



# UNIT 18 NITRO COMPOUNDS

## Structure

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## 18.1 INTRODUCTION

In Unit 17, you studied the chemistry of carboxylic acid derivatives. In this unit, you will study a very important class of nitrogen containing organic compounds called nitro compounds. You may recall that the nomenclature of nitro compounds was discussed in Block 1, Unit 1, Sec. 1.6. The nitro group can be converted to many other functional groups which makes nitro compounds good starting materials for the synthesis of other organic compounds. Let us first study how nitro compounds can be prepared. Then, we will discuss various reactions of nitro compounds. Finally, the uses of nitro compounds will be explained.

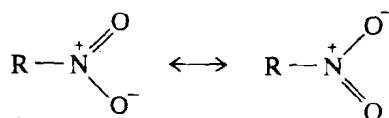
### Objectives

After studying this unit, you should be able to:

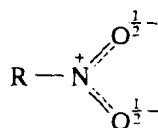
- outline the synthesis of a nitro compound,
- explain the acidic nature of nitro alkanes,
- write reduction products of nitro compounds in different reaction conditions, and
- list the uses of nitro compounds.

## 18.2 STRUCTURE AND PROPERTIES OF NITRO COMPOUNDS

The nitro group,  $-\text{NO}_2$ , which is the functional group of nitro compounds, is a resonance hybrid of two equivalent contributing structures as shown below.



Thus, it can be represented by the following hybrid structure:



Remember that a similar resonance hybrid was written in the case of carboxylate ion.

You can see in the hybrid structure that there is a positive charge on the nitrogen atom and the negative charge is distributed equally on the two oxygen atoms. This separation of charge is reflected in the high dipole moment values for nitro compounds which range between  $11.67 \times 10^{-30} \text{ C m}$  and  $13.35 \times 10^{-30} \text{ C m}$ , depending upon the nature of the hydrocarbon group. Their polar nature is also indicated by their high boiling points.

Nitro Compound
nitromethane
nitroethane
2-nitropropane
1-nitropropane
nitrobenzene

b.p./K
374
387
393
404
484

## Spectral properties of nitro compounds

Aliphatic nitro compounds show an absorption near 270 nm in their ultraviolet spectrum due to  $n \rightarrow \pi^*$  transitions. However, aromatic nitro compounds absorb at longer wavelengths, i.e.,  $\sim 300$  nm, due to the extended conjugation.

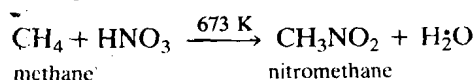
The infrared spectra of nitro alkanes show strong bands at about  $1550\text{ cm}^{-1}$  and  $1375\text{ cm}^{-1}$  whereas aromatic nitro compounds show these absorptions at slightly lower frequencies.

## 18.3 PREPARATION OF NITRO COMPOUNDS

The nitro compounds can be prepared by a number of methods. Let us now study these methods.

### 1. By direct nitration of hydrocarbons

Hydrocarbons can be nitrated using nitric acid. The reaction with aliphatic hydrocarbons requires high temperatures and is carried out in the vapour phase. For example,



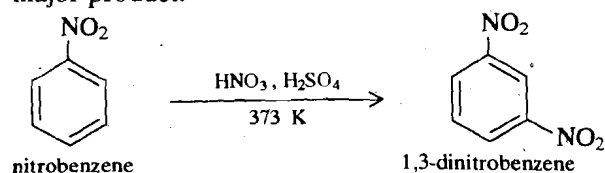
Nitration is accompanied by oxidation.

You have studied, under the nitration of alkanes in sub-Sec. 6.6.2, Unit 6, Block 2, that nitration of higher alkanes yields a mixture of nitroalkanes which are separated using fractional distillation.

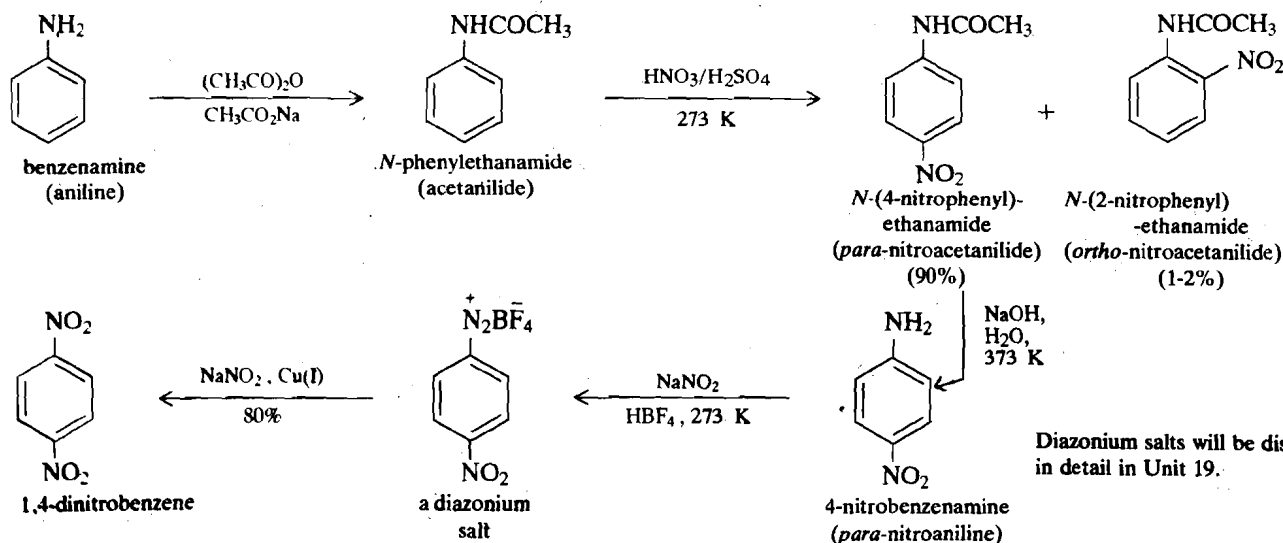
In contrast to this, nitration of aromatic compounds takes place readily in the liquid phase and can be carried out near room temperature or on a steam bath. You have already studied about the nitration of benzene in sub-Sec. 9.6.1, Unit 9, Block 2.

You may recall that nitration of aromatic compounds is an electrophilic substitution reaction, the electrophile being the nitronium ion,  $\text{NO}_2^+$ .

The products of nitration of substituted benzenes depend upon the nature of the substituent groups already present in the molecule. The nitro group itself is *meta*-directing and, therefore, nitration of nitrobenzene yields 1,3-dinitrobenzene as the major product.



1,4-Dinitrobenzene can be prepared by starting with benzenamine. Since the amino group is *o*-, *p*-directing, nitration of benzenamine followed by the conversion of the amino group to nitro group, should give the desired compound. Benzenamine, however, is susceptible to oxidation, so the amino group is first protected by ethanoylation (acetylation). The sequence of reactions is outlined below:

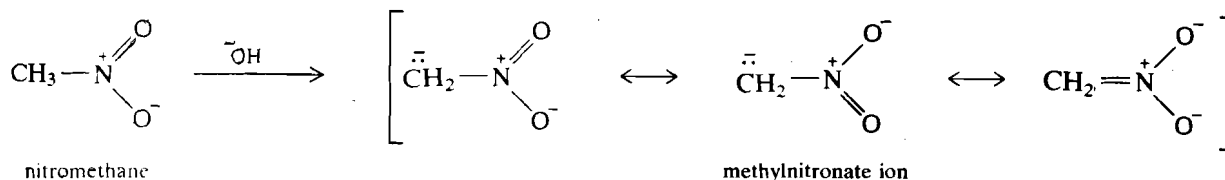


Diazonium salts will be discussed in detail in Unit 19.



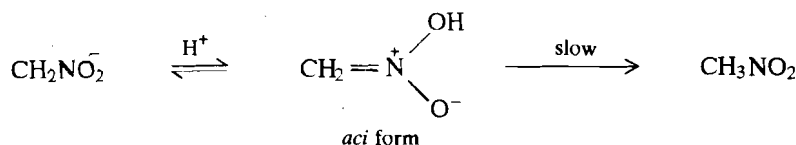
## 1. As weak acids

The hydrogen atoms bonded to the carbon atom carrying the nitro group are acidic in nature. Thus, nitro compounds dissolve in bases like sodium hydroxide. The anion so produced is resonance stabilised as shown below:



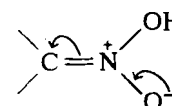
nitroalkane	$pK_a$
nitromethane	10.2
nitroethane	8.5
nitropropane	7.8

On acidification, the anion yields the acidic isomer of nitromethane known as the *aci* form which slowly changes to the more stable nitro form.

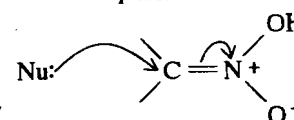


The *aci* form can behave both as a nucleophile as well as an electrophile.

as nucleophile:

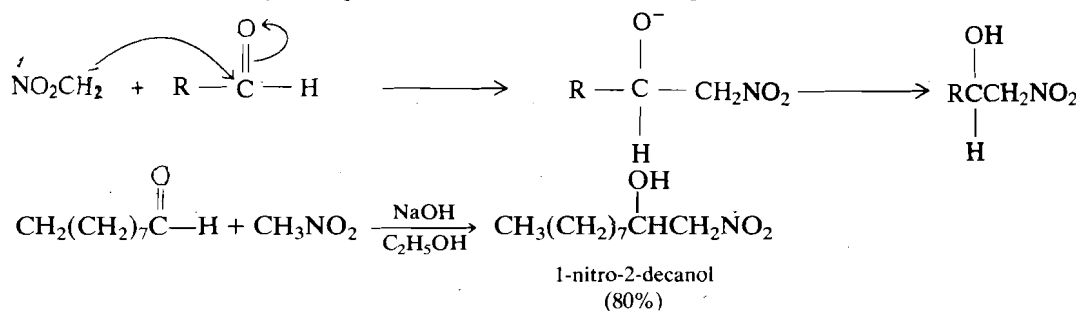


as electrophile:

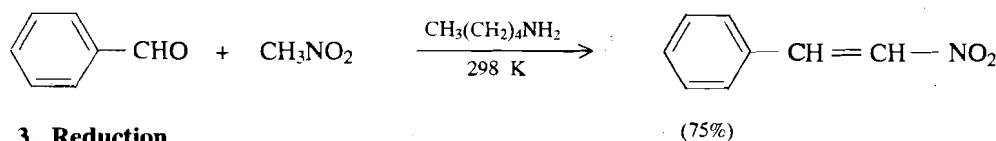


## 2. Henry reaction

The anions obtained from nitroalkanes as explained above can undergo nucleophilic reactions with carbonyl compounds similar to the aldol type addition reaction.

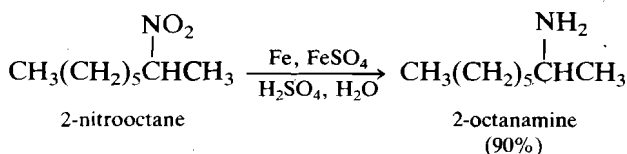


In case of aromatic aldehydes, the product obtained undergoes dehydration as shown below:



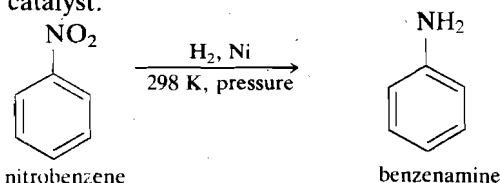
## 3. Reduction

Nitro compounds can be reduced with a variety of reducing agents. Nitroalkanes can be converted to alkanamines as shown below:

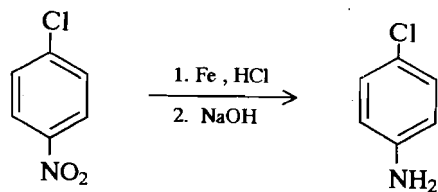


The product of reduction of aromatic nitro compounds depends on the reaction conditions employed. Catalytic reduction and reduction in acidic media yields aromatic amines.

Catalytic hydrogenation is carried out by using platinum, palladium or nickel as the catalyst.



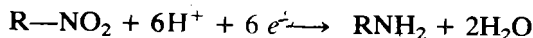
For reduction in **acidic medium** a metal and an acid is used. Usually iron or zinc and hydrochloric acid are taken.



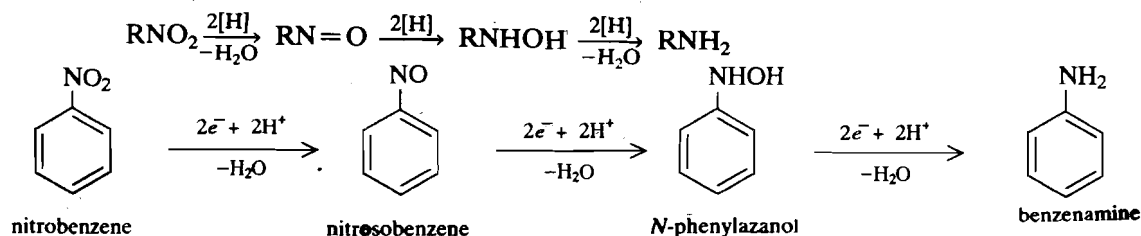
1-chloro-4-nitrobenzene

4-chlorobenzenamine

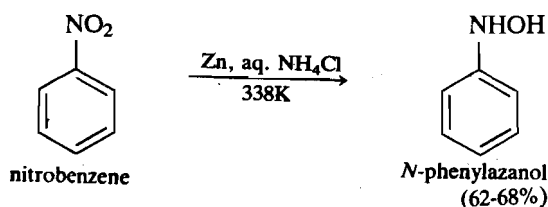
Reduction of a nitro compound to an amine requires six equivalents of the reducing agent, i.e.,



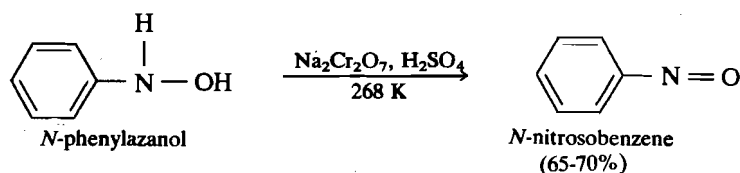
The reduction actually proceeds in a series of two-electron steps via the nitroso compounds ( $\text{R-N=O}$ ) and *N*-substituted azanols ( $\text{RNHOH}$ ) as successive intermediates.



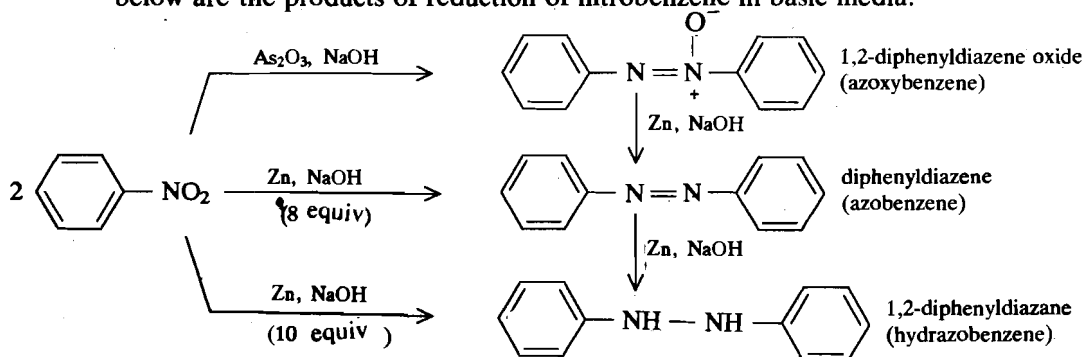
Reduction can be stopped at the *N*-substituted azanol stage when reduction is carried out in **neutral conditions** using zinc and ammonium chloride.



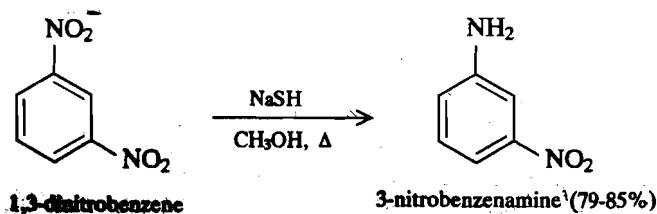
*N*-phenylazanol obtained above can be oxidised to nitrosobenzene.



Reduction of nitro compounds in **basic medium** gives binuclear compounds. Given below are the products of reduction of nitrobenzene in basic media.



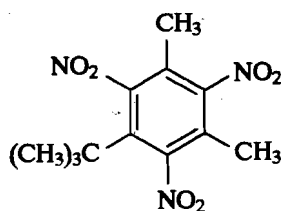
Selective reduction of the nitro group is also possible as shown below:



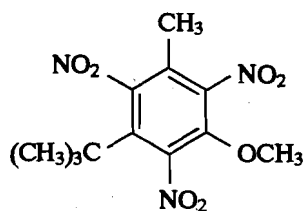
## 18.5 IMPORTANT USES OF NITRO COMPOUNDS

In addition to the synthetic utility of nitro compounds, you have studied that they are used in the preparation of explosives.

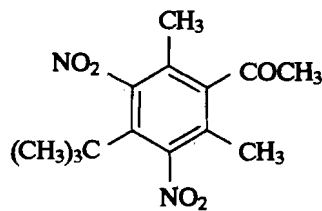
Several polynitro compounds possess an odour resembling musk and are used in perfumery. Some such examples are listed below:



musk xylol

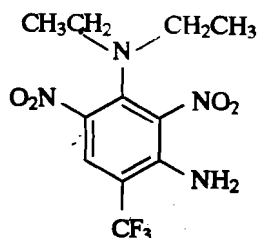


musk ambrette

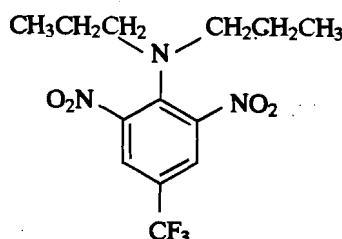


must ketone

Nitro compounds have important herbicidal uses. Some nitro compounds used as weedicides for the cotton, soybean and peanut crops are shown below:



*N,N*-diethyl-6-trifluoromethyl-2,4-dinitro-1,3-benzenediamine  
(dinitramine)



*N,N*-dipropyl-4-trifluoromethyl-2,6-dinitrobenzenamine  
(trifluralin)

## 18.6 SUMMARY

In this unit, you have studied that :

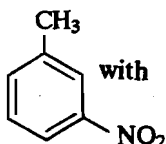
- Drastic conditions are required for the preparation of nitroalkanes whereas aromatic nitro compounds are easier to synthesise.
- Primary and secondary nitro compounds behave as weak acids and they show nitro—acinitro tautomerism.
- Nitro compounds react with carbonyl compounds in alkaline medium to yield aldol type products.
- Nitroalkanes can be reduced to alkanamines.
- Aromatic nitro compounds on catalytic reduction and reduction in acidic conditions yield amines whereas in neutral media the product is *N*-substituted azanol. The reduction in basic media leads to a series of bimolecular reduction products, depending upon the nature of the reducing agent.

## 18.7 TERMINAL QUESTIONS

- 1) Write equations for the reactions of 3-nitropentane with
  - a)  $H_2$ /Catalyst
  - b) dil. NaOH, HCHO

- 2) Write the major product of reduction of

- a) Zn/alc. NaOH
- b) Pt/ $H_2$
- c) Zn/aq.  $NH_4Cl$
- d)  $SnCl_2/HCl$



## 18.8 ANSWERS

## Terminal Questions

