

NITRO COMPOUNDS

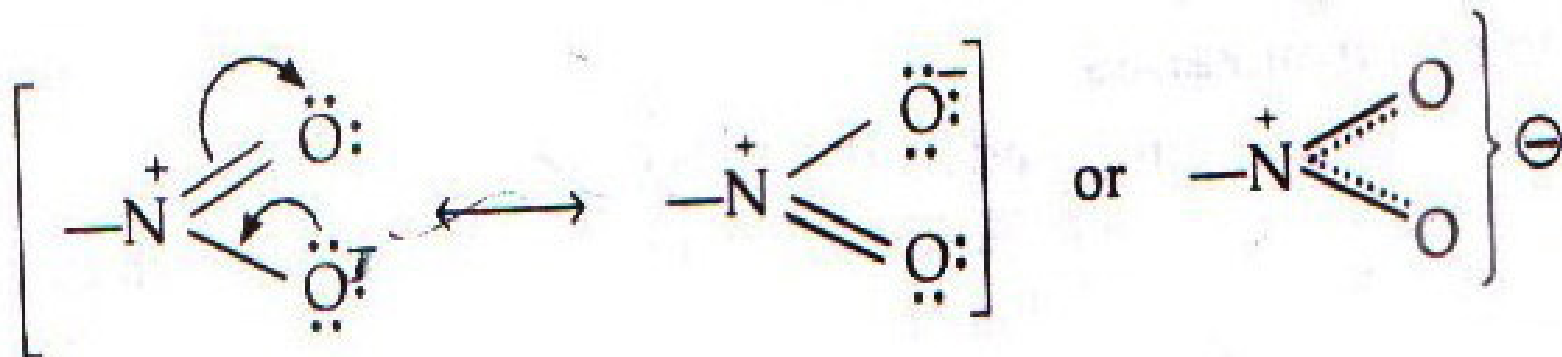
Introduction

Nitro compounds are an important class of organic compounds which may be regarded as derived from hydrocarbons by the replacement of one or more hydrogen atoms by nitro (NO_2) groups. Nitro arenes (i.e. nitro compounds in which $-\text{NO}_2$ group is directly attached to benzene ring) have been used as synthetic reagents since long.

Structure of Nitro group

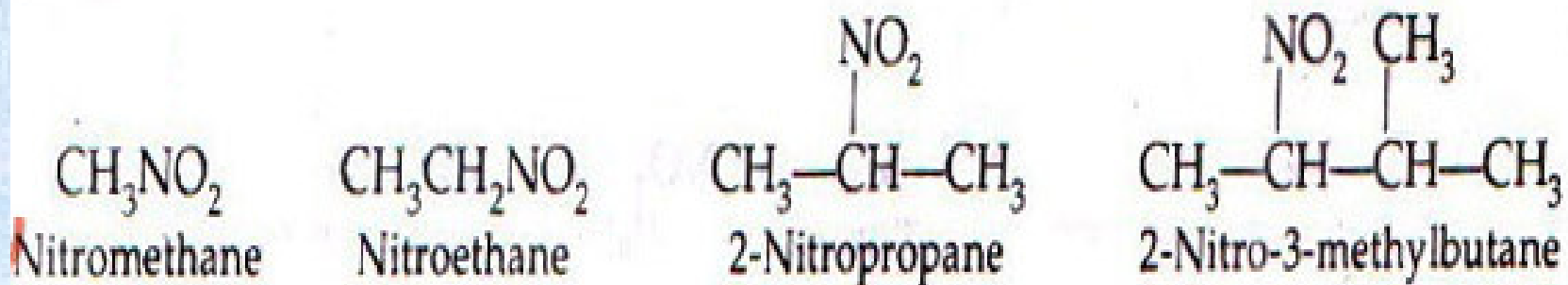
Nitro group is quite often represented as containing a double bond between nitrogen and one oxygen and a co-ordinate or dative bond between nitrogen and other oxygen i.e. $-\text{N} \begin{array}{l} \text{=} \text{O} \\ \text{--} \text{O} \end{array}$

But actually nitro group is stabilized by resonance and is a hybrid of two equal contributing structures:



Nomenclature of nitro compounds

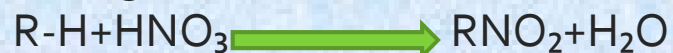
Nitro compounds are named by writing the word nitro before the name of the parent compound.



PREPARATION OF NITRO COMPOUNDS

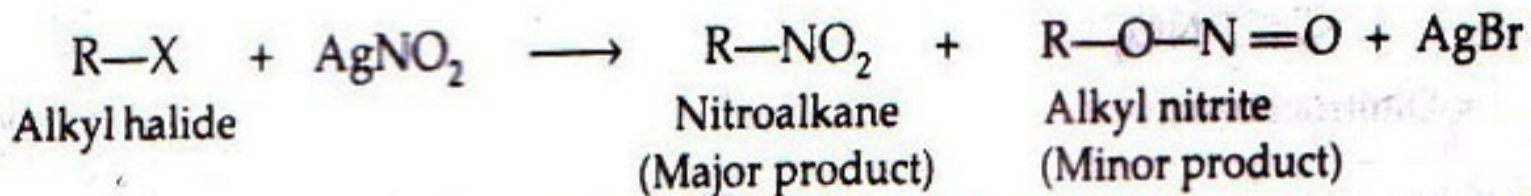
Nitro alkanes are usually prepared by the following methods:

1: **VAPOUR PHASE NITRATION OF ALKANES:** This reaction involves the substitution of a hydrogen atom of the alkane by a nitro *group*. It is carried out in the *vapour state* by heating the alkane with nitric acid at about 700K.

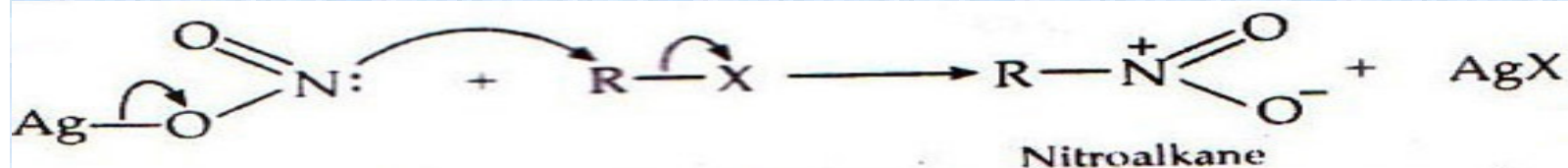


LIMITATIONS OF THE PROCESS: During the nitration of higher alkanes all possible isomeric nitro products are formed. More over rupture of carbon carbon bonds also take place leading to the formation of nitro alkanes containing lesser number of carbon atoms.

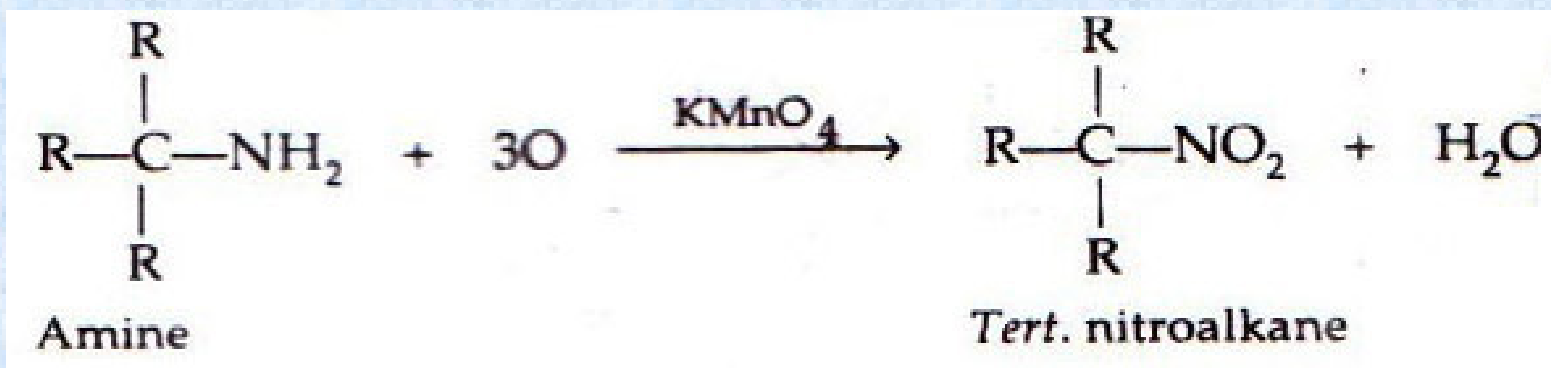
2: **ACTION OF SILVER NITRITE ON ALKYL HALIDES:** This is the method generally employed for the laboratory preparation of nitro alkanes. When heated with silver nitrate alkyl halides undergo *nucleophilic substitution* to form nitro alkanes along with small quantities of alkyl nitrites.



MECHANISM



3: **OXIDATION OF AMINES:** When an amine in which the amino group is attached to a tertiary carbon atom is oxidised potassium permanganate, a tertiary nitro alkane is obtained.



PREPARATION OF NITROARENES

Nitroarenes are almost invariably prepared by direct nitration of arenes. The nitrating agents generally used are

- 1: Concentrated or fuming nitric acid.
- 2: Mixture of concentrated or fuming nitric acid and concentrated sulphuric acid.

3: Mixture of concentrated nitric acid and acetic anhydride or boron trifluoride.

4: Acetyl nitrate

5: Nitrogen peroxide in the presence of anhydrous aluminium chloride.

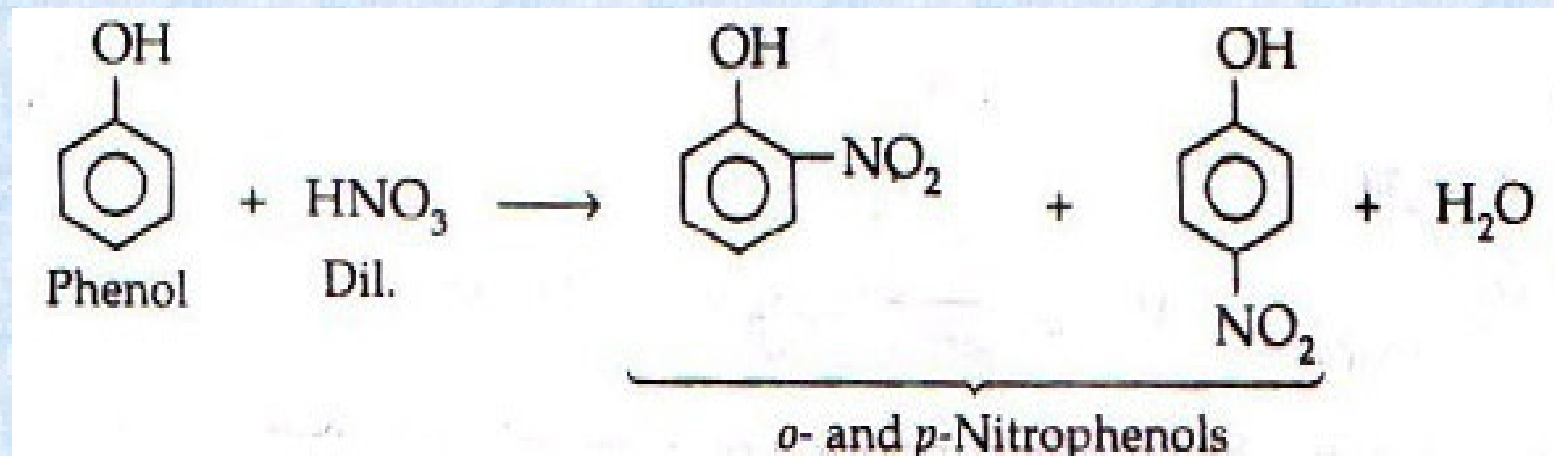
Choice of nitrating agent to be used for nitration of a given compound depends upon following two factors:

1: Nature of compound to be nitrated .

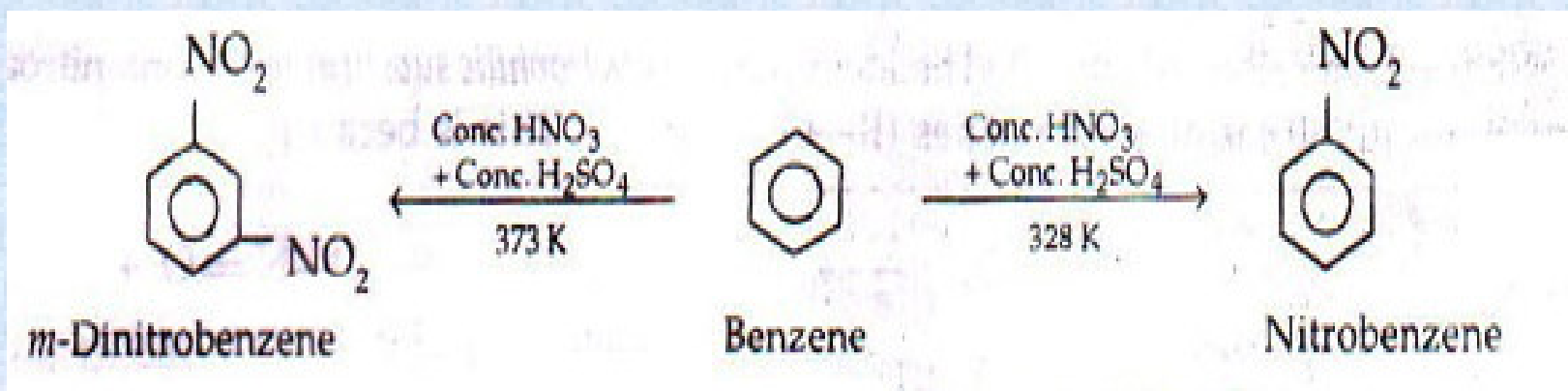
2: No of nitro groups to be introduced.

In the nitration of aromatic compounds containing electron releasing or activating groups

Such as $-NH_2$, $-OH$, $-CH_3$, the reaction takes place readily at room temperature by employing conc. HNO_3 .



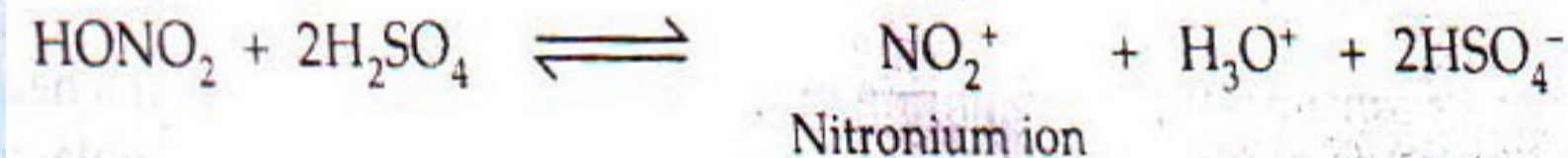
For nitrating compounds containing electron attracting or deactivating group such as –COOH or when it is desired to introduce more than one nitro group a suitably strong nitrating mixture has to be employed and the reaction is carried out at higher temperature. Nitro benzene and m-dinitrobenzene can be obtained from benzene under the conditions shown below :



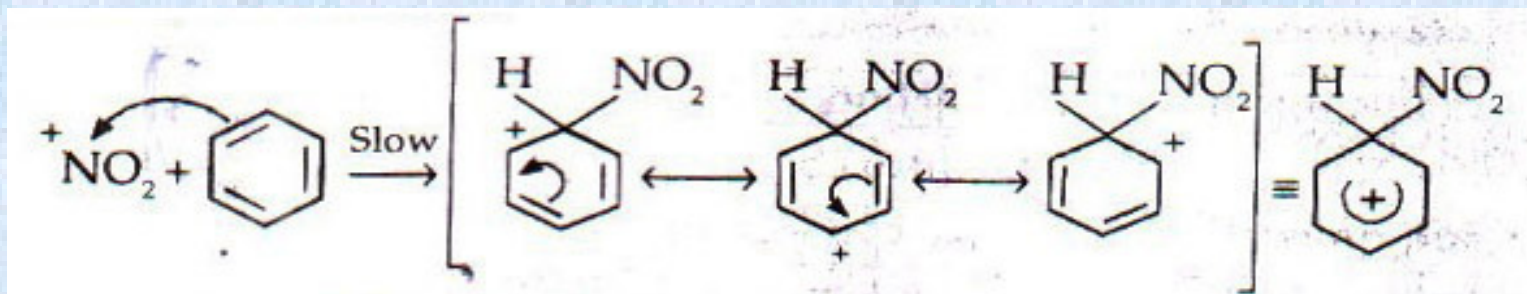
MECHANISM OF NITRATION

Nitration of aromatic compounds involves a nitronium ion as the attacking electrophile. The mechanism may be summed up as follows:

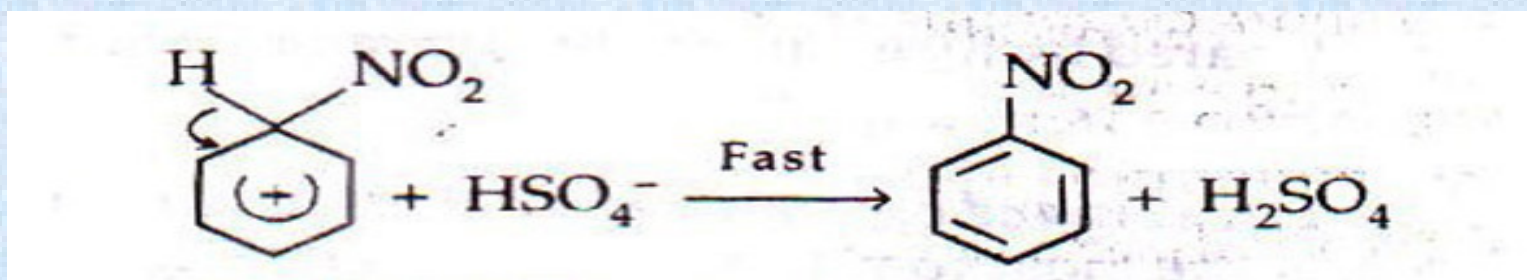
1: *generation of electrophile* :



2: Formation of carbocation



3: Proton transfer from the carbocation to yield the final product



COMPARISON OF NITRATION OF ARENES AND NITRATION OF ALKANES

It may be noted that nitration of arenes takes place at relatively low temperature where as nitration of alkanes requires a very high temperature . This may be due to the fact that the nitration of arenes involves the initial formation of electrophilic reagent while the nitration of alkanes is supposed to involve the initial formation of free radical . The formation of free radical takes through homolysis requires stronger condition than the formation of electrophile that takes place through heterolysis. As such nitration of arenes takes place more easily than nitration of alkanes

PHYSICAL PROPERTIES OF NITRO COMPOUNDS

Nitro alkanes have pleasant smell and are sparingly soluble in water. Aromatic nitro compounds except benzene are yellow crystalline solids. Nitro compounds are heavier than water.

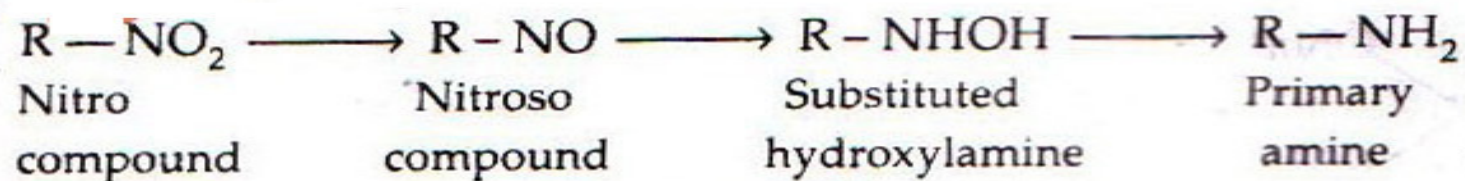
Due to the presence of highly polar nitro group, nitro compounds have strong dipole-dipole interaction. Hence they possess high boiling points, much higher than hydrocarbons of comparable molecular masses.

CHEMICAL REACTIONS OF NITRO ALKANES

1: **ACIDIC NATURE** : Nitro alkanes containing alpha hydrogen atoms exhibit acidic character



2 REDUCTION OF NITRO ALKANES:



The product obtained depend upon the nature of the reducing agent and Ph OF THE REACTION MEDIUM.

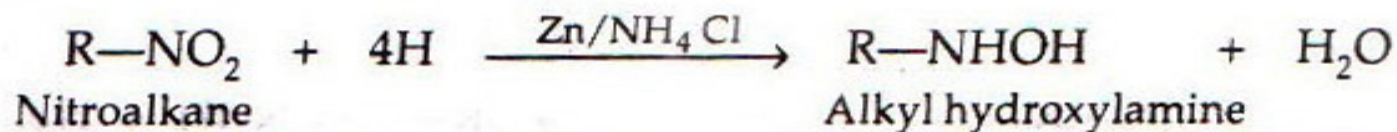
ACIDIC MEDIUM : primary amines are formed.



CATALYTIC REDUCTION:



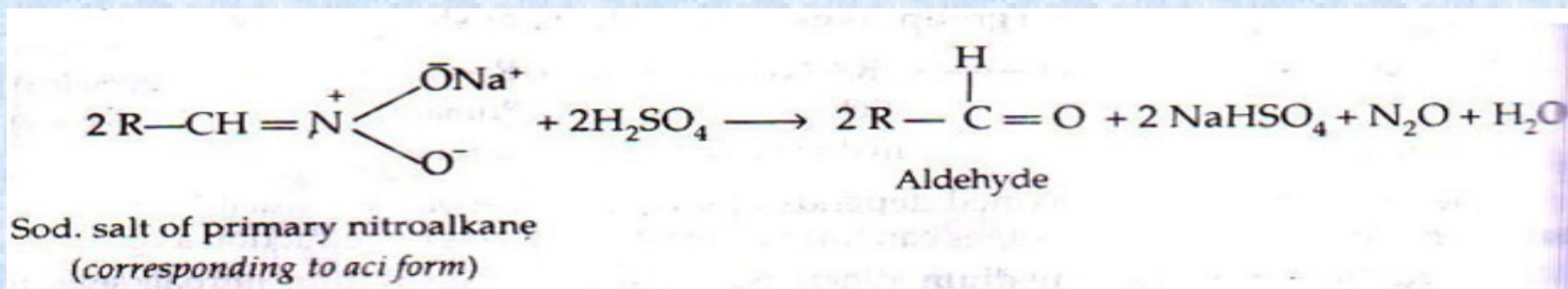
NEUTRAL MEDIUM: hydroxyl amine derivative is obtained.



3 HYDROLYSIS: When boiled with conc. HCl or H₂SO₄, primary nitro alkanes undergo hydrolysis to form carboxylic acids and the corresponding salt of hydroxylamine.

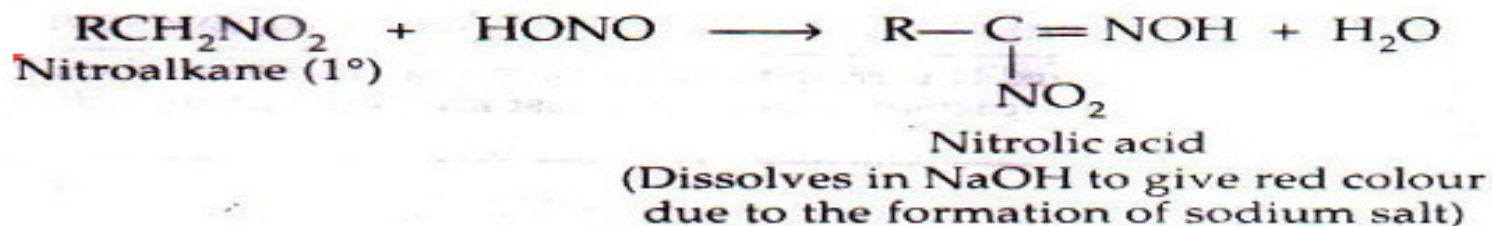


4 NEF REACTION: When sodium salts of primary and secondary nitro alkanes are hydrolysed with dil sulphuric acid aldehydes and ketones respectively are obtained. The reaction proceeds through aci nitro form of nitro alkanes.

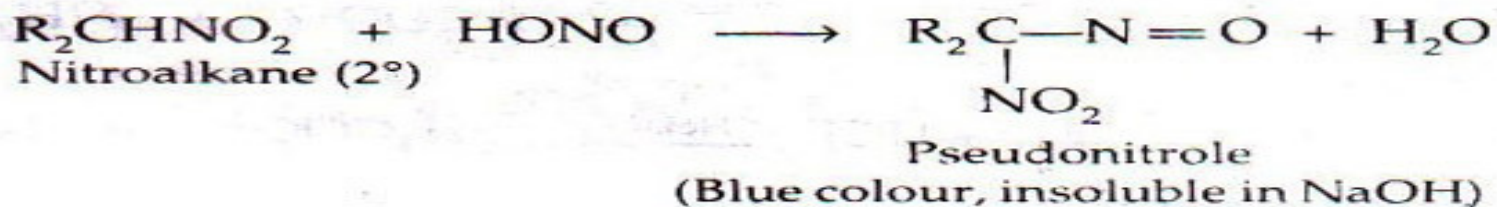


5 ACTION WITH NITROUS ACID:

PRIMARY NITRO ALKANES react with nitrous acid to form nitrolic acids which dissolve in *NaOH* to give a **RED SOLUTION**.



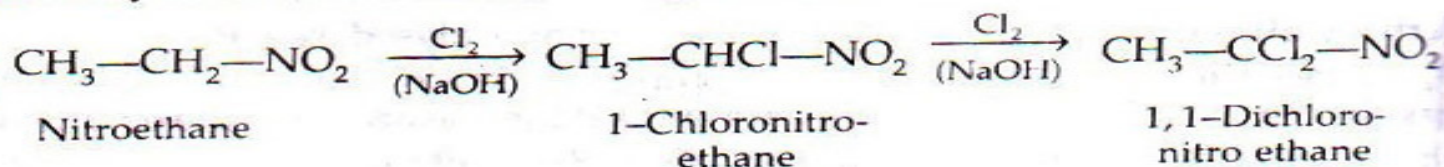
SECONDARY NITRO ALKANES react with nitrous acid to form **pseudonitroles** which have blue colour but do not dissolve in *NaOH*.



TERTIARY NITRO ALKANES do not react with nitrous acid since they do not contain any alpha hydrogen atoms.

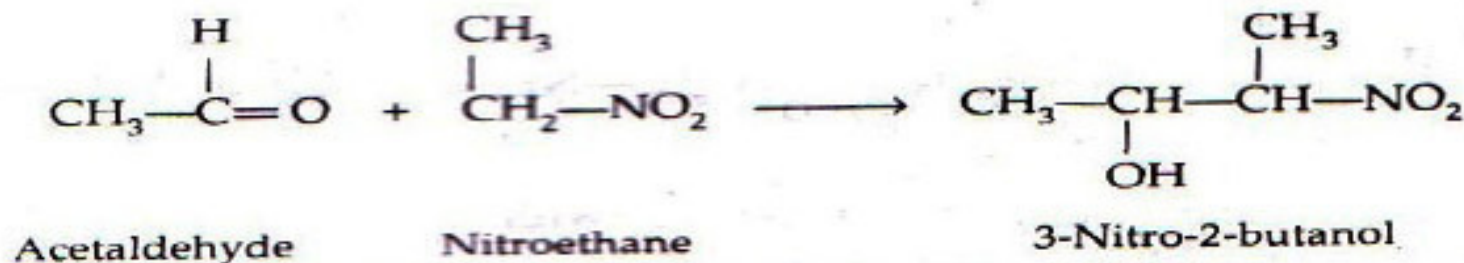
The above test can be used as a test for distinguishing between primary, secondary and tertiary nitro compounds.

6 HALOGENATION: Primary and secondary nitro alkanes undergo halogenation at alpha position



Tertiary alkanes do not undergo halogenation since they do not have alpha hydrogens.

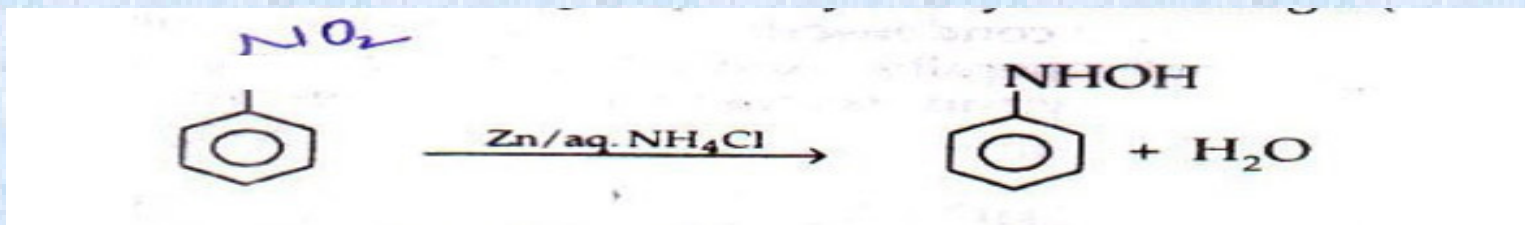
7 CONDENSATION WITH ALDEHYDES: Primary and secondary nitro alkanes undergo aldol type condensation with aldehydes in the presence of a base to form nitro alcohols.



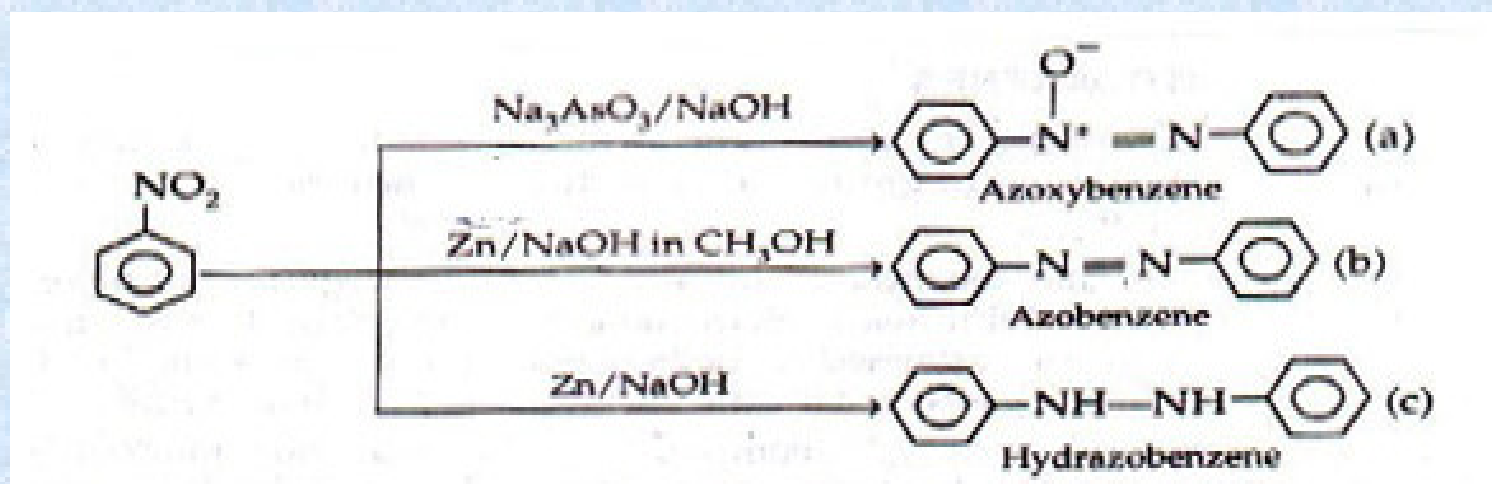
8 MANNICH REACTION : This is a condensation reaction which involves HCHO, Ammonia or a primary or secondary amine (generally taken as hydrochloride) and a compound with at least one active hydrogen.

Catalytic reduction also leads to the formation of aniline

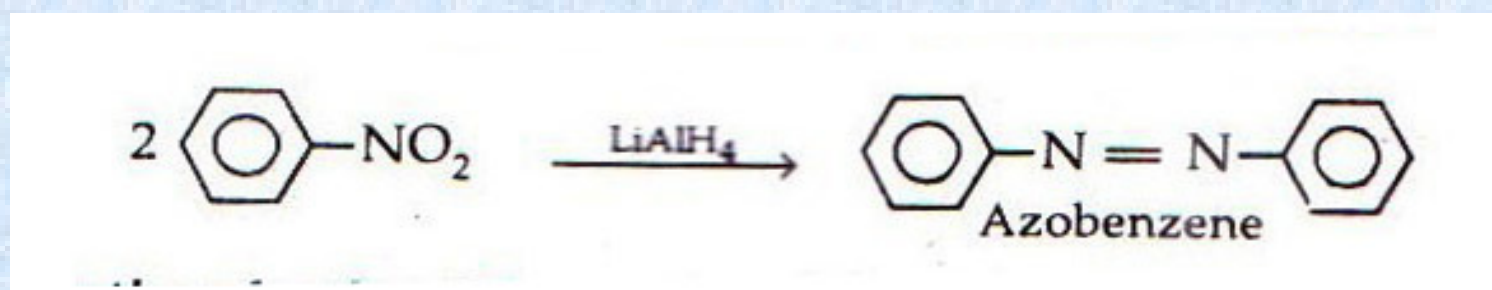
Reduction in neutral medium: The reaction stops at hydroxylamine stage.



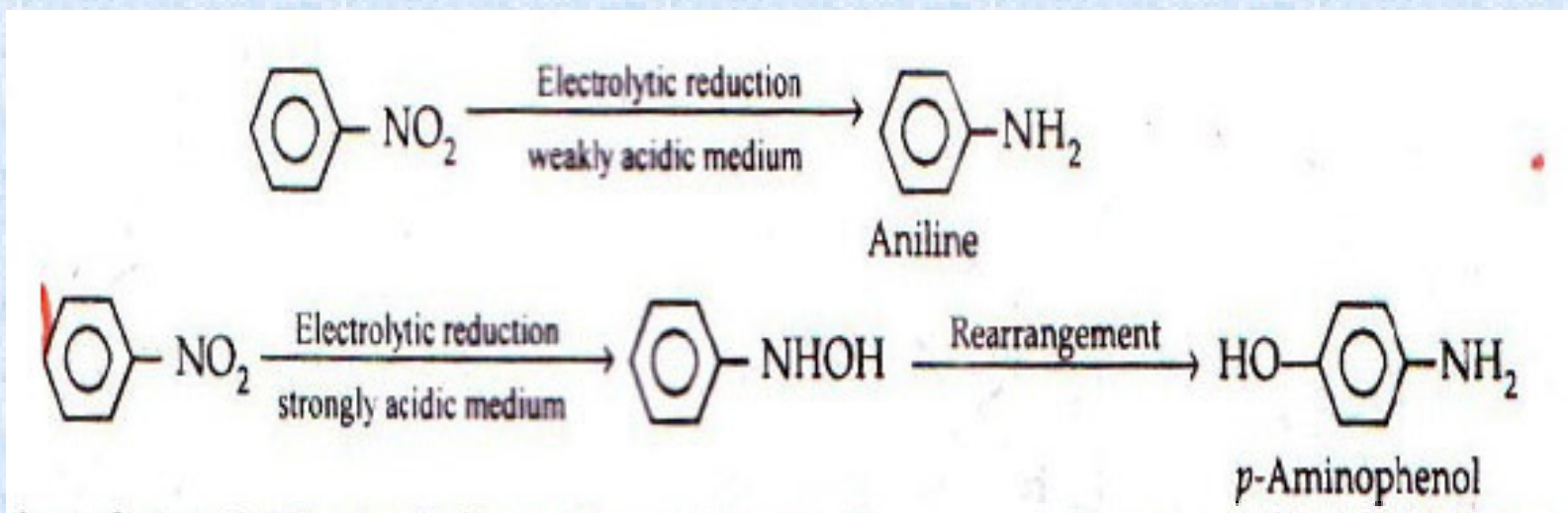
Alkaline medium :



Reduction with LiAlH₄:

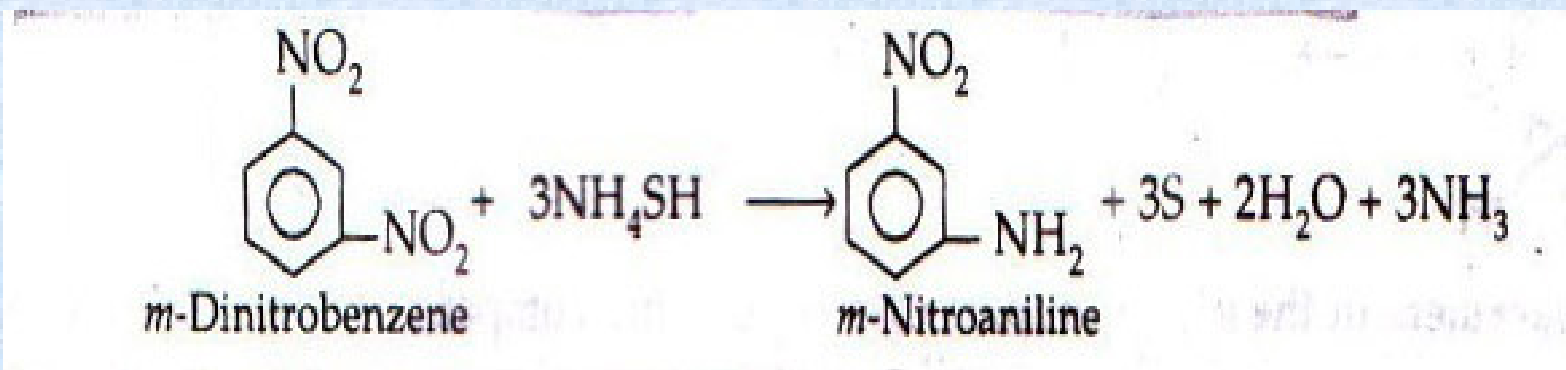


Electrolytic reduction: In weakly acidic medium nitrobenzene gives aniline but in strongly acidic medium p-aminophenol is formed.

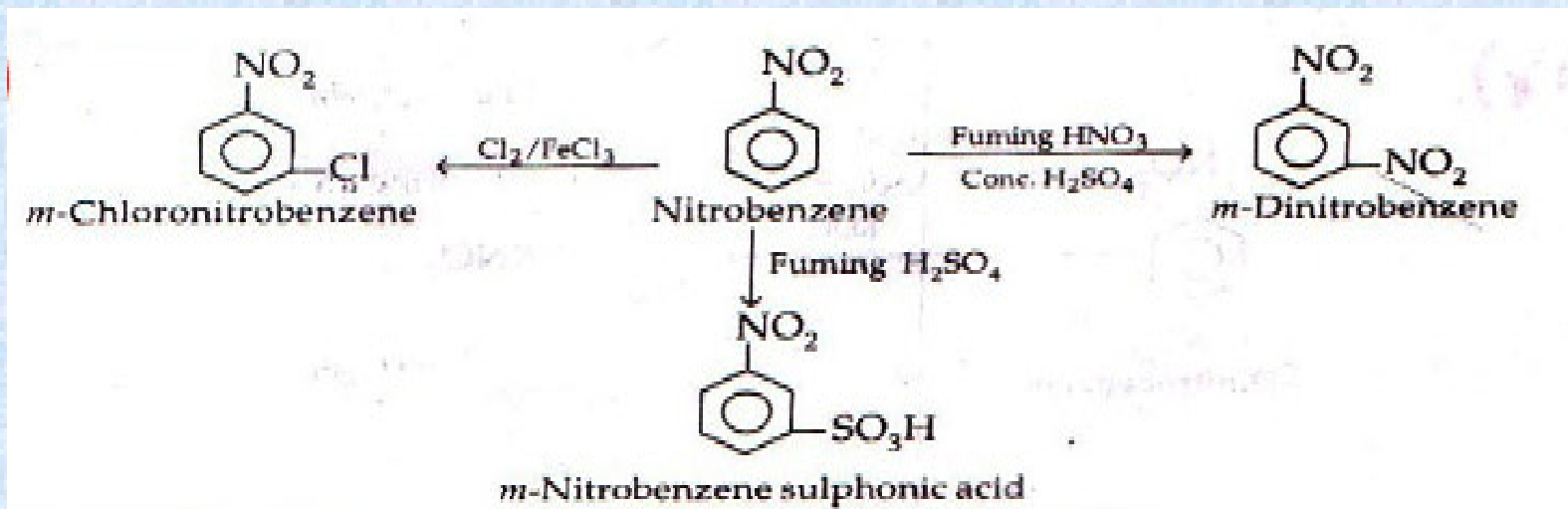


Selective reduction: In case of compounds containing more than one nitro group selective reduction is carried out with a mild reducing agent such as ammonium hydrosulphide.

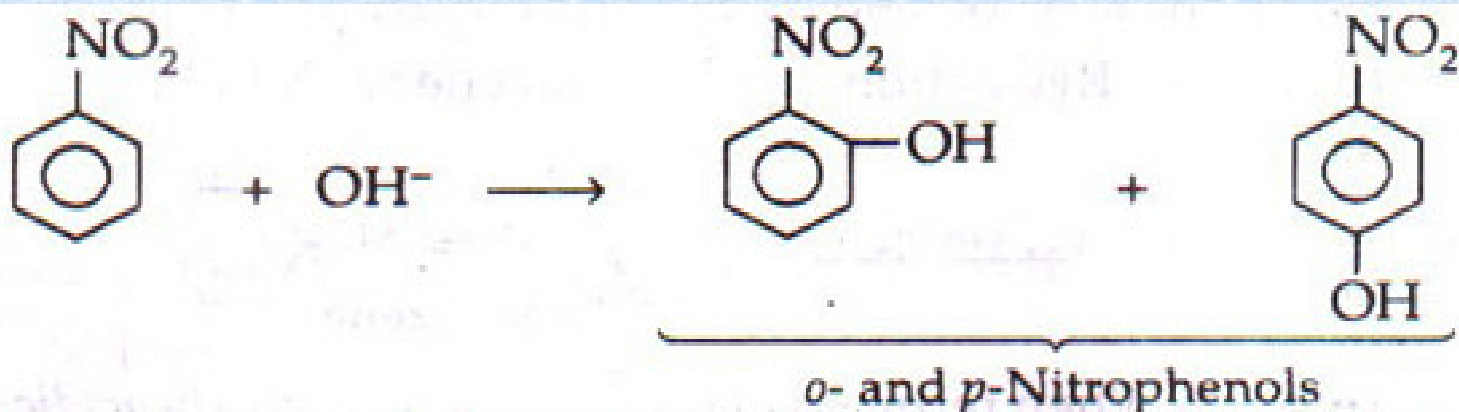
This reduction is called *zinin reduction*.



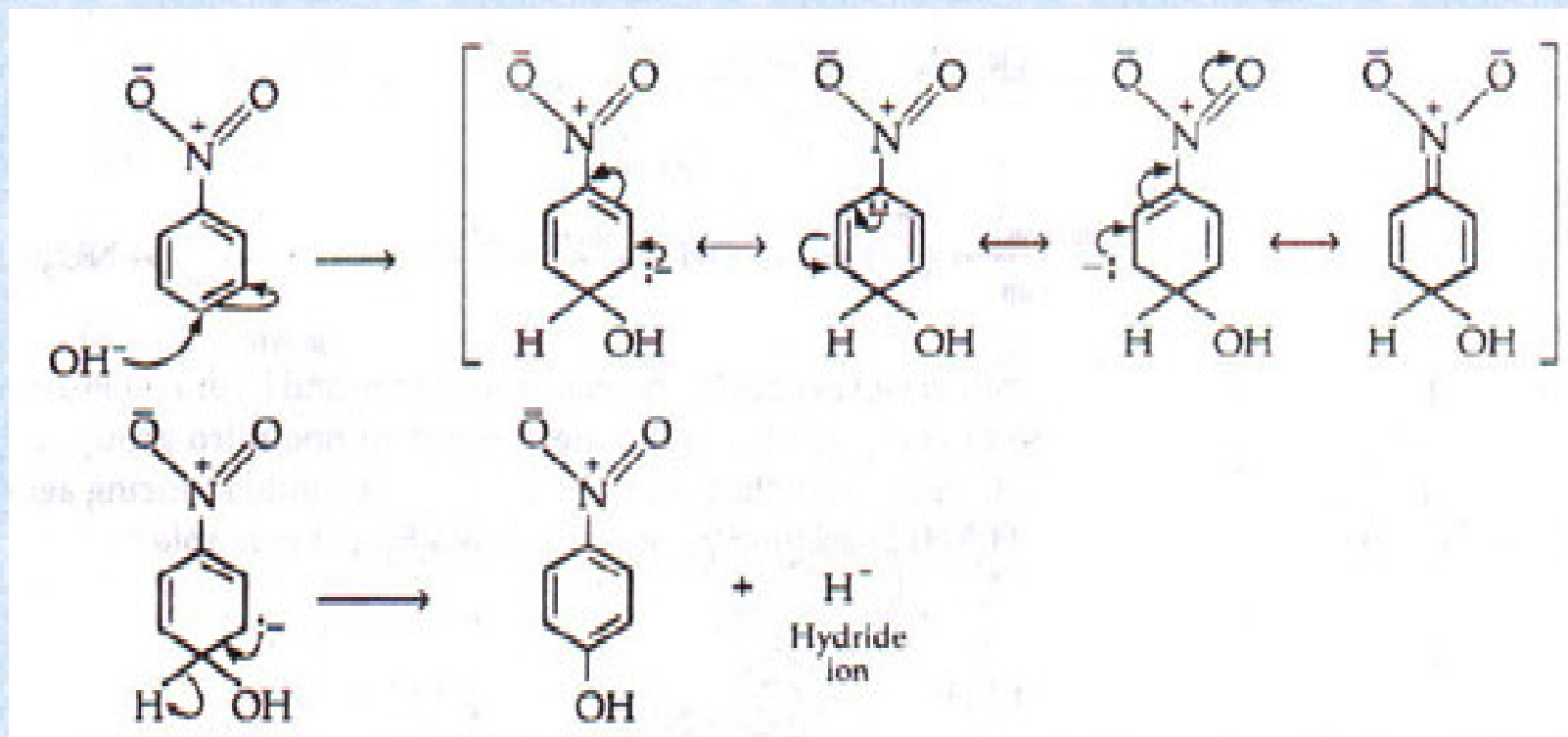
2 Electrolytic substitution: Under strong conditions, nitro compounds may undergo electrophilic substitution at meta position.



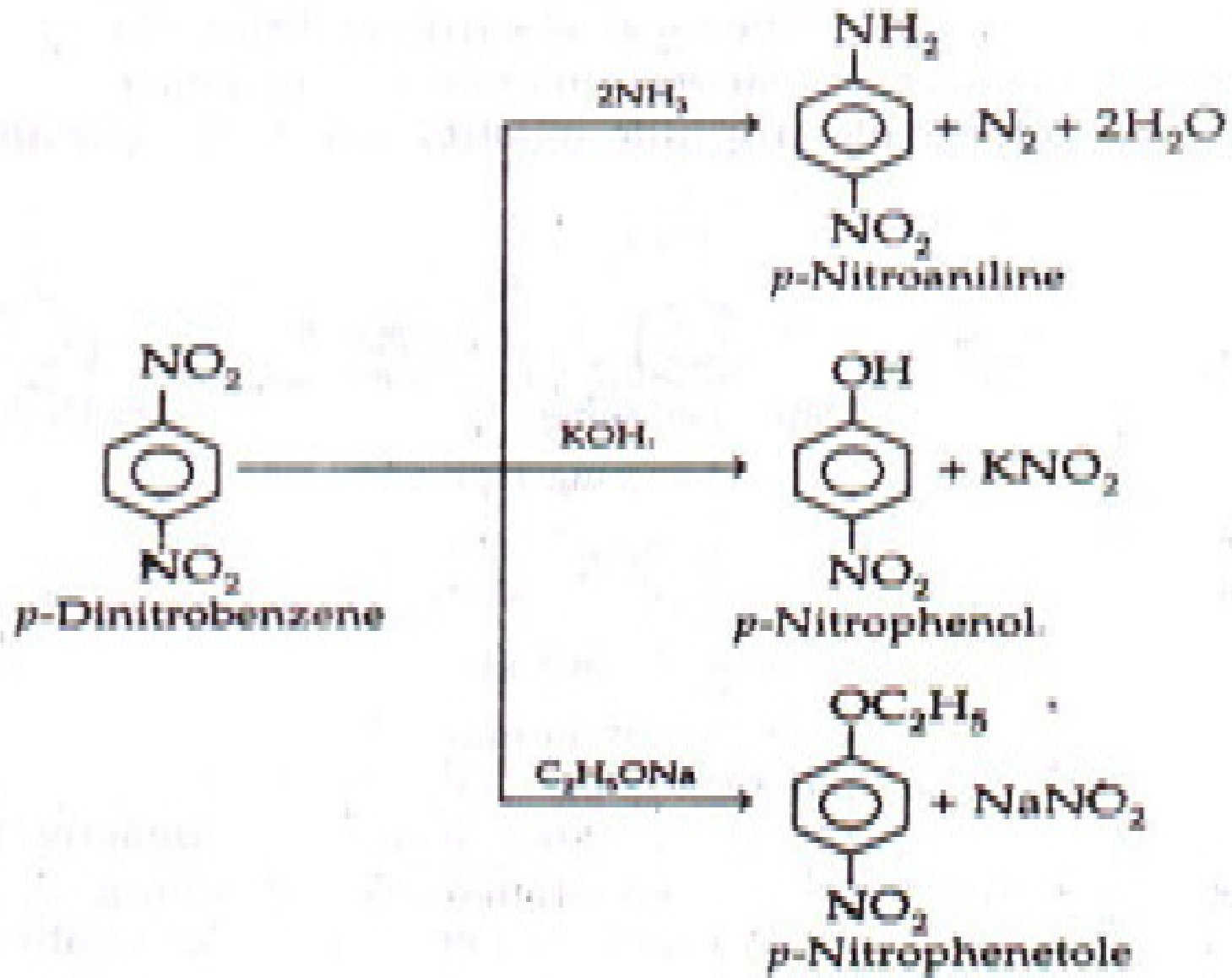
3 Nucleophilic substitution: Nitro benzene on heating with sodium hydroxide gives small amounts of ortho and para nitro phenols.



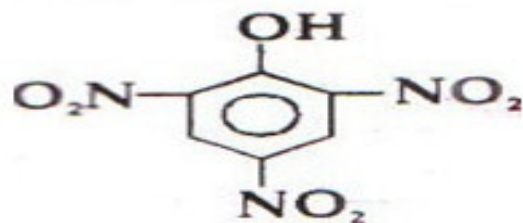
Mechanism:



- 4 Replacement of the nitro group: In case of polynitro compounds one of the nitro groups can be replaced by nucleophilic groups.

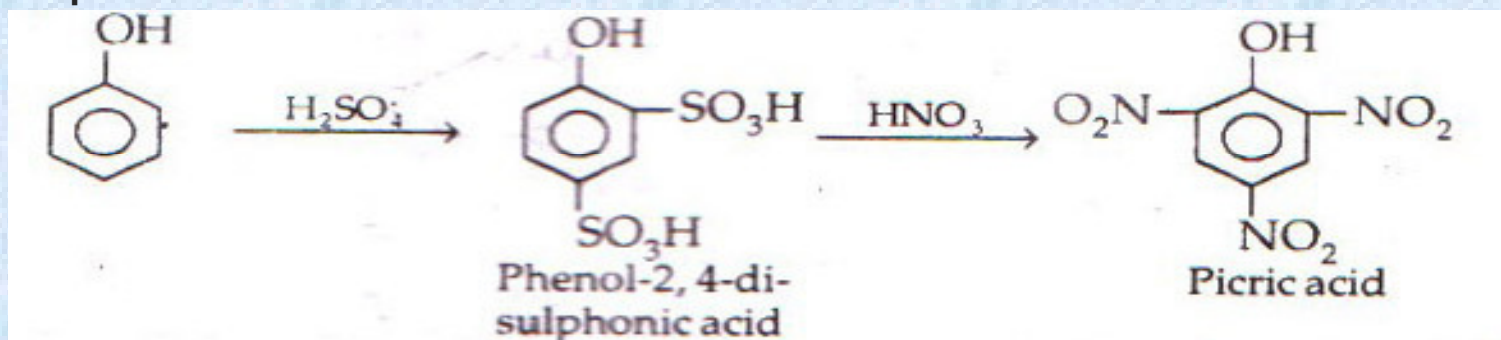


Picric acid

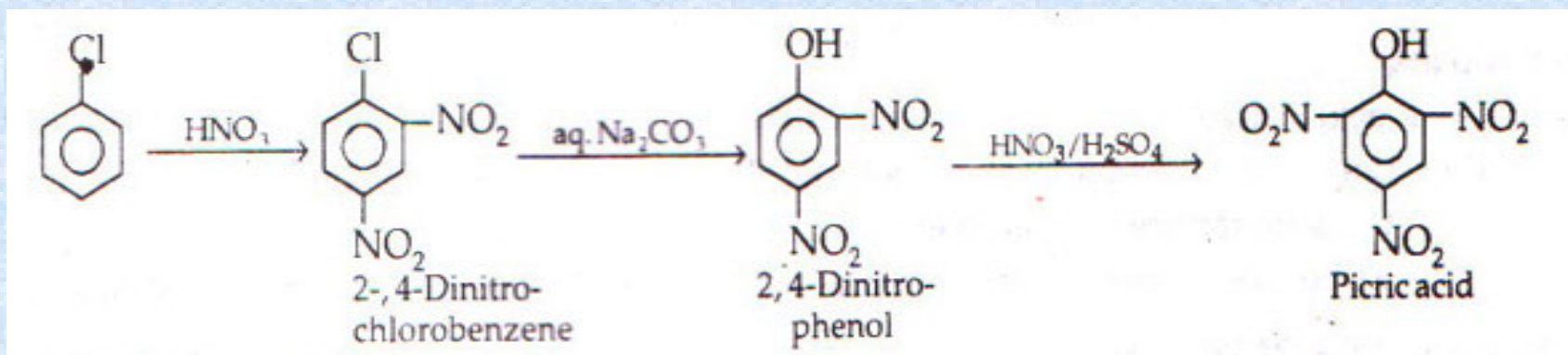


PREPARATION

1 From phenol:



2 From chlorobenzene:

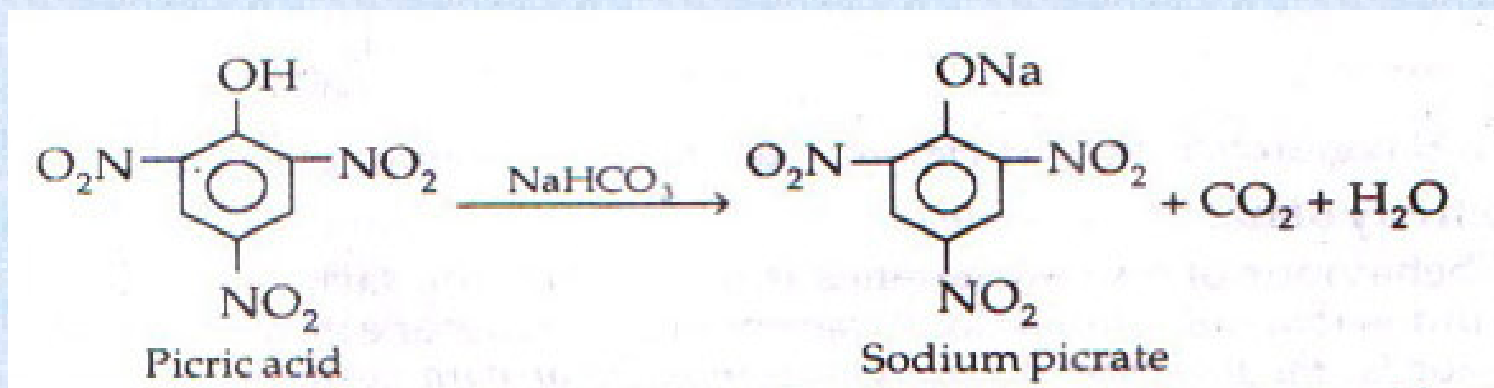


Physical properties

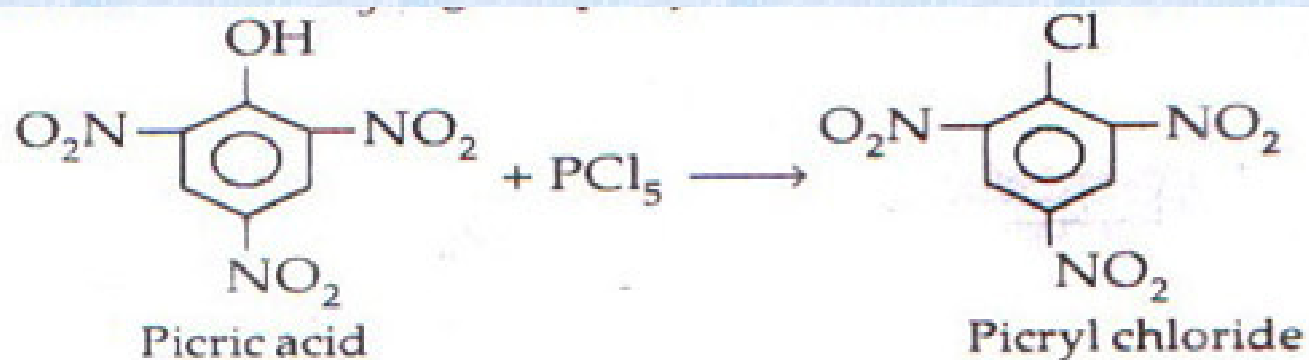
It is a crystalline solid sparingly soluble in water but readily soluble in alcohol and ether.

Chemical properties

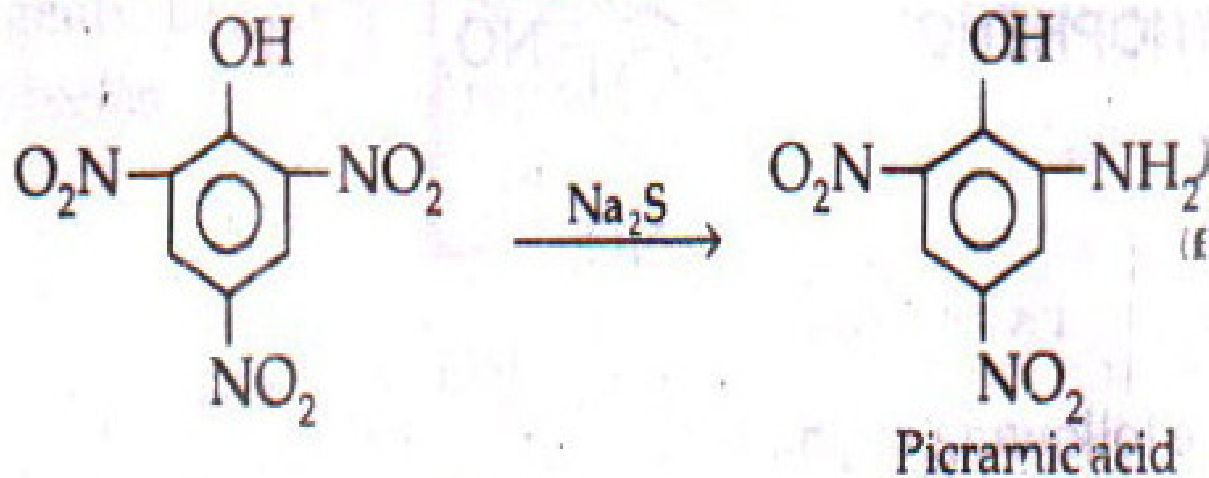
1 Acidic character: Due to the presence of three nitro groups it is much stronger acid than phenols.



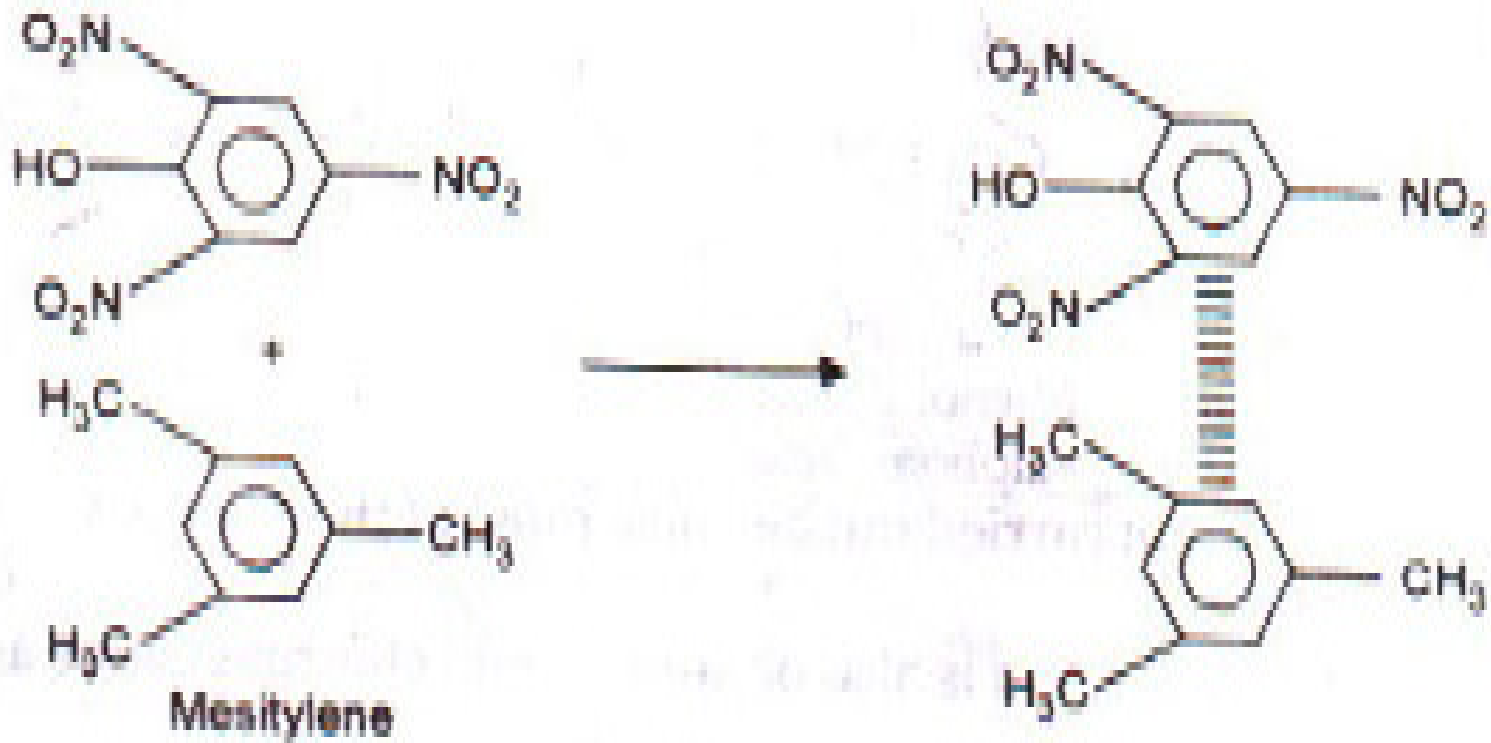
2 Reaction with PCl_5



3 Reaction with Na_2S :



4 Formation with picrates: picric acid reacts with electron rich aromatic compounds such as naphthalene and mesitylenene to form addition products called charge transfer complexes.



USES:

PICRIC ACID IS USED AS:

- 1 An antiseptic and a dye for wool and silk.
- 2 In the manufacture of explosives.
- 3 As a laboratory reagent for the identification of poly nuclear hydrocarbons, amines, alkaloids etc.