,3-tetranitropropane (427, 27); IV did not undergo the Michael reaction with methyl acrylate or acrylonitrile (499, 21). All attempts to isolate potassium 2,2-dinitroethyl acetate (II) or 1,1-dinitroethylene (III) were unsuccessful, but III was postulated as a transitory intermediate, capable of undergoing a Michael reaction with II to form IV. The mechanism of this new reaction was substantiated by extending the reaction of 2-bromo-2,2-dinitroethyl acetate to salts of organic compounds. Thus, treatment of I with sodium 1,1-dinitroethane and sodium phthalimide yielded the sodium salts of 1,1,3,3-tetranitrobutane (V) and 1,1-dinitro-2-phthalimidoethane (VI), respectively.



This evidence indicates that the process of dinitroethylation is a general type of reaction with 2-bromo-2,2-dinitroethyl acetate functioning as a source of 1,1-dinitroethylene which can participate in a Michael type of reaction with other active compounds. The salts formed in the Michael condensation can react further as illustrated in the preparation of 2,2,4,4-tetranitro-1-pentanol (468, 16) from V and formaldehyde, and in the synthesis of methyl 4,4-dinitro-5-phthalimidopentanoate (482, 28) from VI and methyl acrylate.

(3) Reactions of Potassium 2,2-Dinitroethanol

It was found that acidification of potassium 2,2-dinitroethanol to a pH of 4 gave potassium 2,2,4,4-tetranitro-1-butanol (I) (457, 14). The mechanism for this reaction was postulated as also proceeding through the transitory intermediate, 1,1-dinitroethylene.



I

Compound I was converted to 2,2,4,4-tetranitro-1-butanol (paragraph II,D,2,d) and 2,2,4,4-tetranitro-1,5-pentanediol (paragraph II,D,2,a). Treatment of I with strong base yielded dipotassium 1,1,3,3-tetranitropropane (457, 17).

Dipotassium 1,1,3,3-tetranitropropane has also been prepared* by heating an aqueous solution of potassium 2,2-dinitroethanol (pH = 7-8). This reaction has been postulated as proceeding through a Mannich-type reaction.

$$HOCH_2C(NO_2)_2^- \rightleftharpoons CH_2O + HC(NO_2)_2^-$$

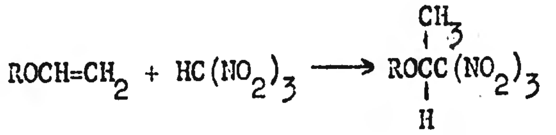
$$HC(NO_2)_2^- + HOCH_2C(NO_2)_2^- \rightleftharpoons H_2O + {}^-(O_2N)_2CCH_2C(NO_2)_2^-$$

---

*Ohio State U., Monthly Letter Report, March 15, 1950.

7. Adducts of Nitroform and Vinyl Ethers

Nitroform added readily to vinyl ethers according to the following equation (404, 53).



$$ROCH{=}CH_2 + HC(NO_2)_3 \longrightarrow RO\overset{CH_3}{\underset{H}{C}}C(NO_2)_3$$

The proof of structure of these adducts was established by reduction to known amines (417, 48). The products and their properties are summarized in Table 16.

TABLE 16

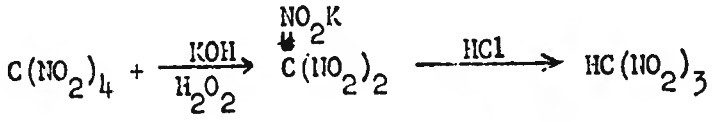
ADDUCTS OF NITROFORM AND VINYL ETHERS

	Nitroform Adduct				
Vinyl Ether	b.p. °C/mm	n_D^{20}	d_{20}^{20}	Yield %	Reference
Ethylvinyl	83-86/1	1.4390	1.3145	68	404, 53
2-Methoxyethylvinyl	82-86/1	1.4470	1.3194	50	404, 53
Isopropylvinyl	75-76/1	1.4390	1.2720	73	404, 53
Isobutylvinyl	82-87/1	1.4389	1.2227	75	404, 53
Dihydropyran	103/1	1.4708	1.3968	81	404, 53

8. Miscellaneous Preparations

a. Nitroform (SPIA Data Sheet - 404, App.)

Nitroform is one of the most important intermediates, because it serves as an excellent means for the introduction of one or more trinitromethyl groups into an organic compound. Because of its importance, a special review has been written on its preparation, properties, and reactions (494). Potassium nitroform was prepared by treating tetranitromethane with potassium hydroxide in the presence of hydrogen peroxide. The salt was isolated from the reaction mixture and treated with acid to give nitroform.



$$C(NO_2)_4 + \xrightarrow[H_2O_2]{KOH} \overset{NO_2K}{C}(NO_2)_2 \xrightarrow{HCl} HC(NO_2)_3$$

A procedure for the preparation and use of nitroform <u>in situ</u> has now been worked out so that the isolation of the hazardous potassium nitroform could be avoided (1083, 31). It was found that the original reaction slurry can be used as a source of nitroform by acidification with a mixture of sulfamic and sulfuric acids, which destroys the nitrous acid as it is formed.

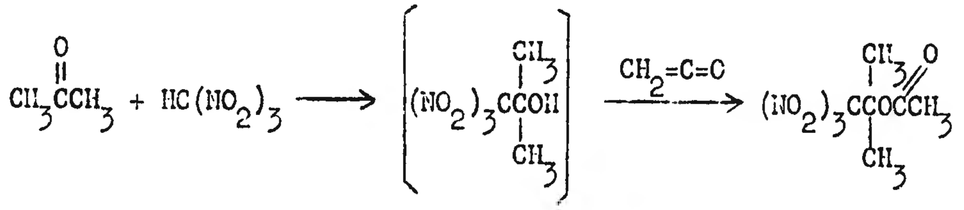
b. Nitroform-Dioxan Complex (SPIA Data Sheet - 404, App.)

Nitroform and dioxan (2:1) react to form a 92% yield of a white crystalline solid, m.p. 44-44.5°, b.p. 61-62°/8 mm (404, 33). This substance has been characterized as being a molecular compound, probably consisting of two molecules of nitroform coordinated with the two oxygen atoms of each dioxan molecule involved in complex formation.

c. Compounds for Use in Chain-Transfer Studies

(1) 1,1,1-Trinitro-2-methyl-2-acetoxypropane

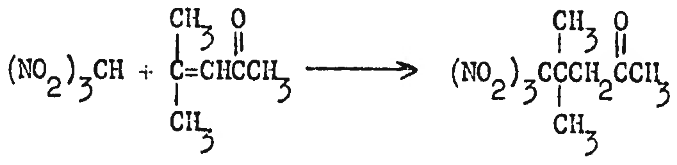
1,1,1-Trinitro-2-methyl-2-acetoxypropane was prepared by treating a solution of nitroform in acetone with ketene (638, 103).*



$$CH_3COCH_3 + HC(NO_2)_3 \longrightarrow \left[(NO_2)_3C(CH_3)_2OH\right] \xrightarrow{CH_2=C=C} (NO_2)_3C(CH_3)_2OCOCH_3$$

(2) 5,5,5-Trinitro-4,4-dimethyl-2-pentanone

5,5,5-Trinitro-4,4-dimethyl-2-pentanone was prepared** by the addition of nitroform to mesityl oxide (638, 104).



$$(NO_2)_3CH + (CH_3)_2C=CHCOCH_3 \longrightarrow (NO_2)_3C(CH_3)_2CH_2COCH_3$$

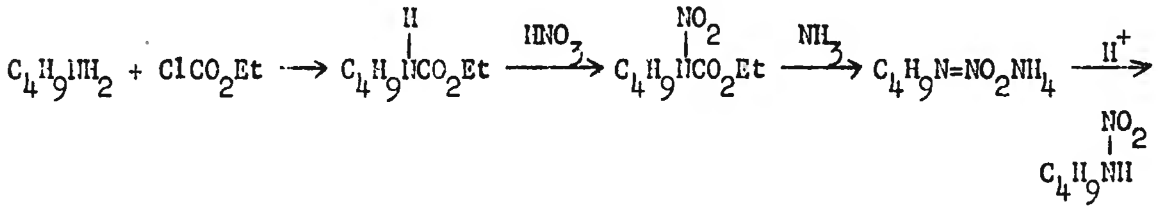
---

*Schenck and von der Forst (BIOS/Gr-2/HEC No. 5475, 27).

**U.S. Rubber Co., Quarterly Report No. 4.

(3) 1-Nitraminobutane

1-Nitraminobutane was prepared by the following series of reactions according to the method of van Erp* (663, 82).



$$C_4H_9NH_2 + ClCO_2Et \longrightarrow C_4H_9\overset{H}{N}CO_2Et \xrightarrow{HNO_3} C_4H_9\overset{NO_2}{N}CO_2Et \xrightarrow{NH_3} C_4H_9N{=}NO_2NH_4 \xrightarrow{H^+} C_4H_9\overset{NO_2}{N}H$$

(4) 2,2,2-Trinitroethyl Propionate

2,2,2-Trinitroethyl propionate was prepared according to the procedure of Marans and Zelinski** with some minor modifications (590, 82).

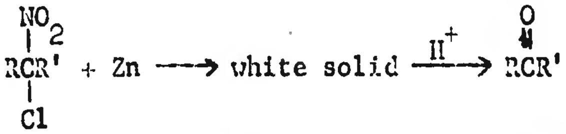
d. tris-(β-Nitroethyl)-hydrazine Hydrochloride

When β-nitroethyl acetate and hydrazine were mixed in aqueous solution, an exothermic reaction took place and a brown oil was formed. This oil was converted into a crystalline hydrochloride salt, the analysis of salt corresponded to tris-(β-nitroethyl)-hydrazine hydrochloride (638, 100).

$$3\ O_2NCH_2CH_2OAc + NH_2NH_2 \xrightarrow{HCl} (O_2NCH_2CH_2)_2N\overset{H\cdot HCl}{\overset{\downarrow}{N}}CH_2CH_2NO_2$$

e. Reaction of gem-Halo Nitro Compounds with Zinc***

It was found that gem-halo nitro compounds react with zinc with the formation of a white solid of unknown structure. Treatment of this product with mineral acid gave a ketone (686, 79):



$$R\underset{Cl}{\overset{NO_2}{C}}R' + Zn \longrightarrow \text{white solid} \xrightarrow{H^+} R\overset{O}{\overset{\|}{C}}R'$$

Methyl 4-ketopentanoate and cyclohexanone were prepared from the corresponding gem-halo nitro compounds by this method.

---

*Rec. trav. chim. 14, 26 (1895).

**J. Am. Chem. Soc. 72, 5329 (1951).

***K. Klager, J. Org. Chem. 20, 646 (1955).

III. POLYMERIZATION STUDIES

A. VINYL POLYMERS

1. Introduction

The successful synthesis of a high-energy unsaturated nitromonomer is but the initial step toward the goal of preparing a nitropolymer propellant. A study of its polymerization, the mechanical properties of the polymer, and its behavior in a propellant composition are the more important steps to be hurdled before a nitromonomer can be successfully transformed into an acceptable propellant.

Of the 57 (successful and attempted) unsaturated nitro compounds discussed in the section devoted to their synthesis, only 12 of the nitromonomers reached the stage to which their polymerization was attempted. Of this number, only six have been studied sufficiently that their polymerization characteristics are well known. However, from a study of these six monomers has come a wealth of information that has defined the general scope of the polymerization of unsaturated nitro compounds. The important revelation that special structures of aliphatic nitro groups participate in the chain-transfer reaction during polymerization has changed the outlook of the synthetic part of the program. The work covering the study of the chain transfer of aliphatic nitro groups has been the subject of a special report and will not be covered in this report except where needed to clarify the discussion (700).

This section of the report records all unsaturated nitromonomers whose polymerization has thus far been attempted on this program.

2. Nitroesters of Unsaturated Acids

a. Introduction

As stated earlier in the report, this class of compounds has been the most fruitful source of nitromonomers of all the various types of chemical compounds studied. Within the class, the acrylates were the easiest to prepare. In studying the polymerization of this class of monomers, the acrylates were again the most fruitful type. However, the utility of a polymer as a propellant ingredient depends upon many things, among which is the average molecular weight of the polymer. From a study of the chain transfer of aliphatic nitro groups, it became apparent that the arrangement of the nitro groups was the most important factor in determining the molecular weight of the polymer. Consequently the nitro groups, being in the alcohol portion of the nitroalkyl acrylates, determine the usefulness of the monomer. Thus, not all nitroalkyl acrylates yield polymers suitable for propellant work. For example, 2,2,2-trinitroethyl acrylate gives a polymer whose average molecular weight is of the order of several thousand. The polymer is hard and brittle and totally unsuited for propellant work. On the other hand, 2,2-dinitropropyl acrylate yields a polymer whose average molecular weight is of the order of 200,000. The mechanical properties of the polymer are sufficiently good to encourage further investigation into its use in propellant compositions.

b. 2,2,2-Trinitroethyl Acrylate

2,2,2-Trinitroethyl acrylate (TNEA) was successfully polymerized, using the common free—radical initiators such as methyl n-amyl ketone peroxide (MAKP), benzoyl peroxide, t-butyl perbenzoate, and cumene hydroperoxide (482, 35). A brief kinetic study of the bulk polymerization was carried out at 30, 40, and 50°C. The rates of polymerization were measured dilatometrically and the rate determined at each temperature was used to determine the overall activation energy of polymerization. The rates were assumed to correspond to a zero-order reaction similar to the chain-type process observed for other vinyl monomers. Using a 0.736% MAKP initiator and 0.134% Accelerator 1000 as activator, the zero-order rate constants were, at 30°C, - 9.035×10^{-1} %/hr; at 40°C, - 27.64×10^{-1} %/hr; and, at 50°C, - 73.33×10^{-1} %/hr. The overall activation energy of polymerization was found to be 20.6 kcal/mole (515, 38). The molecular weights of the polymers formed in the kinetic study were determined osmometrically, using acetone solutions of the polymers. It was found that no correlation of molecular weight with the temperature of polymerization could be made, and further, that very erratic results were obtained from the same samples of polymer. The osmotic molecular-weight determinations gave values ranging from 2800 to 14,200 (540, 2). Since this work was carried out prior to the observation that diffusion of low-molecular-weight polymers through the osmometer membrane occurs quite readily, it seems likely that the reported values for the molecular weight of the polytrinitroethyl acrylate are much too large. Subsequently, it was found that the ready chain-transfer of the trinitromethyl group gave rise to low-molecular-weight polymers. The variation of the density of the polymer with temperature was determined for the range of 25 to 50°C (515, 38).

An attempt to polymerize this monomer, using cationic catalysts such as aluminum chloride or boron trifluoride, at -70°C, failed (515, 47).

c. 2,2-Dinitropropyl Acrylate

In using this monomer, much of the polymerization work has been carried out on composite propellant formulations as the subject of another contract.* This work will not be discussed in this report.

The problem of obtaining dinitropropyl acrylate monomer of sufficient purity to give an acetone-soluble polymer of high relative viscosity, and yet free of polymerization retarders, is discussed elsewhere (paragraph II,A,3). The work reported in this section covers only polymerization and formulation work performed on this contract.

Polymers and copolymers of 2,2-dinitropropyl acrylate (DNPA) have been prepared using free radical initiators. Early polymerizations were carried out in the presence of a high-energy condensation polymer, I-AN, (see paragraph IV,C,3) in order to give a nitropolymer of specific impulse greater than DNPA and of better mechanical properties than I-AN alone. These attempts were not entirely satisfactory, due to the thermally unstable nature of the I-AN polymer and its inhibiting effect upon the polymerization of DNPA (638, 70). The polymerization of DNPA in the presence of ethyl cellulose was performed in order to determine the effect of a non-nitro containing

---

*Contract NOas 54-399c.

substance. In general, the ethyl cellulose appeared to decrease in molecular weight during attempted polymerization of the DNPA. Inasmuch as this approach to a propellant composition appeared unfruitful, the emulsion polymerization of DNPA was next studied in order to produce its homopolymer (PDNPA). The homogeneous emulsions which were obtained gave a 90% conversion of monomer to polymer in 5 hr at 60°C. A redox initiator system was employed using ferrous ion and ammonium persulfate initiator. A typical emulsion recipe contained the following (868, 6):

20 ml DNPA
0.25 g polyvinyl alcohol in 20 ml water
1.70 g Atlas Tween 40
0.25 g ammonium persulfate in 2 ml water
3 mg ferrous sulfate heptahydrate in 1 ml water

The emulsion polymerization technique was later scaled up to 1-1/2 lb DNPA batch size, using a Beken laboratory mixer (907, 46).

In the preparation of a propellant composition, it is desirable to use a fuel binder which can be subjected to molding, casting, or extruding operations, and then subsequently cured to a three-dimensional cross-linked structure, preferably by moderately raising the temperature. This cross-linking imparts dimensional stability to the propellant grain so that it is not easily deformed. In order to achieve this end, dinitropropyl acrylate was copolymerized with minor amounts of acrylic acid and ethylene glycol diacrylate. The reactivity ratios for the acrylic acid copolymer were determined. It was found that r_1 and r_2 were both very close to 1 (868, 11). When copolymers with the ethylene glycol diacrylate (EGDA) were prepared, it was observed that insoluble copolymers resulted when as little as 0.2% of the EGDA was employed (868, 16).

Osmometric molecular-weight determinations of PDNPA produced by bulk or emulsion polymerization ranged from 50,000 to 120,000 (868, 50). An SPIA data sheet for the polymer was published (868, App.).

d. 2,2-Dinitro-1-butyl Acrylate

Dinitrobutyl acrylate (DNBA), like the dinitropropyl acrylate, was subjected to polymerization studies in the hope of obtaining a satisfactory propellant composition. It was also polymerized in the presence of condensation polymers I-AN, I-J, and I-A (paragraph IV,C,3). However, unsatisfactory results were obtained similar to those observed for the DNPA (638, 70; 663, 53; 686, 40).

The rate of bulk polymerization of DNBA has been determined dilatometrically at 40, 50, and 60°C for two different initiator concentrations of azo-<u>bis</u>-isobutyronitrile. With an initiator concentration of 0.25 mole %, the following rates were obtained: at 40°C, 1.43×10^{-5} mole/l/sec; at 50°C, 7.65×10^{-5} mole/l/sec; and at 60°C, 23.6×10^{-5} mole/l/sec. Using these data, an overall activation energy for polymerization of 28.8 kcal/mole was obtained. From similar data obtained by using 0.51 mole % of the same initiator, an activation energy of 29.8 kcal/mole was calculated (686, 4; 712, 4).

Work on the emulsion polymerization of DNBA was performed prior to the work carried out on dinitropropyl acrylate. It was with the DNBA monomer that the successful recipe which was previously listed in the work on DNPA was developed. However, a maximum conversion of only 70% was obtained with DNBA (833, 4).

A study of the variation in molecular weight (determined osmometrically) with intrinsic viscosity of variously prepared DNBA polymers gave the constants of the Mark equation $[\eta] = KM^a$ of $K=1.92 \times 10^{-5}$ and $a=0.840$, using acetone solvent (833, 37). An SPIA data sheet on the polymer was reported (907, App.).

An attempt to cross-link PDNBA by subjecting the polymer to the irradiation from a 1700-Curie Co^{60} source for 96 hr resulted in an acetone-insoluble polymer, green in color, and badly swollen by gas bubbles (907, 69). No further work along this line was performed.

e. 3,3-Dinitro-1-butyl Acrylate

In order to compare the mechanical properties of two isomeric polymers, this monomer was prepared since it is isomeric with 2,2-dinitro-1-butyl acrylate. It was bulk-polymerized at 50°C with 0.5% azo-bis-isobutyronitrile initiator, yielding a 65% conversion to polymer (740, 6). Inasmuch as the synthesis of this monomer was difficult, no further polymerization studies were carried out.

f. 2,2-Dinitro-1-pentyl Acrylate

The polymerization of this monomer was performed on a small scale, and no effort was made to study its polymerization characteristics. The bulk polymerization at 45°C, using 1% MAKP initiator, gave a polymer with an estimated molecular weight of 50,000 to 60,000 (622, 61).

g. 5,5,5-Trinitro-2-pentyl Acrylate

This monomer was polymerized in several exploratory experiments in order to determine whether the trinitromethyl group, further removed from the ester linkage than in trinitroethyl acrylate, would produce a low-molecular-weight polymer by active chain-transfer. Three samples polymerized at 50°C with 0.25, 0.50, and 1.0% MAKP initiator gave polymers with identical relative viscosities in acetone. At a 2% polymer concentration, the relative viscosity in each case was 1.17 (622, 17). From previous experience, this low relative viscosity was known to be related to a low-molecular-weight polymer.

h. 3,5,5-Trinitro-3-aza-1-hexyl Acrylate

The only work performed with 3,5,5-trinitro-3-aza-1-hexyl acrylate was a small-scale experiment to determine the polymerizability of this material. The monomer, a solid, was polymerized in 50% dioxan solution at 50°C, using 1% (based on monomer weight) of azo-bis-isobutyronitrile initiator. An 89% yield of polymer was obtained, which gave a relative viscosity of 1.08 for a 1% acetone solution (740, 5). The molecular weight of the polymer appeared to be low.

i. 2,4,6-Trinitro-2,4,6-triaza-1-heptyl Acrylate

A 2-g sample of this monomer was received from the Naval Ordnance Test Station laboratories, where it was synthesized. Polymerization of the monomer at 50°C in acetone solution (at a concentration of 17.5%) was effected with 1% MAKP (based on monomer) initiator. The polymer was insoluble in acetone, and it precipitated from solution as formed. In 11 days, a 75% yield of polymer was obtained which had a relative solution viscosity of 2.41 for a 2% solution in dimethylformamide (638, 20).

j. 2,2,2-Trinitroethyl Methacrylate

The polymerization of trinitroethyl methacrylate (TNEMA) has been studied extensively. Most of the data was obtained from a study of bulk polymerization; however, solution and emulsion types were investigated also. Most of the work carried out on bulk polymerization was summarized previously in a special report describing the chain-transfer character of the trinitromethyl group (700). Solution polymerizations in dioxan solvent were described for three temperatures (30, 40, and 50°C), and an overall activation energy of 10.2 kcal/mole was calculated (499, 28). Numerous attempts to obtain a satisfactory emulsion-polymerization sample were unsuccessful. The polymer plated out on the vessel walls, and decomposition in the presence of various surface-active agents was noted (515, 40; 563, 2).

Due to the active chain-transfer of the trinitromethyl group, polymers of trinitromethyl methacrylate possess a low molecular weight. The applicability of the isopiestic method for molecular-weight determinations was demonstrated and showed the polymer, obtained by any method, to have a constant molecular weight of 3300 (663, 32). An apparent increase in molecular weight, as determined by the relative viscosity of an acetone solution, was observed when ethylene glycol dimethacrylate (EGDMA) was copolymerized with TNEMA (563, 2). Up to a concentration of 0.8 wt%, the copolymer remained acetone-soluble, but a gel was obtained when the concentration of EGDMA was increased to 0.9%.

Although polytrinitroethyl methacrylate has an estimated specific impulse of 215 lbf sec/lbm, all hope of obtaining a monopropellant from this material was abandoned when it was realized that the polymer was so low in molecular weight that its mechanical properties would be unsuitable in a propellant.

k. Summary and Evaluation

The work on the acrylates has been both fruitful and disappointing. It has been demonstrated that these monomers can be easily polymerized; however, those with the highest specific impulse are the ones that contain the trinitromethyl group, which has been shown to participate in chain-transfer reactions. The result has been to abandon these materials from consideration in propellant work, and to concentrate the effort upon those of lower specific impulse that yield polymers of sufficiently high molecular weight to be of interest. Attention has been diverted from the goal of obtaining a monopropellant to that of obtaining composite nitropolymer propellants.

3. Nitratoesters of Unsaturated Acids

a. Pentaerythritol Acrylate Trinitrate

The specific impulse of the polymer obtained from this monomer was estimated to be 214 lbf sec/lbm. The high calculated impulse made it desirable to study the polymerization of this monomer. Initial attempts revealed that the monomer gave an insoluble gel, unless polymerized in solution (563, 9). Therefore, the rates of polymerization were determined dilatometrically for a 50% acetone solution at 30, 40, and 50°C, using 1% MAKP (based on monomer weight) initiator. The rates calculated for a zero-order reaction were at 30°C, k=2.2%/hr, at 40°C, k=5.3%/hr; and at 50°C, k=10.1%/hr (590, 14). The overall activation energy was calculated to be 14.5 kcal/mole (590, 19).

Further investigation of increasing gel formation with increased monomer concentration in acetone-solution polymerization showed that at 60% monomer concentration and at 1% MAKP initiator, acetone-soluble polymer was obtained after 10 days. If the monomer concentration were increased to 65%, the polymer remained soluble after 2 days at 50°C; but, after 5 days, the polymer was 50% insoluble. At a monomer concentration of 70%, insoluble polymer was formed after only 19 hr at 50°C (638, 20). The relative viscosity of a 2% acetone solution at 25°C was 1.57. Using the isopiestic method for the molecular-weight determination, this polymer had a molecular weight of 5150 (663, 33). An SPIA data sheet on the polymer was published (638, App.).

4. Unsaturated Esters of Nitroacids

a. The Attempted Polymerization of Vinyl 4,4,4-Trinitrobutyrate

Repeated attempts to polymerize or copolymerize this monomer have been unsuccessful. When the bulk polymerization was attempted, using a free radical initiator, the only product obtained, other than monomer, was a solid which was tentatively identified as succinic acid (515, 3). Attempts to polymerize the monomer, using a cationic agent ($AlCl_3$ and BF_3.etherate) at -65°C in ethyl chloride solution, were unsuccessful. Attempts to copolymerize vinyl trinitrobutyrate with vinyl acetate, styrene, or acrylonitrile were also unsuccessful (540, 2; 563, 10; 590, 14). In these cases, it was observed that the un-nitrated monomer also failed to polymerize, indicating that the nitromonomer is an excellent inhibitor for these materials. After complete failure to obtain a polymer under these varied conditions, work on this monomer was abandoned.

5. Esters of Unsaturated Nitroacids

a. The Attempted Polymerization of Methyl α-(2',2'-Dinitropropyl)-acrylate

Attempts to polymerize this monomer, using benzoyl peroxide, MEKP and azo-*bis*-isobutyronitrile, were unsuccessful. Likewise, an attempt to copolymerize it with methyl acrylate also failed (622, 15). The reason for the failure to polymerize may be steric hindrance of the double bond since its structure is similar to methyl α-*t*-butylacrylate, which reportedly does not polymerize.* However, the structure postulated for the monomer has not been

---

*J.W.C. Crawford and S.D. Swift, *J. Chem. Soc.*, *1952*, 1220.

rigorously proved, and there remains some doubt as to its correct constitution. It is possible that, in the dehydrohalogenation reaction creating the double bond, the hydrogen was abstracted from an alternate carbon atom yielding methyl 4,4-dinitro-α-methyl-2-pentenoate, which would not be expected to polymerize (622, 61).

6. Unsaturated Nitroamides

a. N-(3,3-Dinitrobutyl)-acrylamide

This monomer polymerized slowly to give a 48% yield of polymer, after 138 hr at 45°C, using 2% MAKP initiator. The polymer was difficult to purify, because it was apparently plasticized by most organic non-solvents. A relative viscosity (1% concentration in acetone) of 1.17 showed the polymer to be of low molecular weight (712, 3). No further work was performed with this monomer.

7. Summary and Evaluation of the Vinyl Polymers

Of the unsaturated nitromonomers whose polymerization has been studied, the nitroalkyl esters of acrylic acid have been the most interesting. The ease with which they are prepared, and their facile polymerization, make them outstanding among unsaturated nitromonomers. The unfortunate discovery that those particular nitro groupings which possess a large amount of energy (hence, high specific impulse) also possess large chain-transfer constants, has reduced the importance of the unsaturated nitro monomers.

The fact that only the acrylates have been found useful should be subject to further exploitation. Synthetic efforts should be made to develop other high-energy alcohols that do not possess chain-transfer groups. Should this be found possible, then one may predict that the acrylates would again be in a competitive position as potential propellants. This problem, admittedly difficult, deserves support, because the advantages to be found over present propellants would justify the necessary research.

B. ADDITION AND CONDENSATION POLYMERIZATION

1. Introduction

The polymerization studies in this report are divided into two general classes, based on the method of polymer preparation involved. The polymerization of unsaturated nitro compounds, which in general proceeds by a free radical mechanism, is described in a previous paragraph, III,A. Those polymerizations that do not proceed by a free radical mechanism, and in general are ionic in nature, are described in this section.

In the preparation of condensation polymers, polyfunctional monomers react with the accompanying elimination of small molecules such as water, alcohol, or hydrogen chloride. The addition-type polymerization referred to here is actually something of a hybrid between the vinyl and condensation types. The polymerization occurs between polyfunctional monomers to give a product whose simplest structure differs from the structural arrangement of the original monomers. However, no byproducts of the reaction are formed, and the percentage composition is the same as that of the initial mixture of monomers.

The preparation of addition and condensation polymers containing nitro groups for potential use in smokeless propellants required the solution of many problems. The program was planned by first considering all known polymeric systems, and then eliminating the least desirable types on the basis of experience gained with polymers in these laboratories, as well as that obtained from published information. The following types of nitro addition and condensation polymers were investigated:

Polyurethanes
Polyesters
Polyureas
Polyamides
Polyamines
Polyesters

Of these six types, the polyurethanes proved to be the most promising for use in smokeless propellants, hence received the major proportion of the total effort.

In the beginning, a method was needed for determining the relative reactivity of nitromonomers during polymerization. Polymerization reactions that were too slow at the maximum safe temperature indicated the need for more vigorous catalysts. A series of kinetic studies established the relative reactivities of the new nitromonomers that were synthesized, and aided in the search for better catalysts.

An important requirement of a solid propellant is that it be able to resist deformation under stress. It is known that good mechanical properties of an amorphous polymer cannot be achieved until a minimum molecular weight is attained. This critical molecular weight varies somewhat for different polymers; but, in general, a minimum molecular weight of 10,000 is desirable. Thus, it was necessary to determine the optimum conditions for the preparation of linear, high-molecular-weight nitropolymers. This in turn required the determination of physical and mechanical properties of the nitropolymers, and the resultant information served as a guide in the synthesis of new monomers.

In the following sections, the work on these six types of addition and condensation polymers is described in detail. The monomers that have been investigated are listed in Tables 17-20, along with code letters and numbers corresponding to the revised system of nomenclature (772, App. B)

The following general assignments were made:

Diols are characterized by capital letters (A, B. . .)

Diisocyanates are characterized by Roman numbers (I, II . . .)

Diamines are characterized by Greek lower case letters (α, β . . .)

Diacids (acid chlorides, esters) are characterized by Arabic numbers (1, 2 . . .)

Thus, a polyurethane made from the I diisocyanate, 3,3-dinitro-1,5-pentane diisocyanate, and the A diol, 2,2-dinitro-1,3-propanediol, is designated as Polyurethane I-A ; the polyurea made from the I diisocyanate, and the α diamine, 3,3-dinitro-1,5-pentane diamine, is designated as Polyurea I-α . In all reports prior to No. 772, December 1953, Polyurea I-α was designated III-A . The new designations for the monomers were selected to give a minimum amount of change from the old system in effect prior to December 1953.

TABLE 17

DIISOCYANATES

Code	Monomers
I	3,3-Dinitro-1,5-pentane diisocyanate
VI	Methylene diisocyanate
VII	Ethylene diisocyanate
XI	3,3,5,7,7-Pentanitro-1,9-nonane diisocyanate
XII	3,6-Dinitraza-1,8-octane diisocyanate
XIII	3-Nitraza-1,5-pentane diisocyanate
XIV	3,3,5,7,7-Pentanitro-5-aza-1,9-nonane diisocyanate
XV	2-Nitraza-1,4-butane diisocyanate
XVI	2,5-Dinitraza-1,6-hexane diisocyanate

TABLE 18

DIOLS

Code	Monomer
A	2,2-Dinitro-1,3-propanediol
B	1,3-Propanediol
C	2-Nitro-2-ethyl-1,3-propanediol
D	5,7,9-Trinitraza-3,11-dioxa-1,13-tridecanediol
E	3,3-Dinitro-1,5-pentanediol
F	2,2,4,4-Tetranitro-1,5-pentanediol
G	5,7,9,11-Tetranitraza-3,13-dioxa-1,15-pentadecanediol
H	5,5,5-Trinitro-1,2-pentanediol
I	No assignment given because of possible confusion with I-diisocyanate
J	2-Nitro-2-methyl-1,3-propanediol
K	4,4,6,8,8-Pentanitro-1,11-undecanediol
L	4,4,6,6,8,8-Hexanitro-1,11-undecanediol
M	N,N'-*bis*-(2-hydroxyethyl)-oxamide
N	Ethylene glycol
O	5,5-Dinitro-1,2-hexanediol
P	3-Nitraza-1,5-pentanediol
Q	2-Nitro-2-bromo-1,3-propanediol
R	1,4-Butanediol
S	2-Nitro-2-chloro-1,3-propanediol
T	3,6-Dinitraza-1,8-octanediol
U	2-Butyne-1,4-diol

TABLE 19

DIACID CHLORIDES AND DIESTERS

Code	Monomer
1	4,4-Dinitro-1,7-heptanedioyl chloride
2	4,4,6,8,8-Pentanitro-1,11-undecanedioyl chloride
3	(N-Nitro-N-trinitroethyl)-aspartyl chloride
4	(N-Nitro-N-trinitroethyl)-glutamyl chloride
5	Oxalyl chloride and diethyl oxalate
6	4,4,6,8,8-Pentanitro-1,11-undecanediol-*bis*-chloroformate

TABLE 20

DIAMINES

Code	Monomer
α	3,3-Dinitro-1,5-pentane diamine
β	Ethylene diamine
γ	3-Nitraza-1,5-pentane diamine*
δ	3,6-Dinitraza-1,8-octane diamine*
ε	2-Nitraza-1,4-butane diamine*
ζ	2,5-Dinitraza-1,6-hexane diamine*

---

*Prepared and reacted *in situ*.

2. Nitropolyurethanes

a. Introduction

Polyurethanes are obtained by the addition reaction of diisocyanates with diols. In diisocyanate addition reactions, there is no byproduct formed; hence, the polymer resulting from a given set of reactants is more likely to be chemically reproducible from batch to batch. This ability of a reaction to reproduce a polymer of definite composition is indispensable to reproducible ballistic performance. Furthermore, the reaction affords a method for preparing large propellant grains by a casting process.

The feasibility of nitropolyurethanes was examined with the known ethylene diisocyanate, before nitro diisocyanates were prepared (330, 1, 39-41; 345, 24, 30; 371, 24-27). It was found that nitropolyurethanes were formed at moderate (100°C or less) temperatures, using the nitro diols 2,2-dinitro-1,3-propanediol (A), 2-nitro-2-methyl-1,3-propanediol (J), and N,N'-bis-(2-hydroxyethyl)-2,4,6-trinitro-m-phenylene diamine. Although these nitropolyurethanes had insufficient energy for propellant use, it was shown that the urethane nitrogen atoms could, in some instances, be post-nitrated to yield more energetic systems (386, 21).

The advent of nitro diisocyanates and metal chelate catalysts made possible the preparation of high-energy, high-molecular-weight nitropolyurethanes that are suitable for use as propellant binders.

b. Kinetic Studies

(1) Introduction

When the systematic study of nitropolyurethanes was initiated, quantitative data on the reaction rates of nitro monomers was not available. Qualitatively, it was known that nitro groups adjacent to functional groups in a molecule had a pronounced effect on their reactivity. Therefore, a study of the kinetics of nitropolyurethane formation was made with the following objectives:

(a) To quantitatively determine the effect of nitro groups on the reactivity of the functional groups necessary for polymerization.

(b) To quantitatively determine the effect of catalysts upon the rate of reaction.

(c) To aid in the development of optimum methods for preparing high-molecular-weight nitropolyurethanes.

(2) The Effect of Nitro Groups on Rate of Polymerization

The effect of nitro groups on the rate of polyurethane formation was studied by comparing the following reaction rates:

(a) Nitro diisocyanate and nitro diol

(b) Nitro diisocyanate and diol

(c) Diisocyanate and nitro diol

The rate of reaction of 3,3-dinitro-1,5-pentane diisocyanate (I) with 2,2-dinitro-1,3-propanediol (A), and 1,3-propanediol (B) was determined (457, 27, 28, Table 22). The reaction rate of 1,5-pentane diisocyanate with A diol was determined (457, 29, Table 22). Comparing the rate of polyurethane formation in systems I-A and I-B, the reactivity of the hydroxyl groups was lowered by a factor of 50-100, due to the adjacent _gem_-dinitro group. Corroborative evidence of the low rate of I-A formation was obtained by a different method (540, 10). A comparison between I diisocyanate and 1,5-pentane diisocyanate showed that the reactivity of the isocyanate groups was increased by the _gem_-dinitro group.

A decrease in the effect of nitro groups on hydroxyl groups further removed was observed in the reaction of I diisocyanate with 3,3-dinitro-1,5-pentanediol (E) and 5,7,9-trinitro-5,7,9-triaza-3,11-dioxa-1,13-tridecanediol (D) (482, 36,38).

(3) The Effect of Acidic and Basic Catalysts on Rate of Polymerization

The large decrease in the reactivity of the hydroxyl groups in nitro diols showed the need for catalysts in the practical preparation of nitropolyurethanes. This need was emphasized when a second nitro diisocyanate, 3,3,5,7,7-pentanitro-1,9-nonane diisocyanate (XI), became available and its rate of reaction with ethylene glycol (N) was determined (563, 11).

The work of Tarbell, Mallatt, and Wilson indicated that both acidic and basic catalysts were effective in urethane formation.* Boron trifluoride etherate and triethylamine were the most effective catalysts of those studied. Baker and coworkers showed that urethane formation followed second-order kinetics in the presence of basic catalysts and, in the absence of base, the spontaneous reaction was autocatalyzed by the urethane formed.**

The effect of acidic and basic catalysts on the rate of nitropolyurethane I-B formation (482, 42) and nitropolyurethane XI-N formation (563, 11) was studied. Both triethylamine and boron trifluoride etherate catalyzed nitropolyurethane formation, but extensive decomposition accompanied the use of triethylamine. Less-basic materials such as urea, ethyl carbamate, and triphenyl phosphine had little or no catalytic effect. In the more stable XIII-J system, 3-nitraza-1,5-pentane diisocyanate and 2-nitro-2-methyl-1,3-propanediol, the catalytic effect of triethylamine was studied at three catalyst-concentration levels (868, 18).

The use of boron trifluoride etherate as a catalyst was studied intensively in the I-J system. This system was chosen for the following reasons:

---

*Tarbell, Mallatt, and Wilson, J. Am. Chem. Soc. 64, 2229 (1942).
**Baker, et al., J. Chem. Soc. 1947, 713.

(a) Both monomers contained nitro groups.

(b) J-Diol did not interfere with the determination of the isocyanate function.

(c) Both of the monomers and the resulting polymer were soluble in dioxan, a solvent which did not interfere in any way.

(d) J-Diol was commercially available.

The rate of I-J formation was studied at two BF_3 etherate levels (590, 22). It was found that the initially rapid rate decreased as the polymerization proceeded. An attempt was made to determine the cause of the decreased rate (622, 18); it was shown that water, which might arise from decomposition of the nitromonomers, was not acting as a catalyst poison. However, the addition of polyurethane I-J to a mixture of I-J monomers, plus BF_3 etherate, decreased the rate of polymer formation. It was found that portion-wise addition of the catalyst in the I-J system gave the highest overall rate of reaction with the minimum amount of BF_3 etherate (638, 24). Furthermore, it was found that boron trifluoride acted as a chain-terminating agent, hence the minimum amount was desirable (638, 26; 663, 12).

It was concluded that boron trifluoride etherate was an effective catalyst in nitropolyurethane formation, but that it had many disadvantages, such as

(a) An increase in catalyst concentration resulted in a decrease in polymer molecular weight.

(b) The catalyst became inactivated during the reaction.

(c) Interaction between the catalyst and the isocyanate function resulted in inequality of end groups.

It was concluded that basic catalysts are effective in nitropolyurethane formation but must be restricted to those few systems which are stable in the presence of base.

(4) The Effect of Metal Chelates on Rate of Polymerization

The disadvantages in the use of boron trifluoride as a catalyst prompted the search for more effective agents. Petersen reported the use of soluble iron compounds, such as iron acetylacetonate, as catalysts for the preparation of urethanes.* Rate studies on the I-J system, using two similar compounds, chromium acetylacetonate (CrAA) and vanadyl acetylacetonate (VOAA), were extremely encouraging (663, 13). The effect of these materials on I diisocyanate was studied, and it was found that some interaction with the vanadium chelate occurred (663, 13). The chromium chelate, however, caused no appreciable loss in isocyanate function.

Ferric acetylacetonate (FeAA) was much more effective than either the vanadyl or chromium chelates in the polyurethane I-J system (686, 8) and caused no appreciable loss in isocyanate function (712, 9). The variation in rate of I-J formation with temperature in the presence of FeAA was studied (712, 6), and from this data the activation energy was calculated. The variation in rate of I-J formation with FeAA concentration was studied (833, 12).

The polyurethane I-J system was used to compare the catalytic efficiency of other metal acetylacetonates with FeAA (833, 13). The acetylacetonates studied are listed in order of decreasing effectiveness: Iron III >> lead II > copper II > magnanese III > vanadyl II > chromium III = nickel II = cobalt II > cobalt III. The effect of these metal acetylacetonates on the rate of I diisocyanate homopolymer formation was studied (833, 13). The acetylacetonates studied are listed in order of decreasing rate of homopolymer formation: Lead II > copper II > manganese III > vanadyl II > iron III.

It was concluded that iron III acetylacetonate was by far the most effective catalyst for nitropolyurethane formation, and that it had the least effect on the rate of diisocyanate homopolymerization.

---

*Petersen, Ann. 562, 206 (1949).

(5) Comparison of Nitro Diisocyanate Reactivities

As new nitro diisocyanates became available, the rate of reaction of each new diisocyanate with J diol was determined under standard experimental conditions. Because of lack of an analytical method (740, 70), the relative reactivity of 3,3,5,7,7-pentanitro-5-aza-1,9-nonane diisocyanate (XIV) could not be determined. The comparative reactivities of the nitro diisocyanates are listed in Table 21.

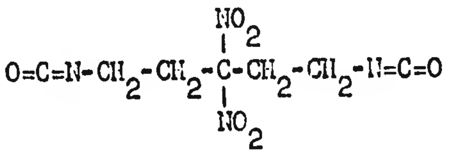
c. Polymerizations

(1) Introduction

In the first phase of the nitropolymer program, a great variety of polymerization reactions were attempted with the available nitro compounds, in an effort to show that stable polymers containing nitro groups could be prepared. The preparation of nitropolyurethanes was one of the first reactions studied, and one of the first to yield a stable nitropolymer (330, 1). At that time, nitrodiisocyanates were not available, and nitropolyurethane preparations were limited to ethylene diisocyanate plus nitro diols.

When the first nitrodiisocyanate, 3,3-dinitro-1,5-pentane diisocyanate (I), became available (see paragraph II,B,3,b of this report), a systematic study of nitropolyurethane formation was initiated. The prime objectives of the program were the preparation and identification of linear nitropolyurethanes having high molecular weight, high specific impulse, and high thermal and impact stability.

(2) Nitropolyurethanes from 3,3-Dinitro-1,5-pentane Diisocyanate (I) (paragraph II,B,3,b)



$$O{=}C{=}N{-}CH_2{-}CH_2{-}\overset{NO_2}{\underset{NO_2}{C}}{-}CH_2{-}CH_2{-}N{=}C{=}O$$

TABLE 21

COMPARISON OF NITRO DIISOCYANATE REACTIVITIES WITH 2-NITRO-2-METHYL-1,3-PROPANEDIOL

Initial Concentration: 1 eq/liter (-OH) and (-NCO) in Dioxan
1×10^{-5} mole/liter Ferric Acetylacetonate

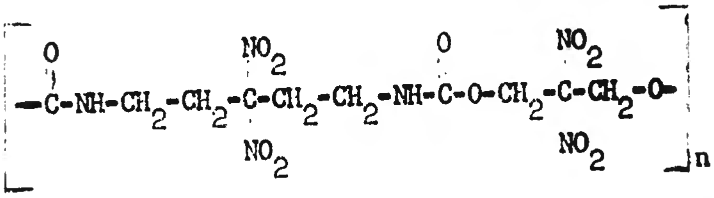
Temperature: 50°C

Code Number	Diisocyanate	k_{50^o} liter/eq. hr	Relative Rate	Reference
I	3,3-Dinitro-1,5-pentane	4.3	215	(712, 7)
XII	3,6-Dinitraza-1,8-octane	0.02	1	(712, 10)
XIII	3-Nitraza-1,5-pentane	0.35	18	(740, 8)
XV	2-Nitraza-1,4-butane	2.0	100	(807, 14)
XVI	2,5-Dinitraza-1,6-hexane	0.7	35	(868, 21)

(a) Introduction

A greater variety of nitropolyurethanes was prepared from I diisocyanate than from any other nitrodiisocyanate. This was partly due to the fact that it was the first nitrodiisocyanate available for study, but mainly to the excellent properties of the polymers prepared from it. Table 22 lists the polyurethanes prepared and some of their more important properties.

(b) Polyurethane I-A from 2,2-Dinitro-1,3-propanediol (paragraph II,D,2,a)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-O-\right]_n$$

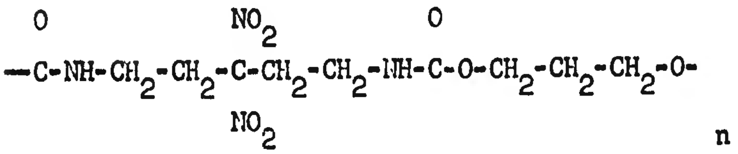
The first attempted polymerization resulted in extensive decomposition (457, 36, 39, 67). The expected polymer was obtained when the reaction was repeated in dioxan solution with BF_3•etherate as catalyst (482, 43, 45-57, 51-53) and a SPIA data sheet was prepared (482, Appendix). Using a large excess of one monomer, low <u>DP</u> polymer was prepared to determine the effect of molecular weight on softening range (499, 44-46). The infrared spectrum was obtained (499, 63). Attempts were made to determine the optimum time and temperature conditions for the polymerization (540, 9, 10). A study of the effect of BF_3 concentration on molecular weight showed that as BF_3 concentration was increased, molecular weight decreased (590, 26. 28, 29). Degradation of the polymer by BF_3 was found to be small (622, 35). The effect of catalyst concentration and polymer concentration on thermal stability was studied (663, 20, 22). The results were inconclusive, since end-group type was not controlled (1004, 6). Optimum conditions for the polymerization were redetermined with metal acetylacetonate catalysts (686, 19-25). Branched polymer was prepared by adding small amounts of <u>tris</u>-(hydroxymethyl)-nitromethane (740, 54,55; 772, 30; 807, 23). The effect of monomer equivalence on molecular weight was determined (807, 25-27). A modified polyurethane, containing some urea linkages, was prepared for use in second-stage crosslinking studies (833, 21-25).

TABLE 22

PROPERTIES OF NITROPOLYURETHANES FROM 3,3-DINITRO-1,5-PENTANE DIISOCYANATE(I)

	Diol	Polymer Empirical Formula	Heat of Combustion cal/g Calc'd	Heat of Combustion cal/g Found	Estimated Specific Imp. lbf sec/lbm	Softening Range °C	Relative Viscosity % Soln	Density g/cc	Stability: KI-Starch at 65.5°C min	Stability: Methyl violet 134.5°C min	Impact cm/2 kg	Preparation Reference
(A)	2,2-Dinitro-1,3-propanediol	$C_{10}H_{14}N_6O_{12}$	2920	2880	174	75-78	1.8 (1%)	1.57	>300	195	100	686, 19-20
(B)	1,3-Propanediol	$C_{10}H_{16}N_4O_8$	3970	3920	<100	50-60	1.5 (1%)	--	>300	>300	>100	457, 56, 57
(C)	2-Nitro-2-ethyl-1,3-propanediol	$C_{12}H_{19}N_5O_{10}$	3887	3918	110	55-65	2.0 (1%)	--	>300	>300	>100	868, 51
(D)	5,7,9-Trinitraza-3,11-dioxa-1,13-tridecanediol	$C_{15}H_{26}N_{10}O_{16}$	3350	3350	179	55-60	1.2 (2%)	--	>300	>300	80	482, 49, 50
(F)	2,2,4,4-Tetranitro-1,5-pentanediol	$C_{12}H_{16}N_8O_{16}$	2720	2756	203	70-80	1.6 (2%)	1.64	12	13	80-85	712, 17
(G)	5,7,9,11-Tetranitraza-3,13-dioxa-1,15-pentadecanediol	$C_{16}H_{28}N_{12}O_{18}$	--	--	188	60-65	1.1 (2%)	--	--	--	**70**	515, 55, 56
(H)	5,5,5-Trinitro-1,2-pentanediol	$C_{12}H_{17}N_7O_{14}$	3076	3096	188	85-95	1.7 (1%)	--	10	78	**85**	686, 25, 26
(J)	2-Nitro-2-methyl-1,3-propanediol	$C_{11}H_{17}N_5O_{10}$	3655	3625	112	60-70	2.5 (1%)	1.47	>300	>300	>100	686, 15-17
(K)	4,4,6,8,8-Pentanitro-1,11-undecanediol	$C_{18}H_{27}N_9O_{18}$	3555	3556	175	35-40	1.5 (2%)	1.50	10	11	>100	590, 32, 33
(L)	4,4,6,6,8,8-Hexanitro-1,11-undecanediol	$C_{18}H_{26}N_{10}O_{20}$	3280	3329	191	30-40	1.4 (2%)	1.55	8	8 (exploded)	>100	590, 34, 35
(M)	N,N'-bis(2-Hydroxyethyl)-oxamide	$C_{13}H_{20}N_6O_{10}$	--	--	94	80-100	1.3 (1%)	--	--	--	>100	622, 22-24
(N)	Ethylene glycol	$C_9H_{14}N_4O_8$	3637	3586	109	40-45	1.6 (2%)	--	--	--	>100	638, 36, 39
(O)	5,5-Dinitro-1,2-hexanediol	$C_{13}H_{20}N_6O_{12}$	3683	3674	148	65-70	1.5 (2%)	--	>300	>300	>100	638, 35, 36
(P)	3-Nitraza-1,5-pentanediol	$C_{11}H_{18}N_6O_{10}$	3643	3615	142	45-55	1.6 (1%)	--	21	--	>100	833, 20, 21
(T)	3,6-Dinitraza-1,8-octanediol	$C_{13}H_{22}N_8O_{12}$	3549	3461	145	65-70	1.4 (1%)	--	>120	--	>100	941, 48

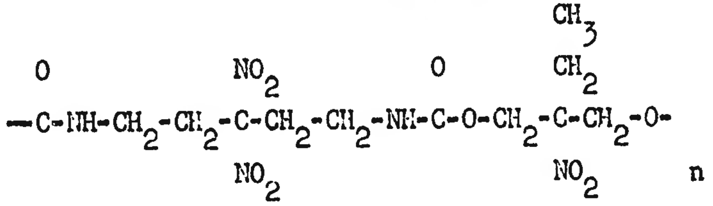
(c) Polyurethane I-B from 1,3-Propanediol



$$-\overset{O}{C}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{C}-O-CH_2-CH_2-CH_2-O-\quad n$$

This polymer was prepared for comparison of physical properties with polyurethane I-A. Dimethylformamide was used as the solvent during one preparation (424, 16, 33); another polymerization was made in bulk (424, 15; 457, 36, 37). The physical properties were determined (457, 70).

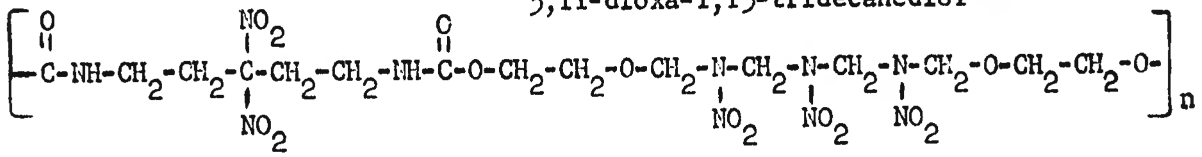
(d) Polyurethane I-C from 2-Nitro-2-ethyl-1,3-propanediol



$$-\overset{O}{C}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{C}-O-CH_2-\underset{NO_2}{\overset{\overset{CH_3}{CH_2}}{C}}-CH_2-O-\quad n$$

This nitrodiol was studied primarily because it was commercially available; after nitration of the urethane linkages, the estimated specific impulse would be sufficiently high for propellant use. The preparation and physical properties were described (868, 31).

(e) Polyurethane I-D from 5,7,9-Trinitraza-3,11-dioxa-1,13-tridecanediol*



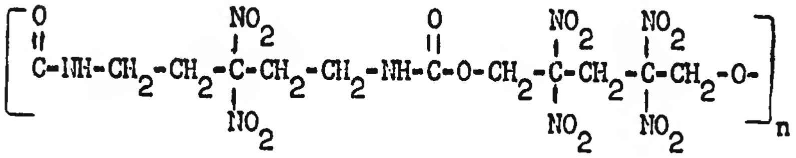
$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-CH_2-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-O-CH_2-CH_2-O-\right]_n$$

The preparation and physical properties of this high-energy polymer were described (482, 49, 51-53; 515, 56). The SPIA data sheet was prepared (482, Appendix).

---

*Obtained from the Naval Ordnance Test Station, Inyokern.

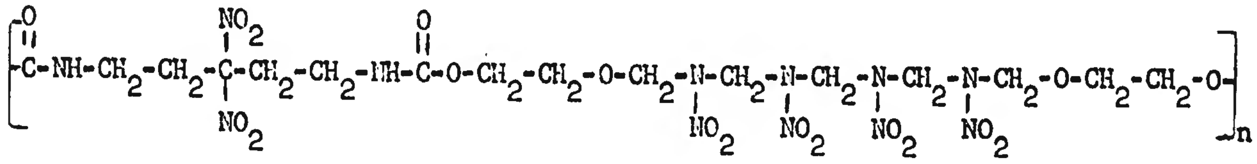
(f) Polyurethane I-F from 2,2,4,4-Tetranitro-1,5-pentanediol (II,D,2,a)



$$\left[\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_2-\overset{NO_2}{\underset{NO_2}{C}}-CH_2-CH_2-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-\overset{NO_2}{\underset{NO_2}{C}}-CH_2-\overset{NO_2}{\underset{NO_2}{C}}-CH_2-O-\right]_n$$

An uncatalyzed polymerization, carried out in dioxan, resulted in very low-molecular-weight polymer (499, 49). The use of BF_3·etherate catalyst improved the molecular weight slightly (499, 49, 50; 515, 48). Ferric acetylacetonate catalysis increased the molecular weight further (712, 17). The SPIA data sheet was prepared (515, Appendix).

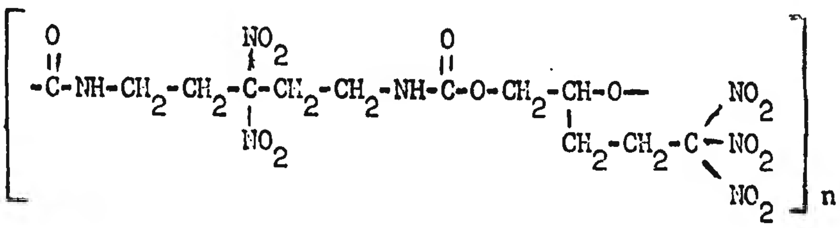
(g) Polyurethane I-G from 5,7,9,11-Tetranitraza-3,13-dioxa-1,15-pentadecanediol*



$$\left[\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_2-\overset{NO_2}{\underset{NO_2}{C}}-CH_2-CH_2-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-O-CH_2-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-\underset{NO_2}{N}-CH_2-O-CH_2-CH_2-O-\right]_n$$

The preparation and physical properties were described (515, 55).

(h) Polyurethane I-H from 5,5,5-Trinitro-1,2-pentanediol (II,D,2,b)



$$\left[-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_2-\overset{NO_2}{\underset{NO_2}{C}}-CH_2-CH_2-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{CH_2-CH_2-C(NO_2)_3}{CH}-O-\right]_n$$

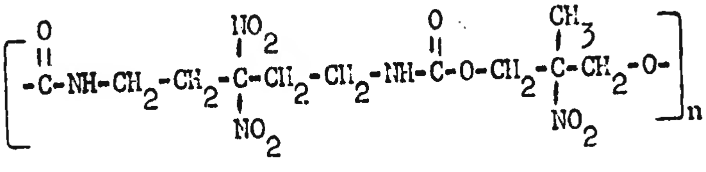
An uncatalyzed polymerization was carried out in dioxan (563, 19). The preparation was repeated, using BF_3·etherate catalyst and varying the ratio of end-group equivalence, in an effort to

---

*Obtained from the Naval Ordnance Test Station, Inyokern.

determine the purity of the N diol (590, 35; 622, 27-30). A study of the effect of BF_3·etherate concentration on the molecular weight was inconclusive (622, 32, 33). Optimum conditions for the polymerization were determined using BF_3·etherate as catalyst (638, 27-33), and using ferric acetylacetonate as catalyst (686, 25, 26; 712, 16, 17).

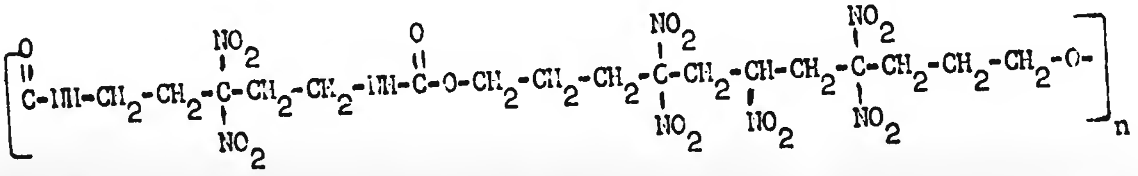
(i) Polyurethane I-J from 2-Nitro-2-methyl-1,3-propanediol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{NO_2}{\overset{CH_3}{C}}-CH_2-O-\right]_n$$

The polymer was prepared in dioxan solution, using BF_3·etherate catalyst, and it was the first example of a tough, fibrous nitropolyurethane (563, 21; 622, 25). The I-J system was used to test the hypothesis that adjustment of end-group equivalence during the polymerization would result in higher-molecular-weight product (638, 26-28). It was found that an excess of either monomer, over that required for precise end-group equivalence, resulted in decreased molecular weight (807, 25). Branched polymer was prepared by incorporating small amounts of tris-(hydroxymethyl)-nitromethane (663, 28, 29). A higher-molecular-weight polymer was obtained using vanadyl acetylacetonate as catalyst (663, 29-31). The optimum conditions for preparing the polymer were determined, using ferric acetylacetonate as catalyst (686, 15-19). The SPIA data sheet was prepared (686, Appendix). The solubility characteristics were determined (967, 5). Polyurethane I-J, number-average molecular weight $M_n \approx 72,000$, was fractionated into twelve portions ranging from $M_n = 800$ to $M_n = 241,000$ (712, 20-24; 740, 34-48). The I-J system was used to determine the suitability for polymerizations of solvents other than dioxan (712, 18, 19; 740, 28).

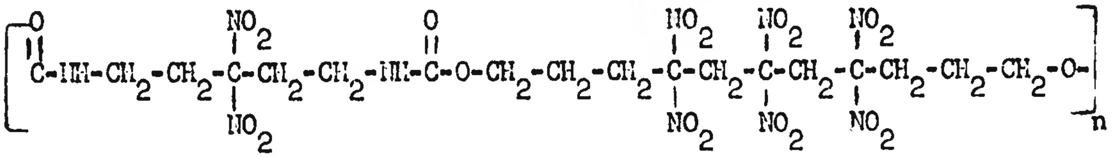
(j) Polyurethane I-K from 4,4,6,8,8-Pentanitro-1,11-undecanediol (II,D,2,b)



$$\left[\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-\underset{NO_2}{CH}-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-CH_2-O-\right]_n$$

The two high-energy undecanediols, K and L, having structures that appeared promising, based on earlier experience with diols A and F, were synthesized for study in the polymerization program. It was known from kinetic studies (III,B,2,b) that increasing the distance between the nitro groups and the hydroxyl function decreased the retarding action of the gem-dinitro structure. Thus, it was believed that diols K and L would have normally reactive hydroxyl groups coupled with a high-energy structure. This hypothesis was substantiated. Polyurethane I-K was prepared in dioxan as a solvent using BF_3•etherate catalyst (590, 32, 33; 622, 27). The data for the SPIA data sheet was obtained (622 Appendix).

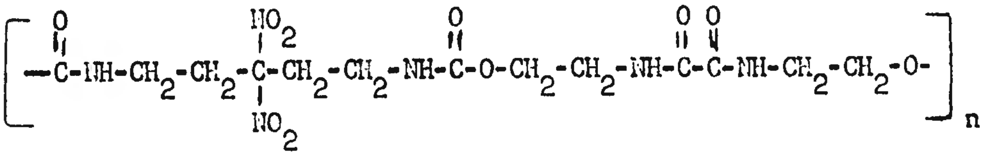
(k) Polyurethane I-L from 4,4,6,6,8,8-Hexanitro-1,11-undecanediol (II,D,2,b)



$$\left[\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-CH_2-O-\right]_n$$

Polyurethane I-L was prepared in dioxan as solvent using BF_3•etherate catalyst (590, 34, 35), and evaluated as described in the SPIA data sheet (622, 41-44).

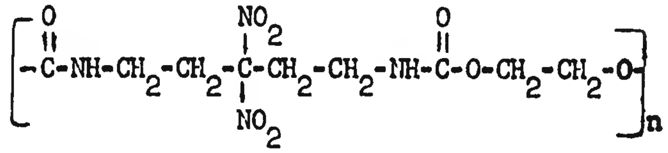
(l) Polyurethane I-M from N,N'-*bis*(2-Hydroxyethyl)-oxamide



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-O-\right]_n$$

It was desirable to study the effect on physical properties of a polymer chain containing both amide and urethane linkages. Polyurethane I-M was prepared in dioxan solution, without the use of a catalyst (622, 23, 24).

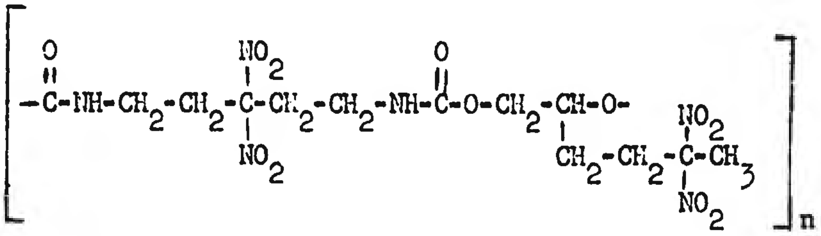
(m) Polyurethane I-N from Ethylene Glycol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\right]_n$$

After nitration of the urethane linkages of polyurethane I-N, the specific impulse would be sufficiently high for propellant use. The preparation and physical properties of polyurethane I-N were described (638, 36).

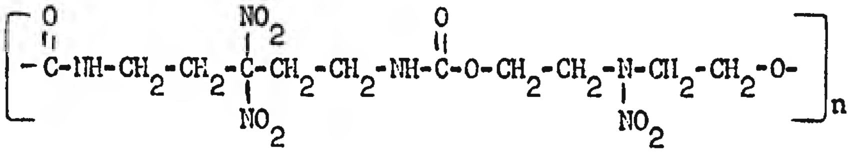
(n) Polyurethane I-O from 5,5-Dinitro-1,2-hexanediol (II,D,2,b)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_3}{\underset{|}{CH}}-O-\right]_n$$

The polymerization was carried out in dioxan as solvent without catalyst at various concentrations of total solids (638, 35, 36). The maximum molecular weight was obtained at 80% solids.

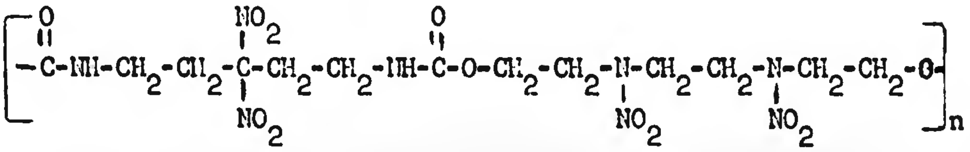
(o) Polyurethane I-P from 3-Nitraza-1,5-pentanediol (II,D,2,h)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-O-\right]_n$$

The polymerization was carried out in dioxan as solvent and ferric acetylacetonate as catalyst (833, 20, 21).

(p) Polyurethane I-T from 3,6-Dinitraza-1,8-octanediol (II,D,2,i)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-O-\right]_n$$

The preparation of this polymer was made in γ-butyrolactone as a solvent, using ferric acetylacetonate as a catalyst (941, 4, 5, 8).

(q) Solvents for Conducting Polymerizations

In addition to the polymerization reactions described, 3,3-dinitro-1,5-pentane diisocyanate was used to screen a variety of solvents to determine those that were compatible with the isocyanate function. (499, 41, 42; 712, 19).

(r) Evaluation of Nitropolyurethanes from 3,3-Dinitro-1,5-pentane Diisocyanate

The fifteen nitropolyurethanes in the (I) series may be divided into three groups, based on estimated specific impulse: Group 1, those having I_{sp} values above 170 lbf sec/lbm; Group 2, those with I_{sp} values in the range 140-170 lbf sec/lbm; Group 3, those with I_{sp} values below 140 lbf sec/lbm.

Group 1 includes polyurethanes I-A, I-D, I-F, I-G, I-H, I-K, and I-L. Polyurethane I-A fulfills the three major requirements of high molecular weight, high energy, and stability. Polyurethane I-D meets the high-energy and stability needs, but fails to meet molecular weight requirements. The molecular weight could undoubtedly be improved by using ferric acetylacetonate catalyst. On the other hand, the supply of D is limited because of the hazardous nature of the preparation. Polyurethane I-F fails in both molecular-weight and stability requirements. Polyurethane I-G, prepared with BF_3·etherate catalyst, was very low in molecular weight. This might be overcome by using ferric acetylacetonate catalyst; however, the preparation of G also contains a hazardous step in the preparation. Polyurethane I-H has poor thermal stability as measured by the KI-starch test. This was at first believed to be due to the trinitromethyl group in the diol; however, polyurethane XIII-H from 3-nitraza-1,5-pentane diisocyanate (XIII) exhibits excellent stability in the KI-starch test. Therefore, further study on the I-H system is warranted since it meets the other requirements. Both polyurethanes I-K and I-L fail the molecular-weight and stability requirements.

Group 2 includes polyurethanes I-O, I-P and I-T. Polyurethane I-T meets molecular-weight and stability requirements. Polyurethane I-O, low in molecular weight, probably could be improved by the use of ferric acetylacetonate. Polyurethane I-P, having a high molecular weight, exhibits only moderate stability.

Group 3 includes polyurethanes I-B, I-C, I-J, I-M and I-N, all of which pass the requirements, other than that of high energy.

The rate of gas evolution by polyurethanes I-A, I-H, I-J and I-O was measured in the Warburg apparatus (686, 50)(see section VI,J). All were stable, evolving less than 0.1 ml gas/100 g polymer/hr.

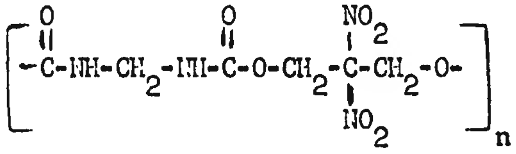
(3) Nitropolyurethanes from Methylene Diisocyanate (VI) (II,B,2,b)

$O=C=N-CH_2-N=C=O$

(a) Introduction

Methylene diisocyanate was synthesized on this program (see paragraph II,B,2,b), because polyurethanes prepared from it and nitrodiols would have slightly higher calculated-specific-impulse values than those prepared from ethylene diisocyanate.

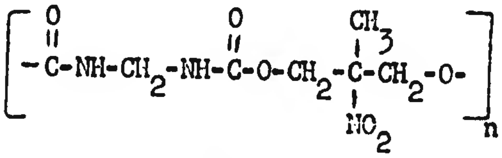
(b) Polyurethane VI-A from 2,2-Dinitro-1,3-propanediol (II,D,2,a)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-O-\right]_n$$

This nitropolyurethane has an estimated specific impulse of 165 lbf sec/lbm (772, Appendix). The first attempt to prepare the polymer resulted in a product having a low nitrogen content (345, 26, 50, 51). A second attempt in dioxan as solvent produced polymer that, when analyzed, was about 1% low in nitrogen (371, 25, 69). A bulk polymerization produced polymer that softened at 135°C and contained the theoretical amount of nitrogen (386, 20, 39 and paragraph (3) page 40).

(c) Polyurethane VI-J from 2-Nitro-2-methyl-1,3-propanediol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{NO_2}{\overset{CH_3}{C}}-CH_2-O- \right]_n$$

The estimated specific impulse is 122 lbf sec/lbm (772, Appendix). The first attempted polymerization in bulk failed (371, 26, 70). Another bulk polymerization produced polymeric material containing the theoretical amount of nitrogen and softening at 135°C (386, 20, 40, 41). The rate of reaction was determined (563, 26); the resulting polymer had a relative viscosity of 1.47, 1% in dimethylformamide at 25°C, and heat of combustion of 3519 cal/g compared to 3574 cal/g calculated (563, 26).

(d) Attempted Polymerizations

Attempts to prepare nitropolyurethanes from methylene diisocyanate and 2,4,6-trinitroresorcinol (345, 26, 51; 371, 25, 68) or N,N'-*bis*-(2-hydroxyethyl)-2,4,6-trinitro-*m*-phenylenediamine (386, 20, 41) failed to yield materials having theoretical analytical values.

(e) Evaluation of Polyurethanes Prepared from Methylene Diisocyanate (VI)

Nitropolyurethanes from methylene diisocyanate, at best, can have only moderately high specific-impulse values. This, together with the fact that one of the intermediates in the preparation, malonyl diazide, is extremely sensitive to impact, precludes any extensive use of VI in nitropolyurethane formation.

(4) Nitropolyurethanes from Ethylene Diisocyanate (VII)

$$O=C=N-CH_2-CH_2-N=C=O$$

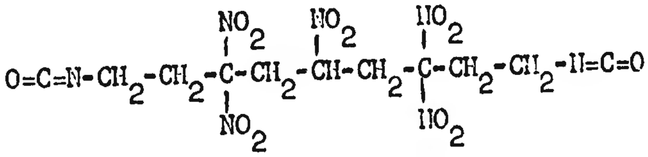
Before nitrodiisocyanates were available, many polymerizations were attempted with ethylene diisocyanate, which had been described earlier by Curtius and Hechtenburg.* In general, poor yields of

---

*J. prakt. chem., [2], 105, 289-318 (1923).

low-molecular-weight materials, having analytical values in poor agreement with theory, resulted (330, 35-42, 111-114; 345, 24, 25, 30, 47, 49, 52; 371, 24-28, 66, 67, 70-72). Further investigation showed that ethylene diisocyanate frequently forms cyclic products along with the desired open-chain derivatives (515, 27-30), hence is unsuitable for the preparation of high-molecular-weight polymers.

(5) Nitropolyurethanes from 3,3,5,7,7-Pentanitro-1,9-nonane Diisocyanate (XI) (II,B,3, Table 6)

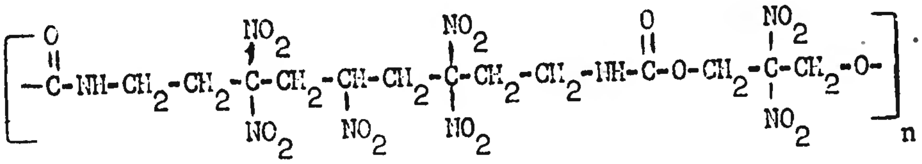


$$O{=}C{=}N{-}CH_2{-}CH_2{-}\underset{NO_2}{\overset{NO_2}{C}}{-}CH_2{-}\overset{NO_2}{CH}{-}CH_2{-}\underset{NO_2}{\overset{NO_2}{C}}{-}CH_2{-}CH_2{-}N{=}C{=}O$$

(a) Introduction

Because of the low stability of the products, only two polymers were prepared from this highly energetic nitrodiisocyanate.

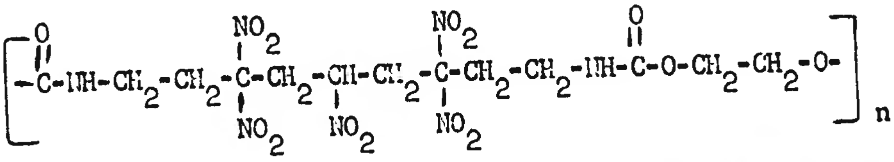
(b) Polyurethane XI-A from 2,2-Dinitro-1,3-propanediol (II,D,2,a)



$$\left[{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_2{-}CH_2{-}\underset{NO_2}{\overset{NO_2}{C}}{-}CH_2{-}\underset{NO_2}{CH}{-}CH_2{-}\underset{NO_2}{\overset{NO_2}{C}}{-}CH_2{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}\underset{NO_2}{\overset{NO_2}{C}}{-}CH_2{-}O{-}\right]_n$$

This polymer has an estimated specific impulse of 203 lbf sec/lbm. It was prepared in dioxan solution with BF_3·etherate catalyst (590, 29, 32). The SPIA data sheet was prepared (622, Appendix).

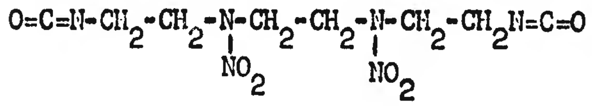
(c) Polyurethane XI-N from Ethylene Glycol



$$\left[{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_2{-}CH_2{-}\underset{NO_2}{\overset{NO_2}{C}}{-}CH_2{-}\underset{NO_2}{CH}{-}CH_2{-}\underset{NO_2}{\overset{NO_2}{C}}{-}CH_2{-}CH_2{-}NH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_2{-}O{-}\right]_n$$

The polyurethane has an estimated specific impulse of 172 lbf sec/lbm. It was prepared in dioxan solution without catalyst (563, 13, 17).

(6) Nitropolyurethanes from 3,6-Dinitraza-1,8-octane Diisocyanate (XII) (II,B,4, Table 7)

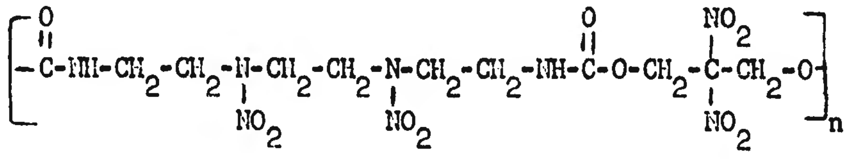


$$O{=}C{=}N-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2N{=}C{=}O$$

(a) Introduction

3,6-Dinitraza-1,8-octane diisocyanate was the first of a series of diisocyanates which contain the nitramino group as the energy source. Kinetic studies showed that the uncatalyzed rate of reaction of XII was about one two-hundreth the rate of 3,3-dinitro-1,5-pentane diisocyanate (see Table 21 of this section). Fortunately, the metal chelate polyurethane catalysts became available (see 2,b,(4) of this section), making it possible to prepare nitropolyurethanes from this energetic monomer. Polyurethanes of the XII series and their more important physical properties are listed in Table 23.

(b) Polyurethane XII-A from 2,2-Dinitro-1,3-propanediol. (II,D,2,a)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{NO_2}{\underset{NO_2}{\overset{|}{\underset{|}{C}}}}-CH_2-O-\right]_n$$

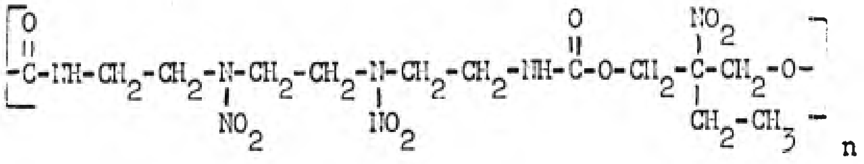
The first preparation of this polymer was made with BF_3'etherate as catalyst (663, 16-17). Subsequent preparations were made with ferric acetylacetonate catalyst (712, 17-18; 740, 28-30; 772, 22). When prepared in dioxan solution, a portion of the product separated as a higher-melting polycrystalline XII-A (712, 17-18). Attempts to increase the yield of polycrystalline XII-A were not successful (740, 28-30; 772, 22). The solubility characteristics were determined (967, 5). A copolymer of XII-A with 3-nitraza-1,5-pentane diisocyanate (XIII) was made in an effort to improve the physical properties of XII-A (868, 34-36). The SPIA data sheet was prepared (941, Appendix).

TABLE 23

PROPERTIES OF NITROPOLYURETHANES FROM 3,6-DINITRAZA-1,8-OCTANE DIISOCYANATE

Diol		Polymer Empirical Formula	Heat of Combustion Calc'd	Cal/g Found	Estimated Specific Impulse lbf sec/lbm	Softening Range °C	Relative Viscosity 1% Solution	Density g/cc	Stability KI-Starch at 65.5°C min	Methyl Violet at 134.5°C min	Impact cm/2 kg	Preparation Reference
(A)	2,2-Dinitro-1,3-propanediol	$C_{11}H_{18}N_8O_{12}$	3188	3284	178	60 to 100	2.0	1.51	21	10	>100	740, 28-30
(C)	2-Nitro-2-ethyl-1,3-propanediol	$C_{13}H_{23}N_7O_{10}$	4068	4133	116	75 to 85	1.4	--	--	--	>100	868, 31, 32
(H)	5,5,5-Trinitro-1,2-pentanediol	$C_{13}H_{21}N_9O_{14}$	3292	3226	175	80 to 90	1.5	1.47	20	25	>100	740, 22
(J)	2-Nitro-2-methyl-1,3-propanediol	$C_{12}H_{21}N_7O_{10}$	--	--	112	75 to 85	1.6	--	--	--	>100	740, 22; 772, 23
(M)	N,N'-bis-(2-Hydroxyethyl)-oxamide	$C_{14}H_{24}N_8O_{10}$	--	--	100	190 to 200	1.3	--	--	--	>100	772, 15
(N)	Ethylene glycol	$C_{10}H_{18}N_6O_8$	3892	3833	118	165 to 170	1.1	--	--	--	>100	772, 16
(O)	5,5-Dinitro-1,2-hexanediol	$C_{14}H_{24}N_8O_{12}$	--	--	148	90 to 100	1.1	--	--	--	>100	772, 17
(T)	3,6-Dinitraza-1,8-octanediol	$C_{14}H_{26}N_{10}O_{12}$	3827	3796	158	75 to 80	1.2	--	120	--	>100	941, 8

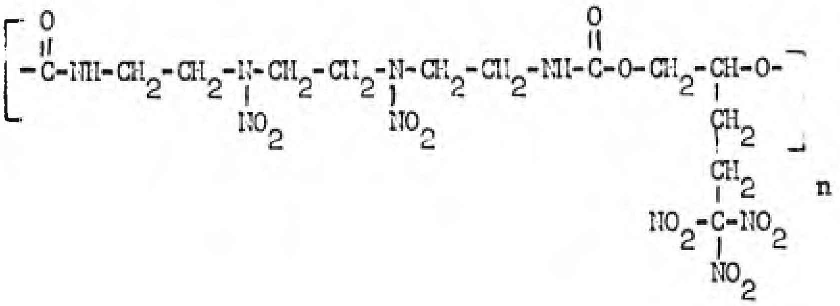
(c) Polyurethane XII-C from 2-Nitro-2-ethyl-1,3-propanediol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{N}-CH_2-CH_2-\underset{NO_2}{N}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{NO_2}{\underset{CH_2-CH_3}{C}}-CH_2-O-\right]_n$$

The commercially available C diol was used to prepare a polymer for use in post-polymerization nitration studies (868, 31-32).

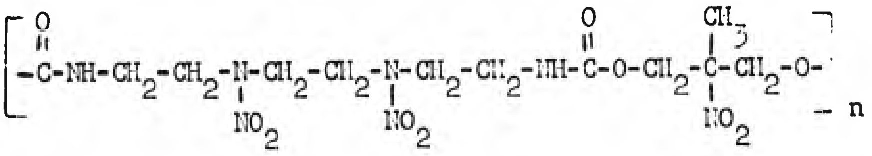
(d) Polyurethane XII-H from 5,5,5-Trinitro-1,2-pentanediol (II,D,2,b)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{N}-CH_2-CH_2-\underset{NO_2}{N}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{\underset{\underset{NO_2}{NO_2-C-NO_2}}{CH_2}}{\underset{CH_2}{CH}}-O-\right]_n$$

Polyurethane XII-H was prepared in dioxan solution using ferric acetylacetonate catalyst (740, 22; 772, 23). The X-ray diffraction pattern showed that the polymer was amorphous.

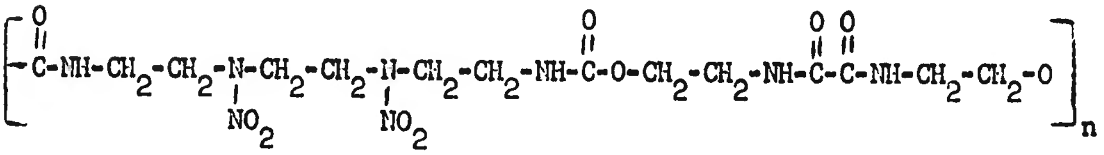
(e) Polyurethane XII-J from 2-Nitro-2-methyl-1,3-propanediol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{N}-CH_2-CH_2-\underset{NO_2}{N}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{CH_3}{\underset{NO_2}{C}}-CH_2-O-\right]_n$$

The commerically available J diol was used to prepare a polymer for use in post-polymerization nitration studies (740, 22).

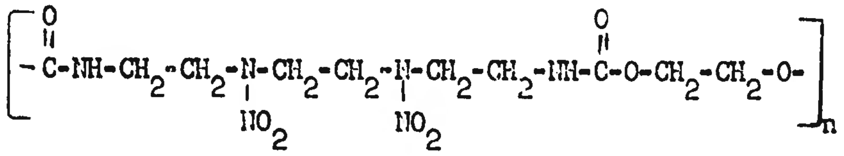
(f) Polyurethane XII-N from N,N'-bis-(2-Hydroxyethyl)-oxamide



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-O\right]_n$$

This low-impulse polymer was prepared for post-polymerization nitration study (772, 15). The X-ray diffraction pattern showed that it was polycrystalline, a fact substantiated by the high softening range of 190-200°C.

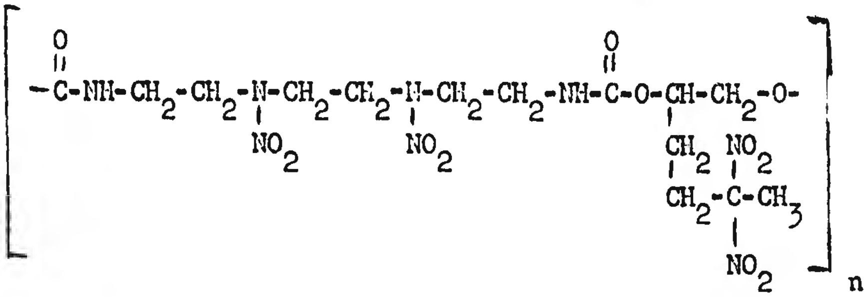
(g) Polyurethane XII-N from Ethylene Glycol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\right]_n$$

This polyurethane was prepared for later nitration study (772, 16).

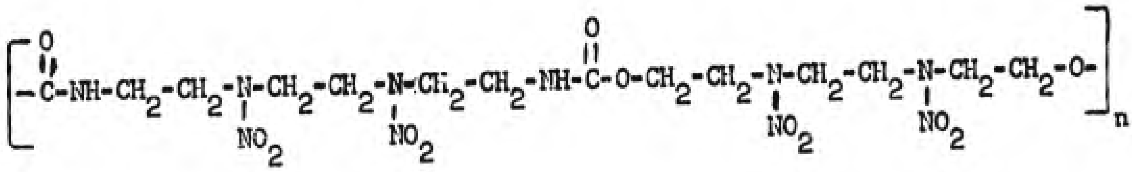
(h) Polyurethane XII-O from 5,5-Dinitro-1,2-hexanediol (II,D,2,b)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-\underset{\underset{CH_2-\overset{NO_2}{\overset{|}{\underset{\underset{NO_2}{|}}{C}}}-CH_3}{\underset{|}{CH_2}}}{\underset{|}{CH}}-CH_2-O-\right]_n$$

This polymer, having a moderate specific impulse, was prepared for evaluation as a propellant binder and for further nitration (772, 17). The X-ray diffraction pattern showed that it was polycrystalline.

(i) Polyurethane XII-T from 3,6-Dinitraza-1,8-octanediol (II,D,2,i)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-O-\right]_n$$

The polyurethane was prepared in γ-butyroacetone as solvent for the monomers; however, after a short reaction period, the polymeric material separated from solution. This undoubtedly limited the molecular weight (941, 8). Although an X-ray diffraction pattern was not obtained, the material having low solubility characteristics (967, 5) appeared to be polycrystalline.

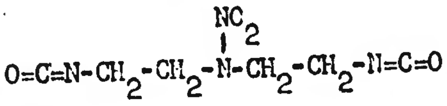
(j) Evaluation of Nitropolyurethanes from 3,6-Dinitraza-1,8-octane Diisocyanate

Group 1 polyurethanes, those with estimated specific impulse values over 170 lbf sec/lbm, include XII-A and XII-H, both of which fulfill the three major requirements of high molecular weight, high energy, and stability.

Group 2 polyurethanes, those with estimated specific impulse values in the range 140-170 lbf sec/lbm, include XII-O and XII-T, both having low molecular weight.

The low-impulse Group 3 includes XII-C, XII-J, XII-M, and XII-N, which were prepared primarily for post-nitration studies. Polyurethanes XII-C and XII-J were amorphous and met the requirements — other than that of high energy. Polyurethanes XII-M and XII-N were polycrystalline and had low molecular weights.

(7) Nitropolyurethanes from 3-Nitraza-1,5-pentane Diisocyanate (XIII) (II,B,4,b)

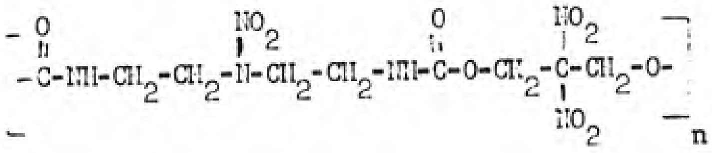


$$O{=}C{=}N-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-N{=}C{=}O$$

(a) Introduction

This nitramino diisocyanate has been used extensively in polymerization reactions, because of its high degree of purity and ease of preparation along with the good physical properties of the resulting polymers. The polymers prepared, along with their physical properties, are listed in Table 24.

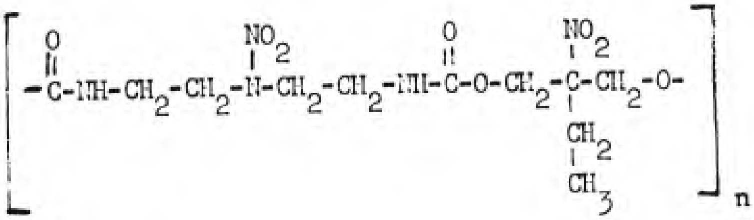
(b) Polyurethane XIII-A from 2,2-Dinitro-1,3-propanediol (II,D,2,a)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-O-\right]_n$$

The initial preparation of XIII-A was made in dioxan solution with ferric acetylacetonate catalyst (740, 23). Adjustment of end-group equivalence resulted in a higher-molecular-weight polymer with greater thermal stability (772, 21, 22). The effect of end-group type on stability was determined (1004, 5-7). Branched polymer was prepared by adding small amounts of tris-(hydroxymethyl)-nitromethane (772, 31, 32; 868, 36). The SPIA data sheet was prepared (941, Appendix).

(c) Polyurethane XIII-C from 2-Nitro-2-ethyl-1,3-propanediol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{\underset{CH_3}{\overset{|}{CH_2}}}{\overset{NO_2}{\overset{|}{C}}}-CH_2-O-\right]_n$$

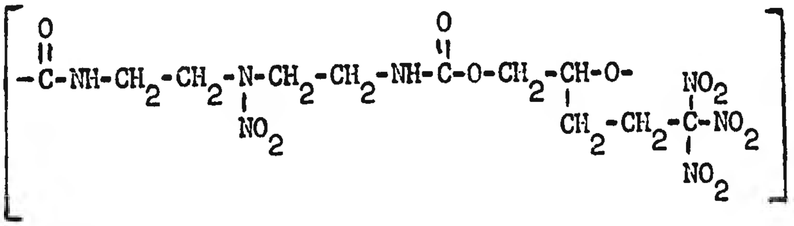
With post-polymerization nitration, the estimated specific impulse of this polymer would be sufficiently high for propellant use. It was prepared in dioxan solution, using ferric acetylacetonate catalyst (868, 32).

TABLE 24

PROPERTIES OF NITROPOLYURETHANES FROM 3-NITRAZA-1,5-PENTANE DIISOCYANATE (XIII)

Diol		Polymer Empirical Formula	Heat of Combustion Calc'd	Cal/g Found	Estimated Specific Impulse lbf sec/lbm	Softening Range °C	Relative Viscosity 1% Solution	Density g/cc	Stability: KI-Starch at 65.5°C min	Stability: Impact cm/2 kg	Stability: Warburg at 65.5°C ml/100g/hr	Preparation Reference
(A)	2,2-Dinitro-1,3-propanediol	$C_9H_{14}N_6O_{10}$	3077	3087	167	60 to 70	1.6	1.65	>300	>100	<0.01	772, 21, 22
(C)	2-Nitro-2-ethyl-1,3-propanediol	$C_{11}H_{19}N_5O_8$	4167	4119	<100	60 to 70	2.3	--	--	>100	--	868, 32
(H)	5,5,5-Trinitro-1,2-pentanediol	$C_{11}H_{17}N_7O_{12}$	--	--	178	90 to 100	2.1	--	60	>100	<0.01	740, 24
(J)	2-Nitro-2-methyl-1,3-propanediol	$C_{10}H_{17}N_5O_8$	--	--	<100	75 to 85	2.5	1.50	>180	>100	--	740, 24, 25
(M)	N,N'-*bis*-(2-Hydroxyethyl)-oxamide	$C_{12}H_{20}N_6O_8$	--	--	<100	130 to 150	1.1	--	--	>100	--	740, 25
(N)	Ethylene glycol	$C_8H_{14}N_4O_6$	3969	3855	<100	185 to 190	1.4	1.576	--	>100	--	868, 33, 34
(O)	5,5-Dinitro-1,2-hexanediol	$C_{12}H_{20}N_6O_{10}$	3904	3829	130	60 to 70	1.4	--	240	>100	<0.1	740, 27
(Q)	2-Nitro-2-bromo-1,3-propanediol	$C_9H_{14}BrN_5O_8$	--	--	--	30 to 70	2.0	--	>60	>100	--	907, 15
(R)	1,4-Butanediol	$C_{10}H_{18}N_4O_6$	--	--	--	80 to 85	--	--	--	--	--	Unpublished Data
(S)	2-Nitro-2-chloro-1,3-propanediol	$C_9H_{14}ClN_5O_8$	--	--	--	--	3.2	--	--	--	--	967, 7
(T)	3,6-Dinitraza-1,8-octanediol	$C_{12}H_{22}N_8O_{10}$	3855	3823	138	75 to 80	1.4	--	>120	>100	--	941, 9
(U)	2-Butyne-1,4-diol	$C_{10}H_{14}N_4O_6$	--	--	--	--	1.2	--	--	--	--	941, 16

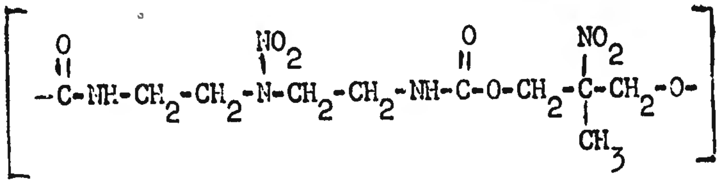
(d) Polyurethane XIII-H from 5,5,5-Trinitro-1,2-pentanediol (II,D,2,b)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{\underset{NO_2}{|}}{N}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{\underset{CH_2-CH_2-\overset{\overset{NO_2}{|}}{\underset{\underset{NO_2}{|}}{C}}-NO_2}{|}}{CH}-O-\right]_n$$

The preparation of this amorphous polymer was conducted in dioxan solution with ferric acetylacetonate catalyst (740, 24). The product was high in molecular weight and had good stability along with high specific impulse.

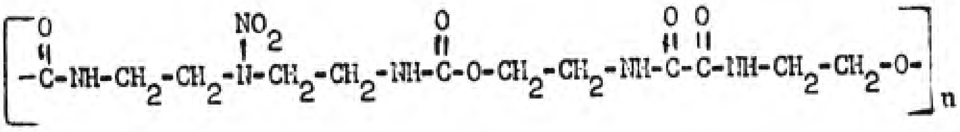
(e) Polyurethane XIII-J from 2-Nitro-2-methyl-1,3-propanediol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{\overset{NO_2}{|}}{N}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{\overset{NO_2}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-O-\right]_n$$

This polymer was prepared for post-polymerization nitration study (740, 24, 25). The solubility of the polymer was determined (967, 5).

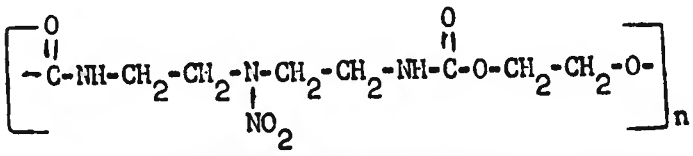
(f) Polyurethane XIII-M from N,N'-bis-(2-Hydroxyethyl)-oxamide



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{\overset{NO_2}{|}}{N}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-O-\right]_n$$

The polycrystalline reaction product separated from the dimethylformamide used as solvent for the monomers (740, 25).

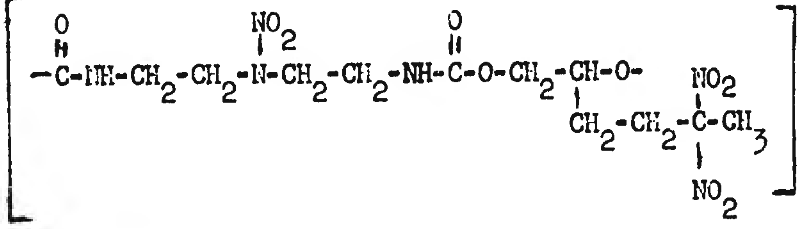
(g) Polyurethane XIII-N from Ethylene Glycol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{\underset{NO_2}{|}}{N}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\right]_n$$

The first preparation of this polycrystalline polymer was made in dimethylformamide, from which the polymer separated at a low degree of polymerization (740, 26). The preparation was repeated in γ-butyrolactone, as solvent, at a higher temperature; the product had a higher molecular weight (868, 33, 34). The solubility was determined (967, 5).

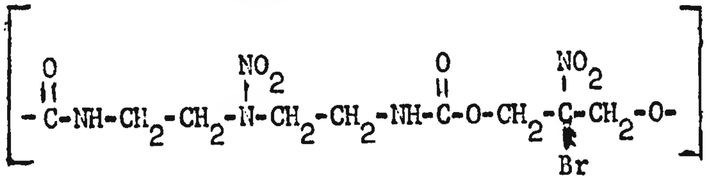
(h) Polyurethane XIII-O from 5,5-Dinitro-1,2-hexanediol (II,D,2,b)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{CH_2-CH_2-\overset{NO_2}{\overset{|}{\underset{NO_2}{\underset{|}{C}}}}-CH_3}{\underset{|}{CH}}-O- \right]_n$$

The amorphous polymer was prepared in dioxan solution (740, 27).

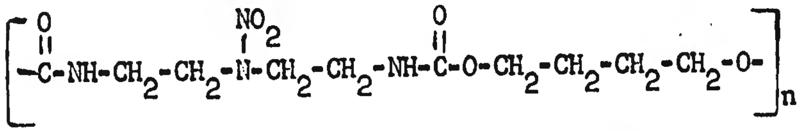
(i) Polyurethane XIII-Q from 2-Nitro-2-bromo-1,3-propanediol (II,D,2,a)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{NO_2}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_2-O- \right]_n$$

This bromine-containing nitropolymer was prepared for study in second-stage cross-linking reactions. The substitution of 2-nitro-2-bromo-1,3-propanediol for a portion of the 2,2-dinitro-1,3-propanediol in the "A" series of polyurethanes would provide active centers for cross-linking reactions, without seriously reducing the specific impulse of the copolymer. It was desirable to prepare the pure bromine-containing polyurethane, and characterize it, before preparing the desired copolymers. (907, 15; 941, 15, 16). Copolymers XIII-CQ 95/5 (941, 11) and XIII-AQ 90/10 (941, 12, 15) were prepared for cross-linking studies (see Section IV).

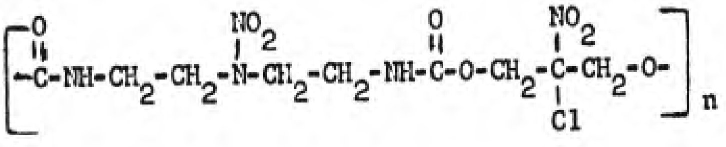
(j) Polyurethane XIII-R from 1,4-Butanediol



$$\left[-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{NH}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}-\right]_n$$

The polymerization was carried out in dimethylformamide solution. Polymer separated from the monomer solution. It softened in the range 80-85°C (unpublished data).

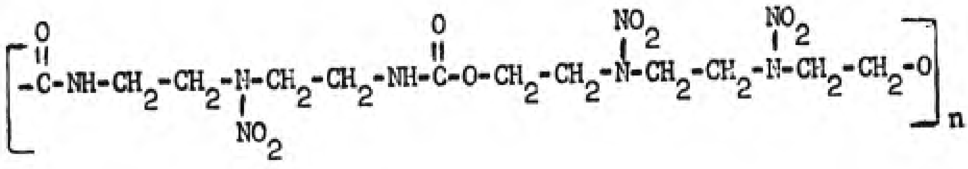
(k) Polyurethane XIII-S from 2-Nitro-2-chloro-1,3-propanediol (II,D,2,a)



$$\left[-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{NH}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\mathrm{CH_2}-\underset{\underset{\mathrm{Cl}}{|}}{\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{C}}}}-\mathrm{CH_2}-\mathrm{O}-\right]_n$$

This polymer was prepared for cross-linking studies (941, 12). Copolymers XIII-CS 90/10 (941, 11) and XIII-AS 90/10 (941, 12) were prepared (see Section IV).

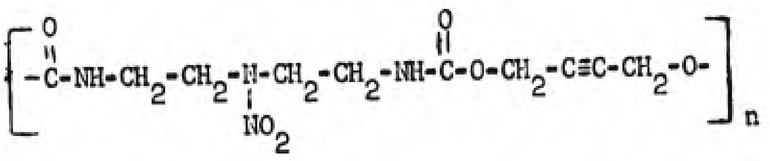
(l) Polyurethane XIII-T from 3,6-Dinitraza-1,8-octanediol (II,B,2,i)



$$\left[-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\underset{\mathrm{NO_2}}{|}}{\mathrm{N}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{NH}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\overset{|}{\mathrm{N}}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{O}\right]_n$$

The polymerization was carried out in γ-butyrolactone solvent, from which the solid polymer slowly separated (941, 9). The solubility was determined (967, 5).

(m) Polyurethane XIII-U from 2-Butyne-1,4-diol



$$\left[-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{NH}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\underset{\mathrm{NO_2}}{|}}{\mathrm{N}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{NH}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}-\mathrm{CH_2}-\mathrm{C}\equiv\mathrm{C}-\mathrm{CH_2}-\mathrm{O}-\right]_n$$

This polymer was prepared for cross-linking studies (941, 16).

(n) Polyurethane from Polyglycidyl Nitrate

The reaction of nitrodiisocyanates with long-chain diols was investigated in an effort to reduce shrinkage and heat of polymerization. With polyglycidyl nitrate of molecular weight of about 1000, some chain-lengthening took place, but high-molecular-weight polymer was not obtained (1083, 10, 11; 1119, 3, 4).

(o) Attempted Polymerization with 2,4,6-Trinitroresorcinol

Previous attempts to prepare polyurethanes from 2,4,6-trinitroresorcinol failed (see paragraph III,B,2,c,(3),(d). Reaction with XIII diisocyanate was attempted, using ferric acetylacetonate catalyst. No polymer was formed; the catalyst was ineffective in the presence of the diol (1048, 4).

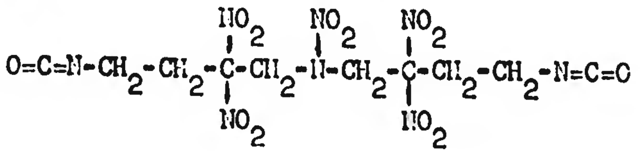
(p) Solvent-Screening with XIII Diisocyanate

In addition to the polymerization reactions described, 3-nitraza-1,5-pentane diisocyanate was used to screen a variety of solvents in order to determine those suitable for use during polymerization (740, 9, 10; 967, 6; 1004, 4, 5).

(q) Evaluation of Nitropolyurethanes from 3-Nitraza-1,5-pentane Diisocyanate

Two of the polyurethanes of the XIII-series, XIII-A and XIII-H, meet all the major requirements of high molecular weight, high energy and stability. The others, though low in estimated specific impulse, were generally obtained in the form of high-molecular-weight polymers with good stability.

(8) Nitropolyurethanes from 3,3,5,7,7-Pentanitro-5-aza-1,9-nonane Diisocyanate (XIV) (II,B,3, Table 6)

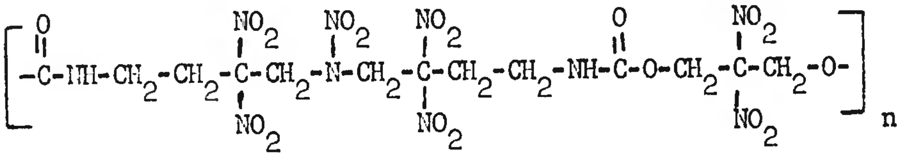


$$O{=}C{=}N\text{-}CH_2\text{-}CH_2\text{-}\underset{NO_2}{\overset{NO_2}{C}}\text{-}CH_2\text{-}\overset{NO_2}{N}\text{-}CH_2\text{-}\underset{NO_2}{\overset{NO_2}{C}}\text{-}CH_2\text{-}CH_2\text{-}N{=}C{=}O$$

(a) Introduction

This highly energetic gem dinitronitramino diisocyanate was difficult to purify, and it could not be analyzed by the standard analytical methods (740, 70; 772, 13). For these reasons, small-scale polymerization experiments were used to estimate the degree of purity of each preparation (772, 13, 14). The physical properties of the three polymers that were prepared are listed in Table 25.

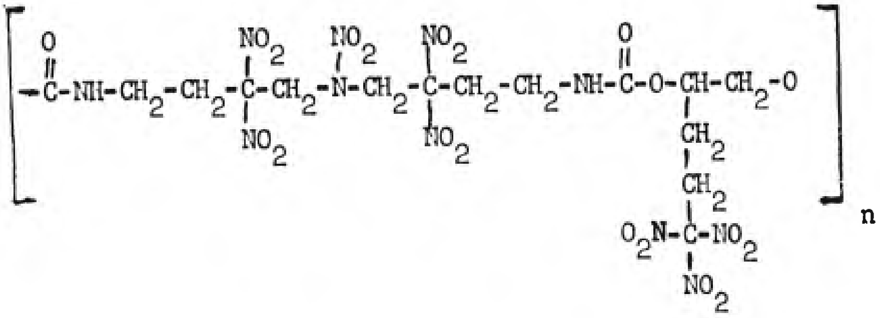
(b) Polyurethane XIV-A from 2,2-Dinitro-1,3-propanediol (II,D,2,a)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-\overset{NO_2}{N}-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-O-\right]_n$$

The high, calculated specific impulse of XIV-A made it one of the most desirable polyurethanes for investigation. Initial attempts to prepare it yielded low-molecular-weight polymer that had poor analytical values (772, 14). After purification of the diisocyanate via the dioxan complex (772, 14), higher-molecular-weight polymer, with better analytical values, was obtained (907, 16, 17).

(c) Polyurethane XIV-H from 5,5,5-Trinitro-1,2-pentanediol (II,D,2,b)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-\overset{NO_2}{N}-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-\underset{CH_2-CH_2-C(NO_2)_3}{CH}-CH_2-O\right]_n$$

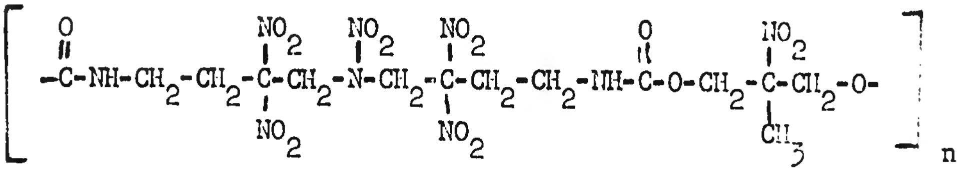
Polyurethane XIV-H was prepared from diisocyanate that had been purified via the dioxan complex (907, 11).

TABLE 25

PROPERTIES OF NITROPOLYURETHANES FROM 3,3,5,7,7-PENTANITRO-5-AZA-1,9-NONANE DIISOCYANATE (XIV)

	Diol	Polymer Empirical Formula	Heat of Combustion Calc'd	Cal/g Found	Estimated Specific Impulse lbf sec/lbm	Softening Range °C	Relative Viscosity 1% Solution	Stability: KI-Starch at 65.5°C min	Stability: Methyl Violet at 134.5°C min	Stability: Impact cm/2 kg	Preparation Reference
(A)	2,2-Dinitro-1,3-propanediol	$C_{13}H_{18}N_{10}O_{18}$	--	--	212	75 to 85	1.6	13	--	40	907, 16, 17
(H)	5,5,5-Trinitro-1,2-pentanediol	$C_{15}H_{21}N_{11}O_{20}$	2805	2949	213	65 to 75	1.2	20	--	65	907, 11
(J)	2-Nitro-2-methyl-1,3-propanediol	$C_{14}H_{21}N_{9}O_{15}$	3116	3159	187	80 to 90	1.7	--	47	--	772, 13, 14

(d) Polyurethane XIV-J from 2-Nitro-2-methyl-1,3-propanediol



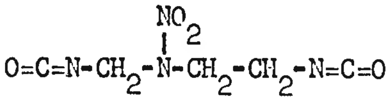
$$\left[-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{NH}-\mathrm{CH_2}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\underset{\mathrm{NO_2}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\mathrm{N}}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\underset{\mathrm{NO_2}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{NH}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{O}-\right]_n$$

The initial preparations with ferric acetylacetonate catalyst gave low-molecular-weight polymer (772, 13, 14). Using diisocyanate purified via the dioxan complex and ferric acetylacetonate catalyst, higher-molecular-weight polyurethane was obtained (868, 32, 33). With BF_3-etherate catalyst, the product had low molecular weight (868, 33).

(e) Evaluation of Nitropolyurethanes from 3,3,5,7,7-Pentanitro-5-aza-1,9-nonane Diisocyanate

The three polymers studied all belong to Group 1, having high energy. Polyurethanes XIV-A and XIV-J were high-molecular-weight polymers that did not meet the stability requirements. Polyurethane XIV-H had fair stability, but it was low in molecular weight.

(9) Nitropolyurethanes from 2-Nitraza-1,4-butane Diisocyanate (XV) (II,B,4, Table 7,(2))



$$\mathrm{O{=}C{=}N}-\mathrm{CH_2}-\overset{\mathrm{NO_2}}{\mathrm{N}}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{N{=}C{=}O}$$

(a) Introduction

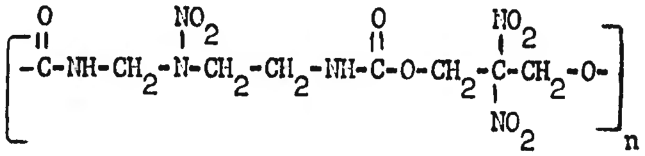
The availability of this short-chain nitramino diisocyanate made possible the preparation of a series of nitropolyurethanes with somewhat higher specific impulse than the corresponding members of the XII series. Kinetic studies showed that XV diisocyanate reacted about six times as fast as XIII, which had already been used successfully in nitropolymer formation (see Table 24). The resulting polymers are described in Table 26.

TABLE 26

PROPERTIES OF NITROPOLYURETHANES FROM 2-NITRAZA-1,4-BUTANE DIISOCYANATE (XV)

	Diol	Polymer Empirical Formula	Heat of Combustion Calc'd	Cal/g Found	Estimated Specific Impulse lbf sec/lbm	Softening Range °C	Relative Viscosity 1% Solution	Density g/cc	Stability		
									KI-Starch at 65.5°C min	Methyl Violet at 134.5°C min	Impact cm/2 kg	Preparation Reference
(A)	2,2-Dinitro-1,3-propanediol	$C_8H_{12}N_6O_{10}$	2748	2717	179	85 to 95	1.8	1.55	120	--	>100	807, 15
(H)	5,5,5-Trinitro-1,2-pentanediol	$C_{10}H_{15}N_7O_{12}$	2954	2931	188	80 to 90	1.5	--	120	>300	55	808, 17
(J)	2-Nitro-2-methyl-1,3-propanediol	$C_9H_{15}N_5O_8$	3497	3512	111	90 to 100	1.8	1.53	>300	--	>100	807, 18
(N)	Ethylene glycol	$C_7H_{12}N_4O_6$	3560	3460	<100	65 to 75	1.3	--	>300	--	>100	833, 17
(O)	5,5-Dinitro-1,2-hexanediol	$C_{11}H_{18}N_6O_{10}$	3643	3571	142	70 to 80	1.1	--	>300	--	>100	833, 20

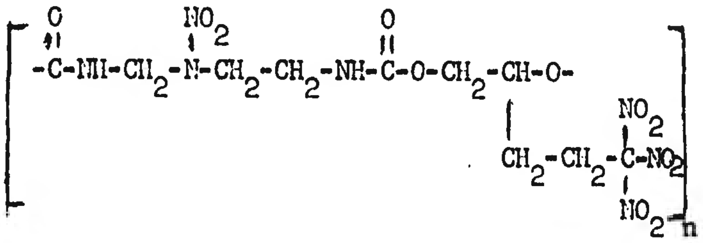
(b) Polyurethane XV-A from 2,2-Dinitro-1,3-propanediol (II,D,2,a)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-O-\right]_n$$

The polyurethane was readily prepared in dioxan solution with ferric acetylacetonate catalyst (807, 15). Data was obtained for the SPIA data sheet (941, Appendix).

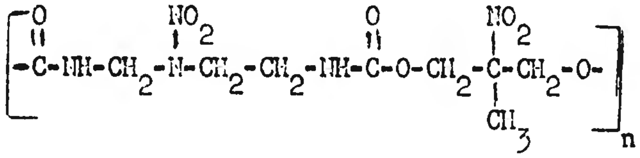
(c) Polyurethane XV-H from 5,5,5-Trinitro-1,2-pentanediol (II,D,2,b)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-NO_2}{\underset{|}{CH}}-O-\right]_n$$

The preparation was similar to that of XV-A above (807, 17, 18).

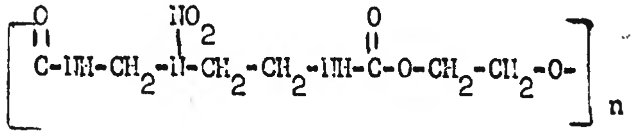
(d) Polyurethane XV-J from 2-Nitro-2-methyl-1,3-propanediol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{CH_3}{\overset{NO_2}{C}}-CH_2-O-\right]_n$$

The polymerization was similar to that of XV-A above (807, 18). The SPIA data sheet was prepared (941, Appendix). The polymer was prepared for further nitration study.

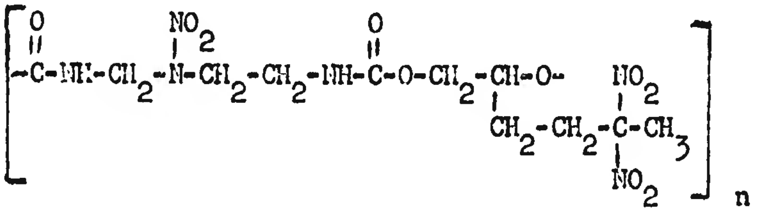
(e) Polyurethane XV-N from Ethylene Glycol



$$\left[\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\right]_n$$

Post-nitration of the urethane linkages would make this polymer suitable for propellant use. It was prepared in dioxan solution, from which some polymeric material separated during the reaction (833, 17).

(f) Polyurethane XV-O from 5,5-Dinitro-1,2-hexanediol (II,D,2,b)



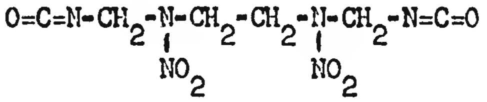
$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{CH_2-CH_2-\underset{NO_2}{\underset{|}{\overset{NO_2}{\overset{|}{C}}}}-CH_3}{\underset{|}{CH}}-O-\right]_n$$

The preparation of this moderately energetic polyurethane was similar to that of XV-N above (833, 20).

(g) Evaluation of Nitropolyurethanes from 2-Nitraza-1,4-butane Diisocyanate

Polyurethanes XV-A and XV-H fulfill the requirements of high molecular weight, high specific impulse, and high stability needed for propellant use. Polyurethanes XV-J and XV-N require post-nitration for increased energy. Polyurethane XV-O is low in molecular weight.

(10) Nitropolyurethanes from 2,5-Dinitraza-1,6-hexane Diisocyanate (XVI) (II,B,4, Table 7)

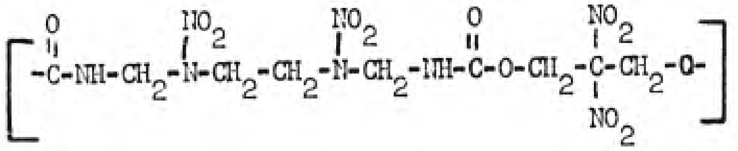


$$O=C=N-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-CH_2-\underset{NO_2}{\underset{|}{N}}-CH_2-N=C=O$$

(a) Introduction

2,5-Dinitraza-1,6-hexane diisocyanate, with two nitramino groups and only four methylene groups, is second only to 3,3,5,7,7-pentanitro-5-aza-1,9-nonane diisocyanate in the amount of energy contributed by diisocyanates. The rate of reaction of XVI with 2-nitro-2-methyl-1,3-propanediol was approximately twice the rate of 3-nitraza-1,5-pentane diisocyanate with the same diol (868, 21, 22), making it easy to prepare polymers from the less reactive diols. Table 27 lists the polymers of the XVI series that were prepared and some of their more important physical properties.

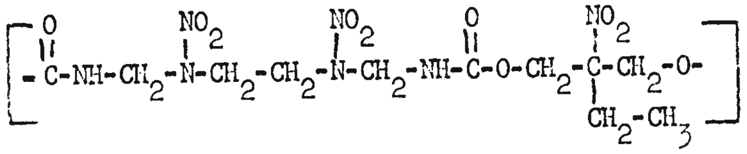
(b) Polyurethane XVI-A from 2,2-Dinitro-1,3-propanediol (II,D,2,a)



$$\left[-\overset{\overset{O}{\|}}{C}-NH-CH_2-\overset{\overset{NO_2}{|}}{N}-CH_2-CH_2-\overset{\overset{NO_2}{|}}{N}-CH_2-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_2-O-\right]_n$$

The initial preparation was carried out in dioxan, which proved to be a poor solvent for the resulting polymer (868, 29). The polymerization was repeated in γ-butyrolactone, in an effort to obtain higher-molecular-weight product (907, 17).

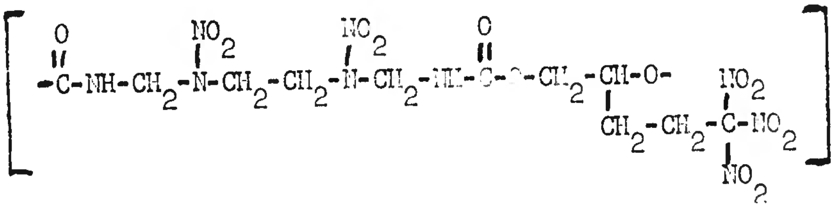
(c) Polyurethane XVI-C from 2-Nitro-2-ethyl-1,3-propanediol



$$\left[-\overset{\overset{O}{\|}}{C}-NH-CH_2-\overset{\overset{NO_2}{|}}{N}-CH_2-CH_2-\overset{\overset{NO_2}{|}}{N}-CH_2-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_2-CH_3}{|}}{\overset{\overset{NO_2}{|}}{C}}-CH_2-O-\right]_n$$

γ-Butyrolactone was used as polymerization solvent with ferric acetylacetonate as catalyst (907, 11, 12).

(d) Polyurethane XVI-H from 5,5,5-Trinitro-1,2-pentanediol (II,D,2,b)



$$\left[-\overset{\overset{O}{\|}}{C}-NH-CH_2-\overset{\overset{NO_2}{|}}{N}-CH_2-CH_2-\overset{\overset{NO_2}{|}}{N}-CH_2-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_2-CH_2-\underset{\underset{NO_2}{|}}{\overset{\overset{NO_2}{|}}{C}}-NO_2}{|}}{CH}-O-\right]_n$$

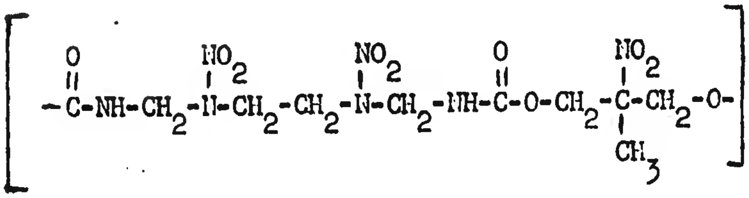
A number of attempts were made to increase the molecular weight of this desirable high-energy polymer (907, 12, 13); both dioxan and γ-butyrolactone were used as solvents.

TABLE 27

PROPERTIES OF NITROPOLYURETHANES FROM 2,5-DINITRAZA-1,6-HEXANE DIISOCYANATE

	Diol	Polymer Empirical Formula	Heat of Combustion Calc'd	cal/g Found	Estimated Specific Impulse lbf sec/lbm	Softening Range °C	Relative Viscosity 1% Solution	Stability KI-Starch at 65.5°C min	Stability Impact cm/2 kg	Preparation Reference
(A)	2,2-Dinitro-1,3-propanediol	$C_9H_{14}N_8O_{12}$	2663	2806	204	85-95	1.3	90	>100	868, 29
(B)	2-Nitro-2-ethyl-1,3-propanediol	$C_{11}H_{19}N_7O_{10}$	3590	3591	130	85-95	1.4	> 80	>100	907, 11, 12
(H)	5,5,5-Trinitro-1,2-pentanediol	$C_{11}H_{17}N_9O_{14}$	2847	2946	202	90-100	1.2	>120	60	907, 12, 13
(J)	2-Nitro-2-methyl-1,3-propanediol	$C_{10}H_{17}N_7O_{10}$	3314	3308	154	100-110	1.6	120	>100	868, 30
(N)	Ethylene glycol	$C_8H_{14}N_6O_8$	3267	3213	130	100-110	1.3	> 80	>100	907, 14
(O)	5,5-Dinitro-1,2-hexanediol	$C_{12}H_{20}N_8O_{12}$	3425	3442	168	75-85	1.2	> 180	>100	907, 14, 15

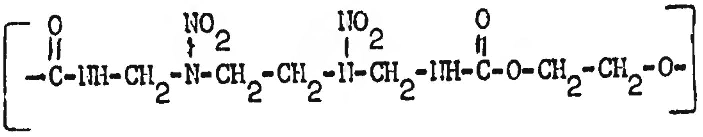
(e) Polyurethane XVI-J from 2-Nitro-2-methyl-1,3-propanediol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{CH_3}{\underset{|}{\overset{NO_2}{\overset{|}{C}}}}-CH_2-O-\right]_n$$

The preparation was carried out in dioxan solution with ferric acetylacetonate catalyst (868, 30). Attempts to determine the molecular weight were unsuccessful, due to the high degree of diffusion through the osmometer membrane (907, 52; 941, 29).

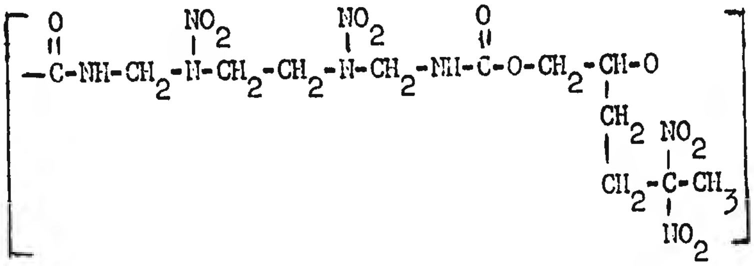
(f) Polyurethane XVI-N from Ethylene Glycol



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\right]_n$$

Although γ-butyrolactone was used as solvent, the entire mixture solidified during the polymerization (907, 14). A better solvent is needed for this preparation.

(g) Polyurethane XVI-O from 5,5-Dinitro-1,2-hexanediol (II,D,2,b)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-NH-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{\substack{|\\ CH_2\\ |\\ CH_2-\overset{NO_2}{\overset{|}{\underset{NO_2}{\underset{|}{C}}}}-CH_3}}{CH}-O\right]_n$$

The preparation was similar to the preparation of XVI-J above (907, 14, 15).

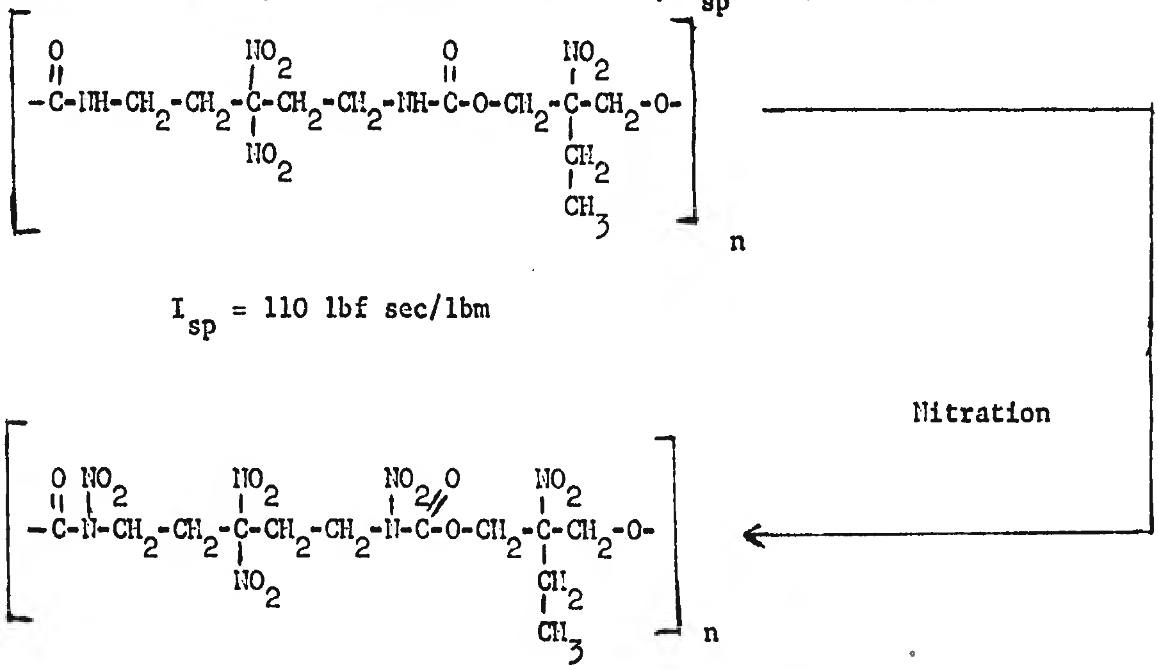
(h) Evaluation of Nitropolyurethanes from 2,5-Dinitraza-1,6-hexane Diisocyanate

Three of the XVI series polyurethanes belong in the high-energy Group 1, including XVI-A, XVI-N, and XVI-O. All had good stability but failed to meet molecular-weight requirements. Polyurethane XVI-J, with intermediate energy, had a higher relative viscosity, but it contained a considerable amount of low-molecular-weight polymer that diffused through the osmometer membrane. Polyurethanes XVI-C and XVI-H, in the low-energy group, had good stabilities but were low in molecular weight. Since none of the XVI series polyurethanes had very high molecular weights (based on relative-viscosity measurements), and yet the polymers had good thermal stability, it was concluded that the XVI diisocyanate may contain some mono-functional impurities that stop the growing polymer chain.

d. Nitration Studies

(1) Introduction

Many of the polyurethanes described in paragraph III,B,2,C would be useful as propellants, only if they could be successfully post-polymerization-nitrated at the urethane linkages. Thus, polyurethane I-C, with an estimated specific impulse of 110 lbf sec/lbm after post-nitration, yields polyurethane I-CN, I_{sp} = 189 lbf sec/lbm.



$$\left[-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{CH_2}}{\overset{NO_2}{C}}-CH_2-O-\right]_n$$

I_{sp} = 110 lbf sec/lbm

$$\left[-\overset{\overset{O}{\|}}{C}-\overset{NO_2}{N}-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-\overset{NO_2}{N}-\overset{\overset{O}{\|}}{C}-O-CH_2-\underset{\underset{CH_3}{CH_2}}{\overset{NO_2}{C}}-CH_2-O-\right]_n$$

I_{sp} = 189 lbf sec/lbm

(The addition of an "N" to the code designation of a polyurethane has been used to indicate that all urethane linkages in the polymer have been nitrated. Thus polyurethane I-C after complete nitration is designated polyurethane I-CN.)

The study of nitration methods applicable to polyurethanes was started at the very beginning of the nitropolymer program, before high-energy monomers were synthesized (330, 39-41; 345, 24, 25, 27; 371, 24-28; 386, 20, 21; 404, 22, 23). In many cases, nitration was accompanied by degradation, which resulted in low yields of thermally unstable products. A method was developed for increasing the thermal stability, in certain instances, by treating the postnitrated polyurethanes with ammonium persulfate (371, 71, 72; 663, 17, 18, 24; 638, 40).

The study of nitration techniques was continued, after higher energy monomers became available, with emphasis being made on methods for increasing the thermal stability of the post-nitrated products. Polyurethanes I-A and I-J (see paragraph III,B,2,c) were used as models in the nitration experiments, representing the high- and low-energy polyurethane groups, respectively. Most of the effort was concentrated on them, and the techniques that were developed were applied in making single preparations of the other post-nitrated polyurethanes listed in Table 28. Post-nitrated polymers in which two nitramino groups were separated by only one methylene group were found to suffer extensive degradation during nitration (563, 25-27; 807, 17, 19). The nitration of polyurethane I-D (see paragraph III,B,2,c,(2),(c)) was accompanied by degradation and nitration of the fragments to give a yield larger than theoretical (515, 60, 61; 563, 25).

In these studies, it was found that the great difference between the heat of combustion of the starting material and the post-nitrated polymer, in conjunction with the high degree of accuracy in the determination of the heat of combustion, made it the most reliable measurement for determining the degree of nitration.

TABLE 20

PROPERTIES OF POST-NITRATED POLYURETHANES

Post-Nitrated Polyurethane	Empirical Formula	Heat of Combustion Calc'd	Cal/g Found	Estimated Specific Impulse lbf sec/lbm	Softening Range °C	Relative Viscosity 2% Solution	Polymer Density min	Stability				References
								Starch-Iodide at 65.5°C min	Methyl Violet at 65.5°C min	Impact cm/2 kg	Warburg at 65.5°C min	
I-AN	$C_{10}H_{12}N_8O_{16}$	2320	2320	226	65-75	1.7	1.72	>360	13	30	0.64	See III,B,2,d,(2)
I-FN	$C_{12}H_{14}N_{10}O_{20}$	2260	2305	234	50-60	1.1	--	--	--	25	--	515, 31; 622, 34, 35
I-HN	$C_{12}H_{15}N_9O_{18}$	2524	2491	226	50-70	1.6	--	5	--	30	1.7	563, 20; 622, 32; 663, 27, 28
I-JN	$C_{11}H_{15}N_7O_{14}$	2871	2881	201	50-60	1.7	--	>240	--	65	1.4	See III,B,2,d,(3)
I-KN	$C_{18}H_{25}N_{11}O_{22}$	3075	3015	209	30-35	1.4	--	10	8	40	--	590, 33, 34
I-LN	$C_{18}H_{24}N_{12}O_{24}$	2858	2823	219	30-35	1.3	---	7	4	35	--	590, 35
I-MN	$C_{13}H_{16}N_{10}O_{18}$	2561	2531	210	85-90	1.2	1.66	19	11	93	--	622, 24, 25; 638, 40, 41; 663, App.
I-NN	$C_9H_{12}N_6O_{12}$	2711	2716	202	40-45	1.5	--	--	--	85	--	638, 39
I-ON	$C_{13}H_{18}N_8O_{16}$	3000	2996	205	55-65	1.4	--	23	>300	100	--	638, 36
I-PN	$C_{11}H_{16}N_8O_{14}$	2886	2844	207	40-50	1.4	--	5	--	75	--	833, 21
XI-AN	$C_{14}H_{17}N_{11}O_{22}$	2420	2424	231	55-60	1.1	--	--	--	26	--	590, 32
XI-HN	$C_{13}H_{17}N_9O_{18}$	2705	2696	217	40-45	1.1	--	--	--	45	--	563, 18
XII-AN	$C_{11}H_{16}N_{10}O_{16}$	2584	2596	221	65-75	1.8 (1% soln)	--	--	--	100	0.34	772, 17-19
XII-HN	$C_{13}H_{19}N_{11}O_{18}$	2749	2712	222	70-80	1.4 (1% soln)	--	3	--	82	--	807, 19, 20
XII-JN	$C_{12}H_{19}N_9O_{14}$	3085	3102	195	60-70	1.2 (1% soln)	--	12	--	50	0.17	772, 19
XII-MN	$C_{14}H_{20}N_{12}O_{18}$	2773	2799	207	65-70	1.03 (1% soln)	--	--	--	90	--	772, 15
XII-NN	$C_{10}H_{16}N_8O_{12}$	3008	2979	197	60-65	1.1 (1% soln)	--	--	--	75	--	772, 16
XII-ON	$C_{14}H_{22}N_{10}O_{16}$	3147	3148	200	85-95	1.1 (1% soln)	--	--	--	90	--	772, 17
XIII-AN	$C_9H_{12}N_8O_{14}$	2388	2375	222	50-60	1.3 (1% soln)	--	4	--	>100	--	740, 23, 24; 807, 21, 22
XIII-HN	$C_{11}H_{15}N_9O_{16}$	2602	2601	211	80-90	1.4 (1% soln)	--	10	--	30	0.12	772, 20
XIII-JN	$C_{10}H_{15}N_7O_{12}$	2964	2994	189	70-80	1.7 (1% soln)	--	10	--	83	--	772, 20, 21; 807, 22, 23
XIII-MN	$C_{12}H_{16}N_{10}O_{16}$	2650	2651	205	65-75	1.1 (1% soln)	--	8	--	47	--	807, 20, 21
XIII-NN	$C_8H_{12}N_6O_{10}$	2845	2832	192	50-60	1.1 (1% soln)	--	10	--	90	0.95	740, 26
XIII-ON	$C_{12}H_{16}N_8O_{14}$	3054	3067	196	50-60	1.2 (1% soln)	--	7	--	90	0.65	740, 27

(2) Nitration of Polyurethane I-A: Polyurethane I-AN

A series of experiments was made in which time, temperature, acid concentration, and dehydrating agent were varied (499, 51-53; 515, 56-60; 563, 23-25). The effect of using technical nitric acid for the nitration, upon the molecular weight and thermal stability of the nitrated product, was studied (590, 37, 38). A variety of methods were tried in an effort to increase the thermal stability of the polymer (663, 17, 18, 23-27; 686, 11-14; 712, 21-16). It was found that degradation during nitration could be minimized by ensuring completely anhydrous conditions. It was also found that purification by reprecipitation into non-aqueous solvents gave products that were stable in the starch-iodide test at 65.5°C. Quantitative measurements of the gassing rates at various temperatures and in the presence of various stabilizers were made, using the Warburg manometer. The temperature dependence of the gassing rate of polyurethane I-AN was determined, and it was found that at temperatures at or above the softening range of the polymer, the decomposition rate was greater, by a factor of ten, than at temperatures below its softening range (740, 10-13). The relative viscosities showed that the decomposition was accompanied by chain degradation. It was concluded that a search should be made for higher-softening and/or crystalline, post-nitrated polyurethanes which should have greater stability. Polyurethane I-AN was fractionated in an effort to remove low-molecular-weight fragments that may have contributed to the high gassing rate at 65.5°C (807, 24, 25); no improvement was observed. The nitration of branched polyurethane I-A resulted in higher molecular weight I-AN (772, 23). The SPIA data sheet was prepared (515, Appendix).

(3) Nitration of Polyurethane I-J; Polyurethane I-JN

The nitration of polyurethane I-J with 100% nitric acid gave completely nitrated polymer in good yield (563, 22; 622, 25). The stability, as measured by the starch-iodide method, was improved by the addition of small amounts of diphenylamine (663, 18, 19). However, gassing was not decreased, and a search was made for other ways of increasing the stability (663, 23, 24). It was found that washing the nitrated polymer with sodium bicarbonate solution at 50-65°C for 2 hr improved the starch-iodide stability without causing serious degradation (686, 14, 15). No improvement in the rate of gassing was observed (686, 51).

(4) Evaluation of Post-nitrated Polyurethanes

None of the post-nitrated polyurethanes meet all of the three major requirements for potential propellant use. Many have low molecular weight which, in some cases, could be improved by applying the techniques developed in nitration studies on the two model polymers. However, all fail the stability requirement. No exact figure has been set as a limit in the Warburg gas-evolution test (see paragraph VI,J), but a comparison with double-base propellant indicates that gas evolution should be less than 0.1 ml/100g/hr (663, 61). Of the post-nitrated polyurethanes tested, only XIII-HN approaches that level of gas evolution. However, polyurethane XIII-HN has low impact stability and poor stability in the starch-iodide test.

3. Nitropolyesters

a. Introduction

The preparation of polyesters by the condensation of dicarboxylic acids with diols is normally accompanied by the elimination of water. The polymerizations, in order to proceed at a reasonable rate, are conducted at relatively high temperatures. In the case of nitro polyesters, the nature of the diacid and diol precludes the use of high temperature; therefore, an alternate procedure was used. The diacids were first converted to the diacid chlorides. Polymerizations were then conducted in anhydrous solvents, from which the evolved hydrogen chloride was swept by a stream of dry nitrogen.

b. Kinetic Studies

(1) Introduction

When the systematic study of nitropolymers was initiated, it was known qualitatively that nitro groups that were adjacent to functional groups in a molecule have a pronounced effect on their reactivity. Therefore, a study of the kinetics of polyester formation was made simultaneously with the nitropolyurethane kinetics study (see III,B,2,b).

(2) The Effect of Nitro Groups on Rate of Polyester Formation

The effect of nitro groups on the rate of polyurethane formation was studied by comparing the following reaction rates:

(a) Nitro diacid chloride and nitro diol
(b) Nitro diacid chloride and diol
(c) Diacid chloride and nitro diol

The rate of reaction of 4,4-dinitro-1,7-heptanedioyl chloride (1) with 2,2-dinitro-1,3-propanediol (A) and 1,3-propanediol (B) was determined (457, 29, 30, 53, 54, 57, 58, Table 22). The reaction rate of 1,7-heptanedioyl chloride with A diol was determined (457, 29, 61, 62, Table 22). Comparing the rate of polyester formation in systems 1-A and 1-B, the reactivity of the hydroxyl groups was lowered by a factor of 10^4, due to the adjacent gem-dinitro group. As other, more energetic diacid chlorides became available, their rates were studied. The rate of reaction of 4,4,6,8,8-pentanitro-1,11-undecanedioyl chloride (2) with A and B diols was studied (540, 4-6). The rate of reaction of N-nitro-N-trinitroethyl aspartyl chloride (3) was studied with A diol and ethylene glycol (N) (540, 4-6). The rate of reaction of N-nitro-N-trinitroethyl glutamyl chloride (4) was studied with N diol (540, 4-6). The rate of reaction of 1 with 3,3-dinitro-1,5-pentanediol (E), with N, and with 5,5,5-trinitro-1,2-pentanediol (H) was studied (540, 4-6; 563, 29, 30).

(3) Conclusions

From these studies, the following conclusions were made: (2) is slower reacting than (1), which is about the same as (3) and (4). The reactivity of the H diol is not greatly affected by the trinitromethyl group. The hydroxyls in E are more reactive than in A — in agreement with their reactivities in polyurethane formation (see III,B,2, b). Since acidic materials other than hydrogen chloride (i.e., nitric oxides resulting from thermal decomposition) were evolved at reaction temperatures as low as 50°C, still lower temperatures must be used for polymerizations with A. This results in prohibitive lengths of time for polyester formation with A. Polyesters using H are practical from a rate standpoint.

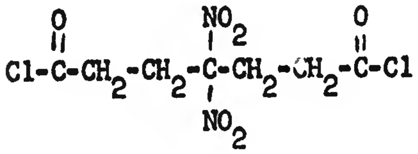
c. Polymerizations

(1) Introduction

Before high-energy diacidchlorides and diols were available, a technique for preparing polyesters was developed with model compounds such as malonyl chloride, oxalyl chloride, and 2-nitro-2-methyl-1,3-propanediol (371, 30, 73, 74). When applied to oxalyl chloride (5) and the unreactive 2,2-dinitro-1,3-propanediol (A), repeated efforts in a variety of solvents failed to product polyester 5-A (345, 28, 54; 371, 30, 73; 404, 34; 417, 17). Post-polymerization nitration was used to prepare a nitropolyester from the reaction product of 5 diacidchloride and N,N'-<u>bis</u>-(2-hydroxyethyl)-oxamide (371, 30, 74).

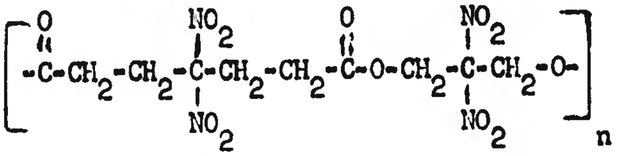
When nitro-diacidchlorides became available, the systematic study of high-energy polyesters was begun. The major objectives of the program were the preparation and identification of linear nitropolyesters having high molecular weight, high specific impulse, and high thermal and impact stability.

(2) Nitropolyesters from 4,4-Dinitro-1,7-heptanedioyl Chloride (1) (II,C,3,c)



$$Cl-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-Cl$$

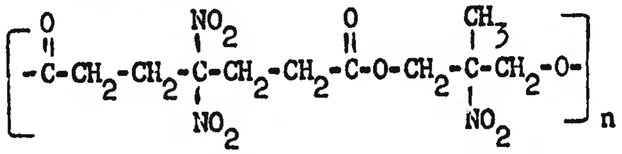
(a) Polyester 1-A from 2,2-Dinitro-1,3-propanediol (II,D,2,a)



$$\left[-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-O-\right]_n$$

The estimated specific impulse of this nitro polyester is 185 lbf sec/lbm (772, Appendix C). Polymeric material, having analytical values in agreement with theory, was obtained from a polymerization carried out in refluxing dioxan (404, 24, 44; 417, 16, 40). A bulk polymerization gave low molecular weight, highly crystalline polymer that contained residual halogen (457, 37, 69, 70). Attempts were made to increase the molecular weight (468, 45, 46, 50, 53). Copolymers of polyester 1-A with polyester 1-H and polyester 1-J, from 5,5,5-trinitro-1,2-pentanediol and 2-nitro-2-methyl-1,3-propanediol, respectively, were made in an effort to reduce the second-order transition temperature (622, 38, 39). The SPIA data sheet was prepared (482, Appendix).

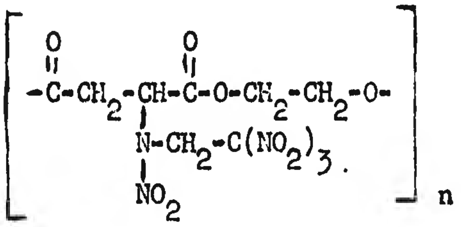
(b) Polyester 1-J from 2-Nitro-2-methyl-1,3-propanediol



$$\left[-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{NO_2}{\overset{CH_3}{C}}-CH_2-O-\right]_n$$

The estimated specific impulse is 130 lbf sec/lbm (772, Appendix C). This polymer was prepared for comparison of its physical properties with those of polyester 1-A (622, 36-38).

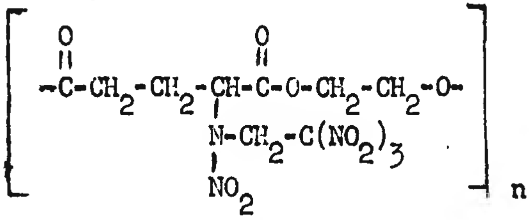
(3) Polyester 3-N from N-Nitro-N-trinitroethylaspartyl Chloride (II,C,2,h) and Ethylene Glycol



$$\left[-\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{\underset{NO_2}{|}}{N-CH_2-C(NO_2)_3}}{\underset{|}{CH}}-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-O-\right]_n$$

This polyester has an estimated specific impulse of 215 lbf sec/lbm (772, Appendix C). The reaction took place readily in dioxan solution but stopped at a low degree of polymerization apparently because the evolved hydrogen chloride reacted with some of the ethylene glycol (540, 8). The polymer contained 3.18% residual chlorine.

(4) Polyester 4-N from N-Nitro-N-trinitroethylglutamyl Chloride (II,C,3,h) and Ethylene Glycol



$$\left[-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{\underset{NO_2}{|}}{N-CH_2-C(NO_2)_3}}{\underset{|}{CH}}-\overset{\overset{O}{\|}}{C}-O-CH_2-CH_2-O-\right]_n$$

The estimated specific impulse is 204 lbf sec/lbm (722, Appendix C). The preparation was similar to that of polyester 3-N and the resulting polymer likewise contained residual chlorine, 1.42% (540, 9).

(5) Attempted Preparation of Polyester 6-J from 4,4,6,8,8-Pentanitro-1,11-undecanediol-bis-chloroformate (II,D,3,e) and 2-Nitro-2-methyl-1,3-propanediol

Reaction at 90°C was very slow and was accompanied by extensive decomposition (622, 36).

(6) Evaluation of Nitropolyesters

The reaction of nitro diacidchlorides with nitrodiols yields only low-molecular-weight polymers. Analysis of the products shows residual chlorine in the polymer. Apparently the anhydrous hydrogen chloride eliminated in the reaction occasionally replaces a hydroxyl group, either on the end of the chain or in a glycol monomer molecule. This halogenated material is monofunctional, causing chain-growth termination.

4. Nitropolyureas

a. Introduction

Polyureas result from the interaction of diisocyanates with diamines. No byproduct results from the reaction, which takes place readily with a large evolution of heat. An attempt to study the kinetics of nitro polyurea formation showed that the reaction was 92% completed within 8 sec at 18°C (475, 30, 31). Before nitro diisocyanates were available, attempts were made to react methylene or ethylene diisocyanate with ethylene dinitramine (345, 46, 47; 371, 34; 386, 24-26, 44). The extensive gas evolution during the reaction was investigated, and it was found that the nitramino group was destroyed in the reaction (404, 26, 27, 45).

Polyureas can also be prepared from a diisocyanate and water, with the accompanying evolution of carbon dioxide. This method was

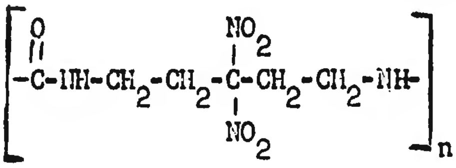
$$RNCO + H_2O \longrightarrow RNHCOOH \longrightarrow RNH_2 + CO_2\uparrow$$

$$RNH_2 + RNCO \longrightarrow RNHCONHR$$

used successfully to prepare nitropolyureas.

The post-polymerization nitration of polyureas would result in products having considerably higher specific impulse. A number of attempts were made to achieve complete nitration of the two nitrogens in each urea linkage. All were unsuccessful in that only one nitrogen per urea linkage could be post-nitrated. More drastic nitration conditions invariably resulted in degradation of the polymer chain.

b. Polyurea I-α from 3,3-Dinitro-1,5-pentane Diisocyanate and 3,3-Dinitro-1,5-pentane Diamine (II,B,3,b)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\right]_n$$

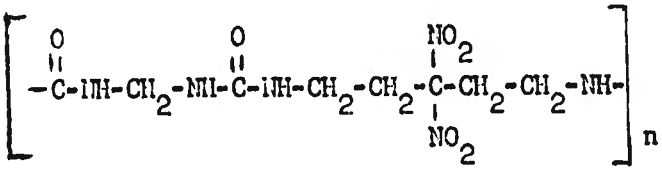
The polyurea from I diisocyanate and α diamine has an estimated specific impulse of 154 lbf sec/lbm (772, Appendix C). The initial preparations were made in a variety of solvents using the free amine (468, 46, 47, 49, 50, 53; 483, 47, 48; 499, 50). The polymers were all low in molecular weight, probably because of monofunctional impurities in the diamine. The SPIA data sheet was prepared (482, Appendix). Later, the method of adding water to the diisocyanate was used to prepare high-molecular-weight I-α (772, 27, 28). A copolymer of polyurea I-α and polyamide 1-α was prepared by the reaction of 4,4-dinitro-1,7-heptanedioic acid (II,C,3,c) with I diisocyanate (482, 48, 49; 499, 48, 49).

A series of attempts were made to effect complete nitration of the urea linkages in polyurea I-α (515, 61-63; 540, 11, 12; 772, 28). The experimentally determined heat of combustion indicated that only half-nitration had taken place. The estimated specific impulse of the half-nitrated product, I-α N/2, is 207 lbf sec/lbm (772, Appendix). The attempted post-nitration of the copolymer described above was unsuccessful (499, 53).

c. Polyureas from Methylene Diisocyanate (VI)

$O=C=N-CH_2-N=C=O$ (II,B,2,b)

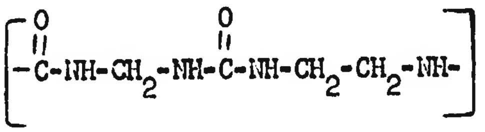
(1) Polyurea VI-α from 3,3-Dinitro-1,5-pentane Diamine (II,B,3,b)



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-NH-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\right]_n$$

The theoretical specific impulse is 122 lbf sec/lbm, which would rise to 208 lbf sec/lbm for the half-nitrated polymer (515, 51; 772, Appendix). Four preparations were made, varying monomer and end-group equivalence (515, 53, 54).

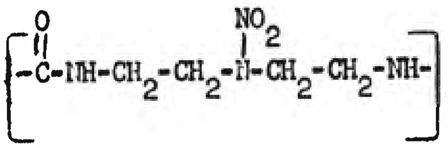
(2) Polyurea VI-β from Ethylene Diamine



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-NH-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-NH-\right]_n$$

The estimated specific impulse of the half-nitrated polyurea is 184 lbf sec/lbm (772, Appendix). Several preparations of VI-β were made with small variations in end-group equivalence ratios (515, 54, 55).

d. Polyurea XIII-γ from 3-Nitraza-1,5-pentane Diisocyanate (II,B,4,b) and Water

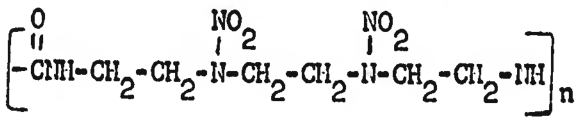


$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH-\right]_n$$

The polymer was prepared by adding a solution of water in dimethylformamide to a cooled solution of the diisocyanate in the same solvent (740, 30-32). The polyurea was insoluble in all solvents, and apparently cross-linked. The preparation was repeated, reversing the order of addition, i.e., the diisocyanate solution was added to the water (772, 26). High-molecular-weight, soluble polymer was obtained.

The preparation of polyurea XIII-γ N/2, estimated specific impulse 193 lbf sec/lbm, was studied. Nitration of the insoluble polyurea XIII-γ resulted in a product that had poor analytical values (740, 32). The nitration was repeated on the soluble XIII-γ. The product had analytical values in agreement with theory, but was low in molecular weight (772, 27).

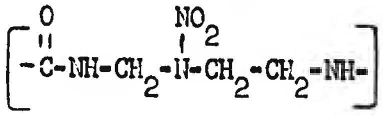
e. Polyurea XII-δ from 3,6-Dinitraza-1,8-octane Diisocyanate (II,B,4, Table 7) and Water



$$\left[-\overset{O}{\overset{\|}{C}}NH-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH\right]_n$$

The polymer was prepared, using the technique described for polyurea XIII-γ, above (772, 24).

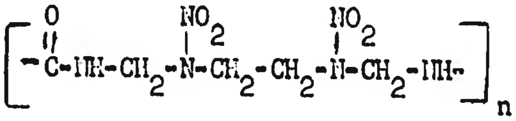
f. Polyurea XV-ε from 2-Nitraza-1,4-butane Diisocyanate (II,B,4, Table 7) and Water



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-NH-\right]$$

The estimated specific impulse is 152 lbf sec/lbm. The polymer was prepared by adding a solution of the diisocyanate in dimethyl formamide to water and cooling (833, 25).

g. Polyurea XVI-ζ from 2,5-Dinitraza-1,6-hexane Diisocyanate (II,B,4, Table 7) and Water



$$\left[-\overset{O}{\overset{\|}{C}}-NH-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-CH_2-\overset{NO_2}{\overset{|}{N}}-CH_2-NH-\right]_n$$

The estimated specific impulse is 189 lbf sec/lbm. The polymer was prepared using the technique of preparing the diamine in situ from the diisocyanate and water (907, 17, 18).

h. Evaluation of Nitropolyureas

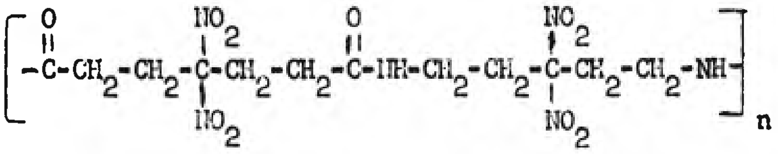
The preparation of nitropolyureas from nitro diisocyanates and water, with the accompanying evolution of carbon dioxide, offers a convenient route for the preparation of linear polymers, but could not be readily employed for the preparation of propellants by a casting technique, as is done with nitropolyurethanes. In general, the nitropolyureas have poor solubility characteristics and would require the synthesis of new, more efficient nitroplasticizers before they could be used as propellants. Only those nitropolyureas with moderate specific impulse have been obtained as high-molecular-weight polymers.

5. Nitropolyamides

a. Introduction

The difficulties experienced in the preparation of nitropolyamides were similar to those encountered in the preparation of nitropolyesters. Preparation via the reaction of diacids with diamines or the polymerization of cyclic lactams generally required temperatures that are too high for high-energy nitro compounds. The reaction of diacid chlorides with diamines takes place readily, but the evolved hydrogen chloride forms a salt with unreacted amino groups, thereby terminating the growing polymer chain. Another method involves the reaction of a diester with a diamine, by the elimination of alcohol, hence it could not be readily used for the preparation of propellants by a casting technique. Attempts to overcome these difficulties in the preparation of nitropolyamides have been unsuccessful.

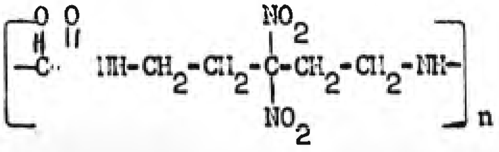
b. Polyamide 1-α from 4,4-Dinitro-1,7-heptanedioyl Chloride (II,C,3,c) and 3,3-Dinitro-1,5-pentane Diamine (II,B,3,b)



$$\left[-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\right]_n$$

The estimated specific impulse is 151 lbf sec/lbm. The use of sodium succinimide to consume the hydrogen chloride that was eliminated in the polymerization reaction gave only low-molecular-weight polymer (468, 47, 48). Using sodium succinimide and the amine in the form of its crystalline hydrochloride resulted in no polymer formation (482, 48). The physical properties were determined (482, 52, 56) and the SPIA data sheet was prepared (482, Appendix).

c. Polyamide 5-γ from Diethyl Oxalate and 3,3-Dinitro-1,5-pentane Diamine (II,B,3,b)



$$\left[-\overset{O\;O}{\overset{\|\;\|}{C}}-NH-CH_2-CH_2-\underset{NO_2}{\overset{NO_2}{C}}-CH_2-CH_2-NH-\right]_n$$

The polyamide, after nitration, would have an estimated specific impulse of 208 lbf sec/lbm (638, 42). The reaction proceeded readily, with noticeable evolution of heat. No suitable solvent was found for keeping the polymer in solution in order to achieve high molecular weight (638, 41, 42). A series of copolymers were made from mixtures of α diamine and hexamethylenediamine, in an effort to increase the solubility of the product (663, 31, 32).

The complete nitration of 5-α to polyamide 5-αN was achieved with acetic anhydride-nitric acid at 30°C (638, 41).

d. Attempted Nitropolyamide Preparations

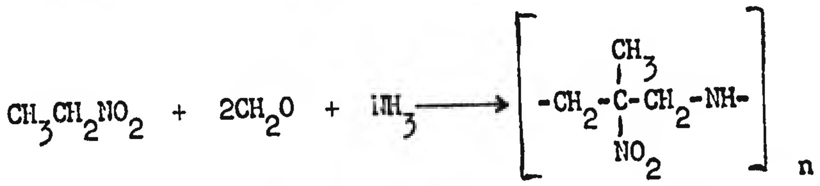
An attempt to polymerize 4,4-dinitro-6-hexanolactam failed (772, 29). The reaction of β,β'-dihydroxyethyl ether dichloroformate with ethylenediamine, followed by post-nitration of the amide linkages, produced a material that did not have the expected analytical values (371, 29, 72, 73). No reaction occurred when ethylene dinitramine was treated with oxalyl chloride (371, 32).

e. Evaluation of Nitropolyamides

The nitropolyamides prepared to date have had very low molecular weights, and their solubility characteristics were poor.

6. Nitropolyamines

Nitropolyamines may be derived from the Mannich reaction. The reaction involves the use of 1 mol of a bifunctional nitro compound, 1 mol of a bifunctional amine, and 2 mols of formaldehyde.



$$CH_3CH_2NO_2 + 2CH_2O + NH_3 \longrightarrow \left[-CH_2-\underset{NO_2}{\overset{CH_3}{C}}-CH_2-NH- \right]_n$$

Post-nitration would yield a polymer with estimated specific impulse of 208 lbf sec/lbm.

Early in the nitropolymer program, it was shown that the preparation of nitropolyamines was feasible (330, 22-24, 100, 101; 345, 23, 45; 371, 32, 33, 77, 386, 22-24, 43; 404, 25, 26, 45). Later a reinvestigation of the Mannich reaction was made, with emphasis being made on the preparation of polyamines from 2-nitro-2-methyl-1,3-propanediol and 2,2-dinitro-1,3-propanediol (622, 42-51).

All attempts to obtain high-molecular-weight polymers failed.

7. Nitropolyethers

Early attempts to prepare nitropolyethers from 2,4,6,-trinitro resorcinol (styphnic acid) (345, 25, 49; 371, 31; 386, 22), 2-nitro-2-methyl-1,3-propanediol (371, 31, 75), and 2,2-dinitro-1,3-propanediol (345, 29, 47) with formaldehyde all failed.

The synthesis of glycidyl-4,4,4-trinitrobutyrate made it possible to study the preparation of nitropolyethers from nitroepoxides (II,D,5,b). The estimated specific impulse of the polymer is 200 lbf sec/lbm (563, 80). A great variety of experimental conditions were used in an effort to obtain high-molecular-weight polymer (563, 35-40; 590, 41, 42; 622, 40-42). All failed in this respect - the best product had a moleculer weight of 1475 ± 20 (622, 42). This product, presumably a long-chain polyether diol, was treated with 3,3-dinitro-1,5-pentane diisocyanate in an attempt to obtain polymer of higher molecular weight. The reaction product softened below room temperature (hitherto unpublished data).

Recently, the advantages of nitropolyurethanes prepared from long-chain nitro-polyether-diols became apparent, and interest in these potential polyurethane monomers was renewed. The preparation of polyglycidyl nitrate and the reaction of this diol with nitrodiisocyanates are currently under investigation (1083, 3-11; 1119, 2-4).

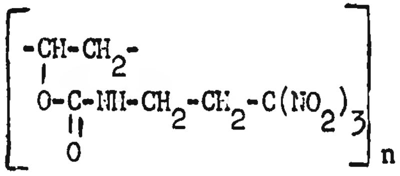
8. Miscellaneous Polymerization Reactions

a. Nitropolymers from Polymers and Nitro Compounds

(1) Introduction

Another approach to the preparation of nitro polymers was investigated. Polymeric materials such as polyvinyl alcohol and cellulose, containing active hydroxyl groups, were treated with nitro isocyanates, nitro acid chlorides, or nitro aldehydes. Unsuccessful attempts were made to nitrate polyglycine (345, 23, 24, 45, 46; 371, 31, 32, 75, 76), polysuccinyl hydrazide (404, 24, 25), poly-N-vinyl-N'-phenyl-urea (330, 32, 106, 107), and poly-N-vinyl-N'-methyl-urea (330, 32, 107, 108). The preparation of polyvinylamine salts, by the reaction of nitro compounds with polyvinylamine, or by the reaction of metallic salts of nitro compounds with polyvinylamine hydrochloride, was studied (330, 26-29, 32, 102-106). It was found that salts of polyvinylamine, and aliphatic nitro compounds, are too unstable to permit their use in propellants.

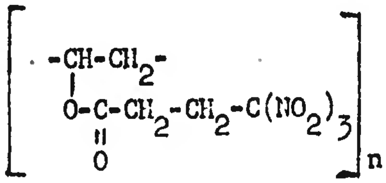
(2) Polyvinyl Alcohol and 3,3,3-Trinitropropyl Isocyanate (II,B, Table 8)



$$\left[\begin{array}{l}-\mathrm{CH}-\mathrm{CH_2}-\\ \ \ |\\ \mathrm{O}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{NH}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{C(NO_2)_3}\end{array}\right]_n$$

Polyvinyl N-(3,3,3-trinitropropyl)-carbamate has an estimated specific impulse of 207 lbf sec/lbm. Low-viscosity-grade polyvinylalcohol was treated with 3,3,3-trinitropropyl isocyanate, with and without the use of solvents, and borontrifluoride catalyst. Unreacted starting materials were recovered (563, 28). Other attempts were made, using polyvinyl alcohol which was specially treated by swelling in water and acetone. Although the product was insoluble in water, elemental analysis showed that only a small portion of the hydroxyls had reacted to form carbamate linkages.

(3) Polyvinyl Alcohol and 4,4,4-Trinitrobutyric Acid (II,C,5,e)



$$\left[\begin{array}{l}-CH-CH_2-\\ \;| \\ O-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-C(NO_2)_3\end{array}\right]_n$$

This nitropolymer has an estimated specific impulse of 214 lbf sec/lbm. Direct esterification of polyvinyl alcohol with 4,4,4-trinitrobutyric acid was tried, using sulfuric acid as catalyst. However, the only product isolated was the original polyvinyl alcohol (563, 34). The chloroacetic anhydride impelling technique[*] was used in a series of reactions under a variety of conditions (563, 35). A small amount of the desired esterification took place (maximum of 3 mol percent). However, mostly polyvinyl chloroacetate was formed. Other attempts were made using 4,4,4-trinitrobutyric anhydride instead of chloroacetic anhydride, zinc chloride being used as catalyst in one experiment and boron trifluoride in another. Polyvinyl alcohol was recovered in both experiments (563, 35; 590, 40).

The action of 4,4,4-trinitrobutyryl chloride on polyvinyl alcohol was studied and found to give a black amorphous solid (590, 39). The evolved hydrogen chloride apparently catalyzed the dehydration of the polyvinyl alcohol to the corresponding conjugated olefinic polymer. The reaction was repeated, using acetic acid-pyridine as a buffer. A substance which contained 3.6% nitrogen was isolated (590, 40).

The reaction between polyvinyl alcohol and 4,4,4-trinitrobutyric anhydride was tried in mixed alkane sulfonic acid solution. The desired reaction did not take place (590, 40).

(4) Polyvinyl Alcohol and 2,3,3-Trinitropropional[**]

Numerous experiments with a variety of solvents failed to yield a completely reacted product (330, 32, 22). One experiment,

---

[*] A. T. Clarke and C. J. Malm, U.S. Patent No. 1,880,808.

[**] Hill and Sanger, *Ber.* *15*, 1906 (1882).

employing the dipotassium salt of the trinitropropionaldehyde in acetic acid to which hydrochloric acid was added, yielded a black plastic mass which gave a qualitative test for nitrogen (330, 108, 109).

(5) Polyvinyl Alcohol and 3-Nitrazabutyl Isocyanate (II,B,5, Table 8)

Polyvinyl alcohol was treated with an excess of the isocyanate in dimethylformamide solution, using ferric acetylacetonate catalyst. A 25% yield of water-insoluble polymer was obtained. The analytical value for nitrogen was 23.18%, as compared to 22.21% N, calculated (1004, 4).

(6) Cellulose and 3-Nitrazabutyl Isocyanate

The reaction of 3-nitrazabutyl isocyanate and cellulose was studied as a model for the desired reaction of cellulose and 3,3,3-trinitropropyl isocyanate (1004, 3). Purified wood pulp was treated with an excess of the isocyanate in several solvents and without solvent, using ferric acetylacetonate catalyst. Using dimethylformamide as solvent, reaction was complete after 89 hr at 50°C.

(7) Cellulose and 3,3,3-Trinitropropyl Isocyanate

The estimated specific impulse of the desired polymer is 212 lbf sec/lbm. Using the optimum conditions that were determined for 3-nitrazabutyl isocyanate (see (6) above), 3,3,3-trinitropropyl isocyanate failed to react (1048, 2-4). Both starting materials were recovered. An earlier attempt, using boron trifluoride catalyst, failed (563, 28). In order to determine whether the insolubility of the cellulose was responsible for the lack of reaction, partially esterified cellulose 4,4,4-trinitrobutyrate (see (8) below), which was soluble in dioxan, was used as starting material. Analysis showed that the nitrogen content was raised from 4.17 to 6.89% (563, 29).

(8) Cellulose and 4,4,4-Trinitrobutyric Acid

The desired polymer has an estimated specific impulse of 219 lbf sec/lbm. Using the impelling technique (see (3), above) a maximum of 10 mol% of available hydroxyls were esterified (563, 30, 32, 33).

Treating the partially esterified cellulose with trinitrobutyric anhydride and catalytic amounts of sulfuric acid raised the nitrogen content to 8.14%, equivalent to the esterification of 18 mol% of the available hydroxyls (563, 33, 34; 590, 40, 41).

b. Attempted Nitropolymer Formation with Chloropicryl Chloride, 1,3,5-Trinitro-2,6-dichlorobenzene

Because of the similarity of the structure of chloropicryl chloride to that of picryl chloride, it was assumed that the two chlorine atoms would react in a manner similar to the chlorine atom in picryl chloride. Although reaction occurred with a variety of amines, amides, ureas and glycols, side reactions prevented the formation of high-molecular-weight nitropolymers (330, 9-17; 90-94).

c. Attempted Nitropolymer Formation with m-Phenylene Diamine and Post-nitration

Polymeric materials were prepared from m-phenylene diamine with ethylene bromide and with ethylene oxide. Post-nitration gave nitropolymers with low thermal and impact stability (330, 17-22, 95-99).

d. Attempted Nitropolymer Formation, Using the Michael Reaction

The use of the Michael reaction was investigated as a source of nitropolymers. The reaction of methyl acrylate with dinitromethane, prepared *in situ* from 2,2-dinitro-1,3-propanediol (II,D,2,a), was used as a model for determining optimum experimental conditions (482, 31, 32). Attempted polymerizations carried out with 2,2-dinitrotrimethylene diacrylate (II,A,3,k) and 2,2-dinitro-1,3-propanediol gave low yields of low-molecular-weight polymers (482, 50, 51).

IV. FORMULATION STUDIES

A. INTRODUCTION

The original goal of the nitropolymer program was the development of a solid, smokeless propellant based on the incorporation of oxidizing groups in an organic polymeric system. This material was to attain a specific impulse of about 210 lbf sec/lbm and should require no inorganic oxidizer. This goal was changed during the years, principally because of two related developments: (a) as time went on, the specific impulse of existing composite propellants was continually raised, requiring an upgrading of the specific-impulse goal of the nitropolymer program to 250 lbf sec/lbm, and (b) the failure to attain high-specific-impulse nitropolymers when (1) post-nitrated polyurethane polymers were discarded due to thermal instability and (2) trinitroethyl esters of unsaturated acids were shown to yield only low-molecular-weight polymers. Because of the above, and since the formulation work was initiated only at an intermediate stage of the program, the work to attain a propellant material composed of all organic substances occupied only a relatively small period in the formulation development. Most of the work was concerned with the incorporation of solid oxidizers.

A second major consideration controlling the scope of the formulation program was that the goal of this ONR-supported program was the development of basic techniques and basic formulations only. Detailed propellant studies, optimization of propellant formulations, and ballistic studies were undertaken in separate research contracts under the Bureau of Aeronautics, the Bureau of Ordnance, and the Air Force. Some of the work performed under these associated contracts was reported with the ONR work; but in each case, a final summary report was published under the separate contracts (see paragraph VI,L). In the discussion below, some of the areas covered by these associated contracts will be outlined, and references to their separate reports will be given. It should be noted, however, that the first energy-containing-binder, composite propellant grain was prepared and fired under the ONR program. This was a Midget-Motor grain, about 4 lb of propellant being used, based on the XII-J nitropolymer (941, 21).

The development of propellant formulation methods falls into two major classes - castable and pressure-formed formulations. Both classes were performed with vinyl-type monomers and polyurethane monomers.

It is important to note that the development of a polyurethane binder for propellants was a unique accomplishment. Besides being a field of polymerization which had not yet reached industrial fruition, its application to solid propellants presented certain peculiar problems which were met and solved on this nitropolymer program. As a direct result, the non-nitro-containing polyurethane propellant system was investigated, and brought to large-scale use at Aerojet, in an amazingly short time.

Early formulation studies drew on the polymerization studies and synthetic studies, but soon the formulation work began to derive certain parameters and requirements, and towards the latter part of the program, the formulation work led the other sections.

B. CASTABLE SYSTEMS

1. Introduction

The castable systems studied fall into two classes: (a) studies with pure organic materials and (b) studies with inorganic oxidizers. The investigation of plasticizers was initiated in the first case, and a wide variety of plasticizers were tested. In general, materials developed by the synthetic section were tested in polymerization. Not all monomers and plasticizers synthesized were tested in the formulation studies, and not all those tested proved satisfactory for further development.

The castable system was developed with a polyurethane-type binder. The research on the use of a vinyl-polymerization-type nitromonomer was performed under Air Force Contract AF 33(616)-2519. This development was carried through to full-scale-motor firings, using dinitropropyl acrylate as the binder monomer. This work is summarized in Aerojet Report No. 1199-5. All castable propellant development under the ONR contract has been restricted to the polyurethane system.

After development of proper formulations and techniques, the formulation work was taken over by associated contracts. However, many formulation samples were prepared on the ONR program for rheological, mechanical, and ballistic evaluation by these other contracts. Table 49 in paragraph VI,L (Rheology) lists the associated contracts and their final reports. Many conclusions as to the applicability of various monomers and plasticizers, in this report, are based on data from these final reports.

2. Studies with Binder Only

a. Introduction

The principal problems to be solved in the development of a nitropolyurethane binder for a castable system were (1) to obtain a dimensionally stable binder, (2) to obtain a bubble-free binder, and (3) to obtain a thermally stable binder. These problems were met and essentially solved with studies on the pure-binder systems. The addition of oxidizer caused few complications that had not already been met and solved. Cross-linking studies soon established the validity of using a trifunctional monomer to obtain a three-dimensional network. The polyurethane system has a specific problem in the handling and use of diisocyanates. These materials readily react with any material that has an active hydrogen, and when water or a carboxylic acid function is present, carbon dioxide is evolved. The techniques of handling these materials and the methods of ensuring the absence of moisture and acidic impurities were developed. In particular, the methods of vacuum-degassing were of the utmost importance. The thermal stability of the various systems examined proved to be largely a function of the plasticizers used; the stabilities of the polyurethane itself had been tested and screened during the polymerization studies (see paragraph III,B).

b. Discussion

The formulation work leading to a castable system with polyurethanes was initiated when attempts were made to prepare nitropolyurethanes with small percentages of cross-linking agent present - 1 to 2% tris-(hydroxymethyl)-nitromethane (nib glycerol) (740, 54). It had earlier been demonstrated that pure linear nitropolyurethanes did not possess the physical and mechanical properties required of a rocket propellant. As expected, it was found that small amounts of cross-linking agent increased the molecular weight of the nitropolymers studied. What would correspond to the first castings with cross-linking agent and nitroplasticizer was performed in an attempt to demonstrate that polyurethane polymerization would take place in the presence of nitro-containing solvents (740, 56). All products remained soluble in acetone, and no good cure was obtained. Bubble formation was pronounced upon attempts to obtain a cure.

Bubble formation during cure, or attempted cure, of the binder mix was observed early in the work. A vacuum-degassing method was observed to be partially effective (772, 32) when used during the cure. This technique was found to be essential in all later casting work. A detailed discussion of all casting problems and their partial solution was given (807, 29). Later studies indicated the necessity for a study of plasticizer purity. In particular, purification of methyl 4,4-dinitropentanoate gave successful gels where none had been obtained before (833, 27). Acidic impurities appeared to be the worst offenders.

All casting studies with binder only were performed with metal chelate catalysts, principally ferric acetylacetonate. Attempts to use tertiary amines were unsuccessful (868, 41).

In general, each polymer system was tested as a pure binder gel before studies with oxidizer were undertaken. In some cases, these studies never progressed to the incorporation of oxidizer, because the pure binder or plasticizer mix could not be prepared in a bubble-free gel. Gels with various propellant ingredients were attempted without oxidizer. A series of carbon blacks, ammonium dichromate, and ethyl orthosilicate were tested at 1% level (907, 24). Most were successful.

Table 29 lists all the binder-only castings reported. Most of these castings were made to determine compatibilities, proper catalyst concentration, or ingredient purity before castings with oxidizer were made.

With the exception of the XII and XVI diisocyanate systems, all the others progresses to oxidizer-loaded castings. The castings in Table 29 were made at various concentrations of catalyst and cross-linking agent, with variations in the cure time. Only the concentration of the cross-linking agent and the particular catalyst are listed. In all cases, the crosslinker was tris-(hydroxymethyl)-nitromethane.

3. Composite Castings

a. Introduction

As soon as it was demonstrated that nitropolyurethanes could be used as a castable binder, attempts were made to incorporate inorganic oxidizer. For reasons of safety, early experiments were with sodium chloride. It was immediately found that the ferric acetylacetonate (FeAA) catalyst was inactivated in the presence of the salt (868, 37). This phenomenon was examined in some detail. It was found that destruction of the catalyst required the presence of the isocyanate function and the salt. This salt effect was found to be general for the usual inorganic oxidizers. It was also observed that above a certain critical concentration (1×10^{-3} molar), the iron catalyst was stable. However, the control of the catalyst proved to be quite difficult, because at this concentration, with the catalyst being so effective, dangerous exotherms and premature polymerizations occurred. Investigations of other catalysts showed that organic tertiary amines were ineffective (868, 4), and that vanadyl acetylacetonate (VOAA) did not exhibit the salt effect, and was a less efficient catalyst and, therefore, was usable in a composite system (868, 42). A later study (1048, 4) screened other metal chelate catalysts, and it was found that FeAA could be used under carefully controlled conditions, with the catalyst being added as a solution in a plasticizer (NPH).

Almost all the formulation work was performed with ammonium perchlorate (AP). A standard bimodal, particle-size mixture was used, i.e., 70% slow speed grind and 30% high speed (Mikro-Atomizer) grind.

TABLE 29

CROSS-LINKED, PLASTICIZED NITROPOLYURETHANE CASTINGS*
(Without Oxidizer)

Polymer System	Plasticizer (Code Name)	% Crosslink	Catalyst	Results	Reference
I-J	MNP	?	VOAA	Good gel	907, 28
↑	NPN	?	↑	Good gel	907, 29
	METNB	?		Good gel	
	TNMCH	?		Rapid decomp.	
	TNEP	?		Incompatible	
	TNKPA	?	↓	Decomposition	
↓ I-J	DNBTNB	?	VOAA	Incompatible	↓
I-A	MDNP	0	FeAA	Low mol wt	740, 56
↑		2	FeAA	No gel	740, 56
	↓	8	VOAA	Good gel	967, 14
	MTNB	0	FeAA	Low mol wt	740, 56
	TNP	0	FeAA	Low mol wt	740, 56
		6	FeAA	Good gel	807, 33
		8	VOAA	Good gel	967, 14
	↓	2	FeAA	Poor gel	740, 56; 772, 32
	DNH	2	FeAA	No gel	772, 32
	DNH	8	VOAA	No gel	967, 14
	NM	4	FeAA	Good gel	807, 33
	DNPNP	8	VOAA	Good gel	967, 14
	TNENP		↑	↑	↑
	EBNP				
	EBDNP				
	DNPN	↓	↓	↓	↓
↓ I-A	DNPDNP	8	VOAA	Good gel	967, 14

---

*See Tables 17-20 (III,B) for polymer nomenclature and Table 30, this section, for plasticizer, catalyst and additive nomenclature.

TABLE 29 (cont.)

Polymer System	Plasticizer (Code Name)	% Crosslink	Catalyst	Results	Reference
I-A	TNKPA	8	VOAA	Decomposition	967, 14
↑	DNBTNB		↑	No gel	
	TNMCH			Poor gel, bubbles	
	TNAHA			Good gel	↓
I-A ↓	MTNAH	↓	↓	Good gel	1004, 9
I-A	TNEDNP	8	VOAA	Gel, incompatible	1004, 9
I-H	various	?	?	Poor gels	907, 28
↑	MNP	0-12	VOAA	Poor gels	967, 15
↓	TNEDNP	8	↑	Gel, incompatible	1004, 9
XIII-J	MDNP	↑		Gel, incompatible	907, 20
↑	MDNP + ENP			Gel, incompatible	907, 22
	ENP			Good gel	907, 23
	MNP			Good gel	
	DNB			Incompatible	↓
	MNP + carbon			Good gel	907, 24
↓	ENP + AD		↓	Good gel	
XIII-J	ENP + EOS		VOAA	Poor gel	↓
XIII-A	DNH	↓	FeAA	Good gel	807, 33
	TNP	8	↑	Gel, incompatible	
	MDNP	4		Good gel	↓
	MDNP	2-10		Good gel	833, 28
↓	TNB	2	↓	No gel	
XIII-A	MNP	2	FeAA	Poor gel, bubbles	↓ 833, 28

TABLE 29 (cont.)

Polymer System	Plasticizer (Code Name)	% Crosslink	Catalyst	Results	Reference
XIII-H	MNP	8	VOAA	No gel	907, 27
↑	MNP	↑	↑	Poor gel	941, 21
	MDNP			Incompatible	907, 27
	MNor			No gel	↑
	TNB		↓	Poor stability	
	DNB		VOAA	Poor gel	
↓	DNB		FeAA	Good gel	
XIII-H	DNH		VOAA	No gel	↓
XIII-O	DNPNP		↑	Good gel	1048, 8
XII-A	MNP			Bubble-filled gel	967, 17
XII-A	NPN			Bubble-filled gel	↑
XII-J	MNP			Good gel	
XII-J	NPN			Good gel	
XIII-H	NPN	↓	↓	Good gel	↓
XVI-H	TNENP	8	VOAA	No gel	1004, 9
XVI-A	DNPNP	?	?	No gel, bubbles	1048, 7

TABLE 30

PLASTICIZER AND ADDITIVE CODE NAMES

Code Name	Chamical Name
AD	Ammonium dichromate
AP	Ammonium perchlorate
C	Carbon
DNB	1,4-Dinitroxybutane
DNBTNB	2,2-Dinitrobutyl 4,4,4-trinitrobutyrate
DNH	5,5-Dinitro-2-hexanone
DNPDNP	2,2-Dinitropropyl 4,4-dinitropentanoate
DNPN	4,4-Dinitropentanonitrile
DNPNP	2,2-Dinitropropyl 4-nitrazapentanoate
EBDNP	Ethylene bis-(4,4-dinitropentanoate)
EBNP	Ethylene bis-(4-nitrazapentanoate)
ENP	Ethyl 4-nitrazapentanoate
EOS	Ethyl orthosilicate
FeAA	Ferric acetylacetonate
MDNP	Methyl 4,4-dinitropentanoate
METNB	2-Methoxyethyl 4,4,4-trinitrobutyrate
MNP	Methyl 4-nitrazapentanoate
MTNAH	Methyl 3,5,5-trinitro-3-azahexanoate
MTNB	Methyl 4,4,4-trinitrobutyrate
NMor	4-Nitromorpholine
NM	Nitromethane
NPN	4-Nitrazapentanonitrile
TNAHA	3,5,5-Trinitro-3-aza-1-hexylacetate
TNB	1,3,3-Trinitrobutane
TNEDNP	2,2,2-Trinitroethyl 4,4-dinitropentanoate
TNENP	2,2,2-Trinitroethyl 4-nitrazapentanoate
TNEP	2,2,2-Trinitroethyl propionate
TNKPA	5,5,5-Trinitro-2-keto-1-pentyl acetate
TNMCH	3-(Trinitromethyl)-cyclohexanone
TNP	5,5,5-Trinitro-2-pentanone
VOAA	Vanadyl acetylacetonate

Only a few castings were made with ammonium nitrate (AN). These castings were with the XIII-J binder system (868, 43; 907, 21). Since the goal of the program was to achieve very high specific impulse, this work was not expanded.

In all cases, the monomer-plasticizer mix was vacuum-degassed at about 50°C until bubbling ceased, and the mix, with added oxidizer and catalyst, was degassed further. Some details of the procedure, including a description of the laboratory-scale equipment used, have been reported (907, 29).

The various polyurethane polymer systems are discussed separately below. In many cases, a particular casting result would be a function of the particular plasticizer used. These plasticizers are discussed separately (IV,E). In some cases, ballistic data, mechanical properties, and densities are reported. No particular reference is given for this type of data, since it is more completely covered in the associated contract reports (see VI,L, Table 49).

b. I-J Castings

The I-J polymer is a relatively low-energy-content binder and was purposely used in the early formulation work for this reason. No particular difficulties arose in the development of a procedure for using I-J, other than the incompatibility of several plasticizers (907, 29). Several ballistic additives were successfully incorporated in these early castings. In general, I-J is an excellent binder system, its only drawbacks being its relatively low specific impulse and the relative difficulty of manufacture of the I diisocyanate (V,B,4). I-J castings appeared to be stronger and more resilient than the XIII-J castings. Table 31 lists the I-J castings reported.

TABLE 31

I-J CASTINGS

Formulation	Catalyst	Cure	Results	Reference
I-J-4X-.6MNP-60AP*	? VO	?	Good gel	907, 28
I-J-8X-.6MNP-60AP	↓	↓	↓	↓
I J-8X-.6MNP-69AP	↓	↓	↓	↓
I-J-8X-.6MNP-69AP + 1C (F-2 black)	↓	↓	↓	↓

c. XIII-J Castings

The specific impulse of the XIII-J system is also relatively low, and much of the early development work was performed with it. As with I-J, no particular difficulties were encountered. Various ballistic modifiers and mixed plasticizers were successfully tested with XIII-J binder (907, 24). An attempt to use technical, unpurified J diol in the casting process was unsuccessful (907, 25). The first nitropolymer propellant grain was a XIII-J casting (941, 21). Table 32 lists the XIII-J castings reported.

TABLE 32

XIII-J CASTINGS

Formulation	Catalyst	Cure hr	Cure °C	Results	Reference
XIII-J-4X-.15MNP-60AP	$7x10^{-5}$ VOAA	16	45	Strong, bubble free	868, 43
XIII-J-4X-.15MNP-60AN	$7x10^{-5}$ VOAA	↓	↓	Strong, bubble free	868, 43
XIII-J-?X-.2 to .3MDNP-45-60AP	? VOAA	↓	↓	Brittle, no gel	907, 20
XIII-J-?X-.2 to .5MNP-20-75AP	↓	↓	↓	Good castings	907, 21
XIII-J-?X-.6MNP-60AN	VOAA	16	45	Hard grainy gel	907, 21

---

*This nomenclature for nitropolymer propellant formulations is used throughout the reports and signifies that the binder is composed of polyurethane I-J, cross-linked with 4 equiv % tris-(hydroxymethyl)-nitromethane, plasticized with methyl 4-nitrazapentanoate (MNP) at a ratio of 0.6 g of plasticizer per gram of I-J-4X binder, and loaded with ammonium perchlorate at a level of 60% based on the total propellant formulation.

TABLE 32 (cont.)

Formulation	Catalyst	Cure hr	Cure °C	Results	Reference
XIII-J-?X-.6$\left(\begin{smallmatrix}\text{MNP}\\ \text{IDNP}\end{smallmatrix}\right)$-60AP	? VOAA	16	45	Good casting	907, 22
XIII-J-?X-.6$\left(\begin{smallmatrix}\text{MNP}\\ \text{TNB}\end{smallmatrix}\right)$-60AP	↓	↓	↓	No gel	↓
XIII-J-?X-.6$\left(\begin{smallmatrix}\text{1MNP}\\ \text{1NMor}\end{smallmatrix}\right)$-60AP	↓	↓	↓	Good casting	↓
XIII-J-?X-1.0$\left(\begin{smallmatrix}\text{1MNP}\\ \text{1DNP}\end{smallmatrix}\right)$-75AP	↓	↓	↓	↓	↓
XIII-J-?X-.6$\left(\begin{smallmatrix}\text{NMor}\\ \text{1DNP}\end{smallmatrix}\right)$-60AP	↓	↓	↓	↓	↓
XIII-J-?X-1.25NMor-60AP	↓	↓	↓	Hard, brittle	907, 23
XIII-J-?X-1.25DNH-60AP	↓	↓	↓	No gel	↓
XIII-J-?X-.6TNB-60AP	↓	↓	↓	Uncastable, prepolymerization	↓
XIII-J-?X-.44TNB-60AP	↓	↓	↓	↓	↓
XIII-J-?X-.6ENP-60AP	↓	↓	↓	Uncastable	↓
XIII-J-?X-1.0MNP-70AP + 0.3C	↓	↓	↓	No cure	907, 24
XIII-J-?X-.6MNP-60AP + 0.5C	↓	↓	↓	Good casting	↓
XIII-J-?X-.6MNP-60AP + 5% Additives	VOAA	16	45	Bubble filled grain	↓

d. I-A Castings

The A diol is one of the two, generally useful, high-energy diols available for formulation work (H diol is the other). From the beginning (941, 19) successful castings were made with the I-A system with no apparent difficulty. For rheological studies, a number of castings were made with the I-A system, wherein variations were made in oxidizer and plasticizer level and in plasticizer kind (967, 13; 1004, 9). The I-A system was chosen for much of the early rheological studies, but processing difficulties made the I diisocyanate less available than the XIII diisocyanate (see paragraph V,B,4). Consequently, most of the nitro-polyurethane development work on the associated BuOrd programs was performed with the XIII diisocyanate, in spite of the apparent merits of the I-A system. Table 33 lists the I-A castings reported.

TABLE 33

I-A CASTINGS

Formulation	Catalyst	Cure hr	Cure °C	Results	Reference
I-A-8X-.63MDNP-60AP	? VOAA	16	45	Good	941, 19
I-A-8X-.68METNB-60AP				Good	
I-A-8X-.7TNB-60AP				Bubble-filled	
I-A-8X-.6NPN-61.6AP				Bubbles	
I-A-8X-.6MNP-60AP				Good	
I-A-8X-.6NPN-60AP				Bubbles	
I-A-8X-.65DNB-60AP				Good	
I-A-8X-.64MDNP-55AP				Good	
I-A-8X-.64MDNP-50AP					
I-A-8X-.64MDNP-65AP					
I-A-8X-.64MDNP-67.2AP					
I-A-8X-.65MDNP-70AP					↓
I-A-8X-.716MDNP-57.5AP					967, 13
I-A-8X-.556MDNP-62.4AP					
I-A-8X-.471MDNP-64.7AP					
I-A-8X-.39MDNP-66.9AP					↓
I-A-8X-.63MDNP-30AP					967, 14
I-A-8X-.63MDNP-35AP					
I-A-8X-.63MDNP-40AP					
I-A-8X-.63MDNP-45AP					
I-A-8X-.63MDNP-63.6AP					
I-A-8X-.63MDNP-65AP	↓	↓	↓	↓	↓
I-A-8X-.63MDNP-66.4AP	? VOAA	16	45	Good	967, 14

TABLE 33 (cont.)

Formulation	Catalyst	hr	°C	Results	Reference
I-A-8X-0.63MDNP-67.2AP	? VOAA	16	45	good	967, 14
I-A-8X-0.63MDNP-68.2AP	? VOAA	16	45	good	967, 14
I-A-8X-0.63MDNP-70AP	? VOAA	16	45	good	967, 14

e. XIII-A Castings

The XIII-A system is the one which has been most widely used in development work. Both ingredients are available on a relatively large scale (section V). The system is adaptable to various processing methods, and it yields a binder of high thermal stability. After early studies indicated the need for an extended degassing time for XIII-A(907, 29), most subsequent studies were successful. The XIII-A system was extensively used in the compression-formed-propellant system (IV,C), in the glass fiber applications, and in the evaluation of monomer purity (IV,D). Table 34 lists the XIII-A castings reported.

TABLE 34

XIII-A CASTINGS

Formulation	Catalyst	Cure hr	Cure °F	Results	Reference
XIII-A-8X-?MNP-60AP-1C	1×10^{-4} VOAA	16	110	Good casting	941, 18
XIII-A-8X-0.6DNPNP-60AP	1×10^{-4} VOAA	24	110	Bubbled castings	1004, 10
XIII-A-8X-0.9NPN-66AP	2×10^{-4} FeAA	16	110	Good casting	1048, 9
XIII-A-8X-0.8NPN-67AP	↓	↓	↓	↓	↓
XIII-A-8X-0.7NPN-68AP	↓	↓	↓	↓	↓
XIII-A-8X-0.6NPN-69AP	↓	↓	↓	↓	↓
XIII-A-8X-0.6DNPNP-63AP	1×10^{-4} FeAA	↓	↓	↓	↓
XIII-A-8X-0.6NPN-69AP	2×10^{-4} FeAA	48	↓	↓	1083, 17, 22
XIII-A-12X-0.6NPN-69AP	2.5×10^{-4} FeAA	24	110	Good casting	1083, 22

f. I-H Castings

The H diol, 5,5,5-trinitro-1,2-pentanediol is the other generally useful, high-energy diol. Considerable difficulty was experienced in obtaining cures with this diol. No practical analytical procedure was available for its assay, and the reactivity of the primary hydroxyl group in the molecule was considerably greater than for those in the α-nitro alcohols. When successful gel castings were made with the I diisocyanate, an oxidizer-loaded casting was successfully reported (967, 16); I-H-8X-0.4MNP-60AP. With this diol, most formulation work was performed with the XIII diisocyanate under the BuOrd contract.

g. XIII-H Castings

As with the I-H system, some difficulty was encountered in obtaining good cures with the H diol. Only unsuccessful castings were reported in first attempts (907, 27; 941, 21). No successful XIII-H castings were reported on this program. The formulation work under the associated BuOrd contract has satisfactorily made the XIII-H propellant (see paragraph VI,L). The H-diol gives more resilient castings than the A or J diols, probably due to internal plasticization from the side chain. This also was observed in the work with the related O diol (see below).

h. XIII-O Castings

The O diol, 5,5-dinitro-1,2-hexanediol is closely related to the H diol. Similar difficulties were found in attempting to use it in a propellant casting. After the binder-only casting (1048, 8) was successful, attempts with oxidizer were largely unsuccessful (1083, 12), except at below-stoichiometric AP content (119, 5). This casting was very resilient. Table 35 lists the XIII-O castings reported. No attempts were made to prepare I-Q castings.

TABLE 35

XIII-0 CASTINGS

Formulation	Catalyst	Cure		Results	Reference
		Time	°F		
XIII-0-8X-0.6NPN-73.4AP	2×10^{-4} FeAA	4 day	110	No gel	1083, 13
XIII-0-8X-0.6NPN-70AP	4×10^{-4} FeAA	7 day	110	Poor gel	↓
		4 day	180	Poor gel	
XIII-0-8X-0.6NPN-70AP	4.4×10^{-4} FeAA	8 day	110	Poor gel	
		1 day	180	Poor gel	
XIII-0-8X-0.4NPN-79AP	4.4×10^{-4} FeAA	7 day	110	Poor gel	
XIII-0-8X-0.6DNPNP-69AP	4.0×10^{-4} FeAA	5 day	110	No gel	
XIII-0-8X-0.6NPN-60AP	4.0×10^{-4} FeAA	2 wk	110	Good casting	1119, 5

i. XII and XVI Diisocyanate Castings

The XII and XVI diisocyanates both melt higher than the I and XIII diisocyanates and higher than the usual degassing temperature, 50°C. For this reason, and the related one of reduced solubility of these diisocyanates in the nitroplasticizers, a higher degassing temperature, 65°C, was attempted for them (967, 16; 1004, 9). The gel castings were partially successful in each case. No composite castings were made with these diisocyanates. This difficulty points up an additional requirement for successful diisocyanate candidates.

j. Copolymer Castings

It was suggested that copolymer castings, e.g., mixed diisocyanates or mixed diols, might yield more resilient propellants. This was attempted and found to be correct. The physical and mechanical evaluation which demonstrated this fact was performed under an associated contract (see Aerojet Report No. 1104). Table 36 lists the copolymer castings reported.

TABLE 36

COPOLYMER CASTINGS

Formulation	Catalyst	Cure hr	Cure °C	Results	Reference
I, XIII*-A-8X-0.6MNP-60AP	? VOAA	24	45	Good castings	967, 18
I-A, H**-8X-0.6MDNP-60AP	? VOAA	24	45	Good castings	967, 18
I-A, H-8X-0.4MNP-60AP	$4x10^{-3}$ VOAA	24	45	Good castings	1004, 7

* Copolymer castings, varying proportions of I and XIII diisocyanates.

** Copolymer castings with varying proportions of A and H diols.

C. NON-CASTABLE SYSTEMS

1. Introduction

The application of nitropolymers and nitromonomers to propellants has most successfully been applied to the castable systems (see previous section).* Under this program, no truly successful system has been developed for the preparation of a propellant that can be compression-formed or extruded, then cured to yield a thermally and dimensionally stable product. Several systems, however, appear to hold considerable promise for further development. The principal problem has been to devise a scheme for a delayed or second-stage cross-linking reaction that can permit compression-molding, or extrusion under moderate conditions, to yield a product which on further cure becomes dimensionally stable at higher temperatures. Several studies have indicated the ready applicability to the molding or extrusion of the linear nitropolymers, but no successful cross-linking system has been developed.

Early studies involved mixed nitropolymers, e.g., linear nitropolyurethane, as a filler for a vinyl monomer which is post-cured. The linear nitropolyurethane exerted too strong an inhibiting action for

---

* Some studies on compression-formed or extruded nitropolyurethanes were performed under Contract AF33(616)-2519, Final Report - Aerojet Report No. 1199-4. Studies on compression-formed or extruded propellants, based on dinitropropyl acrylate, have been successfully performed under Contract NOas 54-399c, Final Report - Aerojet Report No. 1104, and under Contract NOrd 16878, now in progress.

this system to be operable. Later studies in the nitropolyurethane systems examined a number of second-stage cross-linking methods, none of which were successful.

2. Linear-Polymer-Molding Studies

As a means of demonstrating the plastics developed under this contract, compression-molded samples were desired. This work was performed on a laboratory platen press. It was found that the amorphous, linear materials readily yielded clear, light yellow samples which were strong but brittle. The crystalline materials such as polyester 1-A were opaque and even more brittle. Molding conditions were similar for most materials: 80-100°C, 3000-5000 psi. Strands were also desired for the rheology studies. These were made in a typical molding die, since attempts to cut samples from milled sheets were unsuccessful because of their brittleness (590, 46). An attempt to extrude linear polymer I-A was unsuccessful (590, 46). The moldings and extrusions of linear nitropolyurethanes I-A, I-J, and XIII-A with oxidizer present were successfully accomplished.*
It appeared that extrusions with oxidizer (AP) were more readily accomplished than without oxidizer (807, 37). Molding of linear materials with nitroplasticizers successfully yielded tough strands (1119, 8). Table 37 lists the polymers whose molding has been reported, and their references.

TABLE 37

LINEAR NITROPOLYMERS WHICH HAVE BEEN COMPRESSION-MOLDED

Polymer	Reference
Polyurethane I-A	482, 51; 515, 68; 590, 46
Polyurethane I-AN	515, 68; 563, 51
Polyurethane I-F	515, 68
Polyurethane VI-AN	515, 68
Polyurethane I-D	482, 51
Polyurethane I-H	563, 51
Polyurethane I-HN	563, 51
Polyurethane I-G	563, 51

---

*Linear nitropolymers that were milled and extruded with oxidizer were reported under Contract AF33(616)-2519, see Aerojet Report No. 1199-4.

Polymer	Reference	
Polyurethane XIII-J	1119, 8	with and without plasticizers
Polyurethane XIII-A	1119, 8	
Polyurethane I-J	1119, 8	
Polyester 1-A	468, 50; 482, 51; 515, 68; 590, 46	
Polyamide 1-α	468, 51	
Polyurea I-α	468, 50; 482, 51; 515, 68; 590, 46	
Polyurea I-αN	515, 68	
Polyurea VI-α	515, 68	
Poly THEMA*	563, 51	
Poly DNPA**	563, 51	
Poly DNBMA***	563, 51	
Polyurethane I-A	686, 46 with AP and AN	
Polyurethane I-J	686, 46 with AP and AN	
Polyurethane XIII-A	807, 38; 833, 29 with AP	

---

*2,2,2-Trinitroethyl methacrylate

**2,2-Dinitropropyl acrylate

***2,2-Dinitrobutyl methacrylate.

3. Mixed Polymers

One of the first attempts to formulate a nitropolymer propellant material was to use a high-energy linear nitropolyurethane as an oxidizer-filler in a mixture with a nitro-containing vinyl monomer which, on curing, would become the binder. Thus, for example, use could be made of post-nitrated polyurethane I-AN of relatively low molecular weight but of high specific impulse. With 10% DNPA as a binder, such a mixture would have a calculated specific impulse of 221 lbf sec/lbm (638, 70). Mixtures of nitropolymers and vinyl monomers were prepared by mixing on a roller mill, sheeting, and curing in strips (638, 70), or were extruded after mixing on the roller mill (663, 53; 686, 40). Materials were dough-like before cure, and often brittle after curing. The usual precautions were undertaken for excluding air from the samples during cure.

First attempts using several different preparations of polymer I-AN and 10 to 30% DNBA indicated that the vinyl monomer did polymerize, but that the nitropolyurethane was decomposing (638, 70)(III,A,2).

Not all formulations were compatible. Evidence for curing was established by the qualitative evaluation of physical properties and the measurement of the relative viscosity after the cure. Any vinyl polymerization would cause an increase in viscosity. However, decomposition of the nitropolyurethane filler would cause degradation and result in a lowering of viscosity. This was observed (663, 53). The lowering of viscosity was also shown to be due to an inhibiting effect of the decomposition products on the vinyl polymerization (663, 53).

It was also shown that DNBA and DNPA caused degradation of ethyl cellulose (EC) during attempted cures (663, 54). Nitrocellulose and JPN double-base propellant caused a similar degradation (663, 54). Typical nitrocellulose stabilizers were found to decrease this degradation of EC and the nitropolymer I-AN.

Attempts to use nitropolymers I-J and I-A were only partially successful (686, 40). The compatibilities with DNBA and DNPA were investigated. It was found that after partial polymerization of the vinyl monomer, compatible mixtures could be prepared. Studies with methyl methacrylate replacing the nitro vinyl monomer gave additional evidence for the inhibiting action of the nitropolymer (686, 45). Investigations of thermal stabilities at 65.5°C indicated the need for investigation of the gassing rates of these formulations. The use of the Warburg manometric method was initiated for this study (663, 53; 686, 40) (see VI,J).

In view of the instability of polymer I-AN and the inhibiting action of all the nitropolyurethanes on the vinyl monomers, and since no high specific-impulse materials would be prepared, this type of formulation was abandoned.

4. Branched Nitropolyurethane Studies

When it became known that linear nitropolymers could be processed by several different methods but could not offer the physical and mechanical properties required of a rocket propellant, investigations of the effect of branching in the polymer were initiated. Early studies were performed with polymer I-A which was prepared with small amounts (0.5 to 2.0%) of cross-linking agent tris-(hydroxymethyl)-nitromethane (740, 54).

These materials were prepared in dioxan and in nitroplasticizers (740, 56). It was found that the small amount of branching did not appreciably affect the physical properties of the polymer and that some difficulty was encountered in getting branching without insolubilization.

Formulations, without oxidizer, were prepared by mixing branched and cross-linked polymer I-A with a nitroplasticizer in a blendor with water, squeezing out the water on an unheated roller mill, then milling until dry and homogeneous at 150-170°F. These materials were then successfully compression-molded (772, 33). Mechanical properties of these materials were evaluated under a separate contract. The physical and mechanical properties were improved over the linear materials (772, 60).

Moldings and extrusions of branched (1% cross-linker) polymer XIII-A were successfully accomplished in the presence of oxidizer (AP) (807, 37). It was observed that milling operations degraded the polymers sufficiently to destroy the small amount of cross-linking originally present (883, 29). Means of re-establishment of the three-dimensional structure or formation of the cross-linking after the mechanical operations were next desired.

5. Second-Stage Cross-linking Studies

a. Thermal Cross-linking

It was observed that the heating of linear nitropolyurethanes I-A and XIII-A at 150°C caused insolubilization (833, 32) and branched polymers (0.5% cross-linker) became insoluble at a somewhat lower temperature. However, insolubilization did not occur in the presence of plasticizers (833, 33). This thermal cross-linking was further studied with 13 different nitropolyurethanes (868, 45). Table 38 shows the results obtained. It is believed that at 150°C, the polyurethanes exhibit the "abspalter" reaction, the urethane linkage reverses, giving rise to free, reactive isocyanate and hydroxyl groups. The diols are less stable, giving rise to excess isocyanate which reacts with the urethane hydrogen, causing insolubilization. It was concluded that this system did not hold much promise for further development, due to the very high temperatures involved and the attendant decompositions.

TABLE 38

HIGH-TEMPERATURE STUDIES ON LINEAR NITROPOLYURETHANES

Polymer	Relative Viscosity	Solvent	Solubility: After 15 min at 150°C	Solubility: After 75 min at 150°C
I-A	1.61	Acetone	Slowly soluble	Insoluble
I-H	1.60	Acetone	Insoluble	Insoluble
I-J	1.77	Acetone	Soluble	Soluble
XII-A	1.85	DMF	Insoluble	Decomposed
XII-H	1.26	Acetone	Soluble	Insoluble
XII-J	1.62	DMF	Soluble	Insoluble
XIII-A	1.45	Acetone	Slowly soluble	Fumed off
XIII-H	1.53	Acetone	Insoluble	Insoluble
XIII-J	2.32	DMF	Soluble	Insoluble
XV-A	1.47	Acetone	Soluble	Soluble
XV-H	1.22	Acetone	Soluble	Soluble
XV-J	1.78	DMF	Soluble	Soluble
XV-N	1.30	DMF	Soluble	Soluble

Because in the above observed cross-linking method, free isocyanate groups are present, and because the reaction of isocyanates with urea linkages was reported to be 80-100 times faster than with urethane linkages, a nitropolymer containing mixed urethane and urea linkages was studied (833, 21). Polymer I-A was modified by replacement of 33.3% of the A diol with ethanolamine (EA). The resultant copolymer was found to give insolubilization at moderate temperatures (833, 22). This modified I-A polymer was examined for cross-linking , mixed with ammonium nitrate and with plasticizers (833, 31). With dioxan, the formulation became insoluble after 72 hr at 180°F but it failed to become insoluble in the presence of other plasticizers. Addition of basic materials such as dimethylaniline or urea did not improve this cross-linking reaction.

A more recent study of the cross-linking of ethanolamine-modified nitropolymers has been made (1119, 9 and Aerojet Reports No. L831-91 and L831-92). The insolubilization was accomplished with XIII-A-EA copolymer, and it was demonstrated that at least 15% EA was required. Physical and thermal stability studies, however, indicate that EA reduces the thermal stability considerably and that not enough crosslinks are produced to give a dimensionally stable material at 150°F.

b. Cross-linking with Aldehydes

Aldehydes are known to react with amides to form hydroxyalkylamides or methylene-<u>bis</u>-amides. Formaldehyde in particular undergoes this reaction. Attempts to use formaldehyde and glyoxal for cross-linking of nitropolyurethanes was at first reported to be unsuccessful (833, 31). A later study (1004, 15) showed that formaldehyde would cause insolubilization both with and without plasticizers or oxidizers. Polymers I-J, I-A, and XIII-A were used. Further examination indicated that the system did not hold much promise. The degree of cross-linking was sufficient for insolubilization but insufficient for appreciable improvement in physical properties, and all attempts to mold and cure a nitropolymer-formaldehyde mix without bubble formation were unsuccessful (1048, 11).

c. Cross-linking with Peroxides

Attempts to cross-link nitropolyurethanes I-J, XIII-J, and XIII-A with peroxides led to results similar to those obtained with formaldehyde. Insolubilization occurred on heating the polymers with cumene hydroperoxide, dicumyl peroxide, and methyl amyl ketone peroxide, but in no case was a bubble-free strand obtained.

d. Cross-linking with Reactive Centers

Hoping to prepare a nitropolyurethane containing reactive centers that would lend themselves to second-stage cross-linking, nitropolymers with 2-nitro-2-bromo-1,3-propanediol (Q) and 2-nitro-2-chloro-1,3-propanediol (S) were prepared (III,B, Table 24). At first (907, 16), it was thought that these materials gave insolubilization at low temperatures. However, during attempts to prepare copolymers of XIII-J-Q (941, 10), it was observed that inadequate control had been maintained of cross-linking impurities in the various nitromonomers (see paragraph IV,D). Preparations of XIII-Q (941, 10) and XIII-S (967, 7) with isocyanate of high purity could not be cross-linked thermally or in the presence of various reagents. Solutions of XIII-Q in acetone degraded rapidly.

An attempted preparation of a nitropolymer with a reactive hydrogen was unsuccessful. An attempted polymerization of XIII diisocyanate with 2-nitro-1,3-propanediol led to a hard, brittle, completely insoluble mass (941, 15).

e. Two-Stage Polyurethane Formation

The two-stage process involves the preparation of a low-molecular-weight prepolymer (either excess diol or excess diisocyanate may be used), using plasticizers as the polymerization solvent and the subsequent addition of the necessary amount of monomer and cross-linking agent to bring the monomer ratio to unity. Post-cure will then give a three-dimensional system. During the first-stage prepolymer preparation, most of the heat of polymerization is easily removed. The degassing operation is rapidly accomplished during the first stage, as in the usual casting technique. By simply varying the initial monomer ratio, the degree of polymerization of the prepolymer can be adjusted over wide limits. This system was first attempted as a modified casting procedure, but failed, due to too high a viscosity. Prepolymers of the I-A and I-H system were studied (807, 32).

This system seemed to be readily adaptable to the compression molding or extrusion of propellants. After degassing the first stage, the prepolymer-plasticizer solution was transferred to a roller mill, and the oxidizer was milled in. A calculated amount of diisocyanate, to adjust to equivalence (with a hydroxyl end-group prepolymer), was then added and milled to homogeneity. The propellant was then molded, or extruded, and cured. The advantages of this system are (1) the high loadings of oxidizer which may not be attainable in the casting system; (2) the bulk of the exotherm is dissipated during the first-stage; and (3) the prepolymer can be stockpiled for future use (941, 24). The disadvantages include (1) the possible reaction of the diisocyanate, added for the second stage, with atmospheric moisture; (2) the control of the second-stage reaction rate to ensure fabrication of the desired product before gelation. It is exactly on these two points that the system failed.

A series of XIII-J and XIII-A prepolymers of various degrees of polymerization were studied for the effect of DP on the workability of the roller mill. A DP of 12-19 was found to be about optimum (941, 24). Formulations prepared from various DP prepolymers were fabricated, i.e., XIII-J-(or XIII-A)-8X-0.6MNP-60AP. Samples could not be extruded, and some were bubble-filled. All later studies used the XIII-A system. Different plasticizers such as DNPNP and TNENP were investigated (967, 20; 1004, 11). In almost all cases, the molded or extruded samples were bubble-filled or pregelled. Erratic burning rates indicated the bubble and reproducibility difficulties (1004, 11). An attempt to prepare these formulations under anhydrous conditions, using a stream of nitrogen over the roller mill, did not improve the bubble problem (1048, 10).

More recent experience with nitropolymer binder processing, particularly with nitropolymer-fiberglass work,* indicates that low humidity is a requirement for high-density materials. There is no sound reason why the problems of humidity control and gelation control cannot be properly solved.

D. MONOMER QUALITY CONTROL

1. Introduction

The preparation of high-molecular-weight nitropolymers requires monomers of the highest purity. The purity of the monomers used in propellant formulation is likewise of the utmost importance. Problems such as bubble formation, premature gelation, or inadequate pot life, and variation of physical and mechanical properties of the propellant have been directly related to monomer quality. The nitropolymer-propellant-development program has been confronted with problems distinctively different from other propellant-development programs, because the raw materials (the monomers)

---

*Performed under Contract N6onr-46208.

are not commercially available, i.e., manufactured on a large scale. The fact that our monomers have been prepared on laboratory scale has presented a continued problem of reproducibility. Most of the monomers can be assayed for reactive end-groups, but these analytical methods have not been sufficiently sensitive to detect impurities which can render the monomer unusable for most propellant applications. For example, a small percentage of a catalytic impurity, a trifunctional impurity, or a monofunctional impurity cannot be detected in the usual di-n-butylamine titration of XIII diisocyanate. Such problems confront the development of any new polymer system, and must be solved before any reliable evaluation of the utility of the new monomers can be made. These problems have been studied for nitropolyurethane monomers, nitroplasticizers, and dinitropropyl acrylate.

2. Nitropolyurethane Monomers

a. Introduction

The difficulty with small amounts of impurities had been recognized for some time on this program. They were brought to a head when, during a study of second-stage cross-linking, a control run of polymer XIII-J became insoluble under conditions which should have led to soluble, linear polymer (941, 10). A thorough check of a series of batches of various nitromonomers was then made, and a surprising number of batches contained cross-linking and catalytic impurities. On the basis of these observations, a series of tests were devised which successfully detected trace quantities of catalytic impurities, monofunctional impurities, and cross-linking impurities (967, 7).

b. Catalytic Impurity Test

Equivalent quantities of diol and diisocyanate were mixed and held for 18 hr at 50°C, cooled to 25°C, and an empirical flow time was then measured. A flow time of 100 sec for 100 mm was taken as the maximum. If either of the monomers contained catalytic impurities, the flow time was greater, or the mixture even gelled. More recent data indicated that the 18-hr period was unnecessarily long (1083, 15), and the test was modified to 5 hr at 50°C.

c. Polymerization Test

If the monomers pass the above test, they are then polymerized in dioxan solution under carefully controlled conditions. Adjustments of end-group equivalence and additions of catalyst are made until a maximum in the solution viscosity is reached. The relative viscosity of the precipitated polymer is then determined. This controlled polymerization detects catalyst-consuming impurities and impurities that terminate growing chains. If cross-linking impurities are present, insoluble polymer is obtained (967, 11). Inasmuch as the polymerization test is rather time-consuming, it is employed to screen monomer batches that are to be used subsequently in the preparation of high-molecular-weight linear polymer. The relative viscosity parameter has been arbitrarily set at a value of 1.5, at 25°C, for an acetone solution containing 1 g of polymer/100 ml of solution. This corresponds roughly to a molecular weight of 50,000 (1083, 15).

d. Casting Test

Monomers that pass both of the above tests are suitable for all cases. However, actual practice has shown that, for propellant castings, the requirements are less severe, e.g., cross-linking impurity is not too significant for a monomer used in a system to which a cross-linking agent will be added. Several batches of A diol and XIII diisocyanate which failed certain aspects of the above tests were successfully used in castings (1083, 15). The present procedure is now to run a "standard" casting (1083, 21) with the new monomer after it passes the catalytic impurity test. The propellant casting, usually a XIII-A-8X-0.6NPN-69AP-FeAA casting, is examined for pot life, cure time, physical and ballistic properties, bubble formation, etc. If the monomer fails to yield a "good" casting, it may be checked in the polymerization test, or submitted for further purification.

3. Nitroplasticizers

Nitroplasticizer preparations appeared to contain trace impurities similar to those contained in A-diol and XIII-diisocyanate. The only parameter previously tested for nitroplasticizers was their melting points. Presently, however, they are tested by use in a "standard" casting (see above) (1083, 21). If they fail to yield a satisfactory propellant, they are submitted for repurification.

4. Dinitropropyl Acrylate

Dinitropropyl acrylate, DNPA, is the most important nitro-containing vinyl monomer. Most propellant evaluation with DNPA has been performed under other programs (see the Introduction of this section). However, it has been the concern of this program to develop adequate syntheses and monomer quality controls for this monomer (III,A;V,B,6). The principal problems with DNPA have been the presence of polymerization inhibitors and/or retarders and cross-linking impurities (868, 5; 907, 5). This monomer is presently evaluated in a test wherein the relative viscosity of a bulk-polymerized sample is determined after a standard polymerization for 2 hr, and the solubility of the polymer is checked after 20 hr. This test will disclose the presence of inhibitor, retarders, and cross-linking agents (868, 5; 1048, 20).

E. NITROPLASTICIZERS

Nitroplasticizers for nitropolyurethanes and polydinitropropyl acrylate were desired in order to improve the physical properties of these propellant binders. Most of these materials are amorphous polymers. Such polymers can be brought from the glassy, brittle state to the desirable rubbery state, by the addition of plasticizer. A large number of potential nitroplasticizers have been studied. Their synthesis and evaluation have been discussed in a separate section (II,F) of this report. Most of these have been evaluated in castings with various nitropolyurethanes. As the program has progressed, information of the utility of various plasticizers with the nitropolymers that have reached formulation studies has caused most of the plasticizer candidates to be dropped for one or more reasons: volatility, incompatibility, thermal stability, etc. The most effective plasticizers to date have been the esters of 4-nitrazapentanoic acid. They offer a considerable range of properties and energy content and have excellent thermal stabilities.

Table 39 lists the complete evaluation of 14 different nitroplasticizer candidates. The plasticizers are listed in the order of increasing molecular weights, and a marked transition in properties appears around a molecular weight of 280. For the compounds having a molecular weight greater than 280, it is seen generally that melting points are above room temperature, densities are higher, and thermal stabilities are significantly improved. On the basis of thermal stabilities and compatibilities, the two nitrate esters included in the table compare unfavorably with the other plasticizers. The generally unstable trinitromethyl group is shown to produce poor stabilities in METHB and in THP plasticizers. On the other hand, the high-melting-point THENP exhibits excellent stability and represents the highest-energy, most stable plasticizer of the group.

V. PROCESS STUDIES

A. INTRODUCTION

The study of processes for the preparation of nitromonomers, nitroplasticizers, and nitropolymers was inaugurated in answer to the increasing demand for larger quantities of materials for formulation studies and in answer to the question of probable and practical manufacture of such compounds. The processes under investigation concerned the more promising compounds for which laboratory methods of preparation were generally developed to a high degree. The conversion to a pilot-plant scale was quite successful, although problems in the yield and in the quality of certain products were encountered.

As the demand for nitromonomers increased, the emphasis of this study was directed toward the production of these materials, and little time was available for process studies. This resulted in a direct scale-up of some laboratory procedures which were unsatisfactory with regard to the yield and/or the actual process. In these instances, a further study of the problems, on a laboratory scale, was indicated.

TABLE 39

PROPERTIES OF THE NITROPLASTICIZERS

					Physical Properties				Calculated Thermo-Properties	
No.	Plasticizer	Code	Formula	Mole Wt	mp (°C)	bp (°C)	Density (25°C)	Soln. Density[1] (25°C)	I_{sp}[2] lb-sec/lb	CED[3]
1	4-Nitrazapentanonitrile	NPN	$C_4H_7N_3O_2$	129.12	-	120/1mm	1.225	-	145	204
2	Methyl 4-nitrazapentanoate	MNP	$C_5H_{10}N_2O_4$	162.15	-	107/1mm	1.232	-	113	150
3	4,4-Dinitropentanonitrile	DNPN	$C_5H_7N_3O_4$	173.13	-	127/2mm	1.318	-	150	158
4	1,4-Dinitroxybutane	DNB	$C_4H_8N_2O_6$	180.12	13	58/3mm	1.321	-	221	98
5	5,5-Dinitro-2-hexanone	DNH	$C_6H_{10}N_2O_5$	190.16	-	110/1mm	1.245	-	153	205
6	1,3,3-Trinitrobutane	TNB	$C_4H_7N_3O_6$	193.12	-	105/6µ	1.442	-	239	171
7	Methyl 4,4-dinitropentanoate	MDNP	$C_6H_{10}N_2O_6$	206.16	23	115/1mm	1.300	-	162	133
8	5,5,5-Trinitro-2-pentanone	TNP	$C_5H_7N_3O_7$	221.13	43-44	-	1.454	-	228	170
9	1,2,6-Trinitroxyhexane	TNH	$C_6H_{11}N_3O_9$	269.17	-	147/15µ	1.390	-	236	108
10	2,2-Dinitropropyl 4-nitrazapentanoate	DNPNP	$C_7H_{12}N_4O_8$	280.20	39.5-40	-	1.488	1.422	193	127
11	2-Methoxyethyl 4,4,4-trinitrobutyrate	METNB	$C_7H_{11}N_3O_9$	281.18	4	-	1.380	-	201	155
12	2,2,2-Trinitroethyl 4-nitrazapentanoate	TNENP	$C_6H_9N_5O_{10}$	311.17	54.5-55.5	-	1.545	1.504	236	185
13	Ethylene bis-(4-nitrazapentanoate)	EBNP	$C_{10}H_{18}N_4O_8$	322.28	58-59	-	1.399	1.334	114	172
14	Ethylene bis-(4,4-dinitropentanoate)	EBDNP	$C_{12}H_{18}N_4O_{12}$	410.30	39-40	-	1.448	1.427	160	146

	Stability				Compatibility[6]				
No.	KI-Starch[4] (65.5°C)	Warburg (ml/100 g/hr at 65.5°C)	Volatility (g-cm^{-2}-sec^{-1} at 77°C)	Me Violet[5] (134.5°C)	I-A	I-J	XIII-A	XIII-J	I-H
1	1 hr	>0.1	6.8×10^{-8}	>5 hr	Comp.	Comp.	Comp.	Comp.	Comp.
2	>5 hr	Distills	44×10^{-8}	>5 hr	Comp.	Comp.	Comp.	Comp.	Comp.
3	1 hr	Distills	4.7×10^{-8}	68 min	Comp.	Comp.	Comp.	Comp.	Comp.
4	1 hr	Distills	60×10^{-8}	25 min	Comp.	Incomp.	Incomp.	Incomp.	Comp.
5	80 min	Nil	8.0×10^{-8}	33 min	Comp.	Comp.	Comp.	Comp.	Comp.
6	1 hr	0.4	11×10^{-8}	9 min	Comp.	Comp.	Comp.	Comp.	Comp.
7	2.5 hr	Nil	48×10^{-8}	-	Comp.	Comp.	Incomp.	Incomp.	Comp.
8	3 min	Distills	28×10^{-8}	17 min fumed off in 19 min	Comp.	Comp.	Comp.	Comp.	Comp.
9	7 min	0.5	-	20 min	Incomp.	Incomp.	Incomp.	Incomp.	Comp.
10	>5 hr	Nil	Nil	>5 hr	Comp.	Comp.	Comp.	Comp.	Comp.
11	Immed.	0.2	7.1×10^{-3}	12 min fumed off in 14 min	Comp.	Comp.	Incomp.	Incomp.	Comp.
12	>5 hr	-	Nil	60 min	Comp.	Comp.	Comp.	Comp.	Comp.
13	>5 hr	>0.1	Nil	>5 hr	Comp.	Comp.	Comp.	Comp.	Comp.
14	>5 hr	Nil	Nil	>5 hr	Comp.	Comp.	Comp.	Comp.	Comp.

NOTES

[1] Solution density was calculated for the solid plasticizers from density data obtained from solutions of the plasticizers in MNP at 25°C, assuming zero volume of mixing.

[2] Specific impulses were calculated at 1000 psi by the short method (Aerojet Report No. 1205-1).

[3] Cohesive energy densities, CED, were calculated from latent heats of vaporization, which were estimated from boiling-point data. The CED values for the solid plasticizers were calculated from group contribution data (Aerojet Report No. 868, p. 60).

[4] Picatinny Arsenal No. 1401.

[5] OSRD 3401, p. 8.

[6] Compatibility tests were performed as follows: 0.8 g of polymer and 0.2 g of plasticizer are dissolved in acetone (tetrahydrofuran for XIII-J series), and the solvent is allowed to evaporate at 110°F for 16 to 24 hours. The formation of an opaque film is taken as the criterion of incompatibility. The polymers used in the compatibility tests are polyurethanes derived from the following monomers:

Code	Diisocyanate
I	3,3-Dinitro-1,5-pentane diisocyanate
XIII	3-Nitraza-1,5-pentane diisocyanate
	Diol
A	2,2-Dinitro-1,3-propanediol
H	5,5,5-Trinitro-1,2-pentanediol
J	2-Nitro-2-methyl-1,3-propanediol

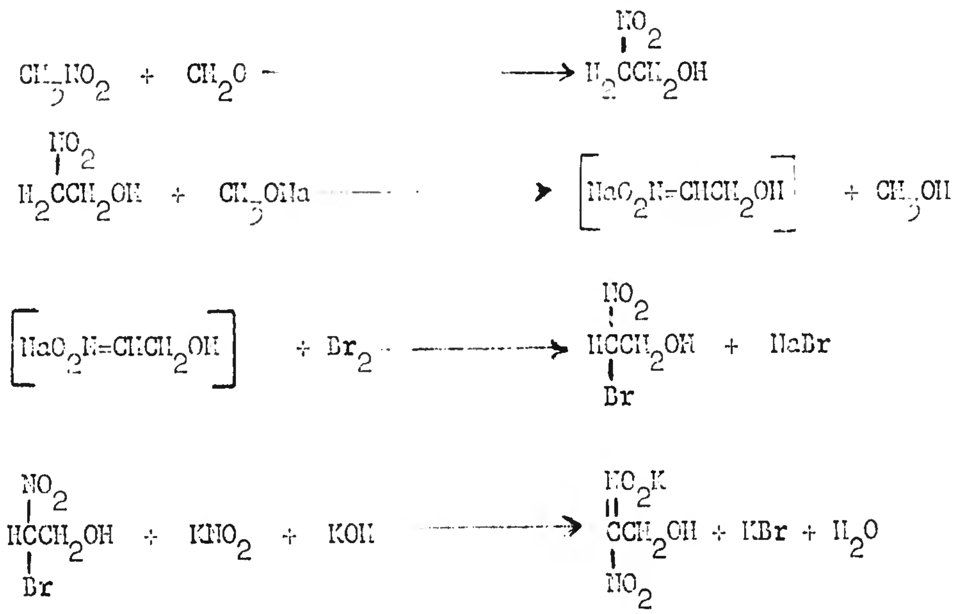
In Table 40, there is presented a summary of all nitromonomers and nitroplasticizers prepared in the chemical pilot plant. The nitropolymer systems which were studied are shown in Table 41 and processing equipment is described in Table 42. Included below is a discussion of the method of preparation of each compound, including intermediates, carried out on pilot-plant scale.

B. NITROMONOMERS

1. 2,2-Dinitroethanol

a. Discussion

2,2-Dinitroethanol was found to be a very valuable chemical intermediate during the early stages of the nitropolymer program. Its preparation and subsequent reactions are discussed elsewhere in this report (II,D,2,a). Until the discovery of the oxidative nitration method for the preparation of *gem*-dinitro compounds (417, 28-32), 2,2-dinitroethanol was prepared from nitromethane by this series of reactions:



$$CH_3NO_2 + CH_2O \longrightarrow H_2\overset{NO_2}{\overset{|}{C}}CH_2OH$$

$$H_2\overset{NO_2}{\overset{|}{C}}CH_2OH + CH_3ONa \longrightarrow \left[NaO_2N{=}CHCH_2OH\right] + CH_3OH$$

$$\left[NaO_2N{=}CHCH_2OH\right] + Br_2 \longrightarrow H\overset{NO_2}{\overset{|}{\underset{\underset{Br}{|}}{C}}}CH_2OH + NaBr$$

$$H\overset{NO_2}{\overset{|}{\underset{\underset{Br}{|}}{C}}}CH_2OH + KNO_2 + KOH \longrightarrow \overset{NO_2K}{\overset{\|}{\underset{\underset{NO_2}{|}}{C}}}CH_2OH + KBr + H_2O$$

Although overall yields were low, no feasible alternative method was available, and considerable effort was expended toward improvement of the process.

TABLE 40

PILOT-PLANT PREPARATIONS
MONOMERS AND PLASTICIZERS

No.	Compound	Batches No.	Batches Average Size lb mole	Batches Average Yield %	References
1	2-Nitroethanol	--	0.166	40.0	417, App.
2	2-Bromo-2-nitroethanol	--	0.015	91.0	417, App.
3	Potassium 2,2-dinitroethanol	--	0.013	33.0	417, App.
4	Di-(β-cyanoethyl)-ammonium nitrate	12	0.430	76.5	907, 35; 941, 26; 967, 25; 1004, 17
5	Di-(β-cyanoethyl)-nitramine	10	0.320	72.3	907, 35-36; 941, 26; 967, 25; 1004, 17
6	Di-(β-carboxyethyl)-nitramine	12	0.258	86.6	907, 36; 941, 26; 967, 25; 1004, 17
7	4-Nitraza-1,7-heptanedioyl chloride	12	0.125	81.2	907, 36; 941, 26; 967, 25; 1083, 27
8	3-Nitraza-1,5-pentane diisocyanate	17	0.063	62.3	907, 36; 941, 26; 967, 24; 1004, 17; 1083, 24
9	2,2-Dinitro-1,3-propanediol	4	0.426	46.0	1004, 17
10	2,2-Dimethyl-5-nitro-5-hydroxmethyl-1,3-dioxane	6	0.440	65.3	907, 38-39; 941, 27
11	2,2-Dimethyl-5,5-dinitro-1,3-dioxane	6	0.250	37.6	907, 39; 941, 27
12	Methyl 4,4-dinitro-1,7-heptanedioate	10	0.485	41.5	907, 37; 941, 27; 967, 25; 1004, 17; 1048, 17
13	4,4-Dinitro-1,7-heptanedioic acid	9	0.228	69.3	907, 38; 941, 27; 967, 25; 1004, 17

TABLE 40 (cont.)

No.	Compound	Batches			References
		No.	Average Size lb mole	Average Yield %	
14	4,4-Dinitro-1,7-heptanedioyl chloride	6	0.119	64.5	941, 27; 967, 24; 1004 17; 1048, 17; 1083, 24
15	3,3-Dinitro-1,5-pentane diisocyanate	12	0.027	36.1	967, 24; 1004, 17; 1048, 17; 1083, 24
16	5,5,5-Trinitro-2-keto-1-pentanol	3	0.0235	74.0	1083, 24
17	5,5,5-Trinitro-1,2-pentanediol	2	0.0372	72.8	1083, 25
18	2,2-Dinitropropanol, crude	6	0.446	59.2	907, 41; 1004, 17
19	2,2-Dinitropropanol, purified	7	0.439	40.6	967, 25; 1048, 17
20	2,2-Dinitropropyl acrylate	3	0.070	33.1	1048, 17
21	2,2,5-Trimethyl-5-nitro-1,3-dioxane		0.462	46.8	907, 40
22	2-Nitro-2-methyl-1,3-propanediol	1	0.147	98.3	907, 40
23	bis-Nitric acid salt of 3,6-diaza-1,8-octane dinitrile	1	0.250	69.0	1004, 19
24	3,6-Dinitraza-1,8-octane dinitrile	1	0.172	70.0	1004, 19
25	3,6-Dinitraza-1,8-octanedioc acid	1	0.114	52.3	1004, 19
26	2,2-Dinitropropyl 4-nitrazapentanoate	1	0.055	76.8	1083, 25

TABLE 40 (cont.)

No.	Compound	Batches No.	Batches Average Size lb mole	Batches Average Yield %	References
27	Nitric acid salt of 4-azapentanonitrile	7	0.681	71.4	907, 42; 967, 25; 1004, 18
28	4-Nitrazapentanonitrile	7	0.358	86.7	907, 42; 967, 25; 1004, 18; 1048, 17
29	4-Nitrazapentanoic acid	3	0.383	53.6	1004, 17; 1083, 25
30	Methyl 4-nitrazapentanoate	3	0.291	72.7	907, 42; 967, 25
31	4,4-Dinitropentanoic acid	1	0.275	53.5	1004, 19
32	4-Azapentanonitrile	3	0.408	67.4	907, 42

TABLE 41

PILOT-PLANT PREPARATIONS NITROPOLYMERS

No.	Type of Polymer System	Total No. of Batches	Av Relative Viscosity 1% in Acetone	References
1	Polyurethane I-A-0.5X	2	Insoluble	807, 23; 833, 36
2	Polyurethane I-A	5	2.47*	833, 36; 868, 48; 907, 44
3	Polyurethane I-J	1	2.03	907, 44
4	Polyurethane XIII-A	7	1.78*	833, 36; 868, 48; 907, 44; 941, 27
5	Polyurethane XIII-J	3	Insoluble	833, 36; 907, 44
6	Polyurethane XIII-A-0.5X	2	1.87	833, 36; 907, 44
7	Poly 2,2-Dinitro-1-propyl acrylate	1	1.27	907, 44

---

*These values do not include the relative viscosities of insoluble polymer obtained when benzene was used as a solvent for the polymerization.

TABLE 42

PILOT-PLANT PROCESSING EQUIPMENT

Item	Description	Function	Reference
Mixer	(2) 50-gal jacketed, stainless steel reaction vessels, complete with agitators	Preparations involving temperature-controlled reactions at high or low (vacuum) pressures	907, 33
Mixer	100 gal-jacketed, glass-lined reaction vessel, complete with agitator	Large reactions involving corrosive chemicals	
Condenser	25-sq ft fixed-tube, stainless-steel condenser, equipped with a portable rack.	To be used with 50-gal kettles for distillations	
Centrifuge	20-in. basket-type centrifuge	Filtrations	
Filter	20-in. porcelain Buchner funnel	Filtration of large quantities of shock-sensitive materials	907, 34
Filter	7-in., 20-plate pressure filter	Clarification of solutions, recovery of silver fines in oxidative nitration reactions	907, 34
Tanks	100 and 200-gal glass-lined tanks, complete with agitators	Liquid-liquid batchwise extractions and reactions which involve no outside means of controlling temperature	
Dryer	8-cu ft stainless steel vacuum dryer	Drying of hygroscopic or water-reactive products	
Mixer	1-gal Beken dispersion blade mixer	Solution and emulsion polymerizations	772, App.
Filter press	1/2-cu ft plate and frame filter press	Filtrations	
Mill	Morehouse mill	Work-up of nitropolyurethanes	686, App.

b. 2-Nitroethanol

2-Nitroethanol was prepared by the method of Gorsky and Makarow.[*] This method involved the condensation of nitromethane and formaldehyde. The study was divided into two phases; (1) a continuous process, which was unsuccessful because of low yields of product and large manpower requirements (345, 12), and (2) a batch process (345, 12). Using the latter process, sufficient material was processed for use on this program.

The batch process was developed to large laboratory scale using the techniques described in the "Laboratory Preparation of 2-Nitroethanol" (417, Appendix C). A study of azeotropic distillation (461, 21; 457, 21) resulted in a safer technique for the distillation of the final product, and permitted the reaction to be run on a somewhat larger scale. Using this modified distillation procedure, the batch size was increased and conditions were varied until these optimum conditions were found:

(1)	Reaction size, g mol	75.6
(2)	Molar ratio, nitromethane/formaldehyde	6.3/1
(3)	Moles of catalyst (K_2CO_3)	0.0145
(4)	Reaction time, hr	0.75
(5)	Recovered nitromethane, %	93.25
(6)	Yield of 2-nitroethanol, %	40.0

Using the above conditions, a number of runs were made, with satisfactory results being obtained. However, no product was obtained in attempting to increase the batch size to 225 moles. Attempted recovery of nitromethane in this run resulted in a violent explosion (482, 61). No reasons were found for the explosion, and the reaction was not repeated on this scale.

c. 2-Bromo-2-nitroethanol

The original procedure for the preparation of 2-bromo-2-nitroethanol involved the addition of bromine to a methanol solution of the sodium salt of 2-nitroethanol, removal of the solvent, and final distillation

---

[*] Gorsky and Makarow, Ber. 67B, 996 (1934).

of the product at reduced pressure. It was found that the formation of higher boiling contaminants could be minimized by reversing the order of addition so that bromine was always in excess (404, 40). With this procedure, an average yield of 91%, based on 2-nitroethanol, was obtained.

Because of the distinct limitations of available equipment, the scale-up factor for this preparation was quite small. However, utilizing the above-described method (417, Appendix), a semi-continuous process was devised whereby one operator could maintain a series of small (5 liter) reactors, and thus produce sufficient quantities of 2-bromo-2-nitroethanol to satisfy the requirements of this program.

d. Potassium 2,2-Dinitroethanol

Potassium 2,2-dinitroethanol was prepared by the reaction of potassium nitrite, potassium hydroxide, and 2-bromo-2-nitroethanol in methanol solution. Due to the numerous competing reactions in the preparation of this compound, it was believed that no significant improvement of the yields (30-35%) could be attained, and major effort was expended toward obtaining a pure product. A study of the fractional crystallization of the crude material revealed the presence of large amounts of inorganic salts (386, 12). These were largely removed by a cold slurry-washing technique. A slight improvement in yield and purity was also found when 2-bromo-2-nitro ethanol was used, which had been prepared while maintaining bromine in excess during the reaction. Adopting these modifications, a standard procedure for the preparation of potassium 2,2-dinitroethanol was developed (417, Appendix), which was employed for all succeeding batches.

e. 2,2-Dinitroethanol

2,2-Dinitroethanol was prepared by the acidification of potassium 2,2-dinitroethanol. The use of equivalent amounts of sulfuric acid for this reaction resulted in improved yields of crude product (417, 11). When the reaction was run by passing a stream of anhydrous hydrogen chloride into a suspension of the potassium, dinitroethanol and crystallizing the resultant oil from ethyl chloride, a 44% yield of crystalline product was obtained (417, 11; 417-A, 16). However, the isolation of the free 2,2-dinitroethanol was considered quite hazardous, and this reaction was run only on a small, laboratory scale.

f. Conclusions and Recommendations

Considerable effort was expended in the study of the reactions leading to 2,2-dinitroethanol; however, with the development of new procedures for producing gem-dinitro compounds, this study was terminated. Overall yields for this series of synthesis were quite low, and the purification procedures for the majority of the compounds were hazardous.

In the event that further investigation of these reactions was initiated, the following items would possibly result in increased yields of product, or reduce the hazardous nature of a particular process:

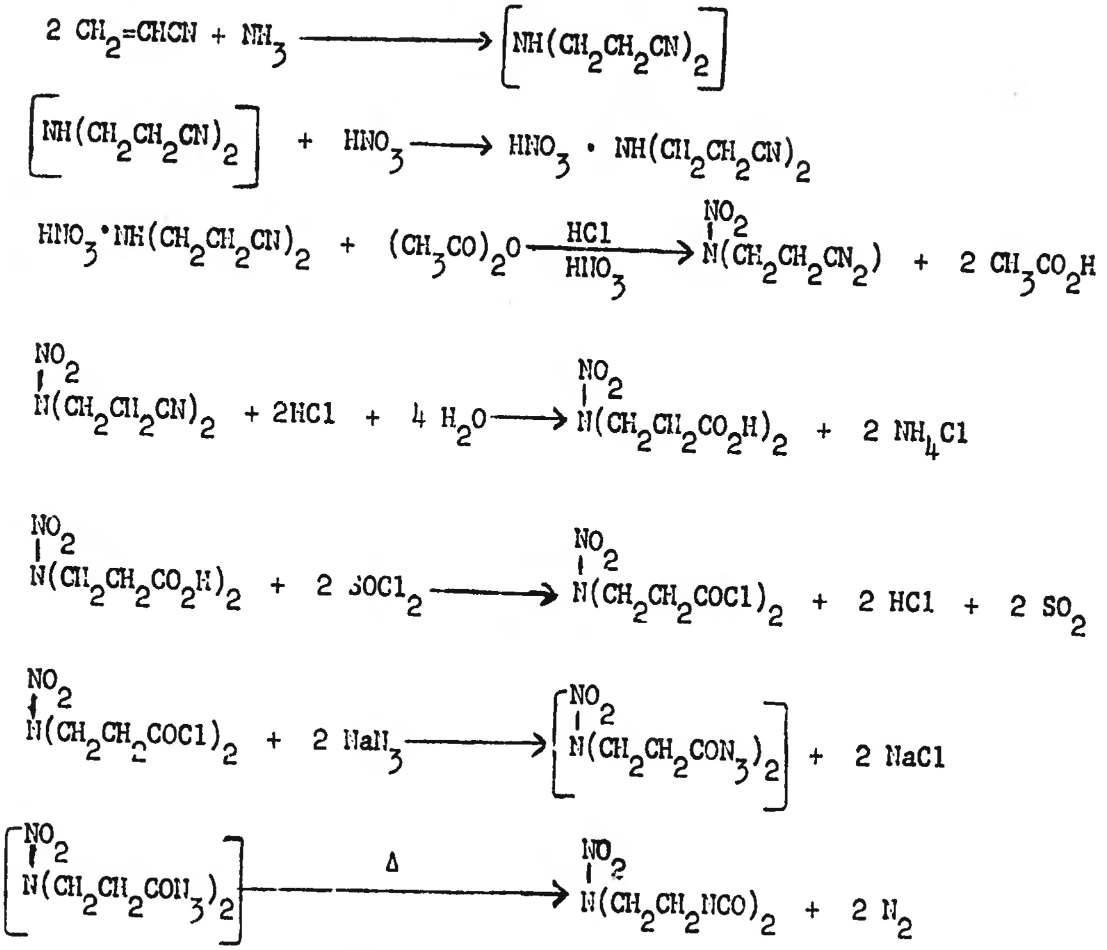
(1) Continuous process for production of 2-nitroethanol, using aqueous formaldehyde

(2) Improved purification technique for the isolation of 2-nitroethanol and 2-bromo-2-nitroethanol.

2. 3-Nitraza-1,5-pentane Diisocyanate

a. Discussion

3-Nitraza-1,5-pentane diisocyanate is one of the most promising diisocyanates developed on this program. The synthesis and reactions of this compound are discussed in paragraph II,B,4,b, and polymerization and formulation studies are found in paragraphs III,A and IV,B and IV,C. The preparation of this valuable nitromonomer from ammonia and acrylonitrile proceeds as follows:



$$2\,CH_2{=}CHCN + NH_3 \longrightarrow \left[NH(CH_2CH_2CN)_2\right]$$

$$\left[NH(CH_2CH_2CN)_2\right] + HNO_3 \longrightarrow HNO_3 \cdot NH(CH_2CH_2CN)_2$$

$$HNO_3{\cdot}NH(CH_2CH_2CN)_2 + (CH_3CO)_2O \xrightarrow[HNO_3]{HCl} \overset{NO_2}{\overset{|}{N}}(CH_2CH_2CN_2) + 2\,CH_3CO_2H$$

$$\overset{NO_2}{\overset{|}{N}}(CH_2CH_2CN)_2 + 2HCl + 4\,H_2O \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2CO_2H)_2 + 2\,NH_4Cl$$

$$\overset{NO_2}{\overset{|}{N}}(CH_2CH_2CO_2H)_2 + 2\,SOCl_2 \longrightarrow \overset{NO_2}{\overset{|}{N}}(CH_2CH_2COCl)_2 + 2\,HCl + 2\,SO_2$$

$$\overset{NO_2}{\overset{|}{N}}(CH_2CH_2COCl)_2 + 2\,NaN_3 \longrightarrow \left[\overset{NO_2}{\overset{|}{N}}(CH_2CH_2CON_3)_2\right] + 2\,NaCl$$

$$\left[\overset{NO_2}{\overset{|}{N}}(CH_2CH_2CON_3)_2\right] \xrightarrow{\Delta} \overset{NO_2}{\overset{|}{N}}(CH_2CH_2NCO)_2 + 2\,N_2$$

This series of reactions, leading to the diisocyanate, was described in an early report (712, 50-52). Scale-up of these reactions to pilot-plant scale size was accomplished, using slight modifications of the laboratory procedures (907, 35-36). Yields, in most instances, were comparable with those obtained in the laboratory.

b. Di(β-cyanoethyl)-ammonium Nitrate

This compound was prepared by the addition of acrylonitrile to aqueous ammonia, followed by nitration of the intermediate, di-(β-cyanoethyl) [illegible] (90/, 35). Optimum yields were realized when a 100% excess of ammonia was used in the formation of the intermediate amine. After removal of the water and excess ammonia by distillation <u>in vacuo</u>, the crude amine was dissolved in methanol, and reacted with an equivalent quantity of 67% nitric acid to yield the crystalline di-(β-cyanoethyl)-ammonium nitrate. Yields are based on the starting material, acrylonitrile, and are very good for this two-step procedure.

c. Di(β-cyanoethyl)-nitramine

Di(β-cyanoethyl)-nitramine was prepared by the hydrochloric acid-catalyzed nitration of di(β-cyanoethyl)-ammonium nitrate. The concurrent addition of di-(β-cyanoethyl)-ammonium nitrate, a 20% excess of anhydrous nitric acid, and catalytic amounts of hydrochloric acid to an 80% excess of acetic anhydride gave maximum yields of the product (907, 35).

d. Di-(β-carboxyethyl)-nitramine

Di-(β-cyanoethyl)-nitramine was hydrolyzed in 31.45% hydrochloric acid solution to yield the corresponding di-(β-carboxyethyl)-nitramine. Direct conversion to pilot-plant scale was achieved, with high purity product being obtained in near-quantitative yields (907, 36).

e. 4-Nitraza-1,7-heptanedioyl Chloride

4-Nitraza-1,7-heptanedioyl chloride was prepared by the action of thionyl chloride on di-(β-carboxyethyl)-nitramine. The laboratory preparation was effected, using a large (250%) excess of thionyl chloride, with the latter serving as a solvent for the reaction (712, 52). However, for large-scale preparations, this method was unsatisfactory because of the problems involved in the recovery of the thionyl chloride. The scale-up of this reaction to pilot-plant size was accomplished by the use of a slight excess of thionyl chloride (50%) with chloroform employed as a solvent (907, 36). The use of catalytic amounts (ca. 0.1%) of pyridine served to reduce the reaction time. Prolonged heating of the reaction mixture or the use of excessive amounts of catalyst resulted in the formation of undesirable side-products (1083, 26). After isolation, the solvent-damp material could be utilized for the preparation of the corresponding diisocyanate (1083, 26). The yields from pilot-plant batches were approximately 10% lower than the quantitative conversion obtained on laboratory scale.

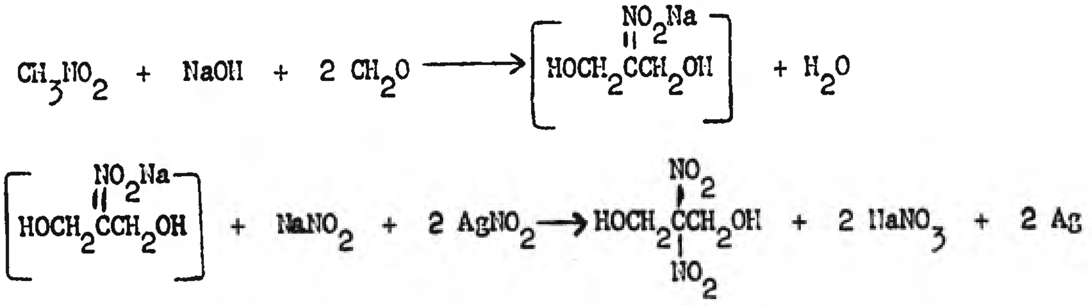
f. 3-Nitraza-1,5-pentane Diisocyanate

3-Nitraza-1,5-pentane diisocyanate was prepared by the initial reaction of 4-nitraza-1,7-heptanedioyl chloride and sodium azide with the subsequent rearrangement of the diazide to the diisocyanate. On a laboratory scale, this reaction was carried out by batch-wise rearrangement of the diazide (712, 53). However, this thermally initiated rearrangement was hazardous, and the reaction was accomplished on a pilot-plant scale by continuous addition of a cold, dry chloroform solution of the diazide to distilling chloroform. Using this procedure, the amount of diazide undergoing rearrangement during any given period in the reaction was minimized. The use of toluene as a crystallization solvent was initiated in order to avoid the use of large quantities of the more volatile and hazardous diethyl ether (907, 36). Preparations of 3-nitraza-1,5-pentane diisocyanate employing these modifications of the laboratory process resulted in high purity product, although yields were somewhat lower than the 75-85% yields attained in the laboratory. These lower yields were possibly due to the increased solubility of the diisocyanate in toluene.

3. 2,2-Dinitro-1,3-propanediol

a. Discussion

2,2-Dinitro-1,3-propanediol is valuable as an intermediate in the preparation of *gem*-dinitro compounds (paragraphs II,B and II,C and II,D) and as a monomer for polymerization studies (paragraph III,B). The use of the oxidative nitration reaction made the preparation of this compound possible from two commercially available materials: nitromethane and *tris*-(hydroxymethyl)-nitromethane. The more feasible process was the preparation from nitromethane, which proceeded according to the following equations:

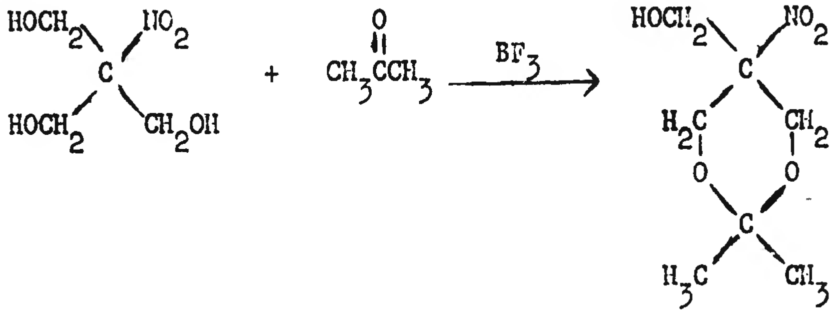


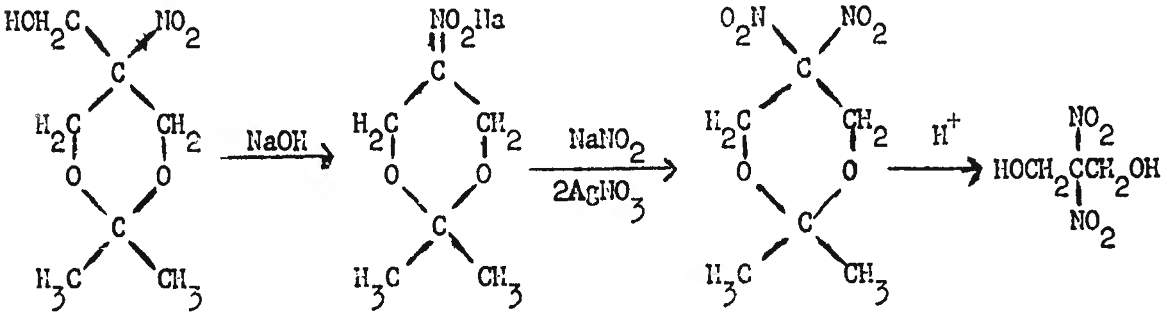
$$CH_3NO_2 + NaOH + 2\ CH_2O \longrightarrow \left[HOCH_2\overset{NO_2Na}{\overset{\|}{C}}CH_2OH\right] + H_2O$$

$$\left[HOCH_2\overset{NO_2Na}{\overset{\|}{C}}CH_2OH\right] + NaNO_2 + 2\ AgNO_2 \longrightarrow HOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OH + 2\ NaNO_3 + 2\ Ag$$

This process was outstanding because it was carried out in one step, without isolation of the intermediate sodium 2-nitro-1,3-propanediol. However, isolation and purification of the product was difficult, and an alternative process was studied on a pilot-plant scale for the preparation of high quality material.

It was known that high-purity 2,2-dinitro-1,3-propanediol could be prepared by the hydrolysis of 2,2-dimethyl-5,5-dinitro-1,3-dioxane (663, 73-74). This compound was prepared from tris-(hydroxymethyl)-nitromethane according to the following equations:





Laboratory investigations indicated that this process could be adapted to pilot-plant scale (686, 62-64). On a laboratory scale, overall yields were somewhat lower than those obtained by the aforementioned reaction, but pure diol was obtained after one recrystallization.

b. Preparation of 2,2-Dinitro-1,3-propanediol from Nitromethane

Crude 2,2-dinitro-1,3-propanediol was prepared on pilot-plant scale by the initial formation of sodium 2-nitro-1,3-propenadiol in situ, followed by the oxidative nitration reaction* (1004, 18). Silver losses were minimized by maintaining a 5% excess of sodium 2-nitro-1,3-propanediol during the reaction. After filtration of the silver, extraction of the product with ethyl acetate, concentration of the extracts, and prolonged cooling (-10°C), a crude, crystalline product was obtained. The yields shown in Table 40 are for crude material and do not represent losses incurred during subsequent laboratory purification. Additional product was present in the filtrates, which was treated with methyl acrylate to form methyl 4,4-dinitro-1,7-heptanedioate in low yield (1048, 23).

c. Preparation of 2,2-Dinitro-1,3-propanediol from tris-(Hydroxymethyl)-nitromethane

(1) Discussion

2,2-Dinitro-1,3-propanediol was prepared by the hydrolysis of 2,2-dimethyl-5,5-dinitro-1,3-dioxane, which was obtained by the oxidative nitration of 2,2-dimethyl-5-nitro-5-hydroxymethyl-1,3-dioxane. The preparation of the intermediates was accomplished on pilot-plant scale, but the subsequent hydrolysis was carried out in the laboratory. Although higher quality diol was obtained using this method, it was more laborious, and excessive silver losses were experienced during the oxidative nitration reaction.

(2) 2,2-Dimethyl-5-nitro-5-hydroxymethyl-1,3-dioxane

tris-(Hydroxymethyl)-nitromethane was treated with acetone in the presence of an equivalent amount of boron trifluoride. The conversion of this process to that of the pilot plant resulted in yields comparable with previous laboratory work (907, 38).

(3) 2,2-Dimethyl-5,5-dinitro-1,3-dioxane

2,2-Dimethyl-5,5-dinitro-1,3-dioxane was prepared by the deformylation and oxidative nitration of 2,2-dimethyl-5-nitro-5-hydroxymethyl-1,3-dioxane (907, 39), using a direct scale-up of the laboratory procedure (686, 64). Yields were much lower than those obtained

---

*Aeroplex Report No. 632, Vol I, Section V, p. 125.

from laboratory experiments; 40% as compared with 70%. In addition, work-up of the reaction mixture was laborious because of fine silver, which was difficult to filter. Excessively high losses of silver were encountered during the reaction, which made this process unattractive for continued use (1004, 18).

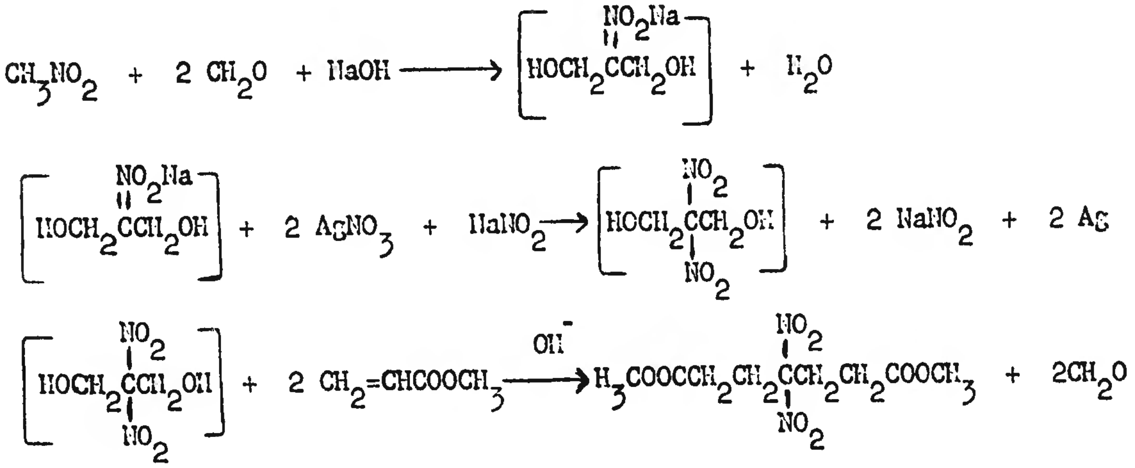
d. Conclusions and Recommendations

The preparation of 2,2-dinitro-1,3-propanediol from nitromethane is superior from the economic viewpoint due to (1) higher yields, (2) less manpower requirements, and (3) lower silver losses. However, the material obtained by this procedure is difficult to purify, and if extensive purification of the diol is to be avoided, the preparation from tris-(hydroxymethyl)-nitromethane is the preferred process.

4. 3,3-Dinitro-1,5-pentane Diisocyanate

a. Discussion

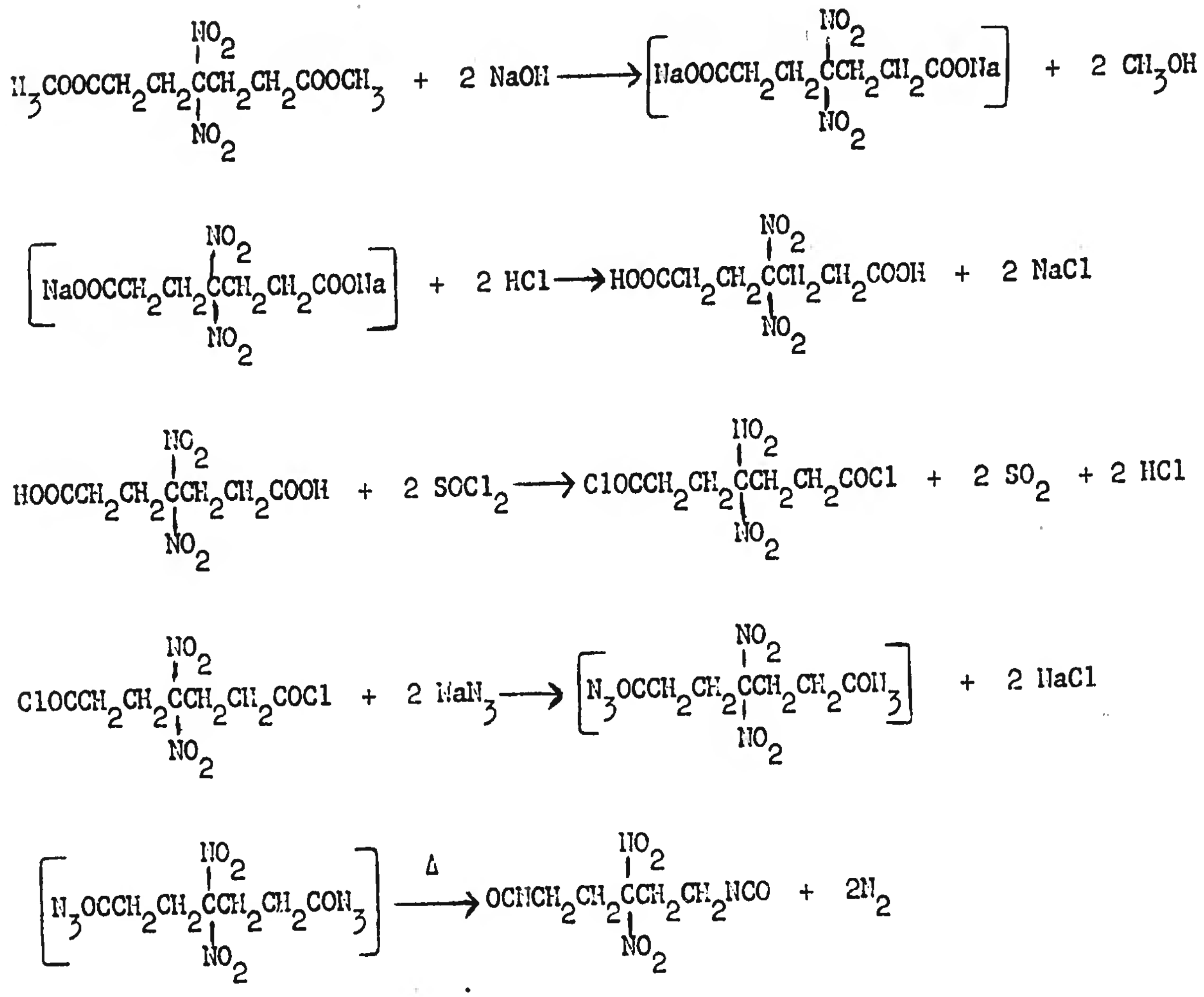
3,3-Dinitro-1,5-pentane diisocyanate is another important diisocyanate developed on this program. The preparation of this compound is discussed in paragraph II,B,3,b, and its uses as a monomer in polymerization and formulation studies are described in paragraphs III.B and IV,B,3. Pilot-plant preparation, using nitromethane as a starting material, involved the following reactions.



$$CH_3NO_2 + 2\ CH_2O + NaOH \longrightarrow \left[HOCH_2\overset{NO_2Na}{\overset{\|}{C}}CH_2OH\right] + H_2O$$

$$\left[HOCH_2\overset{NO_2Na}{\overset{\|}{C}}CH_2OH\right] + 2\ AgNO_3 + NaNO_2 \longrightarrow \left[HOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OH\right] + 2\ NaNO_2 + 2\ Ag$$

$$\left[HOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2OH\right] + 2\ CH_2{=}CHCOOCH_3 \xrightarrow{OH^-} H_3COOCCH_2CH_2\underset{NO_2}{\overset{NO_2}{C}}CH_2CH_2COOCH_3 + 2CH_2O$$



$$H_3COOCCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2COOCH_3 + 2\ NaOH \longrightarrow \left[NaOOCCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2COONa\right] + 2\ CH_3OH$$

$$\left[NaOOCCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2COONa\right] + 2\ HCl \longrightarrow HOOCCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2COOH + 2\ NaCl$$

$$HOOCCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2COOH + 2\ SOCl_2 \longrightarrow ClOCCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2COCl + 2\ SO_2 + 2\ HCl$$

$$ClOCCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2COCl + 2\ NaN_3 \longrightarrow \left[N_3OCCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CON_3\right] + 2\ NaCl$$

$$\left[N_3OCCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CON_3\right] \xrightarrow{\Delta} OCNCH_2CH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2NCO + 2N_2$$

Initial preparation of this compound involved the use of potassium 2,2-dinitroethanol (V,B,1,e) for the preparation of the intermediate 2,2-dinitro-1,3-propanediol. The discovery of the oxidative nitration method for the preparation of this compound (468, 27-28) and its reaction in situ with methyl acrylate made possible the large-scale preparation of the intermediate, methyl 4,4-dinitro-1,7-heptanedioate.* Succeeding preparations of the corresponding diacid* and acid chloride were also successfully accomplished on pilot-plant scale (907, 37-38; 941, 26). However, attempts to scale-up the preparation of the diisocyanate were unsuccessful because of difficulties encountered in the isolation of the product (967, 25-26; 1004, 18; 1048, 23; 1083, 25).

---

*Aerojet Report No. 622, Part V, p. 122.

b. Methyl 4,4-Dinitro-1,7-heptanedioate

Methyl 4,4-dinitro-1,7-heptanedioate was prepared from nitromethane in three steps. The first step involved the preparation of 2,2-dinitro-1,3-propanediol, using the oxidative nitration reaction. The diol was not isolated following the removal of the metallic silver but was deformylated to dinitromethane and combined with an excess of methyl acrylate to form the desired ester. Best results were achieved when the methyl acrylate was maintained in 15% excess, based on nitromethane. The use of this procedure resulted in higher yields than were anticipated on the basis of previous laboratory preparations.

c. 4,4-Dinitro-1,7-heptanedioic Acid

4,4-Dinitro-1,7-heptanedioic acid was obtained by the addition of equivalent amounts of 50% sodium hydroxide solution to a methanol solution of methyl 4,4-dinitro-1,7-heptanedioate. Acidification of the reaction mixture, using a 5% excess of 31.45% hydrochloric acid, yielded the 4,4-dinitro-1,7-heptanedioic acid* (907, 38). The yields, averaging 70%, are somewhat lower than quantitative, laboratory-established yields, using an acidic hydrolysis with refluxing hydrochloric acid (461, 28). However, the use of the basic hydrolysis permitted the preparation of larger quantities of material with available equipment. Recrystallization of the crude acid from boiling water (3:1 weight ratio of water to acid) including treatment with "Nuchar" carbon black (1.5% by weight of acid), resulted in 95% recovery of purified acid (1048, 23).

d. 4,4-Dinitro-1,7-heptanedioyl Chloride

4,4-Dinitro-1,7-heptanedioyl chloride was obtained by the pyridine-catalyzed action of thionyl chloride on 4,4-dinitro-1,7-heptanedioic acid. The pilot-plant preparation was effected in the same manner as was used for the preparation of 4-nitraza-1,7-heptanedioyl chloride. Near-quantitative conversion of the acid was obtained with initial pilot-plant preparations (941, 26). Purification of later materials by recrystallization from chloroform, following a treatment with "Carbolac" carbon black, resulted in lower yields (1048, 23).

---

*Aerojet Report No. 622, Part V, p. 122.

e. 3,3-Dinitro-1,5-pentane Diisocyanate

This diisocyanate was prepared from 4,4-dinitro-1,7-heptanedioyl chloride by rearrangement of the intermediate diazide (967, 25-26). Extensive laboratory investigations resulted in a satisfactory procedure that was adapted to pilot-plant scale (686, 70). As with the aforementioned preparation of 3-nitraza-1,5-pentane diisocyanate (V,B,2,f), the rearrangement of the diazide was accomplished by portionwise addition of a chloroform solution of the diazide to distilling chloroform. Crystallization of the diisocyanate, after removal of the chloroform in vacuo, was accomplished using toluene as a solvent. In all cases, the isolation of the compound was difficult due to finely crystalline product, and low yields were obtained. Substitution of ether as a solvent (1004, 18) and/or purification of the intermediates (1048, 23-24) failed to improve the isolation, purity, or yield of product.

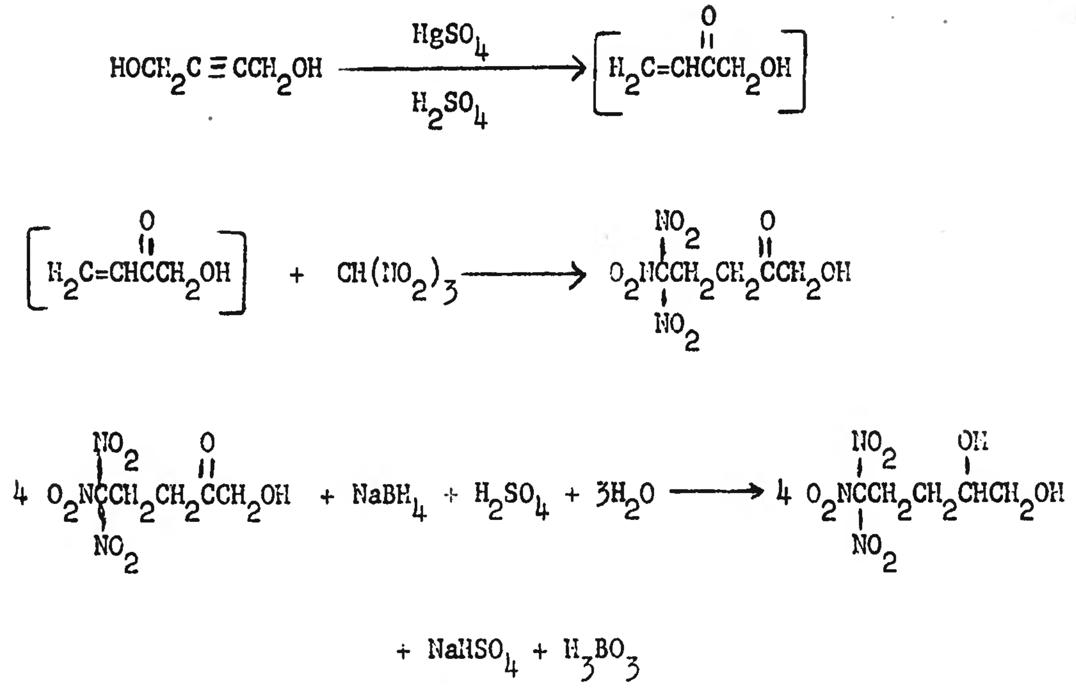
f. Conclusions and Recommendations

Inasmuch as numerous successful preparations of the diisocyanate were carried out on laboratory scale, it is believed that the basic process is sound. However, due to the low yields and difficulties of isolation of product, the preparation has been discontinued, on pilot-plant scale, until a re-evaluation of the process can be carried out in the laboratory (1083, 25).

5. 5,5,5-Trinitro-1,2-pentanediol

a. Discussion

The high-energy diol, 5,5,5-trinitro-1,2-pentanediol, is the only nitroform derivative adapted to pilot-plant scale on this program. The initial laboratory preparation and subsequent reactions of this compound are discussed in paragraph II,D,2,b,(5). This compound was utilized in polymerization and formulation studies. Results of these studies are in paragraphs III,B and IV,B. The preparation of this compound proceeds as follows:



$$HOCH_2C\equiv CCH_2OH \xrightarrow[H_2SO_4]{HgSO_4} \left[H_2C{=}CH\overset{\overset{\displaystyle O}{\|}}{C}CH_2OH\right]$$

$$\left[H_2C{=}CH\overset{\overset{\displaystyle O}{\|}}{C}CH_2OH\right] + CH(NO_2)_3 \longrightarrow O_2N\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2OH$$

$$4\ O_2N\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2OH + NaBH_4 + H_2SO_4 + 3H_2O \longrightarrow 4\ O_2N\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2\overset{OH}{C}HCH_2OH$$

$$+ NaHSO_4 + H_3BO_3$$

This procedure involved the initial formation of hydroxymethyl vinyl ketone, followed by the Michael addition of nitroform to the ketone, to produce the 5,5,5-trinitro-2-keto-1-pentanol. After isolation, this latter compound was reduced to the corresponding diol (515, 4-5; 540, 38-40).

Although the diol and the intermediate keto-alcohol were quite stable, the synthesis required the isolation of hazardous potassium nitroform (prepared from tetranitromethane) as an intermediate step in the preparation of nitroform. However, concurrent with initial pilot-plant runs, a method was developed for the preparation of nitroform *in situ* (1083, 31-32).

b. 5,5,5-Trinitro-2-keto-1-pentanol

The preparation of 5,5,5-trinitro-2-keto-1-pentanol involved the initial isomerization of 1,4-butynediol, in aqueous solution, using mercuric sulfate and sulfuric acid as catalysts, at an elevated temperature (50-52°C). The resulting solution of hydroxymethyl vinyl ketone was then added to an aqueous solution of nitroform. The product was isolated by extraction and crystallization techniques (515, 4-5).

For initial pilot-plant runs, the intermediate preparation of potassium nitroform was carried out in a series of small laboratory reactors. After isolation, the products were combined and acidified with dilute sulfuric acid to yield nitroform (1083, 26-27). In succeeding preparations, nitroform was prepared in situ, using a modified process (1083, 31-33). The latter involved the acidification of potassium nitroform, in the original reaction mixture, with a mixture of sulfamic and sulfuric acids. The sulfamic acid served to stabilize the reaction mixture by destroying nitrous acid, thus avoiding the possible formation of unstable nitroso-nitroform.

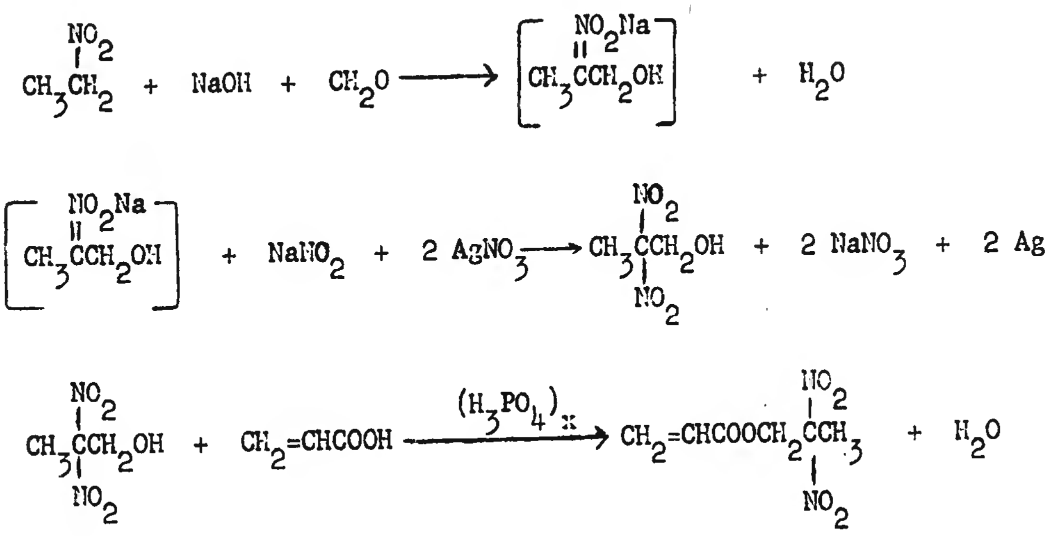
c. 5,5,5-Trinitro-1,2-pentanediol

5,5,5-Trinitro-1,2-pentanediol was prepared on pilot-plant scale (1083, 27) by a direct scale-up of the laboratory procedure (563, 61-63). This method involved the addition of aqueous sodium borohydride solution to a methanol solution of 5,5,5-trinitro-2-keto-1-pentanol, while maintaining the pH of the reaction mixture at 3 to 4 by the simultaneous addition of dilute (5N) sulfuric acid. After extraction with methylene chloride and concentration of the extracts in vacuo, the diol was obtained in crystalline form. Reported average yields (Table 1) are for thrice-crystallized product. A reduction in the amount of sodium borohydride, from 100% excess to equivalent amounts, had no adverse effect on the good yields obtained for this reaction.

6. 2,2-Dinitro-1-propyl Acrylate

a. Discussion

2,2-Dinitro-1-propyl acrylate is the most promising vinyl-type monomer developed on this program. Methods of preparation and polymerization studies of this compound are discussed in paragraphs II,A,3,e and III,A,2,c. The method selected for pilot-plant study involved the preparation of 2,2-dinitro-1-propanol and the subsequent esterification with acrylic acid. The series of reactions leading to 2,2-dinitro-1-propyl acrylate are as follows:



$$\overset{NO_2}{\overset{|}{CH_3CH_2}} + NaOH + CH_2O \longrightarrow \left[CH_3\overset{NO_2Na}{\overset{\|}{C}}CH_2OH \right] + H_2O$$

$$\left[CH_3\overset{NO_2Na}{\overset{\|}{C}}CH_2OH \right] + NaNO_2 + 2\,AgNO_3 \longrightarrow CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2OH + 2\,NaNO_3 + 2\,Ag$$

$$CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2OH + CH_2{=}CHCOOH \xrightarrow{(H_3PO_4)_x} CH_2{=}CHCOOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_3 + H_2O$$

In the pilot-plant scale-up of most processes, the product yields were of major importance, but the prime concern in the above method was the purity of the product, 2,2-dinitropropyl acrylate. High-purity monomer, for use in polymerization studies, is defined as monomer which, after polymerization, yields a high-molecular-weight, acetone-soluble polymer, indicating the absence of polymerization retarders or cross-linking contaminants. Such material was obtained by purification of the intermediate, 2,2-dinitro-1-propanol, and/or final purification of the acrylate.

b. 2,2-Dinitro-1-propanol

(1) Discussion

2,2-Dinitro-1-propanol was prepared by a variety of methods (paragraph II,D,2,a,(3)). The two outstanding methods selected for process studies were (1) the oxidative nitration reaction using sodium 2-nitro-1-propanol and (2) the ter Meer reaction using 1-chloro-1-nitromethane. The oxidative nitration procedure was utilized for large-scale preparation of this compound.*, ** Its major disadvantage was the necessary purification of the crude alcohol. The alternate method, the ter Meer reaction, offers the advantage of a low-cost preparation by the elimination of the purification procedure.

---

*Process Development of 2,2-Dinitropropyl Acrylate, LAMS 1974.

**Aerojet Report No. 649, Part V, pp. 173-180.

(2) 2,2-Dinitropropanol by the Oxidative Nitration Reaction

2,2-Dinitropropanol was prepared from nitroethane by the initial formation of sodium 2-nitro-1-propanol in situ, followed by the oxidative nitration reaction. The compound was isolated by extraction with ethyl acetate or ethylene dichloride, and the extracts were concentrated by vacuum distillation techniques. This crude concentrate was of sufficient purity for use in reactions other than the preparation of 2,2-dinitropropyl acrylate which required a purified alcohol. High purity material was achieved by the deformylation of the crude 2,2-dinitropropanol to potassium 1,1-dinitroethane and reformation of 2,2-dinitropropanol by the addition of formaldehyde and sulfuric acid. The pure compound was obtained by extraction and concentration of the extracts. The concentrate was cooled for 18-24 hr (-10°C), and the crystalline 2,2-dinitropropanol was removed by filtration. The use of toluene as a selective solvent for 2,2-dinitropropanol was shown by another investigator.* It was reported that material obtained with this solvent did not require purification before conversion to the 2,2-dinitro-1-propyl acrylate. This procedure is currently being investigated on this program.

(3) 2,2-Dinitropropanol by the ter Meer Reaction

Although 2,2-dinitropropanol was not prepared on a pilot-plant scale by means of the ter Meer reaction** (II,D,2,j), a discussion of laboratory studies is included in this section, because of the possible future use of this procedure. The ter Meer process involved the preparation of 1,1-dinitroethane from 1-chloro-1-nitroethane, potassium carbonate, and potassium nitrite, followed by the addition of aqueous formaldehyde to yield 2,2-dinitropropanol (1119, 26-27). The isolation of the product was accomplished in the manner described in the preceding paragraph. In two runs, conflicting data were obtained with regard to the

---

*Process Development of 2,2-Dinitropropyl Acrylate, LAMS 1974.
**V.E. ter Meer, Ann. 181, 4 (1876).

quality of the alcohol. From one run, acceptable 2,2-dinitropropyl acrylate was obtained after esterification of the alcohol with acrylic acid. However, with the second run, purification of the alcohol was necessary before satisfactory ester was obtained.

c. 2,2-Dinitro-1-propyl Acrylate

The pilot-plant preparation of 2,2-dinitropropyl acrylate was effected by direct esterification of acrylic acid with purified 2,2-dinitropropanol in polyphosphoric acid solution using a 5% excess of acrylic acid. After a short reaction period, the mixture was quenched in water-ice, the ester was extracted with benzene, and the extracts were washed with dilute aqueous solutions of sodium hydroxide and sodium bisulfite. The benzene solution was next dried over sodium sulfate, concentrated in vacuo to about one-fourth the original volume, and treated with magnesium oxide. After removal of the magnesium oxide by filtration, the remaining solvent was removed by vacuum distillation.

Material processed in this manner has, in all cases, produced high-quality polymer. Average yields are higher than for ester obtained by vacuum-steam distillation or by normal vacuum distillation techniques (1048, 18-19). In some cases, magnesium oxide-purified acrylate has retained some methylene blue inhibitor which resulted in a longer induction period for polymerization (1048, 20). The average yields shown in Table 40 are not indicative of yields currently being obtained for this reaction. An average yield of 75% is now realized.

d. Conclusions and Recommendations

High yields of acceptable 2,2-dinitro-1-propyl acrylate were obtained by the above esterification procedure. With few exceptions, the yields and the quality of the 2,2-dinitropropyl acrylate were reproducible.

The use of unpurified 2,2-dinitropropanol, prepared by either the ter Meer reaction or toluene extraction in the oxidative-nitration reaction, would make this process even more attractive, due to the high cost of the present purification procedure.

7. 2-Nitro-2-methyl-1,3-propanediol

a. Discussion

2-Nitro-2-methyl-1,3-propanediol is a commercially available nitromonomer which has been used on this program in polymerization (paragraph III,B) and formulation (paragraph IV,B) studies. The commercially available material is contaminated with tris-(hydroxymethyl)-nitromethane, which prohibits the use of such material, since high-molecular-weight, linear nitropolyurethanes are nonattainable in the presence of the triol. Removal of this impurity was effected by conversion of the diol to the corresponding ketal, 2,2,5-trimethyl-5-nitro-1,3-dioxane, and reformation of the diol by hydrolysis, using a direct scale-up of the laboratory procedures (686, 60-61; 638, 80). However, pilot-plant preparations resulted in the introduction of another impurity into the compound. This impurity evidenced itself as a vigorous catalyst in subsequent polymerizations, when incontrollable rates were encountered (907, 39-40). In a further search for a satisfactory method of removing the cross-linking impurity from commercially available 2-nitro-2-methyl-1,3-propanediol, laboratory work revealed that two recrystallizations of the diol from water gave a pure material, in 40 to 50% recovery, with no trace of crosslinking agent (941, 31-32).

b. 2,2,5-Trimethyl-5-nitro-1,3-dioxane

2,2,5-Trimethyl-5-nitro-1,3-dioxane was prepared by the addition of acetone to 2-nitro-2-methyl-1,3-propanediol in the presence of boron trifluoride. Neutralization of the boron trifluoride was effected by pumping the reaction mixture into a cold aqueous solution of trisodium phosphate. The ketal was purified by recrystallization from hot acetone. The low yields obtained were possibly due to this purification procedure (907, 39).

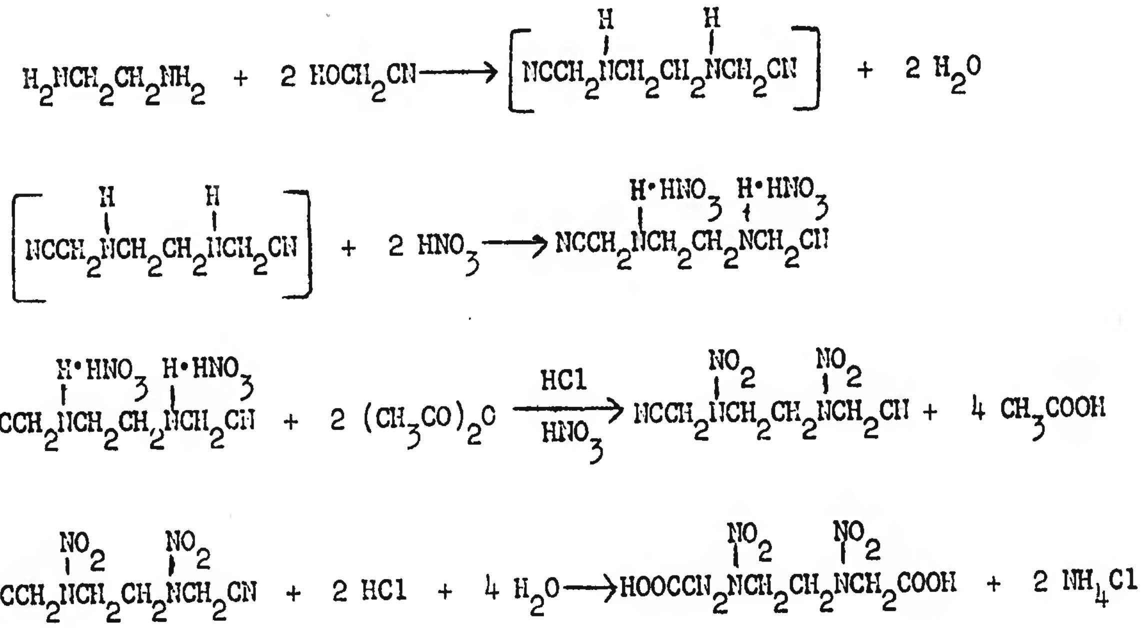
c. 2-Nitro-2-methyl-1,3-propanediol

The hydrolysis of 2,2,5-trimethyl-5-nitro-1,3-dioxane to 2-nitro-2-methyl-1,3-propanediol was carried out in a heterogeneous water and ethylene dichloride mixture, at reflux temperature, in the presence of catalytic amounts of trifluoroacetic acid. After recrystallization from ethylene dichloride, the diol was obtained in quantitative yields (907, 40).

8. 3,6-Dinitraza-1,8-octanedioc Acid

a. Discussion

3,6-Dinitraza-1,8-octanedioc acid is used as an intermediate in the synthesis of 2,5-dinitraza-1,6-hexane diisocyanate. The acid is prepared from ethylene diamine and glycolonitrile by the following reactions:



$$H_2NCH_2CH_2NH_2 + 2\ HOCH_2CN \longrightarrow \left[NCCH_2\overset{H}{N}CH_2CH_2\overset{H}{N}CH_2CN\right] + 2\ H_2O$$

$$\left[NCCH_2\overset{H}{N}CH_2CH_2\overset{H}{N}CH_2CN\right] + 2\ HNO_3 \longrightarrow NCCH_2\overset{H\cdot HNO_3}{N}CH_2CH_2\overset{H\cdot HNO_3}{N}CH_2CN$$

$$NCCH_2\overset{H\cdot HNO_3}{N}CH_2CH_2\overset{H\cdot HNO_3}{N}CH_2CN + 2\ (CH_3CO)_2O \xrightarrow[HNO_3]{HCl} NCCH_2\overset{NO_2}{N}CH_2CH_2\overset{NO_2}{N}CH_2CN + 4\ CH_3COOH$$

$$NCCH_2\overset{NO_2}{N}CH_2CH_2\overset{NO_2}{N}CH_2CN + 2\ HCl + 4\ H_2O \longrightarrow HOOCCH_2\overset{NO_2}{N}CH_2CH_2\overset{NO_2}{N}CH_2COOH + 2\ NH_4Cl$$

The reactions closely parallel those used for the preparation of di-(β-carboxyethyl)-nitramine (V,B,2,a) and 4-nitrazapentanoic acid (V,C,1,a).

b. bis-Nitric Acid Salt of 3,6-Diaza-1,8-octane Dinitrile

3,6-Diaza-1,8-octane dinitrile was obtained by the condensation of ethylene diamine and glyconitrile. The crude diaza compound was formed in situ and treated with a 10% excess of 67% nitric acid to yield the corresponding bis-nitric acid salt of 3,6-diaza-1,8-octane dinitrile (1004, 19). The reported yield shown in Table 40 is for this two-step process.

c. 3,6-Dinitraza-1,8-octane Dinitrile

The conversion of the bis-nitric acid salt of 3,6-diaza-1,8-octane dinitrile to 3,6-dinitraza-1,8-octane dinitrile was effected by a hydrochloric acid-catalyzed nitration in acetic acid-anhydrous nitric acid. The concurrent, portion-wise addition of the hydrochloric acid, nitric acid, and the nitric acid salt to the acetic anhydride was incorporated into the process to prevent excessive loss of the volatile catalyst. After quenching the reaction mixture in water, the product was obtained in fine crystalline form (1004, 19).

d. 3,6-Dinitraza-1,8-octanedioc Acid

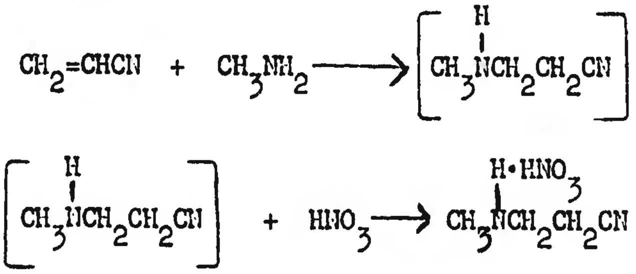
3,6-dinitraza-1,8-octane dinitrile was hydrolyzed in 31.45% hydrochloric acid to yield 3,6-dinitraza-1,8-octanedioc acid. This process was not satisfactory, because of the large amounts of foaming which occurred during the decomposition of the intermediate imino hydrochloride, requiring the use of a reaction vessel that had a capacity several times the volume of the original reaction mixture (1004, 19).

C. NITROPLASTICIZERS

1. 2,2-Dinitropropyl 4-Nitrazapentanoate

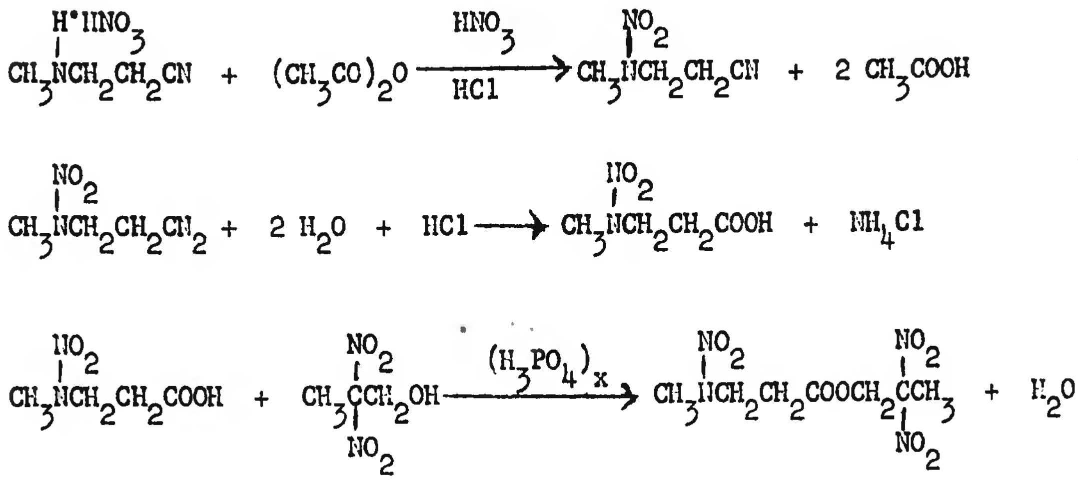
a. Discussion

2,2-Dinitropropyl 4-nitrazapentanoate is a nitroester which was prepared on this program (paragraph II,E,2,b) for use as a high-energy plasticizer in formulation studies (paragraph IV,B). The ester was prepared from acrylonitrile and methylamine by the following series of reactions:



$$CH_2{=}CHCN + CH_3NH_2 \longrightarrow \left[CH_3\overset{H}{N}CH_2CH_2CN \right]$$

$$\left[CH_3\overset{H}{N}CH_2CH_2CN \right] + HNO_3 \longrightarrow CH_3\overset{H\cdot HNO_3}{N}CH_2CH_2CN$$



$$CH_3\overset{H\cdot HNO_3}{N}CH_2CH_2CN + (CH_3CO)_2O \xrightarrow[HCl]{HNO_3} CH_3\overset{NO_2}{N}CH_2CH_2CN + 2\ CH_3COOH$$

$$CH_3\overset{NO_2}{N}CH_2CH_2CN_2 + 2\ H_2O + HCl \longrightarrow CH_3\overset{NO_2}{N}CH_2CH_2COOH + NH_4Cl$$

$$CH_3\overset{NO_2}{N}CH_2CH_2COOH + CH_3\underset{NO_2}{\overset{NO_2}{C}}CH_2OH \xrightarrow{(H_3PO_4)_x} CH_3\overset{NO_2}{N}CH_2CH_2COOCH_2\underset{NO_2}{\overset{NO_2}{C}}CH_3 + H_2O$$

The initial preparation of intermediates leading to 4-nitrazapentanoic acid was carried out in these laboratories under another contract.* This series of reactions was, in many respects, analogous to the reactions used in the preparation of 4-nitraza-1,7-heptanedioic acid (V,B,2,a). Process studies of the intermediate 2,2-dinitro-1-propanol were discussed elsewhere in this section (V,B,6,b).

b. Nitric Acid Salt of 4-Azapentanonitrile

4-Azapentanonitrile was prepared by the Michael reaction of an 11% excess of aqueous monomethylamine (40%) and acrylonitrile. The compound was not isolated, but after removal of the water by distillation in vacuo and dissolution in methanol, it (the compound) was converted to the corresponding nitric acid salt by the addition of a 20% excess of anhydrous nitric acid. The average yield (Table 40) was based on the two-step process, indicating an average yield of 85% for each step.

c. 4-Nitrazapentanonitrile

4-Nitrazapentanonitrile was prepared by the hydrochloric acid-catalyzed nitration of the nitric acid salt of 4-azapentanonitrile. The quantities of reactants and the reaction conditions paralleled those used in preparation of di-(β-cyanoethyl)-nitramine (paragraph V,B,2,6). However, the product was not crystalline and isolation was accomplished by extraction with methylene chloride. These extracts were washed with sodium bicarbonate solution and were concentrated by distillation in vacuo.

---

*Aerojet Report No. 801, Contract N7onr-46203, pp. 12-13.

d. 4-Nitrazapentanoic Acid

4-Nitrazapentanoic acid was obtained by the hydrolysis of 4-nitrazapentanonitrile in 31.45% hydrochloric acid solution. After removal of the precipitated ammonium chloride, the reaction mixture was extracted with methylene chloride in a continuous, liquid-liquid extractor (1004, 19). Simple extraction or crystallization techniques were not applicable for separation of the 4-nitrazapentanoic acid, because of its high solubility in hydrochloric acid (967, 26-30). Initial yields were low, indicating incomplete extraction of product (1004, 19). An extension of the extraction times has resulted in a large increase in yields (unpublished).

e. 2,2-Dinitropropyl 4-Nitrazapentanoate

2,2-Dinitropropyl 4-nitrazapentanoate was prepared by the addition of 2,2-dinitropropanol to equivalent quantities of 4-nitrazapentanoic acid in polyphosphoric acid solution. After a reaction period of 2 hr at 80°C, the reaction mixture was quenched in a water-ice mixture, and the resultant crystals were washed repeatedly with water, followed by crystallizations from methanol. Prior to crystallization, the methanolic solutions were treated with "Nuchar" and "Carbolac" carbon blacks.

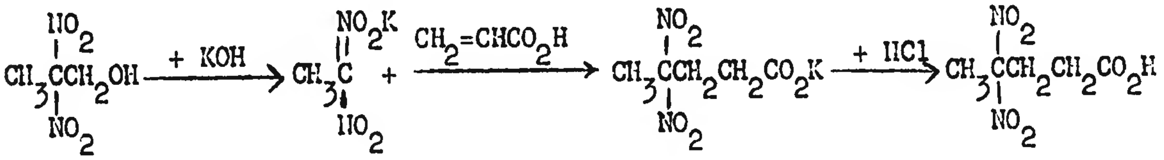
This procedure was a direct scale-up of the optimum conditions found on laboratory scale (1048, 25). However, attempts to increase the batch size, using laboratory equipment, resulted in low yields of product (1083, 27). The high yields obtained in the pilot plant were attributed to more efficient stirring of the viscous, heterogeneous reaction mixture (1083, 26).

2. Methyl 4-Nitrazapentanoate

Methyl 4-nitrazapentanoate was one of the first nitraza compounds which showed promise as a nitro plasticizer (paragraph IV,E). This compound was prepared by the methanolysis of 4-nitrazapentanonitrile in the presence of concentrated sulfuric acid. The crude ester was obtained by extraction of the diluted reaction mixture, and the excess solvent was removed by distillation at reduced pressure. Purification of the material was carried out on laboratory scale (907, 42). Average yields (Table 402) were based on the nitric acid salt of 4-azapentanonitrile which had been used in preparing the 4-nitrazapentanonitrile.

3. 4,4-Dinitropentanoic Acid

4,4-Dinitropentanoic acid was prepared as an intermediate in the preparation of nitroplasticizers (paragraph II,E,3). This compound was prepared from 2,2-dinitropropanol and acrylic acid by the following series of reactions.



$$CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2OH \xrightarrow{+\ KOH} CH_3\overset{NO_2K}{\underset{NO_2}{C}} + \xrightarrow{CH_2=CHCO_2H} CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2K \xrightarrow{+\ HCl} CH_3\overset{NO_2}{\underset{NO_2}{C}}CH_2CH_2CO_2H$$

The reactions involved the initial preparation of potassium 1,1-dinitroethane by the addition of aqueous potassium hydroxide to a methanol solution of 2,2-dinitropropanol. After isolation, the potassium dinitroethane was slurried with water and combined with a 10% excess of acrylic acid, at an elevated temperature (40-45°C), for 3 to 5 hr. The free 4,4-dinitropentanoic acid was obtained by acidification of the reaction mixture with a 10% excess of 31.45% hydrochloric acid solution (1004, 19).

D. NITROPOLYMERS

1. Polyurethanes

The preparation of nitropolyurethanes was studied on pilot-plant scale in order to solve many problems that were either not encountered, or were of small importance on laboratory-scale preparations. This study was conducted using the techniques developed in the laboratory (paragraph III,B) and a Beken dispersion-blade mixer (paragraph V,E). In Table 41 are shown the various types of polyurethanes, both linear and branched, that were selected for this study.

In early runs, extended addition times of the diisocyanate solution to the diol-catalyst mixture were adapted to allow the heat of reaction, 52 kcal/mole for formation of the urethane linkage, to be removed and to prevent overheating of the reaction mixture (807, 23). In later runs, the addition time was reduced to 0.25 hr, and the reaction temperature easily was maintained by judicious use of the heat exchange system (907, 43).

The use of laboratory pilot batches for the determination of the monomer equivalence to be used for the larger Beken batch was satisfactory for preparations of branched polyurethanes (833, 33-36). However, this method failed when used for the preparation of linear polymers. The linear polymers required additional adjustments to reach monomer equivalence, and the mix periods were much longer before high-molecular-weight polymers were attained (868, 46).

An efficient means of following the rate of polymerization in the mixer was needed in order to know when to terminate the reaction. Methods studied included the use of an ammeter to measure the load on the motor during stirring (807, 24), infrared spectrophotometry to measure disappearance of (-OH) or (-NCO) groups (868, 46), solution viscosity measurements of a diluted sample (833, 35), and solution viscosity measurements of the mix. Due to its ease and simplicity, the latter method proved to be most satisfactory (907, 43).

The use of benzene as a heterogeneous solvent for the reaction mixture was studied in an attempt to produce a fine granular polymer which could easily be removed from the reaction mixture. All polymer processed with this method had unfavorable physical characteristics (low-molecular-weight, insoluble material), and considerable difficulties were encountered during the polymerizations (833, 34). Purified dioxane or acetone proved to be the best solvents for all systems studied on this scale. Optimum monomer concentration was 50 wt%, but batches with monomer concentrations of 75 wt% were carried out (807, 23). An attempt to use technical-grade acetone as a solvent resulted in a low-molecular-weight polymer (941, 27).

For use in formulation studies, the complete removal of solvent from the polymer was essential. Attempts to leach out the reaction solvent, using a second solvent in which the polymer was insoluble, were unsuccessful (868, 46-47). The solvent was incompletely removed when the reaction mixture was rolled on a heated roller mill, also (833, 34). The greatest success was attained when the crude polymer was diluted with acetone to a concentration of 2-5% and precipitated into water, using the Morehouse mill (paragraph V,E). However, polymer processed in this manner required a long drying period for complete removal of the water (868, 47; 907, 45).

The reproducibility and uniformity of the polymers were determined by physical measurements and thermal-stability tests. In general, with both the linear and branched polymers, these tests have shown that the physical properties of the products were reproducible, although the reaction time and equivalence factors differed from batch to batch.

2. Polyacrylates

The emulsion polymerization of 2,2-dinitropropyl acrylate was accomplished in the Beken mixer, using a direct scale-up of laboratory procedures (868, 5). The 65% conversion of monomer to polymer was lower than the near-quantitative conversion obtained on laboratory scale. The lower yield was possibly due to the stainless-steel reaction vessel, inasmuch as an excess of ferrous ion was known to suppress the conversion. However, the relative viscosity of the polymer was comparable with the values obtained from laboratory-prepared polymers.

No difficulties in operational techniques were encountered, but the isolation of the polymer was very laborious and time-consuming, and a suitable workup method which would reduce the numerous steps would be desirable (907, 46-47).

E. FACILITIES

Conversion of a laboratory preparation to pilot-plant scale required suitable equipment in order that the transformation could be accomplished in an efficient and economical manner. Equipment used on this program included hardware designed for the study of processes with conditions equivalent to those encountered in large-scale production. In addition, large-scale laboratory equipment was available for the study of reactions on a smaller scale. In Table 42 are shown the major items of equipment which were used in this study.

VI. PHYSICAL STUDIES

A. SPECIFIC IMPULSE CALCULATIONS

1. Introduction

It was apparent, early in the program, that some means of screening proposed structures for application to solid propellants must be used. Calculations of specific impulse would accomplish this screening, in that many structures of too low an energy content would be rejected at the outset. The early goals of the program included a specific impulse (I_{sp}) range of 200-225 lbf sec/lbm. When this goal was raised and it became apparent that solid oxidizers would be used in a composite system, this method of screening of proposed structures became less effective. Repeated calculations have shown that the specific impulse of the binder has only a small effect on the specific impulse of the composite propellant, provided enough oxidizer has been added. The important variable has now become the amount of oxidizer to be added to the nitropolymer to reach optimum specific impulse. The calculation is still an important parameter of any new monomer or plasticizer, and this calculation is of considerable importance in ranking possible choices.

2. Discussion

Several short calculation methods have been examined for use on this program. The first was that of Sayward (345, 67). This was soon abandoned for a modification of the more accurate method of Hirschfelder and Sherman (371, 84). Their method assumes a flame temperature of about 2500°K (I_{sp} 190-235). The accuracy of this short method, when compared to the exact, long method using mobile equilibria, was shown to be excellent

(686, 37) with or without added oxidizers. Specific-impulse calculations for materials with flame temperatures that differ considerably from 2500°K will not have this accuracy. However, the values are useful for exploratory work. The only data required for the calculation are the heat of formation of the material and its elemental structure.

When it was found that interest in the nitropolymer program included composite systems with solid oxidizers, the short method of calculation was expanded (686, 34). Nomographs were prepared for the calculation of any mixture of nitropolymer and oxidizer (ammonium nitrate or ammonium perchlorate).

The calculated specific impulses for various monomers and their combinations (polymers) were tabulated several times, as indicated below in Table 43. Early tabulations included numerous hypothetical monomers which were never prepared and monomers which were not usable for a variety of reasons. These tabulations were continually reviewed for currency with regard to new monomers and changes in calculations (principally, changes in heats of combustion values (VI,A,3). The early tabulations included polyesters, polyureas, polyamides and polyformals which were abandoned at later stages of the program. The last tabulation (967, Appendix) is complete for nitropolyurethanes and is included as Table 44. A summary of I_{sp} values for many nitroplasticizers will be found in Table 39 (paragraph IV,E).

3. Heat-of-Combustion Calculations

For this calculation, the heat of formation is required. This may be derived from the heat of combustion. When an experimental value is not available, this may be calculated. A brief review of available prediction methods led to the selection of the method of Kharasch (345, 63) by which the heat of combustion may be calculated as a sum of structural factors. This calculation has been presented in detail with a tabulation of the corrective terms for various structural groups (345, 63).

TABLE 43

REFERENCES FOR SUMMARY TABULATIONS OF SPECIFIC-IMPULSE CALCULATIONS

Reference	Remarks
386, 50	Includes polyureas, polyamides, polyamines, polyesters, polyurethanes, polyformals. Does not include post-nitrated polymers.
417A, 40	Includes only post-nitrated derivatives of polyurethanes, polyureas, polyamines. Uses new assignment of correction terms for heat-of-combustion calculation.
424, 47	Revision of calculations in 386, 50 for un-nitrated polymers using new heat-of-combustion terms.
540, App.	Revision of all values, including new monomers, for polyesters, polyamides, polyureas, polyamines, polyurethanes, polyformals with post-nitration.
590, 43	Revision and enlargement - new monomers.
663, App.	Revision and enlargement. Also includes vinyl polymers.
686, 34	Calculations of a few examples with solid oxidizers. Nomographs for other calculations are given.
772, App.	Revision. Only polyurethanes, polyesters, polyureas, and polyamides, with and without post-nitration.
967, App.	Revision, polyurethanes only, un-nitrated. Uses new heat-of-combustion correction terms.

TABLE 44

ESTIMATED SPECIFIC IMPULSES OF CONDENSATION POLYMERS — POLYURETHANES IN LBF-SEC/LBM

Code	Code: Diisocyanate / Diol	I 3,3-Dinitro-1,5-pentane Diisocyanate	XI 3,3,5,7,7-Pentanitro-1,9-nonane Diisocyanate	XII 3,6-Dinitraza-1,8-octane Diisocyanate	XIII 3-Nitraza 1,5-pentane Diisocyanate	XIV 3,3,5,7,7-Pentanitro-5-aza-1,9-nonane Diisocyanate	XV 2-Nitraza 1,4-butane Diisocyanate	XVI 2,5-Dinitraza-1,6-hexane Diisocyanate	XVII 2-Nitraza-1,3-propane Diisocyanate
A	2,2-Dinitro-1,3-propanediol	174	203	178	167	212	179$^{(7)}$	204$^{(8)}$	203
B	1,3-Propanediol	*			*	179			
C	2-Nitro-2-ethyl-1,3-propanediol	110	163	116	*	178	*	130$^{(9)}$	*
D	5,7,9-Trinitraza-3,11-dioxa-1,13-tridecanediol		194	175	157	202			
F	2,2,4,4-Tetranitro-1,5-pentanediol	203	214	199	198	221			
G	5,7,9,11-Tetranitro-3,13-dioxa-1,1,5-pentadecanediol	188	202	186	124	208			
H	5,5,5-Trinitro-1,2-pentanediol	188	205	185	178	213	188	202	199
J	2-Nitro-2-methyl-1,3-propanediol	112	174$^{(1)}$	112$^{(3)}$	*	187$^{(6)}$	111	154	132
K	4,4,6,8,8-Pentanitro-1,11-undecanediol	175	193		154				
L	4,4,6,6,8,8-Hexanitro-1,11-undecanediol	191	204		186				
M	N,N'-bis(2-hydroxyethyl) oxamide	*	140		*				*
N	Ethylene glycol	109	172$^{(2)}$	118$^{(4)}$	*$^{(5)}$	188	*	130$^{(10)}$	112
O	5,5-Dinitro-1,2-hexanediol	148		148	130		142	168$^{(11)}$	167
P	3-Nitraza-1,5-pentanediol	142		140	118				148
Q	2-Nitro-2-bromo-1,3-propanediol	141							
R	1,4-Butanediol	*			*			117	
T	3,6-Dinitraza-1,8-octanediol	145		158	138		152	176	166

---

*Specific impulse less than 100 lbf-sec/lbm

(1) Previously reported I_{sp} 179 lbf-sec/lbm (Aerojet Report No. 772, Appendix C, Table I)

(2) Previously reported I_{sp} 175 lbf-sec/lbm (Aerojet Report No. 772, Appendix C, Table I)

(3) Previously reported I_{sp} 135 lbf-sec/lbm (Aerojet Report No. 772, Appendix C, Table I)

(4) Previously reported I_{sp} 117 lbf-sec/lbm (Aerojet Report No. 772, Appendix C, Table I)

(5) Previously reported I_{sp} 142 lbf-sec/lbm (Aerojet Report No. 772, Appendix C, Table I)

(6) Previously reported I_{sp} 189 lbf-sec/lbm (Aerojet Report No. 772, Appendix C, Table I)

(7) Previously reported I_{sp} 185 lbf-sec/lbm (Aerojet Report No. 805, p. 16)

(8) Previously reported I_{sp} 198 lbf-sec/lbm (Aerojet Report No. 868, p. 25)

(9) Previously reported I_{sp} 143 lbf-sec/lbm (Aerojet Report No. 907, p. 8)

(10) Previously reported I_{sp} 148 lbf-sec/lbm (Aerojet Report No. 907, p. 9)

(11) Previously reported I_{sp} 147 lbf-sec/lbm (Aerojet Report No. 907, p. 10)

The heat of combustion has also found considerable use, in this program, as a parameter for proof of structure. The heats of combustion of a large number of nitro compounds were determined experimentally (see VI,C). During the course of this work, it was found that certain of the corrective terms had to be modified so that predicted values would check with experimental values. This was of special importance to the specific-impulse calculation. As these new correction terms were calculated, the calculated specific impulses were also modified.

The only nitro-group value included in the original compilation of Kharash terms was +13.0 kcal/mole for an aliphatic nitro compound (345, 65). For the polynitro compounds prepared on this contract, a considerable number of other terms were required. These are compiled in Table 45. These data, combined with the earlier compilation, complete the terms needed for our work. The method of obtaining a new correction term is detailed in two reports (417A, 24; 907, 47).

B. SOLID PROPELLANT INFORMATION AGENCY DATA SHEETS

Solid-Propellant-Information Agency data sheets were prepared for a number of compounds and polymers. When completed, these data sheets were incorporated in the quarterly reports. Considerable physical data have been obtained on compounds other than those which were reported on SPIA data sheets. In general, only those compounds which appeared of general interest and the purity of which was assured were submitted for SPIA data sheets.

The SPIA data sheets for a typical solid 2,2-dimethyl-4-(3',3',3'-trinitropropyl)-1,3-dioxolane, and a typical polymer, XIII-A,* are shown below to indicate the type of data collected. Table 46 lists all the compounds and polymers for which SPIA data sheets have been completed.

---

*For this and subsequent nitropolymer code designations, see paragraph III,B,1.

TABLE 45

CORRECTION TERMS FOR HEAT-OF-COMBUSTION CALCULATIONS (LATEST DETERMINATION)

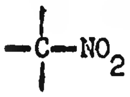
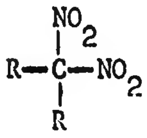
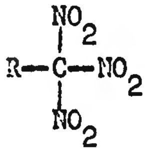
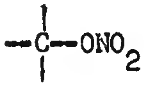
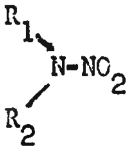
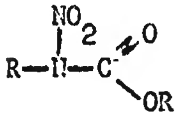
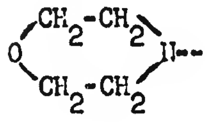
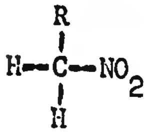
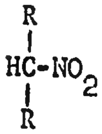
Structural Group	Correction, kcal/mole	Reference
 $-\overset{\vert}{\underset{\vert}{C}}-NO_2$	+13	345, 65
 $R-\overset{NO_2}{\underset{R}{C}}-NO_2$	+34	907, 50
 $R-\overset{NO_2}{\underset{NO_2}{C}}-NO_2$	+56	907, 50
 $-\overset{\vert}{\underset{\vert}{C}}-ONO_2$	+1	417A, 26
 $-\overset{\vert}{N}-\overset{\vert}{N}-$	+41	417A, 29
	+12	907, 50
misc. nitramines	0-46	417A, 36
	+21	907, 50
	+6	868, 50

TABLE 45 (cont.)

Structural Group	Correction, kcal/mole	Reference
 $H-\overset{R}{\underset{H}{C}}-NO_2$	+13	345, 65 907, 50
 $H\overset{R}{\underset{R}{C}}-NO_2$	+13	907, 50
 $R\overset{R}{\underset{R}{C}}-NO_2$	+3	907, 50

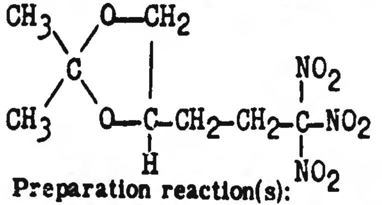
SPIA/M3

Data Questionnaire on

COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound farther. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, APL/JHU, 8621 Georgia Avenue, Silver Spring, Maryland. As additional information on the same or new compounds accrues, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

COMPOUND: 2,2-Dimethyl-4(3',3',3'-trinitropropyl)-
Name 1,3-dioxolane
Empirical formula $C_8H_{13}N_3O_8$
Structure: (configuration)



Information submitted by:
Activity Aerojet Engineering Corp.
Person G. Linden, R. Parrette
Date

Preparation reaction(s): $CH_3COCH_3 + (NO_2)_3CCH_2CH_2CHOHCH_2OH \longrightarrow$ above product + water

1. Quantitative analysis: (% by weight)

	Carbon	Hydrogen	Oxygen	Nitrogen		
Calculated from formula	34.41	4.69		15.05		
By determination	34.83	4.90		14.65		

Impurity from melting point curve, <0.05 mol percent.

2. Burning properties: (compared to nitrocellulose, under nitrogen at atmospheric pressure:)
(faster? slower? residue? etc.)

3. Stability and Sensitivity: Plot any graphs on separate sheet. Discuss methods used when they vary from references. Give temperature used. (Use separate sheet if necessary.)

	Name of test	Recommended method	
a.	Impact Sensitivity	OSRD 3185	
b.	Thermal Stability	OSRD 3401 p.8	134.5°C, methyl violet paper.
c.	Vacuum Stability	OSRD 3401 p.10	
d.	Temperature of Explosion	OSRD 3401 p.6	
e.	Temperature of Ignition	OSRD 3401 p.6	
f.	Thermal Stability, 65.5°C	Picatinny Arsenal	Report No. 1401, 1.3 g sample, KI-starch paper.
g.			
h.	Impact Stability	Bureau of Mines,	Bull. No. 346, 2 kg wt, 50% shots.

RESULTS OF ABOVE TESTS

	Reference compound (designation-TNT, Tetryl, N.C., etc.)	New Compound test results
a.		
b.	Nitrocellulose, 30 min, no color	Melted, and colored paper, 17 min
c.		
d.		
e.		
f.	Nitrocellulose, 10 min, no color	No color or change, 5 hr
g.		
h.	RDX, 34 cm	>100 cm

4. Heat of formation: (ΔH) ± -128 (Indicate sign) Kg. calories at 25°C., 1 atm. pressure

SPIA/M3

	By Experiment		By Calculation	Method Description or reference. Separate sheet if necessary.
5. Energy of explosion (Q) (at 25°C, H_2O liquid)		cal/gm		
6. Heat of combustion (H_c) (at 25°C, H_2O liquid)	3828	cal/gm	3900	Aerojet Report 417A
7. Specific impulse (I_{sp}) calc:		lb-sec/lb		

8. Physical form of compound (viscous liquid, crystalline type, etc.) Medium, white, rod crystals.

9. Simple microscope analysis data: (crystal studies)

10. Density (Macro method) ______ gm/cm³. (Micro or other method) 1.477 gm/cm³. (Explain on separate sheet any unique methods you use.)

11. Index of refraction: ($n_D^{25°C.}$) ______ 12. Color White 13. Odor None.

14. pH at 25°C. 5.1 (Method reference OSRD 3401 p.4, or OSRD 5968. Indicate method used, i.e. solvent and concentrations used. pH indicator paper or Beckman pH meter.)

Water, saturated solution, Beckman meter

15. Hygroscopicity:

	New Compound	Reference Compound ______ (designation)
Visible change on exposure to ambient air.	Highly hygroscopic	Decomposes to form
% wt Increase by* (a) or (b) (Strike out method (a) or (b) if not used.)	acetone	(If other than below methods are used, explain on separate sheet.)

*Method:

(a) The sample (approx. 5-10 g. of whole grain small powder or 1 grain of large powder) is placed in a glass weighing bottle. The weighing bottle (cover removed) is placed in a vacuum drying oven for 5 hrs. @ 55°C. Remove weighing bottle from oven, cover with glass stopper, cool in a desiccator and weigh accurately. This is taken as original dry weight of sample. Then place weighing bottle (cover removed) in a humidor (a 10-in. desiccator is a satisfactory vessel) containing 1 liter of 18.6 ± .5% H_2SO_4. (This gives relative humidity 90 ± .25%). Place in an oven maintained at 30 ± 2°C. On the fourth day remove weighing bottle from the humidor, cover with glass stopper, cool in a desiccator and weigh. Then return to humidor for 24 hours, cool and reweigh. Continue daily weighings until constant weight indicates sample has reached equilibrium with 90% R.H. The % weight increase is then reported as hygroscopicity of the sample.

(b) An alternate method is in OSRD 3401 p.3.

16. Volatility: Report as rate of loss in wt % per unit area (for liquid samples measure the surface area; for solids, the sample should be screened between 100-120 mesh U.S. Standard certified sieve) per 4 hrs., after constant rate of loss is obtained during three consecutive 4-hr. periods at (a) 25°C in a vessel through which a stream of dry air is forced, (b) in an oven at 65.5°C or (c) under other test method or conditions.

(Description or reference to other test or conditions used. Use separate sheet if necessary.)

Volatility results on:	New Compound	Reference Compound ______ (designation)
	a.	a.
	b.	b.
	c.	c.

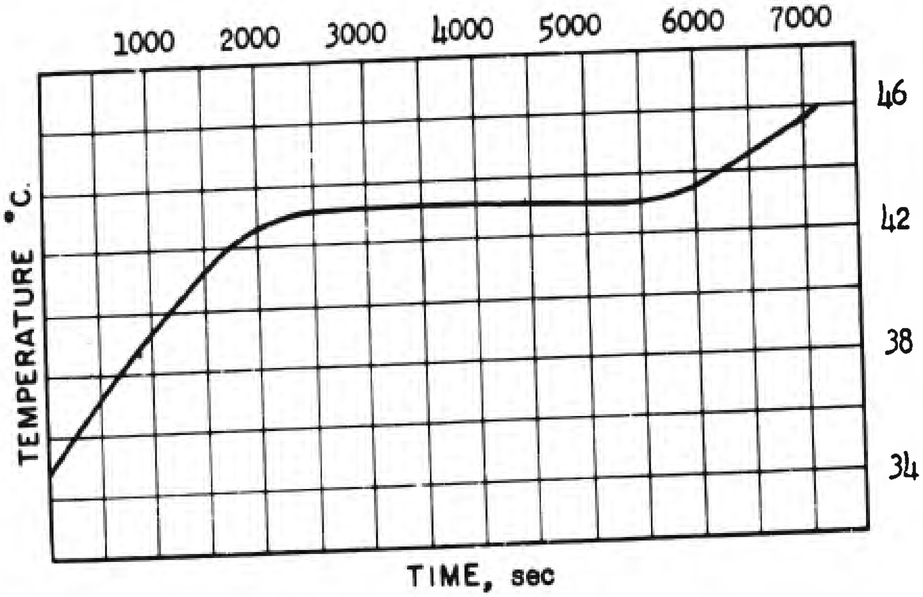
17. Boiling point, or decomposition temperature: ______ °C. (underline which temperature is reported)

18. Heat of Vaporization: ______ g-cal./gm ______ BTU/lb.

19. Heat of Fusion: ______ g-cal./gm ______ BTU/lb.

20. Melting point 43.1 °C.

21. Melting point vs. Time Curve: (Please mark the coordinates with scale values that apply to the compound under study.)



22. Solubility of new compound:

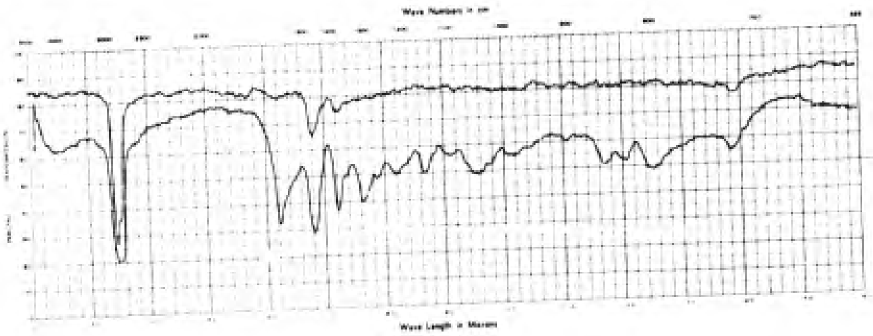
< 0.01 g/100 ml H_2O at 25°C. ________ g/100 ml H_2O at ________ °C.

620 g/100 ml acetone (name material used as solvent) at 25 °C.

424 g/100 ml toluene (name material used as solvent) at 25 °C.

23. Viscosity of the new compound and its solutions:

	NEW COMPOUND wt. % in solution	SOLVENT NAME	SOLVENT Wt. % in solution	VISCOSITY at Centipoises	TEMP. °C.	METHOD USED reference
a.	100		NONE		25	
b.	100		NONE		25	
c.	95	N.C. (13.15% N.)	5			
d.						
e.						
f.						



Upper Curve - Crystal oil

Lower Curve - 2,2-Dimethyl-4-(3',3',3'-trinitropropyl)-1,3-dioxolane, suspension in crystal oil.

Samp. Cell - NaCl, no spacer

Comp. Cell - NaCl block

12 min scan

14 April 1952

SPIA/M3

Under compatability we are considering the ability of two compounds to be in intimate contact (Note OSRD 5758 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the following: (a) Standard stability tests. (b) Simple observations of exudation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Separate the sheets with strips of cigarette paper or carbon paper and compress the stack in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 28 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber. Test performed by dissolving sample and standard substance in a common solvent drying rapidly on a glass plate, and examining the resulting film for clarity and homogeneity.

25. Compatability with ethyl cellulose:

26. Compatability with nitrocellulose: Ratio, $\frac{\text{wt sample}}{\text{wt NC}}$: :
20/80 Compatible
50/50 Compatible
80/20 Compatible

27. Compatability with rubber: Ratio, $\frac{\text{wt sample}}{\text{wt rubber}}$: :
20/80 Compatible
50/50 Compatible
80/20 Compatible

28. Compatability with ____:

29. Polymerizing properties of the new compound:
(a) By itself Might polymerize in presence of acidic catalysts
(b) In mixtures (with additives)
(c) Inhibiting action on polymerization of:
Thiokol
Methacrylate
Other compounds

30. Availability
a. Amount now available? Research quantities
b. When was available material first prepared?
c. Amount prepared at that time?
d. Is large production feasible?
e. Plant capacity in existance, lbs/day?
f. Outline steps for a quantity production method

31. Additional information: (toxicity, hazards, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.) This compound is very readily hydrolyzed by water especially in presence of acid catalysts.

SPIA/M3

Data Questionnaire on

COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

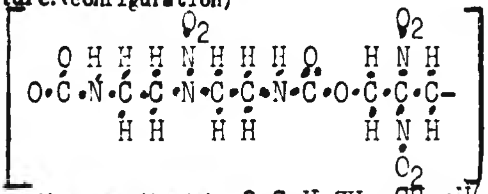
Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound farther. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, APL/JHU, 8621 Georgia Avenue, Silver Spring, Maryland. As additional information on the same or new compounds accrues, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

COMPOUND:

Name Polymer of 3-nitraza-1,5-pentane diisocyanate and 2,2-dinitro-1,3-propanediol

Empirical formula $C_9H_{14}N_6O_{10}$ (366.25)

Structure: (configuration)



Information submitted by:

Activity

Person J. Mishima, J. R. Fischer

Date

Preparation reaction(s): $O{:}C{:}N\cdot CH_2\cdot CH_2\cdot N(NO_2)\cdot CH_2\cdot CH_2\cdot N{:}C{:}O + OH\cdot CH_2\cdot C(NO_2)_2\cdot CH_2OH$ — Fe acetylacetonate $\longrightarrow [O\cdot CO\cdot NH\cdot CH_2\cdot CH_2\cdot N(NO_2)\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot O\cdot CH_2\cdot C(NO_2)_2\cdot CH_2\cdot]_n$

1. Quantitative analysis: (% by weight)

	Carbon	Hydrogen	Oxygen	Nitrogen		
Calculated from formula	29.51	3.85		22.95		
By determination	30.81	4.33		22.90		

2. Burning properties: (compared to nitrocellulose, under nitrogen at atmospheric pressure:)

(faster? slower? residue? etc.)

3. Stability and Sensitivity: Plot any graphs on separate sheet

Discuss methods used when they vary from references. Give temperature used. (Use separate sheet if necessary.)

	Name of test	Recommended method	
a.	Impact Sensitivity	OSRD 3185	
b.	Thermal Stability	OSRD 3401 p.8	
c.	Vacuum Stability	OSRD 3401 p.10	
d.	Temperature of Explosion	OSRD 3401 p.6	
e.	Temperature of Ignition	OSRD 3401 p.6	
f.	Thermal Stability	Picatinny Arsenal No. 1401	1.3-g sample, KI-starch paper
g.	Impact Sensitivity	Bureau of Mines Bull. No. 346	2-kg wt, 50% shots
h.			

RESULTS OF ABOVE TESTS

	Reference compound (designation-TNT, Tetryl, N.C., etc.)	New Compound test results
a.		
b.		
c.		
d.		
e.		
f.	Nitrocellulose, 10 min, no color	20 min
g.	RDX, 28 cm	>100 cm
h.		

4. Heat of formation: (ΔH) ± −44.96 (Indicate sign) **Kg. calories at 25°C., 1 atm. pressure**

	By Experiment	By Calculation	Method Description or reference. Separate sheet if necessary.
5. Energy of explosion (Q) (at 25°C. H_2O liquid)	cal/gm		
6. Heat of combustion (H_c) (at 25°C. H_2O liquid)	3181 cal/gm	3077 cal/gm	Aerojet Report 417-A
7. Specific impulse (I_{sp}) calc:	168 lb-sec/lb	181 lb-sec/lb	

8. Physical form of compound (viscous liquid, crystalline type, etc.) A flexible solid

9. Simple microscope analysis data: (crystal studies) An amorphous solid

10. Density (Macro method) 1.531 gm/cm3. (Micro or other method) ______ gm/cm3. (Explain on separate sheet any unique methods you use.)

11. Index of refraction: ($n_D^{25°C.}$) ______ 12. Color cream 13. Odor none.

14. pH at 25°C. 5.70 (Method reference OSRD 3401 p.4, or OSRD 5968. Indicate method used, i.e. solvent and concentrations used. pH indicator paper or Beckman pH meter.)
Saturated solution in water using a Beckman pH meter-model

15. Hygroscopicity:

	New Compound	Reference Compound ______ (designation)
Visible change on exposure to ambient air.		
% wt Increase by* (a) or (b) (Strike out method (a) or (b) if not used.)		(If other than below methods are used, explain on separate sheet.)

*Method:

(a) The sample (approx. 5-10 g. of whole grain small powder or 1 grain of large powder) is placed in a glass weighing bottle. The weighing bottle (cover removed) is placed in a vacuum drying oven for 5 hrs. @ 55°C. Remove weighing bottle from oven, cover with glass stopper, cool in a desiccator and weigh accurately. This is taken as original dry weight of sample. Then place weighing bottle (cover removed) in a humidor (a 10-in. desiccator is a satisfactory vessel) containing 1 liter of 18.6 ± .5% H_2SO_4. (This gives relative humidity 90 ± .25%). Place in an oven maintained at 30 ± 2°C. On the fourth day remove weighing bottle from the humidor, cover with glass stopper, cool in a desiccator and weigh. Then return to humidor for 24 hours, cool and reweigh. Continue daily weighings until constant weight indicates sample has reached equilibrium with 90% R.H. The % weight increase is then reported as hygroscopicity of the sample.

(b) An alternate method is in OSRD 3401 p.3.

16. Volatility: Report as rate of loss in wt % per unit area (for liquid samples measure the surface area; for solids, the sample should be screened between 100-120 mesh U.S. Standard certified sieve) per 4 hrs., after constant rate of loss is obtained during three consecutive 4-hr. periods at (a) 25°C in a vessel through which a stream of dry air is forced, (b) in an oven at 65.5°C or (c) under other test method or conditions. ______
(Description or reference to other test or conditions used. Use separate sheet if necessary.)

Volatility results on:	New Compound	Reference Compound ______ (designation)
	a.	a.
	b.	b.
	c.	c.

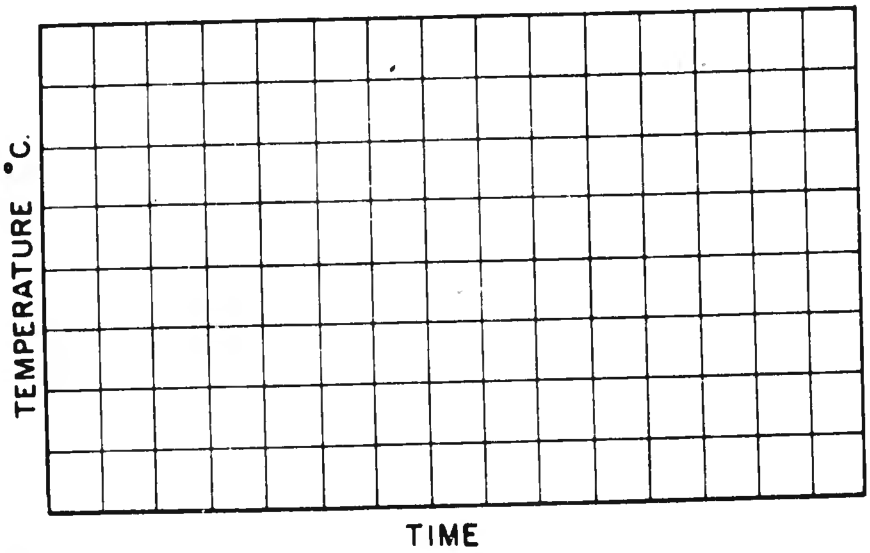
17. Boiling point, or decomposition temperature (underline which temperature is reported) ______ °C.

18. Heat of Vaporization: ______ g-cal./gm ______ BTU/lb.

19. Heat of Fusion: ______ g-cal./gm ______ BTU/lb.

20. Softening Range: 60-70°C.

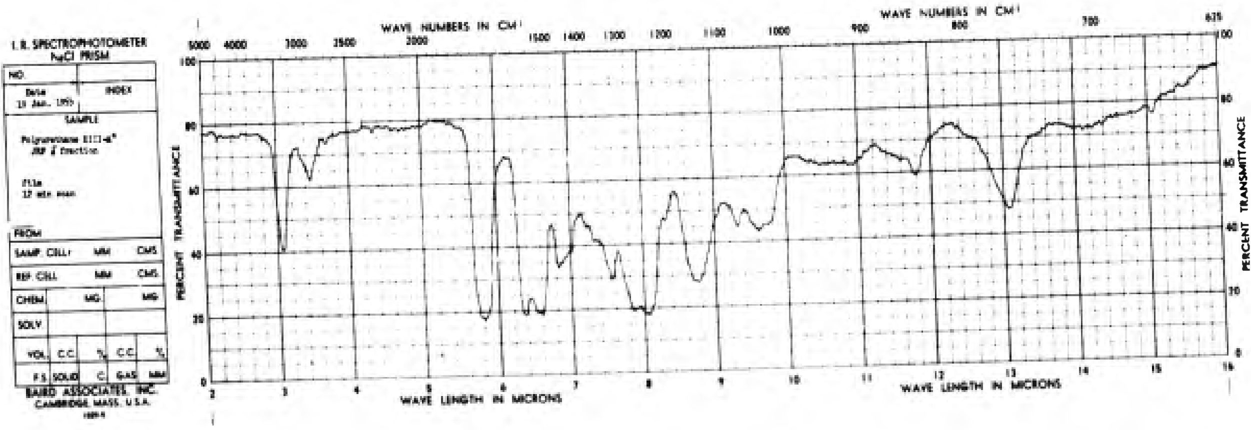
21. **Freezing point vs. Time Curve:** (Please mark the coordinates with scale values that apply to the compound under study.)



22. **Solubility of new compound:**

0.0046 g/100 ml H_20 at 25°C. ________ g/100 ml H_20 at ________ °C.

Methanol	0.0009 g/100 ml
n-Hexane	Insoluble
Benzene	Insoluble
Ethyl acetate	Miscible
Dioxane	Soluble
Carbon tetrachloride	Insoluble
Acetone	Miscible
Dimethyl formamide	Miscible



Under compatability we are considering the ability of two compounds to be in intimate contact (Note OSRD 5758 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the following: (a) Standard stability tests. (b) Simple observations of exudation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Separate the sheets with strips of cigarette paper or carbon paper and compress the stack in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 28 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber.

25. Compatability with ethyl cellulose:

26. Compatability with nitrocellulose: Ratio, wt sample/wt NC
20:80 compatible
50:50 compatible
80:20 compatible

27. Compatability with rubber: Ratio, wt sample/wt rubber
20:80 incompatible
50:50 incompatible
80:20 incompatible

28. Compatability with ________:

29. Polymerizing properties of the new compound:
- (a) By itself
- (b) In mixtures (with additives)
- (c) Inhibiting action on polymerization of:
  - Thiokol
  - Methacrylate
  - Other compounds

30. Availability
- a. Amount now available?
- b. When was available material first prepared?
- c. Amount prepared at that time?
- d. Is large production feasible?
- e. Plant capacity in existance, lbs/day?
- f. Outline steps for a quantity production method

31. Additional information: (toxicity, hazards, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.)

TABLE 46

COMPOUNDS AND POLYMERS - SPIA DATA SHEETS

Compound	Ref.*
2-Nitroethanol	371
1,4-Dinitro-2,3-butanediol	371
2,2-Dinitro-1,3-propanediol	371
4,4-Dinitro-1,7-heptanedioic acid	386
Nitroform-dioxan	404
Nitroform	404
1,1,1,3-Tetranitropropane	417A
2,2-Dinitropropyl acrylate	424
2,2,2-Trinitroethanol	424
3,3-Dinitro-1,5-pentane diisocyanate	424
Methyl 4,4,6,6-tetranitrocaproate	468
3,3-Dinitro-1,5-pentanediamine	468
2,2,4,4-Tetranitrobutyl acetate	468
2,2,2-Trinitroethyl methacrylate	482
2,2-Dinitro-1-butanol	499
2,2,4,4-Tetranitro-1,5-pentanediol	499
2,2,2-Trinitroethyl acrylate	515
Vinyl 4,4,4-trinitrobutyrate	515
2,2-Dinitrobutyl acrylate	515
4,4,6,8,8-Pentanitro-1,11-undecanedioic acid	563
4,4,6,6,8,8-Hexanitro-1,11-undecanedioic acid	563
N-Trinitroethyl-N-nitroaspartic acid	563
Pentaerythritol acrylate trinitrate	590

Polymer**	Ref.*
Polyester 1-A	482
Polyamide 1-α	482
Polyurea I-α	482
Polyurethane I-D	482
Polyurethane I-A	482
Polyurethane I-AN	515
Polyurethane I-F	515
Polyurethane XI-A	622
Polyurethane I-K	622
Polyurethane I-L	622
Polyurethane I-MN	663
Poly-petrin acrylate	638
Polyurethane I-J	686
Poly-dinitrobutyl acrylate	907
Poly-dinitropropyl acrylate	907
Polyurethane XV-J	941
Polyurethane XIII-A	941
Polyurethane XV-A	941
Polyurethane XII-A	941

---

*SPIA data sheets are normally inserted as appendices to the reports.

**See paragraph III,B,1 and III,B,2,c for polymer code designations.

TABLE 46 (cont.)

Compound	Ref.[*]
4,4,6,8,8-Pentanitro-1,11-undecanediol	590
4,4,6,6,8,8-Hexanitro-1,11-undecanediol	590
1,2-bis(4,4,4-Trinitrobutyroxy)-ethane	590
Nitroallyl acetate	622
1,2-bis-(4,4,4-Trinitrobutyroxy)-propane	622
5,5,5-Trinitro-2-keto-1-pentanol	622
1,2,3-tris-(4,4,4-Trinitrobutyroxy)-propane	622
2,2-Dimethyl-4-(3',3',3'-trinitropropyl)-1,3-dioxolane	622
1,5-bis-(4,4,4-Trinitrobutyroxy)-3-oxapentane	622
2-Methoxyethyl trinitrobutyrate	622
5,5,5-Trinitro-1,2-pentanediol	638
3-Nitraza-1,5-pentane diisocyanate	807
2-Nitraza-1,4-butane diisocyanate	833
Methyl 4,4-dinitrovalerate	941

---

[*] SPIA data sheets are normally inserted as appendices to the reports.

C. DETERMINATION OF HEATS OF COMBUSTION

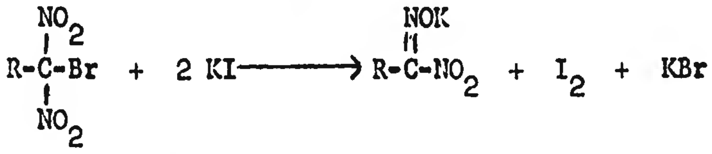
The determination of the heat of combustion of nitro compounds serves as an excellent means for verifying the structure of a compound. It has been found particularly advantageous in the study of the purity of polymers and in the study of reactions performed on polymers, e.g., post-nitration. Determinations were made using a Parr adiabatic calorimeter. Several modifications of the original operating procedure were reported (386, 48; 424, 42) which led to an estimated accuracy of a few tenths of one percent. Early data had been reported as heat of combustion at constant volume. However, for an accurate comparison with the calculated values using the Kharash contribution values, these had to be recalculated to enthalpy of combustion. This correction was small (1 to 2%), and the results were tabulated (563, 40). The precision of a number of duplicate determinations was calculated (563, 42): estimated standard deviation = 27.5 cal/g for values ranging 2000 to 4000 cal/gm.

One singular difficulty was observed and corrected (740, 33; 772, 36). Combustion of several post-nitrated polymers gave values which checked poorly with predicted ones, and a large inorganic residue was found. Apparently these materials gave large amounts of oxides of nitrogen, rather than reduction of the nitro groups to nitrogen. These oxides reacted exothermically with the chamber walls to give nickel salts. This was obviated by the use of a Pyrex liner, which was adopted as a standard technique.

In general, the heat of combustion of a compound was reported with its synthesis; however, several tabulations, by no means complete, have been made of some determinations. These are found in the following reports: 563, 40; 712, 25; 772, 39; 807, 40; 907, 49. Many values will be easily found in the SPIA data sheets (paragraph VI,B).

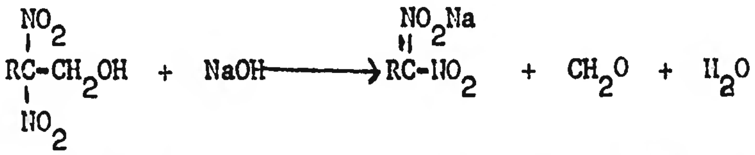
D. ANALYTICAL PROCEDURES

During the course of synthetic and polymerization work, several different analytical procedures were developed or modified specifically for nitromonomers. During early stages of the program, several terminal bromodinitro compounds were synthesized. A procedure which quantitatively analyzed for this functional group was developed (417, Appendix). This procedure was based on the following equation:



$$R\text{-}\overset{NO_2}{\underset{NO_2}{C}}\text{-}Br + 2\ KI \longrightarrow R\text{-}\overset{NOK}{\overset{\|}{C}}\text{-}NO_2 + I_2 + KBr$$

Use was made of the deformylation reaction to analyze 2,2-dinitro-1-alkanols (499, 64). Titration of such monomers with sodium hydroxide was quantitative.



$$R\overset{NO_2}{\underset{NO_2}{C}}\text{-}CH_2OH + NaOH \longrightarrow R\overset{NO_2Na}{\overset{\|}{C}}\text{-}NO_2 + CH_2O + H_2O$$

Examples of monomers on which this technique was used extensively are 2,2-dinitro-1-propanol, 2,2-dinitro-1,3-propanediol (monobasic only), and 2,2,4,4-tetranitro-1,5-pentanediol (dibasic).

Polymerization work with isocyanates required an analytical method for the isocyanate function which would not interact with nitro groups. The use of di-n-butylamine in dioxane proved successful (424, 15). Only one polynitro isocyanate failed in this procedure: 3,3,5,7,7-pentanitro-5-aza-1,9-nonane diisocyanate (XIV diisocyanate) (740, 70).

E. DENSITY DETERMINATIONS

The densities of various nitromonomers, nitroplasticizers, and nitropolymers, and their formulations, were desired for a variety of reasons: for SPIA data sheets, for determination of cohesive energy densities, and as a control on the reproducibility of propellant formulations (907, 52). Two methods were successfully used: the micro determination of NOL (563, 47) and the liquid displacement technique (907, 52; 967, 30). The NOL micro determination method worked well for crystalline materials. However, both methods appeared to fail when applied to the high-molecular-weight, fibrous nitropolymers (941, 29). Successful, reliable determinations were possible by these methods only after the polymers had been pressed into pellets and the pellets crushed before the determination (967, 30).

Numerous density values are reported in the SPIA data sheets (paragraph VI,B), and these have not been separately compiled. A compilation has been made of the values for a number of nitroplasticizers (967, 23) and nitropolymers (967, 30). Some of these are disclosed in Table 47.

TABLE 47

REPRESENTATIVE DENSITIES OF SOME NITROPLASTICIZERS AND NITROPOLYMERS

Compound	Density, g/ml, 25°C
4-Nitrazapentanonitrile	1.225
2,2-Dinitropropyl 4-nitrazapentanoate	1.488
2,2,2-Trinitroethyl 4-nitrazapentanoate	1.545
Ethylene bis-(4-nitrazapentanoate)	1.399
Ethylene bis-(4,4-dinitropentanoate)	1.448
Polyurethane XII-H	1.465
Polyurethane XIII-A	1.532
Polyurethane XV-A	1.553
Polyurethane XV-J	1.537

F. ABSORPTION SPECTRA

1. Infrared Absorption

The infrared spectra for many nitromonomers, plasticizers, and polymers were reported in the SPIA data sheets (see paragraph VI,B). In almost all cases, the observed bands correlated well with literature values. In several cases, the infrared spectra were used to speculate on such things as structure of methylene diisocyanate polymers (563, 48), association of nitroalcohols (499, 58), and structure of post-nitrated polyurethanes (515, 66). In general, the techniques employed were fairly standard: for liquids, either solution or a thin cell was used; crystalline solids were run in solution, or in a mull in crystal oil (mineral oil) or Fluorolube (622, 51); polymers were run in solution, in a film, cast on mercury (482, 51), or on polyethylene (482, 51; 622, 51).

2. Ultraviolet Absorption

The ultraviolet-absorption spectra of aliphatic nitro compounds has been given an extensive review (417A, 44). This included a complete literature review for aliphatic carbon-nitro compounds and spectra determined at Aerojet. Techniques, equipment, calculations, and theory were all covered in detail. Actual absorption curves were given for nitromethane; methazonic acid; dinitromethane; nitroform; tetranitromethane; nitroethane; 1-nitropropane; 2-nitropropane; 1-nitro-1-propene; 1-nitro-1,3-pentadiene; nitroethanol; dinitroethanol; trinitroethanol; 2-nitro-1-butanol; 2-nitro-2-methyl-1-propanol; 2-nitro-2-methyl-1,3-propanediol; 2-nitro-2-ethyl-1,3-propanediol; phenylnitromethane; nitroacetic acid; 2,2-dinitropropane; 1,1,1,3-tetranitropropane; 2,2-dinitro-1,3-propanediol; and 4,4-dinitro-1,7-heptanedioic acid. In addition to the above, the following absorption curves were reported elsewhere: 3,3-dinitro-1,5-pentanediamine; methyl 4,4,6,6-tetranitrocaproate; and 2,2,4,4-tetranitrobutyl acetate (468, 57).

G. DETERMINATION OF PURITY BY MELTING-POINT METHOD OF SMIT

One of the most useful techniques for the determination of purity of crystalline monomers and plasticizers is the Smit method. For a compound which is stable at its melting point, this method can give the estimated mole percent of impurity and the estimated freezing point at 100% purity. The equipment, theory, and techniques have been described (345, 60; 386, 47), and a description was later published in the open literature.* This method was used on almost all compounds reported in the SPIA data sheets since it served to screen any materials of questionable purity (386, 47).

H. DETERMINATION OF MOLECULAR WEIGHT

1. Introduction

The principal parameter for control of polymerizations is molecular weight. It was apparent early in the nitropolymer program that accurate means of measuring molecular weights would be needed. Osmometric

---

*L. T. Carleton, Anal. Chem., 27 845 (1955).

methods were chosen for early study. When it became known that the nitropolymers produced by thermal or acid catalysis were of low molecular weight (in the range of 2,000 to 20,000), another technique was needed. Thus, the isopiestic method was successfully applied to these rather low polymers. With the advent of metal chelate catalysis, high-molecular-weight polymers were prepared, and osmometry was more profitably used.

2. Osmometric Method

The first attempts at osmometry on nitropolymers made use of the Schulz osmometer (457, 37). This apparatus yielded results with considerable scatter and required a relatively long equilibration time. A new instrument, based on that of Zimm and Myerson (468, 48), was investigated and found to be satisfactory. The equipment was checked with polyvinyl chloride (468, 49) and polyethylmethacrylate (499, 60). It was soon apparent that nitropolymers, at this stage of the program, had a molecular-weight range of about 2,000-20,000 and that poor precision in the determinations was resulting (515, 47, 63), due to this range and due to diffusion of low-molecular-weight fragments through the membrane.

The problem of diffusion through the membrane continued to plague the osmometry studies throughout the program. Several methods for attaining a rapid equilibrium,and the use of as many as six osmometers at once, were tried in order to increase the precision of the measurements (563, 42; 686, 26; 712, 26; 740, 34). Most of these methods were only moderately successful.

Besides the use of molecular-weight determinations in controlling polymerization studies, certain fundamental information was derived for the relationship of viscosity vs molecular weight for several nitropolymers. This was accomplished for nitropolyurethane I-J (712, 26; 740, 34; 772, 41) and polydinitrobutyl acrylate (807, 41; 833, 37). The constants for the Staudinger equation ($[\eta] = KM^a$) were determined in each case. The determinations of molecular weight for various preparations of poly-dinitropropyl acrylate are also recorded (868, 50).

Acetone was the solvent chosen for most nitropolymers. With one polymer, XVI-J, which was insoluble in acetone, two different solvents were tried. γ-Butyrolactone failed because no reliable value of the percent diffusion could be determined on account of the high boiling point of the solvent (907, 52). A run in tetrahydrofuran was unsuccessful due to too high a percent diffusion (941, 29).

3. Isopiestic Method

The isopiestic method of molecular-weight determination was chosen to study polymers of low molecular weight (2000-30,000), when the osmometric method proved to be too erratic. The theory, techniques, and equipment for the isopiestic method has been described in detail (638, 53).* Early work on polymer I-A (638, 53) indicated some decomposition in the solvent, acetone; later studies were restricted to materials which passed other stability tests (663, 32). In the detailed molecular-weight study of polyurethane I-J, the molecular weights of several of the lower fractions were determined isopiestically (740, 38; 772, 41).

The precision of the isopiestic method, as used on this program, has been shown to be excellent. Two cases were examined. Some Thiokol resins, the molecular weights of which had been determined cryoscopically, were checked, and a fraction of polyurethane I-J with a molecular weight which had been determined osmometrically was also run (807, 42). These determinations showed an excellent correlation with the other two independent determinations.

4. Other Methods

Two other methods of molecular-weight determination were examined. The ebullioscopic method was unsuccessful, because of the tendency of the nitropolymers to decompose at the boiling point of the solvent (540, 12; 638, 53). The viscosity method gave reproducible results, but it has the disadvantage of giving only relative values of molecular weight (540, 12).

---

*The results of this study were later published in the open literature: R. L. Parrette, J. Polymer Sci., 15 447 (1955).

I. SEPARATION PROCESSES

During the course of research on new nitromonomers, several purification processes were examined which differed considerably from the usual distillation or recrystallization techniques. Recourse to these procedures was taken when the common purification procedures failed because of the presence of a complex mixture or thermal stability problems.

In an attempt to purify nitroethyl acrylate, a thermal-diffusion apparatus was investigated (424, 41). This apparatus was shown to be effective for a heptane-toluene mixture, but when tried on nitroethyl acrylate, no separation, as measured by refractive index, was observed.

For the purification of trinitroethyl acrylate, the use of a countercurrent-distribution apparatus (Craig apparatus) was investigated (499, 64). The apparatus was checked out with a mixture of 2,2-dinitropropanediol and 2,2,4,4-tetranitropentanediol, using di-n-butyl ether and water. The separation was excellent. The apparatus was successfully applied to the purification of trinitroethyl acrylate (499, 6; 515, 2, 64), yielding crystalline material having a correct heat of combustion (540, 33).

In a study related to larger-scale synthesis of 4-nitrazapentanoic acid, extraction from aqueous hydrochloric acid with methylene chloride was examined in detail (967, 26). It was demonstrated that the changing distribution ratio observed could be attributed to an association or dimerization of the acid molecules.

J. THERMAL STABILITY STUDIES

All the compounds on which SPIA data sheets were filed, and numerous others, were examined for thermal stability by two standard tests: the 65.5°C potassium iodide-starch test and the 134.5°C methyl violet test. The SPIA data sheets give the references for these tests. These tests proved most useful in screening monomers, polymers, and propellant formulations. They were effectively used as controls in the long and detailed studies on the preparation and stabilization of post-nitrated polymers (590, 37) and also in the early propellant-formulation studies (663, 60; 686, 49).

It was observed that materials which passed the 65.5°C - potassium iodide - starch test could still be inadequate for formulation work, e.g., materials which decomposed to yield a non-oxidizing gas. As a convenient means of measuring gas evolution, use was made of the Warburg manometer, widely used in the biological fields. (No Taliani or vacuum-stability apparatus was used on this program.) The adaptation and technique for measuring gas evolution in this apparatus has been described in detail (663, 60; 686, 49). Little correlation was observed between gassing rates and the 65.5° potassium iodide-starch test (663, 60). The Warburg gassing rate was used as a valuable research tool in studies of stabilization of post-nitrated polymers (710, 10), propellant formulations (663, 60; 686, 49), nitroplasticizer screening (967, 31), and investigations of the effect of polymer end groups on thermal stability (1004, 5). A modified procedure was described for more accurate use of the Warburg apparatus (967, 31).

K. X-RAY DIFFRACTION OF NITROPOLYMERS

As part of the fundamental study of the newly derived nitropolymers, it appeared of importance to determine their molecular pattern, amorphous or crystalline. The X-ray diffraction patterns for five polymers were reported under this contract (563, 40). A number of other polymer examples were so studied as part of the rheological examination of nitropolymers under an associated contract* (712, 36; 740, 50). The results of these studies are compiled in Table 48.

L. RHEOLOGY

Since the principal aim of the nitropolymer program was to develop a promising solid propellant, it became necessary to obtain data concerning the mechanical behavior of the candidate materials. This work was originated on the ONR program in 1951. Most of the time was spent on assembling sample fabrication equipment and evaluating various techniques for handling the polymers (540, 20; 563, 50). The first rheological equipment, a Cope and Cope constant-stress rheometer, was installed and used on this program.

---

*Contract NOas 53-618c. A final report for this contract is Aerojet Report No. 817. See paragraph VI.L. for discussion of the relationships of the contracts.

TABLE 48

X-RAY DIFFRACTION PATTERN OF NITROPOLYMERS

Reference	Nitropolymer	Results of Analysis of X-Ray Diffraction Pattern
563, 40	Polyester 1-A	Crystalline
563, 40	Polyurea I-α	Amorphous
563, 40 712, 37	Polyurethane I-A	Amorphous
712, 37	Polyurethane I-H	Slightly crystalline
712, 37	Polyurethane I-J	Amorphous
712, 37 740, 50	Polyurethane XII-A	Strongly crystalline
	Polyurethane XII-H	Amorphous
	Polyurethane XII-AN	Moderately crystalline
	Polyurethane XIII-A	Amorphous
	Polyurethane XIII-AN	Amorphous
	Polyurethane XIII-H	Amorphous
	Polyurethane XIII-M	Strongly crystalline
	Polyurethane XIII-N	Strongly crystalline
	Polyurethane XIII-O	Moderately crystalline
	Polyurethane XIII-J	Amorphous
	Polyurethane XIII-NN	Amorphous
	Polyurethane XIII-ON	Amorphous
	Polyurea XIII-γ	Strongly crystalline
	Polyurea XIII-γN	Amorphous
	Polyurethane I-D	Amorphous
740, 50	Polyurethane I-G	Moderately crystalline

Since that early period, all rheological and ballistic investigation of nitropolymers has been performed under contracts other than N7onr-462. Some of the work performed under these other contracts was reported in combined reports submitted under this contract. However, in all cases, complete final reports have been filed for these other contracts, and it would be a needless duplication to include such summaries here. The reader is referred to the summary reports listed in Table 49.

TABLE 49

REFERENCES FOR RHEOLOGICAL AND BALLISTIC EVALUATION OF NITROPOLYMERS

Contract No.	Period Covered	Aerojet Final Report No.
NOas52-359	May 1951 to Sept 1952	649
NOas53-618c	Dec 1952 to Feb 1954	817
NOas54-399c (NOrd 16584)	May 1954 to March 1956	1104
NOrd 16878	April 1956 to March 1957	(in progress)

M. MISCELLANEOUS PHYSICAL-PROPERTY STUDIES

1. Introduction

Several miscellaneous physical-property studies were undertaken. In general these studies were not extensive.

2. Vapor-Pressure Measurements

In the early stages of the nitropolymer-development program, nitroethanol was an important intermediate. Its vapor pressure (345, 58) and that of its acrylate (404, 60) were determined, using an isoteniscopic apparatus. For vapor-pressure measurements near the solidification point, the isoteniscopic apparatus was not suitable. A simple U-tube-type apparatus was assembled and used for vapor-pressure measurements on nitroform (404, 58).

3. Potentiometric Titrations

At an early stage in the program, a compilation of potentiometric titration curves for new nitromonomers was undertaken. It was anticipated that this technique would be useful for determination of purity, or for structure-proof studies (see paragraph VI,D). Titration curves for the following compounds were reported: nitroethanol; 2-bromo-2-nitroethanol; 2,2-dibromo-2-nitroethanol; trinitroethanol; nitroform (404, 58); 3,3-dinitro-1,5-pentanediamine; methyl 4,4,6,6-tetranitrocaproate; 2,2,4,4-tetranitrobutyl acetate (468, 56); 2,2-dinitrobutanol; and 2,2,4,4-tetranitropentanediol (499, 56).

4. Solubility Parameters

From the solubility of a compound in several solvents, the entropy of fusion and the solubility parameter can be determined. This was determined for 2,2-dinitro-1,3-propanediol (590, 43), 1,5-bis-(4,4,4-trinitrobutyroxy)-3-oxapentane (638, 44) and 1,2,3-tris-(4,4,4-trinitrobutyroxy)-propane (638, 44). An attempt to determine the solubility parameter for polyester 1-A was unsuccessful (638, 45). A detailed discussion of the theory and method used was given (638, 46).

VII. SAFETY

A. INTRODUCTION

The general field of propellant and explosives research necessarily introduces a hazard to laboratory personnel, due to the inherent nature of the materials being processed. Throughout the work on this program, every effort was exerted to prevent accidents and to safeguard the personnel from injury. A constant watch was maintained to eliminate dangerous practices and to minimize the hazards associated with the operations.

B. DISCUSSION

From the inception of this program, all standard safety practices and devices were utilized in these laboratories. Personal safety items such as safety shoes, safety glasses, and flame-proof laboratory coats were mandatory for all personnel; and conventional safety devices, such as acid carriers, asbestos gloves, safety shields, and laboratory tongs, were available in each laboratory. In addition, a number of specialized safety items were designed and built for use in this program.

The Safety Committee, composed of laboratory personnel, made periodic inspections of the laboratories to ensure that all safety practices were being complied with.

Despite the rigid safeguards, a number of fume-offs, explosions, and fires occurred (468, 65; 482, 61; 540, 53; 590, 85; 638, 105). In each case, an evaluation of the preparation was made, and corrective measures were incorporated into the process to prevent a recurrence. In no case, throughout the entire program, did any injury, other than minor cuts and burns, occur to personnel.

C. SAFETY EQUIPMENT

1. Safety Shields

For normal laboratory use, the 2-ply safety glass, steel-framed shield, available from Fisher Scientific Co. was satisfactory (468, 60). For extremely hazardous operations, a 1.5-in.-thick safety glass, mounted in a steel frame (468, 60), or a 0.25-in. steel-plate shield containing a safety-glass sight slit, proved to be more satisfactory (468, 60). For larger-scale operations, portable shields, mounted on wheels, were utilized (540, 53). A stationary safety shield was mounted around a large laboratory evaporator (540, 53).

2. Air Bath for Vacuum Distillations

Many nitro compounds encountered in this project were liquids which required a distillation in order to be purified. In this laboratory, a standard practice was adapted wherein all new nitro compounds were distilled in quantities of 0.5 to 5.0 g from a simple two-bulb tube inserted in a metal air bath. This air bath is made of welded, 1/16-in. steel, lined with asbestos paper, and has replaceable safety-glass windows on each side. It is heated on the bottom of one end by means of a small Bunsen flame. Both a diagram and a photograph of this air bath are shown in an early report (468, 61).

3. Remote Control Laboratory

One laboratory was specially equipped for extra-hazardous reactions. One wall is of light, plastic-covered-wire construction. The remaining three walls and ceiling are constructed of reinforced concrete 2 ft thick. A special window of multiple-ply safety glass is placed in the center of one concrete wall, and direct observation of reactions is made by means of angular mirrors. All services may be controlled from outside the laboratory, and a special pulley arrangement has been devised for remotely opening and closing stopcocks. To warn personnel when a hazardous reaction is in operation (468, 65), large signs are placed on each side of the entrance to this laboratory.

4. Water Flooding System

In many chemical reactions which become uncontrollable, the hazards and damages that result could be minimized by flooding the reaction system when the temperature exceeds a predetermined limit. Such a system was designed and placed into operation in this laboratory.

Essentially, this device consists of a thermoregulator, which is inserted into the reaction medium. When the reaction temperature reaches the set point on the thermoregulator, electrical contact is made and a mercury-to-mercury relay is energized. This energizes a power relay, which opens a solenoid valve. Water flows through the valve and into the reaction mixture. The volume of water may be adjusted by means of an electronic timer. A more detailed description and a schematic diagram of this device is shown in an early report (482, 58).

5. Storage Vessels

In order to minimize the hazard of storing and handling sensitive crystalline material, it has become the practice in these laboratories to place 50 gm, or more, of a crystalline explosive material in polyethylene containers. These are now available commercially in a wide variety of sizes and shapes, and they come equipped with pressure-tight covers. The polyethylene is practically indestructible, except by explosion or flame, and makes an excellent storage container (540, 53).

APPENDIX A

COMPOUND INDEX

(Numbers indicate pages in the body of the report)

APPENDIX B

FORMULA INDEX

(Numbers indicate pages in the body of the report)

CONFIDENTIAL

CONFIDENTIAL

$C_7H_{11}N_3O_9$	2-Methoxyethyl 4,4,4-trinitrobutyrate, 107, 110, 207, 210, 215, 230, 231, 278
$C_7H_{11}N_5O_{10}$	2,2,4,6,6-Pentanitroheptane, 120, 121
$C_7H_{12}N_2O_6$	4,4-Dinitro-1-pentyl acetate, 11
	Methyl 3-nitraza-1,6-hexanedioate, 52, 64, 65
$C_7H_{12}N_4$	4,6-Diaza-1,9-nonane dinitrile, 71
$C_7H_{12}N_4O_6$	Polyurethane XV-N, 176, 177, 178, 223
$C_7H_{12}N_4O_8$	3,5,5-Trinitro-3-aza-1-hexyl acetate, 109, 112, 208, 210
$C_7H_{12}N_4O_8$	2,2-Dinitropropyl 4-nitrazapentanoate, 108, 111, 207, 209, 210, 215, 226, 231, 234, 256, 258, 281
$C_7H_{12}N_6O_8$	2,4,6-Trinitraza-1-heptyl acrylate, 134
	poly-2,4,6-Trinitraza-1-heptyl acrylate, 134
$C_7H_{13}NO_4$	Methyl 4-methyl-4-nitropentanoate, 89
	2,2,5-Trimethyl-5-nitro-1,3-dioxan, 101, 234, 254
$C_7H_{13}NO_5$	2,2-Dimethyl-5-hydroxymethyl-5-nitro-1,3-dioxan, 99, 101, 233, 243, 244
$C_7H_{13}N_3O_7$	Isobutyl 1,1,1-trinitroisopropyl ether, 125
$C_7H_{14}ClN_3O_6$	Methyl 6-amino-4,4-dinitrohexanoate hydrochloride, 75, 77
$C_7H_{14}N_2O_6$	4,4-Dinitro-1,7-heptanediol, 91
$C_7H_{14}N_4O_6$	Methyl 4-nitro-2,4,7-triaza-1,8-octanedioate, 44
$C_7H_{14}N_6O_5$	Polyurea XII-δ, 194
$C_7H_{14}N_6O_6$	4,4-Dinitro-1,7-heptanedioyl hydrazide, 41
$C_8H_6N_6O_{16}$	*bis*-(2,2,2-Trinitroethyl) fumarate, 20, 21
	bis-(2,2,2-Trinitroethyl) maleate, 20
$C_8H_7NO_2$	β-Nitrostyrene, 119, 120
$C_8H_8N_6O_{15}$	4,4,4-Trinitrobutyric anhydride, 74, 75, 199, 201

DISTRIBUTION LIST

	No. of Copies
Chief of Naval Research Department of the Navy Washington 25, D. C. Attn: Code 429 VIA: BAR	11
BAR/Azusa	1
Department of the Air Force Hq. USAF, DCS/D Attn: AFDRD-AN Washington 25, D. C.	1
Commander Wright Air Development Center Wright-Patterson Air Force Base, Ohio Attn: WCLPN-3	1
Commander Wright Air Development Center Wright-Patterson Air Force Base, Ohio Attn: WCRRC	1
Commanding General Aberdeen Proving Ground Maryland Attn: Ballistic Research Laboratories ORDBG-BLI	2
Commanding General Frankford Arsenal Bridge and Tacony Streets Philadelphia, Pennsylvania Attn: Pitman-Dunn Laboratory	1
Department of the Army Office, Chief of Ordnance Washington 25, D. C. Attn: ORDTU	1
Commanding Officer Office of Ordnance Research Box CM Duke Station Durham, North Carolina	1

DISTRIBUTION LIST (cont.)

	No. of Copies
Commanding Officer Picatinny Arsenal Dover, New Jersey Attn: Library	2
Commanding General Redstone Arsenal Huntsville, Alabama Attn: Technical Library	2
Commanding General Ordnance Ammunition Command Joliet, Illinois Attn: ORDLY-R-T	1
Department of the Navy Bureau of Ordnance Washington 25, D. C. Attn: Ad3, Technical Library	1
Department of the Navy Bureau of Ordnance Washington 25, D. C. Attn: ReW3a	1
Department of the Navy Bureau of Ordnance Washington 25, D. C. Attn: ReS6	1
Commanding Officer U. S. Naval Air Rocket Test Station Lake Denmark Dover, New Jersey Attn: Technical Library	1
Commanding Officer U. S. Naval Powder Factory Indian Head, Maryland Attn: Research and Development Department	2
Commander U. S. Naval Ordnance Laboratory White Oak Silver Spring, Maryland Attn: Library	1

DISTRIBUTION LIST (cont.)

	No. of Copies
Commander U. S. Naval Ordnance Test Station China Lake, California Attn: Technical Library Branch	3
Director U. S. Naval Research Laboratory Washington 20, D. C. Attn: Chemistry Division, Code 6130	1
Commanding Officer Office of Naval Research Branch Office 86 E. Randolph Street Chicago 1, Illinois	1
Commanding Officer Office of Naval Research 1030 E. Green Street Pasadena, California	1
Department of the Navy Bureau of Aeronautics Washington 25, D. C. Attn: TD-4	1
Allegany Ballistics Laboratory P. O. Box 210 Cumberland, Maryland	1
Armour Research Foundation of Illinois Institute of Technology Technology Center Chicago 16, Illinois Attn: Propulsion and Structural Research; Department M	1
Atlantic Research Corporation 812 North Fairfax Street Alexandria, Virginia	1
U. S. Department of the Interior Bureau of Mines 4800 Forbes Street Pittsburgh 13, Pennsylvania Attn: Division of Explosives Technology Region V	2

DISTRIBUTION LIST (cont.)

	No. of Copies
Catholic University of America 7th St. and Michigan Ave., N. E. Washington 17, D. C. Attn: F. O. Rice	1
E. I. du Pont de Nemours and Company 10th and Market Streets Wilmington, Delaware Attn: W. F. Jackson	1
Experiment, Incorporated P. O. Box 1-T Richmond 2, Virginia Attn: Librarian	1
Hercules Powder Company Wilmington, Delaware Attn: A. M. Ball	1
Director Jet Propulsion Laboratory 4800 Oak Grove Drive Pasadena, California	1
Arthur D. Little, Inc. 30 Memorial Drive Cambridge 42, Massachusetts Attn: W. A. Sawyer	1
Arthur D. Little, Inc. 30 Memorial Drive Cambridge 42, Massachusetts Attn: G. R. Handrick	1
Naval Ordnance Research School of Chemistry University of Minnesota Minneapolis 14, Minnesota Attn: B. L. Crawford, Jr.	1
National Fireworks Ordnance Corp. West Hanover, Massachusetts Attn: S. J. Porter	1

DISTRIBUTION LIST (cont.)

	No. of Copies
Ohio State University Research Foundation Columbus 10, Ohio Attn: H. Shechter	1
Phillips Petroleum Company Room 402 Adams Building Bartlesville, Oklahoma Attn: L. E. Taylor	1
Project Squid Princeton University Princeton, New Jersey Attn: Librarian	1
Purdue University Department of Chemistry Lafayette, Indiana Attn: H. Feuer	1
Rohm and Haas Redstone Arsenal Research Division Huntsville, Alabama Attn: Librarian	3
Solid Propellant Information Agency Applied Physics Laboratory The Johns Hopkins University Silver Spring, Maryland Attn: P. K. Reily, Jr.	8
Standard Oil Company Research Department P. O. Box 431 Whiting, Indiana Attn: W. H. Bahlke	1
Thiokol Chemical Corporation Redstone Division Huntsville, Alabama Attn: Technical Director	2
Thiokol Chemical Corporation Elkton Division Elkton, Maryland Attn: D. W. Kershner	1

DISTRIBUTION LIST (cont.)

	No. of Copies
Olin Mathieson Chemical Corporation East Alton, Illinois Attn: R. A. Cooley	1
Reaction Motors, Inc. Denville, New Jersey Attn: Librarian	1
Phillips Petroleum Company P. O. Box 548 McGregor, Texas Attn: E. Z. Lang	2
B. F. Goodrich Company Research Center Brecksville, Ohio Attn: Vice President/Research	1
American Machine and Foundry Company Mechanics Research Department 1104 South Wabash Avenue Chicago 5, Illinois	1
Commercial Solvents Corporation Terre Haute, Indiana Attn: J. Martin	1
Rocketdyne North American Aviation, Inc. 6633 Canoga Avenue Canoga Park, California Attn: Librarian, Dept. 596-3	2
Bell Aircraft Corporation P. O. Box 1 Buffalo, New York Attn: D. F. Zeman	1

DISTRIBUTION LIST (cont.)

	No. of Copies
Olin Mathieson Chemical Corporation New Haven, Connecticut Attn: R. B. Murphy	1
Grand Central Rocket Company P. O. Box 111 Redlands, California	1
Lockheed Aircraft Corporation Missile Systems Division Van Nuys, California Attn: E. Robertson	1
Wyandotte Chemicals Corporation Wyandotte, Michigan Attn: J. Ohliger Department of Contract Research Research and Development Division	1
Vitro Laboratories 200 Pleasant Valley Way West Orange, New Jersey Attn: Library	1
U. S. Atomic Energy Commission University of California Radiation Laboratory Technical Information Service P. O. Box 808 Livermore, California Attn: M. Edlund	1
Dr. E. Gruber Head, Plastics Research General Tire & Rubber Co. Research Laboratory Akron, Ohio	1
Thomas L. Jacobs Chemistry Department University of California Los Angeles, California	1

DISTRIBUTION LIST (cont.)

	No. of Copies
Dr. D. V. Sickman Explosives Division Naval Ordnance Laboratory White Oak, Silver Spring 19, Md.	1
Dr. William F. Sager Department of Chemistry George Washington University Washington, D. C.	1
Commanding Officer Chemical Corps Chemical and Radiological Laboratories Army Chemical Center, Maryland Attn: Technical Library	1
Bureau of Ordnance Department of the Navy Washington 25, D. C. Attn: Re06	1
University of Michigan Ann Arbor, Michigan Attn: Dr. C. S. Rondestvedt Department of Chemistry	1
Los Alamos Scientific Laboratory Los Alamos, New Mexico Attn: Technical Library	2
Commander U. S. Naval Air Missile Test Center Point Mugu, California Attn: Technical Library	1
Internal Distribution	44

UNCLASSIFIED

UNCLASSIFIED