Nitro Compounds

Dr. Irshad Ahmad Bhat
Assistant Professor
Govt. Sheikh-Ul-Alam Memorial Degree College, Budgam

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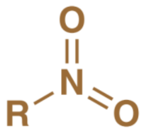
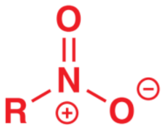


incorrect structure
for the nitro group



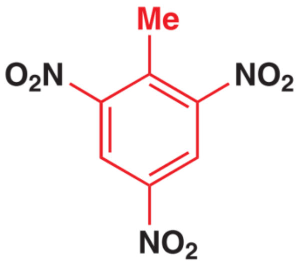
the nitro
group

nitrogen cannot
have five bonds!

delocalization in the nitro group

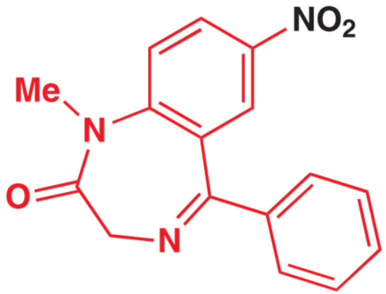
can be drawn as
(both NO bonds
identical)

defensive nitroalkene from termite soldiers



TNT

Explosive

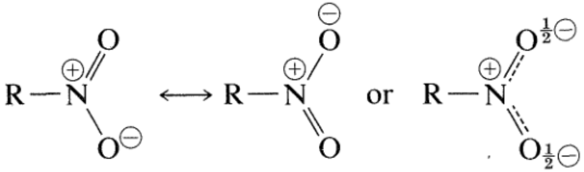


nitrazepam

Sleeping Pill

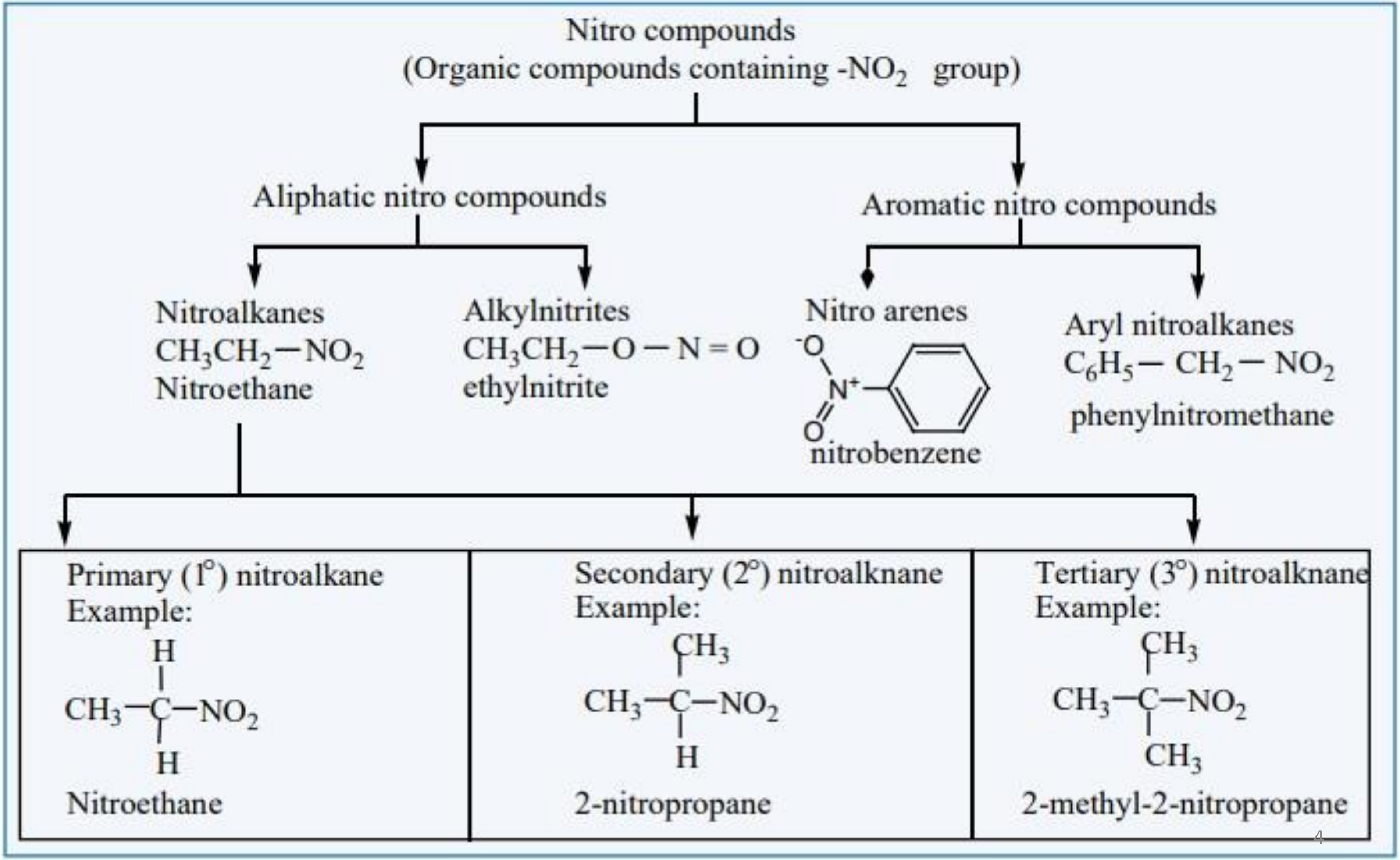
Nitro Compounds

Nitro compounds are a very important class of nitrogen derivatives. The nitro group, −NO2−NO2, like the carboxylate anion, is a hybrid of two equivalent resonance structures:



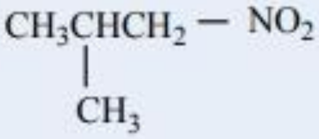
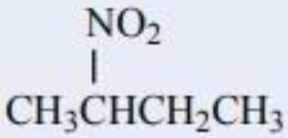
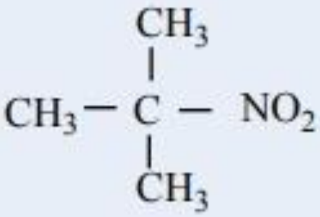
The hybrid structure has a full positive charge on nitrogen and a half-negative charge on each oxygen. This is in accord with the high dipole moments of nitro compounds, which fall between 3.5D and 4.0D, depending upon the nature of R-group. The polar character of the nitro group results in lower volatility of nitro compounds than ketones of about the same molecular weight; thus the boiling point of nitromethane (MW 61) is 101°C, whereas 2-propanone (MW 58) has a boiling point of 56°C. Surprisingly, the water solubility is low; a saturated solution of nitromethane in water is less than 10% by weight, whereas 2-propanone is completely miscible with water.

Nitro groups of nitroalkanes can be identified by strong infrared bands at about 1550cm^{-1} and 1375cm^{-1}, whereas the corresponding bands in the spectra of aromatic nitro compounds occur at slightly lower frequencies. A weak $n \rightarrow \pi*$ transition occurs in the electronic spectra of nitroalkanes at around 270nm; aromatic nitro compounds, such as nitrobenzene, have extended conjugation and absorb at longer wavelengths (~330nm).



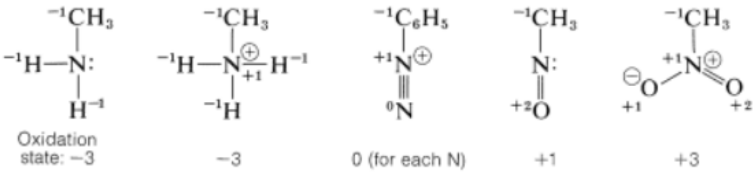
Nitro compounds
(Organic compounds containing $-NO_2$ group)

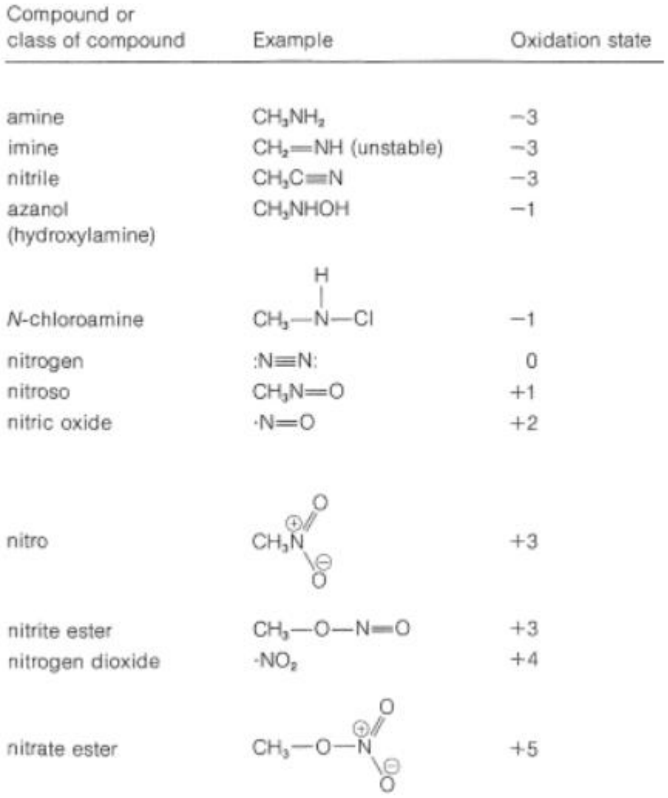
- Aliphatic nitro compounds
  - Nitroalkanes
    $CH_3CH_2-NO_2$
    Nitroethane
    - Primary (1°) nitroalkane
      Example:
      $CH_3-\overset{H}{\underset{H}{C}}-NO_2$
      Nitroethane
    - Secondary (2°) nitroalknane
      Example:
      $CH_3-\overset{CH_3}{\underset{H}{C}}-NO_2$
      2-nitropropane
    - Tertiary (3°) nitroalknane
      Example:
      $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-NO_2$
      2-methyl-2-nitropropane
  - Alkylnitrites
    $CH_3CH_2-O-N=O$
    ethylnitrite
- Aromatic nitro compounds
  - Nitro arenes
    nitrobenzene
  - Aryl nitroalkanes
    $C_6H_5-CH_2-NO_2$
    phenylnitromethane

Isomerism	**Structural formula of isomers**
Chain isomerism: They differ in the length of carbon chain.	$CH_3CH_2CH_2CH_2-NO_2$ 1 - nitrobutane and $CH_3\underset{\underset{CH_3}{\vert}}{C}HCH_2-NO_2$ 2 - methyl - 1-nitropropane
Position isomerism: They differ in the position of nitro group.	$CH_3CH_2CH_2CH_2-NO_2$, 1 - nitrobutane $CH_3\overset{\overset{NO_2}{\vert}}{C}HCH_2CH_3$ 2 - nitrobutane and $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}}-NO_2$ 2 - methyl - 2-nitropropane
Functional isomerism: Nitroalkanes exhibit functional isomerism with alkylnitrites	$CH_3CH_2CH_2CH_2-NO_2$ 1 - nitrobutane and $CH_3CH_2CH_2CH_2-O-N=O$ butyl nitrite

Different Oxidation States of Nitrogen in Organic Chemistry

Nitrogen has a wide range of oxidation states in organic compounds. We can arrive at an arbitrary scale for the oxidation of nitrogen in much the same way as we do for carbon. We simply define elementary nitrogen as the zero oxidation state, and every atom bonded to nitrogen contributes -1 to the oxidation state if it is more electropositive than nitrogen and +1 if it is more electronegative. Doubly bonded atoms are counted twice, and a formal positive charge associated with nitrogen counts as +1.



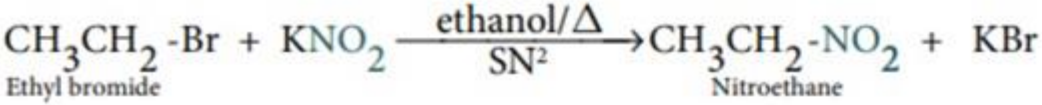


Compound or class of compound	Example	Oxidation state
amine	CH_3NH_2	−3
imine	$CH_2{=}NH$ (unstable)	−3
nitrile	$CH_3C{\equiv}N$	−3
azanol (hydroxylamine)	CH_3NHOH	−1
N-chloroamine	$CH_3{-}\overset{H}{\overset{\mid}{N}}{-}Cl$	−1
nitrogen	$:N{\equiv}N:$	0
nitroso	$CH_3N{=}O$	+1
nitric oxide	$\cdot N{=}O$	+2
nitro	$CH_3\overset{\oplus}{N}({=}O)O^{\ominus}$	+3
nitrite ester	$CH_3{-}O{-}N{=}O$	+3
nitrogen dioxide	$\cdot NO_2$	+4
nitrate ester	$CH_3{-}O{-}\overset{\oplus}{N}({=}O)O^{\ominus}$	+5

Preparation of nitroalkanes

From alkyl halides: (Laboratory method)

a) Alkyl bromides (or) iodides on heating with ethanolic solution of potassium nitrite gives nitroethane.

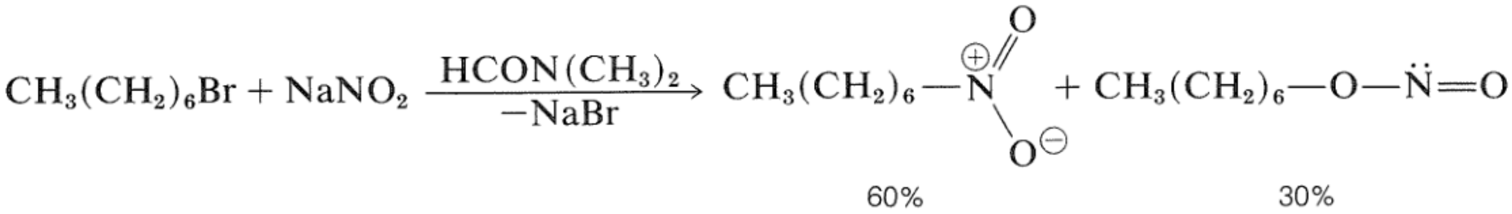


$$\underset{\text{Ethyl bromide}}{CH_3CH_2\text{-}Br} + KNO_2 \xrightarrow[SN^2]{\text{ethanol}/\Delta} \underset{\text{Nitroethane}}{CH_3CH_2\text{-}NO_2} + KBr$$

The reaction follows SN2 mechanism.

This method is not suitable for preparing nitrobenzene because the bromine directly attached to the benzene ring cannot be cleaved easily.

As will be seen from, formation of the nitrite ester by O- instead of N-alkylation is a competing reaction:



Silver nitrite sometimes is used in preference to sodium nitrite, usually in diethyl ether as solvent:

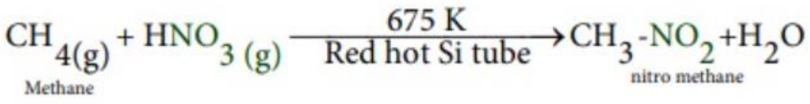
$$\mathrm{ICH_2CO_2C_2H_5 + AgNO_2 \xrightarrow{0^\circ,\ ether} O_2NCH_2CO_2C_2H_5 + AgI}$$

ethyl nitroethanoate
77%

Vapour phase nitration of alkanes: (Industrial method)

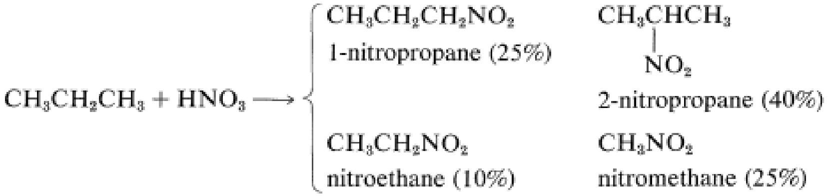
Another reaction of commercial importance is the nitration of alkanes to give nitroparaffins. Such reactions usually are carried out in the vapor phase at elevated temperatures using nitric acid (HNO_3) or nitrogen tetroxide (N_2O_4) as the nitrating agent. In contrast the nitration of aromatic compounds can be carried out in liquid phase as well.

Gaseous mixture of methane and nitric acid passed through a red hot metal tube to give nitromethane.



$$\underset{\text{Methane}}{CH_{4(g)}} + HNO_{3\,(g)} \xrightarrow[\text{Red hot Si tube}]{675\ K} \underset{\text{nitro methane}}{CH_3\text{-}NO_2} + H_2O$$

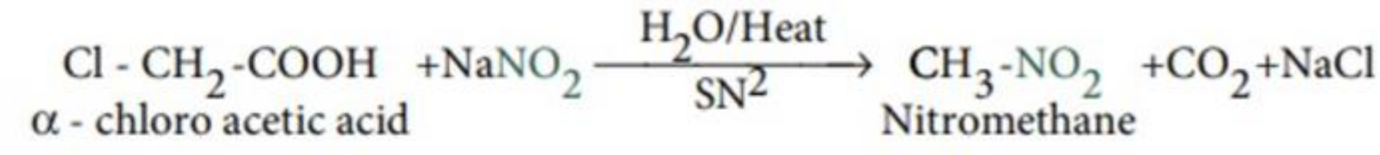
All available evidence points to a radical mechanism for nitration, but many aspects of the reaction are not fully understood. Mixtures are obtained; nitration of propane gives not only 1- and 2-nitropropanes but nitroethane and nitromethane:



In commercial practice, the yield and product distribution in nitration of alkanes is controlled as far as possible by the judicious addition of catalysts (e.g., oxygen and halogens), which are believed to raise the concentration of alkyl radicals. The products are separated from the mixtures by fractional distillation.

From a- halocarboxylic acid

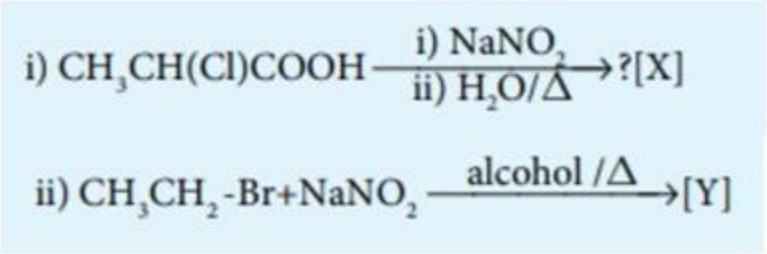
α- choloroacetic acid when boiled with aqueous solution of sodium nitrite gives nitromethane.



$$\underset{\alpha\text{ - chloro acetic acid}}{Cl\text{ - }CH_2\text{-}COOH} + NaNO_2 \xrightarrow[SN^2]{H_2O/Heat} \underset{\text{Nitromethane}}{CH_3\text{-}NO_2} + CO_2 + NaCl$$

Evaluate yourself

Find out the product of the following reactions.

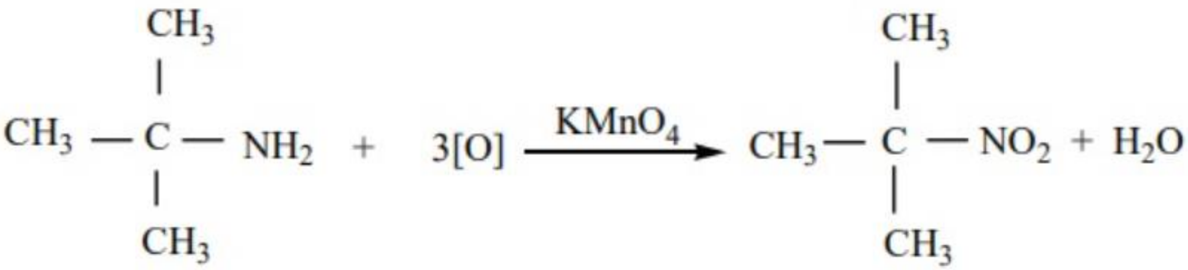


i) $CH_3CH(Cl)COOH \xrightarrow[\text{ii) }H_2O/\Delta]{\text{i) }NaNO_2} ?[X]$

ii) $CH_3CH_2\text{-}Br + NaNO_2 \xrightarrow{\text{alcohol }/\Delta} [Y]$

4) Oxidation of tert – alkyl amines

tert – butyl amine is oxidised with aqueous $KMnO_4$ to give tert – nitro alkanes.



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-NH_2 + 3[O] \xrightarrow{KMnO_4} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-NO_2 + H_2O$$

tert-butylamine

2 - methyl - 2 - nitro propane

5) Oxidation of Oximes

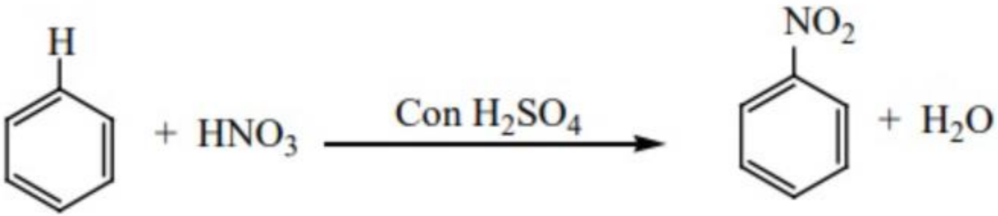
Oxidation of acetaldoxime and acetoneoxime with trifluoroperoxy acetic acid gives nitroethane (1°) and 2 – nitropropane (2 °) respectively.

$$\underset{\text{Acetaldoxime}}{CH_3\text{-}CH{=}N\text{-}OH} \xrightarrow[{[O]}]{CF_3COOOH} \underset{\text{Nitroethane}}{CH_3CH_2\text{-}NO_2}$$

Preparation of Nitroarenes

1) By Direct nitration

When benzene is heated at 330K with a nitrating mixture (Con.HNO_3 + Con.H_2SO_4) , electrophilic substitution takes place to form nitro benzene. (Oil of mirbane)

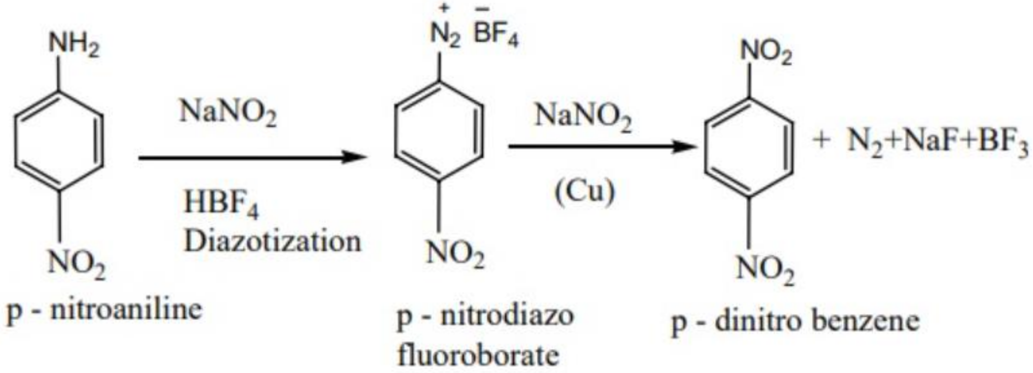


On direct nitration of nitrobenzene m- dinitrobenzene is obtained

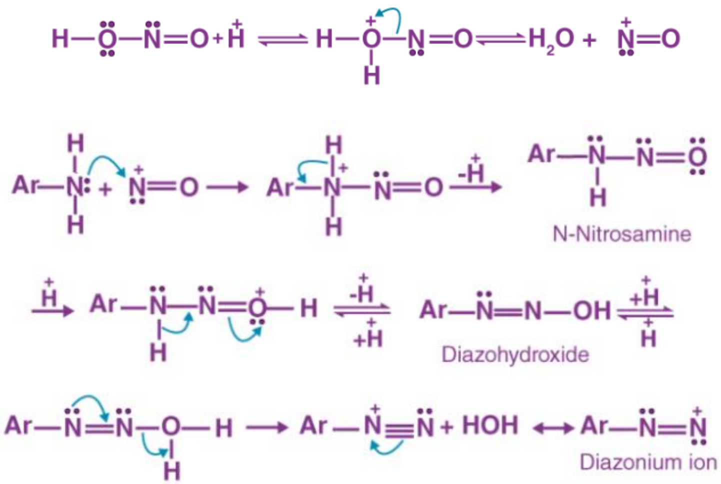
2) Indirect method

Nitration of nitro benzene gives m-dinitrobenzene. The following method is adopted for the preparation of p-dinitrobenzene.

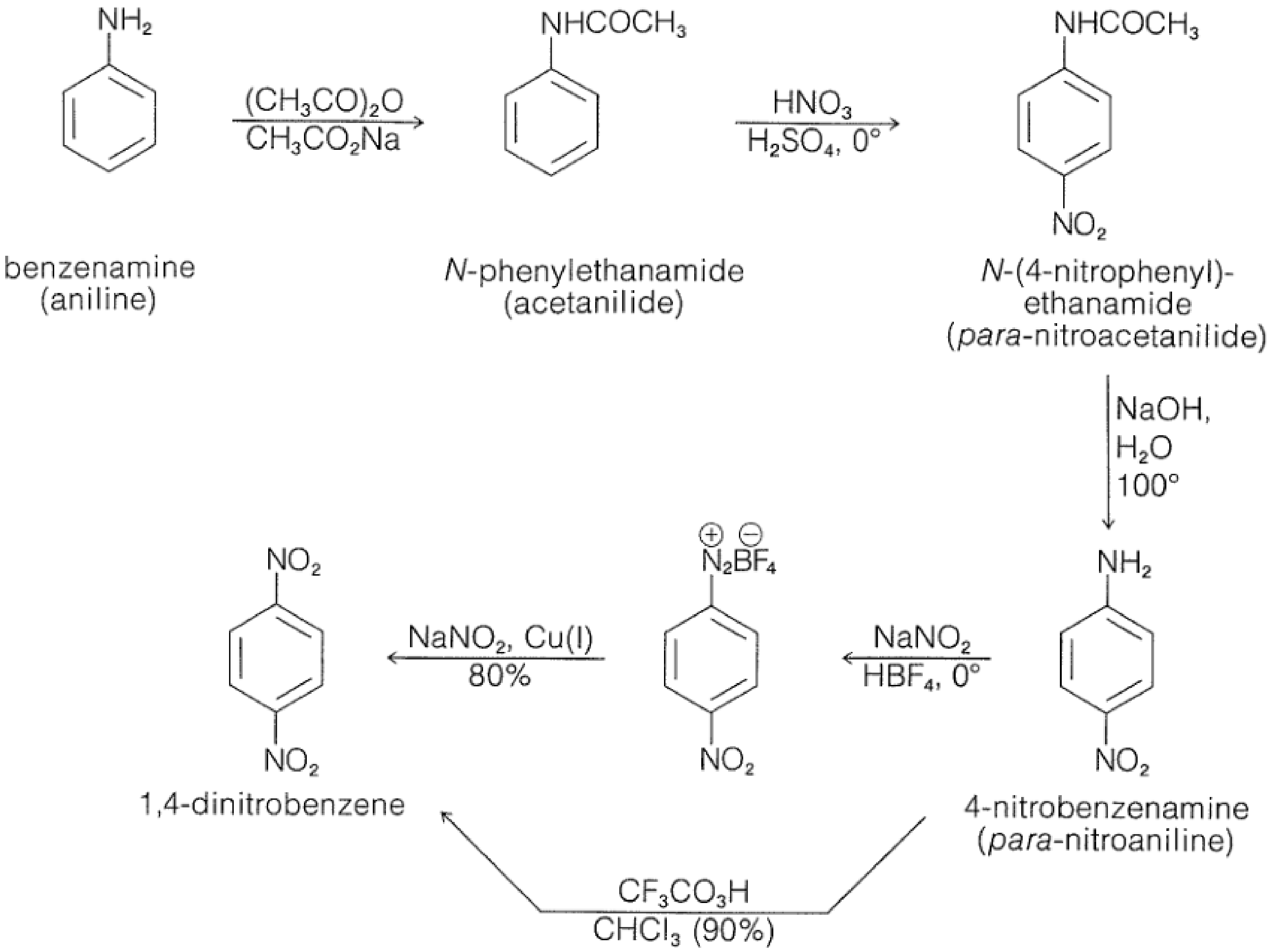
For example



Mechanism of diazotization

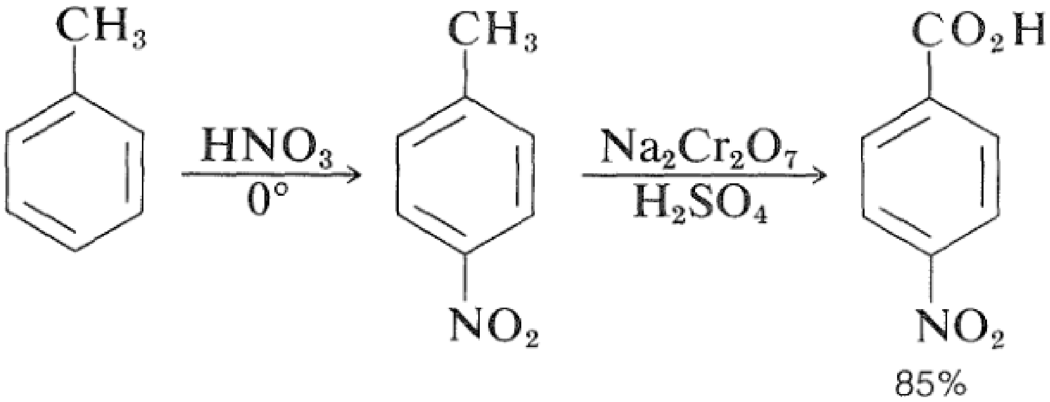


Indirect synthesis of *p*-substituted nitrobenzenes



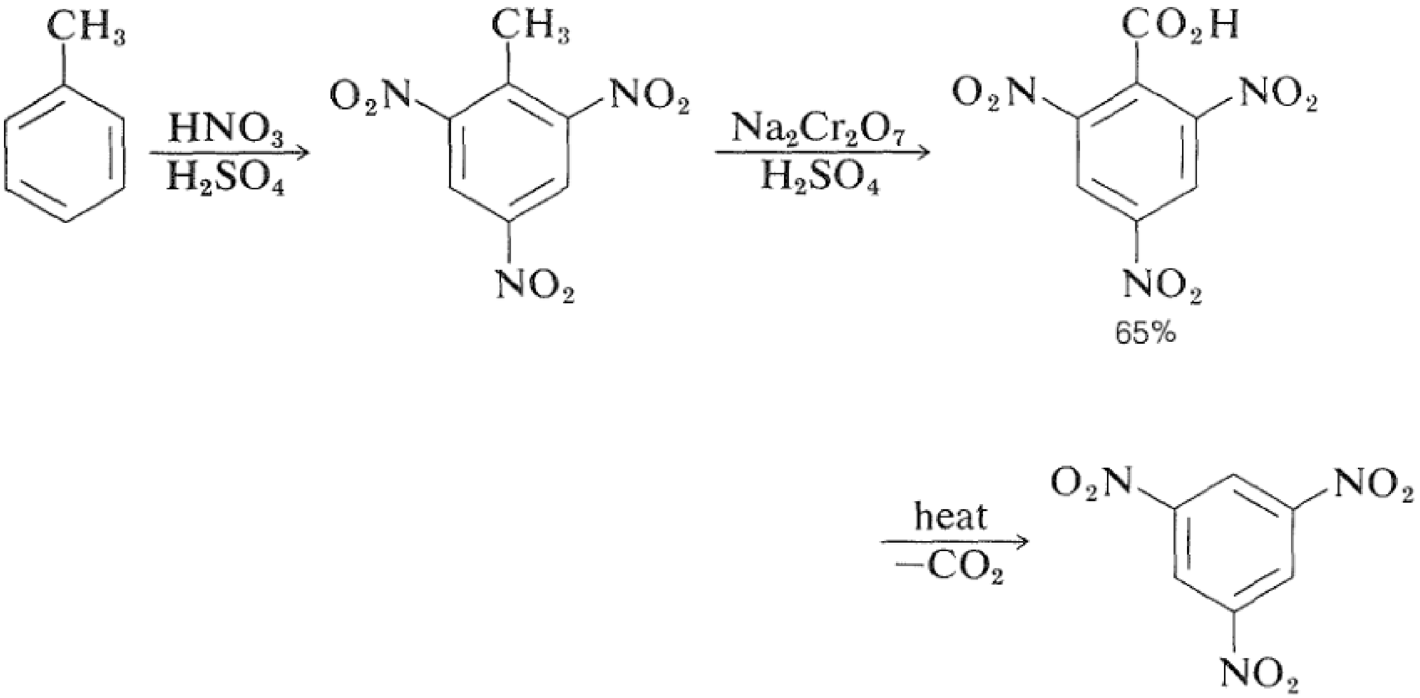
Indirect synthesis of *p*-substituted nitrobenzenes

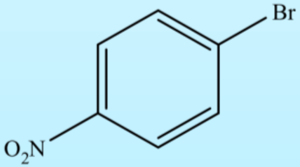
The same approach can be used to synthesize 4-nitrobenzoic acid. The methyl group of methylbenzene directs nitration preferentially to the 4 position, and subsequent oxidation with chromic acid yields 4-nitrobenzoic acid:



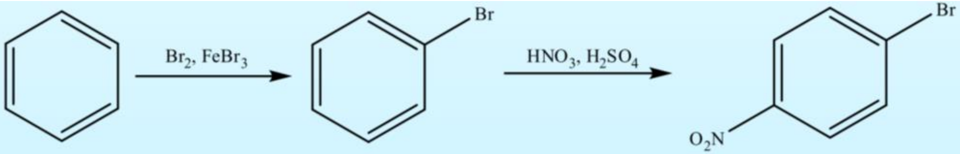
Indirect synthesis of *p*-substituted nitrobenzenes

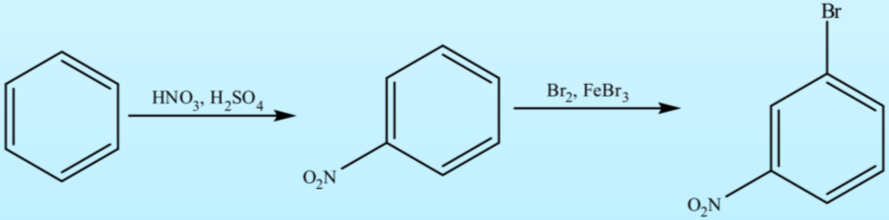
In some cases it may be necessary to have an activating group to facilitate substitution, which otherwise would be very difficult. The preparation of 1,3,5-trinitrobenzene provides a good example; direct substitution of 1,3- dinitrobenzene requires long heating with nitric acid in fuming sulfuric acid. However, methylbenzene is converted more readily to the trinitro derivative and this substance, on oxidation and decarboxylation yields 1,3,5-trinitrobenzene:





- It can be synthesized in two ways,
  - first bromination followed by nitration
  - first nitration followed by bromination

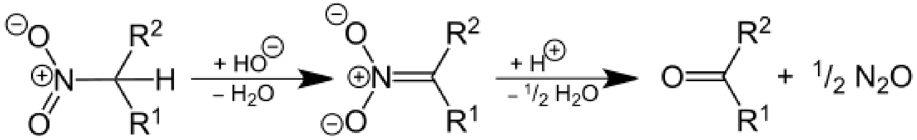




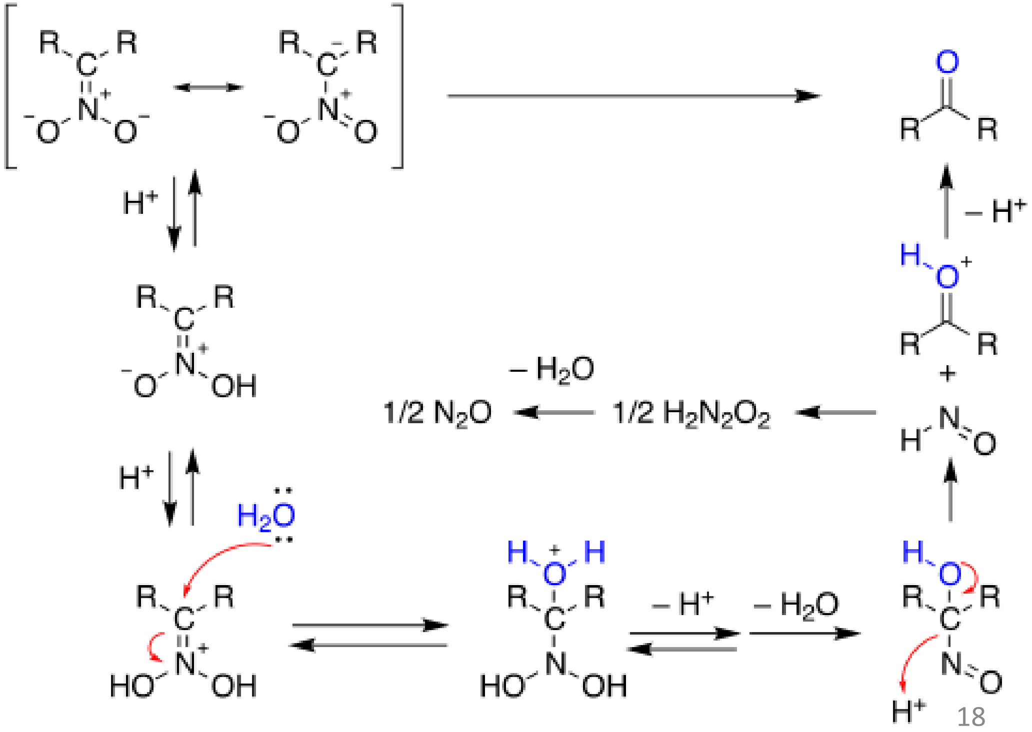
- In the first case, Br present on benzene ring directs NO_2 group to para position and required product is obtained
- whereas, in the second case, NO_2 group directs Br to meta position and unwanted product is obtained

Properties of Nitro compounds

Nef Reaction: Conversion of nitro compounds to carbonyl compounds that involves acid/base hydrolysis of a salt of a primary or secondary nitroalkane ($R{-}NO_2$) to an aldehyde ($R{-}CH{=}O$) or a ketone ($R_2C{=}O$)

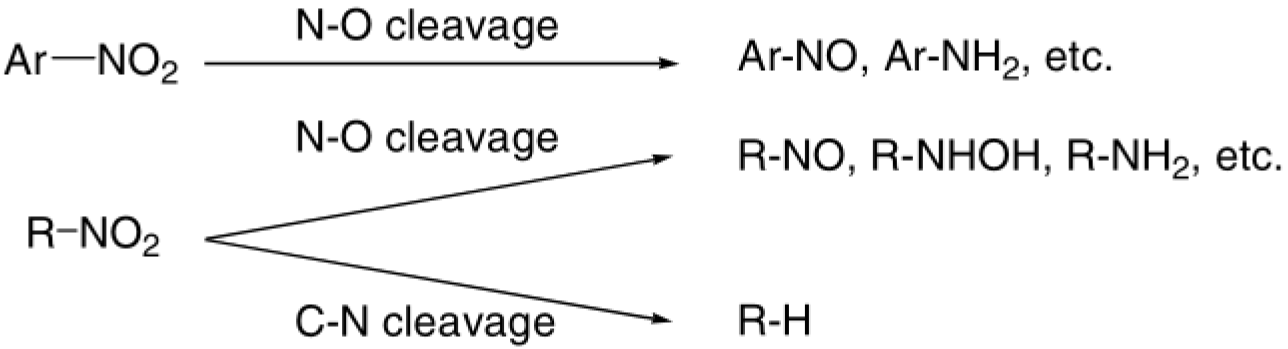


Proposed Mechanism



Chemical reduction of nitro compounds to amines

Reduction of aromatic and aliphatic nitro compounds gives various nitrogen compounds, such as amines, imines, and oximes, where the N–O bonds are cleaved, which is one of the basic reactions of nitro compounds. The sequence of nitration and reduction is the most important method for the preparation of aromatic amines. In aliphatic cases, the recent development of the stereoselective nitro-aldol and Michael reaction using aliphatic nitro compounds makes this conversion important as a tool for the stereoselective synthesis of biologically active amino compounds.



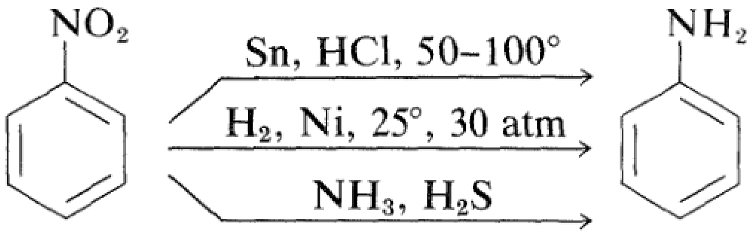
$Ar-NO_2 \xrightarrow{\text{N-O cleavage}} Ar\text{-}NO,\ Ar\text{-}NH_2$, etc.

$R-NO_2 \xrightarrow{\text{N-O cleavage}} R\text{-}NO,\ R\text{-}NHOH,\ R\text{-}NH_2$, etc.

$R-NO_2 \xrightarrow{\text{C-N cleavage}} R\text{-}H$

Chemical reduction of nitro compounds to amines

Reduction of nitro compounds occurs readily with a variety of reducing agents and such reductions afford a particularly useful synthesis of aromatic amines



The reduction of a nitro compound to an amine requires six equivalents of reducing agent:

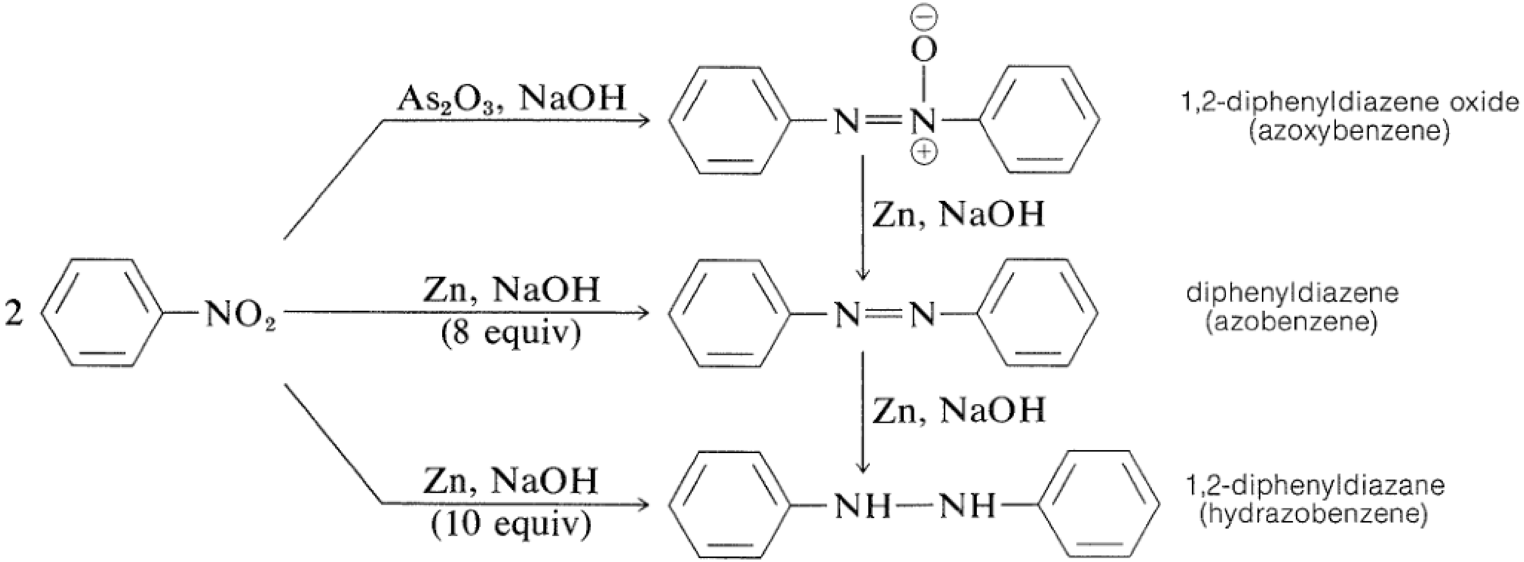
$$R{-}NO_2 + 6H^{\oplus} + 6e^{\ominus} \longrightarrow RNH_2 + 2H_2O$$

One would not expect such a reduction to occur in a single step. Indeed, reduction is stepwise and proceeds through a string of intermediates, which. with strong reducing agents in acid solution, have at most a transient existence. The intermediates formed successively from RNO, by increments of two equivalents of reducing agent are nitroso compounds, R-N=O, and N-substituted azanols (hydroxylamines), RNHOH:

$$RNO_2 \xrightarrow[-H_2O]{2[H]} RN{=}O \xrightarrow{2[H]} RNHOH \xrightarrow[-H_2O]{2[H]} RNH_2$$

Chemical reduction of nitro compounds to amines

Reduction of aryl nitro compounds with less-powerful reducing agents, especially in alkaline media, gives what may appear to be a mysterious conglomerate of bimolecular reduction products. For example, with nitrobenzene,



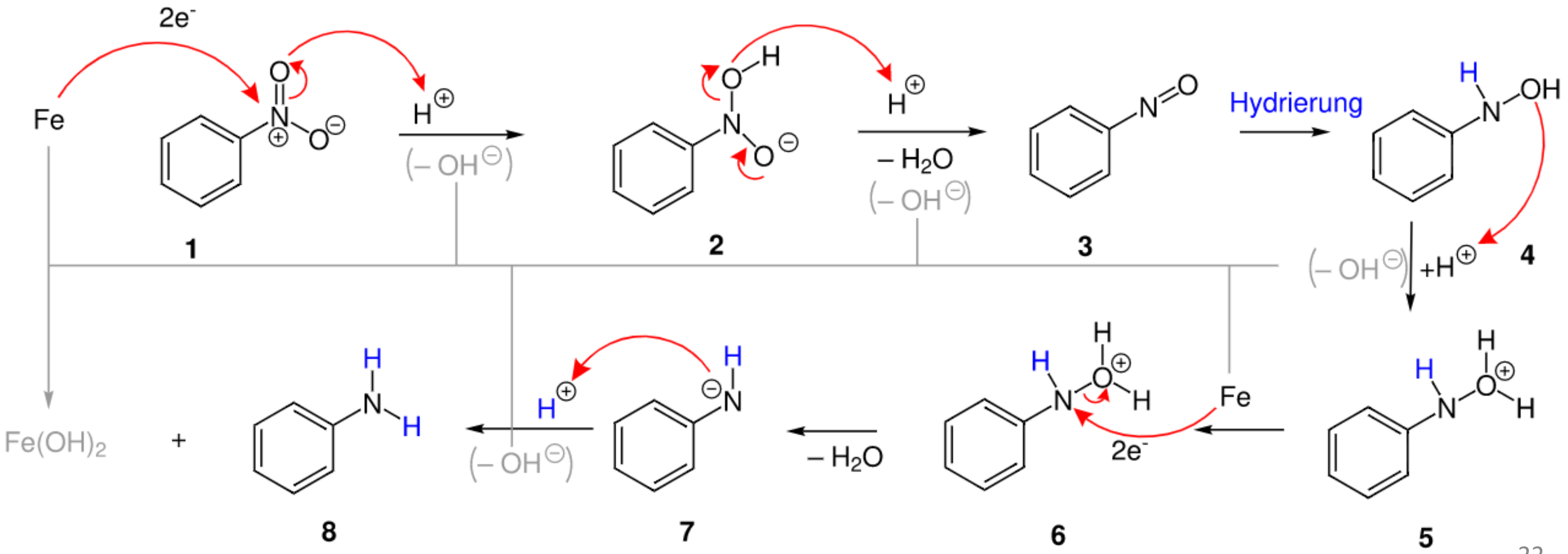
All of these substances can be reduced to benzenamine with tin and hydrochloric acid. As a result, each could be, but not necessarily is, an intermediate in the reduction of nitro compounds to amines. Formation of the bimolecular reduction products is the result of base-induced reactions between nitroso compounds and azanols or amines and possibly further reduction of the initially produced substances

Chemical reduction of nitro compounds to amines

Béchamp reduction: is a chemical reaction that converts aromatic nitro compounds to their corresponding anilines using iron as the reductant.

The reaction was first used by Antoine Béchamp to reduce nitronaphthalene and nitrobenzene to naphthylamine and aniline, respectively. The Béchamp reduction is broadly applicable to aromatic nitro compounds. Aliphatic nitro compounds are however more difficult to reduce, often remaining as the hydroxylamine. Tertiary aliphatic nitro compounds, however, are converted in good yield to the amine using the Béchamp reduction.

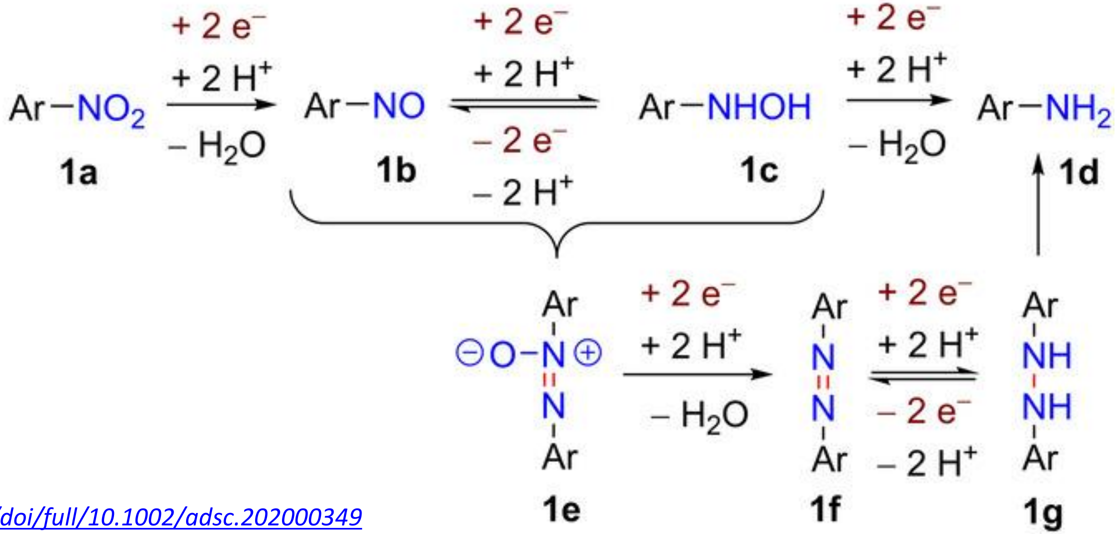
The reduction proceeds in a multistep manner. First, the nitro group is reduced to nitroso, which undergoes hydrogenation to a hydroxylamino group prior to further reduction to the amine.



Electrolytic reduction of nitro compounds to amines

The nitroaryl electroreduction played a very important role at the beginning of the 20th century and eventually led to a significant increase in the understanding of organic electrochemical phenomena.

Reducing nitroaryls (**1a**,) with electricity can yield nitroso compounds (**1b**), hydroxylamines (**1c**) and anilines (**1d**) as products. As the nitroso group is more easily reducible than the nitro group, obtaining nitroso derivatives by directly reducing a nitro group is difficult and it requires, for example, specific electrode materials. In contrast, hydroxylamines usually form straight from the nitro reduction. It is important to mention that the hydroxylamines are very prone to oxidation and they form readily the $2\ e^-/2\ H^+$ redox-pair with the corresponding nitroso system. This is one of the reasons why the final reduction to the aniline is difficult and why divided cells are often mandatory to obtain anilines or nitroso compounds on a preparative scale. Moreover, nitroso intermediates and hydroxylamines can condense to afford azoxybenzenes (**1e**), which can be subsequently electroreduced to azobenzenes (**1f**), or further to hydrazobenzenes (**1g**). Also, azobenzenes and hydrazobenzenes form reversible $2\ e^-/2\ H^+$ redox-pairs.



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5. https://onlinelibrary.wiley.com/doi/full/10.1002/adsc.202000349