



# An efficient process for the synthesis of *gem*-dinitro compounds under high steric hindrance by nitrosation and oxidation of secondary nitroalkanes

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## ABSTRACT

A new nitrosation and oxidation process to synthesize *gem*-dinitro compounds was accomplished by using nitryl chloride as nitrosation reagent and ozone as oxidizing agent. The main features of the present protocol include the compatibility to substances with high steric hindrance, high yields and mild reaction conditions. A plausible mechanism involving the formation of an intermediate of *gem*-nitrosnitro compound by means of single electron transfer was also proposed.

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## Introduction

For centuries, extensive efforts have been devoted to the development of new high energy density materials (HEDMs) that meet the criteria of both higher energy and better safety properties [1–5]. Due to the positive correlation between detonation velocity, detonation pressure, specific impulse and density, the demand for higher energy density is gradually increasing [6]. Currently, there are several known functionalities that can increase the density of energetic compounds, such as nitro, azido, nitroxy, nitramino, difluoramino, *gem*-difluoramino and *gem*-dinitro. It is critical to introduce suitable functionalities with certain number on the skeletons of target energetic compounds due to the inherent contradiction between detonation performance and stability.

Polynitroaliphatic compounds have not found widespread use as either commercial or military explosives up to now because most of them, containing internal *gem*-dinitroaliphatic functionality, have high chemical and thermal stability. But this property is of great importance nowadays owing to the increasing requirement of energetic compounds with low sensitivity and good heat-resistance. Besides, *gem*-dinitro groups can give the energetic

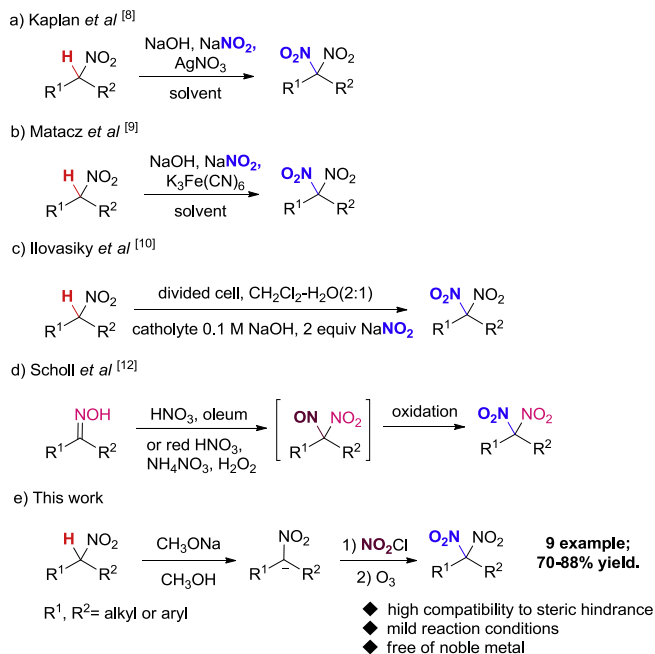
compounds higher density and better oxygen balance in comparison with aromatic C-nitro compounds.

Although a large number of *gem*-dinitro compounds have been synthesized [7], the methods for efficiently and simply constructing *gem*-dinitro functionality are still limited. Generally, there are two approaches to do this work. One is oxidative nitration of nitroalkanes under basic conditions. For example, Kaplan and co-workers prepared *gem*-dinitro compounds from sodium nitronates with AgNO<sub>3</sub>/NaNO<sub>2</sub> through a free radical mechanism (Scheme 1a) [8]. However, this method has the fatal drawback in heavy use of expensive AgNO<sub>3</sub> as oxidant. Subsequently, some efforts had been made to use much cheaper oxidants such as stoichiometric potassium ferricyanide or catalytic amount of potassium ferricyanide with stoichiometric amount of persulfate anion as co-oxidant (Scheme 1b), but still no obvious improvement in reaction yield had been achieved [9]. In addition, under electrochemical conditions, sodium nitronates can react directly with sodium nitrite to afford *gem*-nitro compounds (Scheme 1c) [10]. Lister and co-workers improved this process and their following project was to investigate pilot-plant scale reaction [11]. The other approach for constructing *gem*-dinitro functionality is tandem nitrosation-oxidation of oximes by Scholl method [12] via the intermediate of pseudonitrole [13] (Scheme 1d).

As potential candidates of HEDMs, polynitroadamantanes have attracted widespread attention [14]. In 1988, the oxidative

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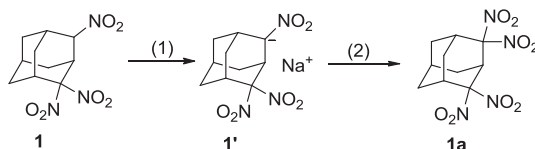


**Scheme 1.** Processes for the synthesis of *gem*-dinitro compounds.

nitration of nitroadamantanes with AgNO<sub>3</sub>/NaNO<sub>2</sub> was studied by Archibald and co-workers [15]. For example, 2-nitroadamantane was converted to 2,2-dinitroadamantane in 89% yield while both 2,4-dinitroadamantane and 2,6-dinitroadamantane did not give *gem*-dinitro derivatives by this methods. Meanwhile, direct nitration of 2,4-adamantanedione resulted in the Nef reaction product 2,4-adamantanedione and the intramolecular ring-closure byproduct 2,4-dinitro-2,4-dinitrosoadamantane [16]. For 2,6-dinitroadamantane, its *gem*-dinitro product 2,2,6,6-tetranitroadamantane can be achieved by reaction in NaOH/C(NO<sub>2</sub>)<sub>4</sub> system. However, this protocol failed for the case of 2,4-dinitroadamantane. The reason might be assigned to the high steric hindrance. In fact, there are no reports on the synthesis of polynitroadamantanes that contain seven or more nitro groups.

**Table 1**

Preparation of 2,2,4,4-tetranitroadamantane through nitrosation and oxidation of 2,2,4-trinitroadamantane.<sup>a</sup>



Entry	Nitrating reagent	Usage [equiv.]	Temperature [°C]	Time [h]	Yield <sup>c</sup> [%]
1	NaNO <sub>2</sub> <sup>b</sup>	5	20	1	–
2	N <sub>2</sub> O <sub>4</sub>	15	–30	2	35
3	NOCl	15	–30	2	16
4	NO <sub>2</sub> BF <sub>4</sub>	15	–30	2	20
5	NO <sub>2</sub> Cl	15	–30	2	66
6	NO <sub>2</sub> Cl	20	–30	2	76
7	NO <sub>2</sub> Cl	25	–30	2	77
8	NO <sub>2</sub> Cl	20	–50	2	83
9	NO <sub>2</sub> Cl	20	–70	2	87
10	NO <sub>2</sub> Cl	20	–70	1	61
11	NO <sub>2</sub> Cl	20	–70	3	85
12	NO <sub>2</sub> Cl	20	–70	4	85

<sup>a</sup> Reaction conditions: (1) compound **1** (1 mmol), CH<sub>3</sub>ONa (1.1 mmol), CH<sub>3</sub>OH (5 mL), RT, 4 h; (2) compound **1'**, nitrating or nitrosating reagents, CH<sub>2</sub>Cl<sub>2</sub> (100 mL); then ozone was bubbled into the system until the system became colourless.

<sup>b</sup> AgNO<sub>3</sub> (3 mmol, 3 equiv.), ethanol (10 mL), water (10 mL).

<sup>c</sup> Isolated yield.

In order to synthesize polynitroadamantanes containing more *gem*-dinitro groups, more efficient processes for introducing *gem*-dinitro functionality to carbons with high steric hindrance are still required. In this paper, an efficient process for the conversion of nitroalkanes to *gem*-dinitro compounds *via* nitrosation with nitryl chloride and oxidation with ozone is reported.

## Results and discussion

Eaton and co-workers [17] tried to synthesize octanitrocubane by direct electrophilic nitration of various alkali salts of heptanitrocubane with N<sub>2</sub>O<sub>4</sub>, NO<sub>2</sub>Cl, NO<sub>2</sub>BF<sub>4</sub>, NO<sub>2</sub>PF<sub>6</sub> and some nitrate esters but failed at all. Finally, they accomplished this target through the tandem reactions of nitrosation and oxidation. Some similar reaction process that electrophilic reagents reacted directly with metal salts were also reported [18]. Refer to this method, 2,2,4-trinitroadamantane (**1**) was used as the model substrate to optimize the reaction conditions and the results were listed in Table 1.

Firstly, the oxidative nitration with AgNO<sub>3</sub>/NaNO<sub>2</sub> was attempted, but no target product 2,2,4,4-tetranitroadamantane (**1a**) was obtained (Table 1, Entry 1). When a large excess of N<sub>2</sub>O<sub>4</sub> (15 equivalents) was used and the reaction was carried out at –30 °C, the green nitrosation intermediate was observed. But unfortunately, the effort to separate it out of the reaction mixture failed. After oxidizing with ozone, the target product **1a** was isolated in an overall yield of 35% (Table 1, Entry 2). It was once thought to be an electrophilic reaction between nitronium ion (NO<sup>+</sup>) and carbon anion in the first step. But when NOCl [19] was used as nitrosating reagent, the target product **1a** was obtained in much lower yield of 16% (Table 1, Entry 3). As a result, the formation of pseudonitrole might not be the classical electrophilic nitrosation process. NO<sub>2</sub>BF<sub>4</sub> and NO<sub>2</sub>Cl were used as nitrating agents long before [20]. To our surprise, when highly active nitrating reagents NO<sub>2</sub>BF<sub>4</sub> or NO<sub>2</sub>Cl were applied, the green nitrosation intermediate still formed according to the experimental phenomena. With the inletting of ozone, the green mixture gradually changed to colourless and afforded **1a**. For the case of NO<sub>2</sub>BF<sub>4</sub>, the yield was still very low and comparable to that of NOCl (Table 1, Entry 4). To our delight, the yield was dramatically elevated to 66% when

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