Unit 15 · Nitro Compounds

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Organic Chemistry (Units 8–17 together): 33 of 75 marks; 2 MCQs, 3 short and 2 long questions
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** MCQ: electrolytic reduction of nitrobenzene in acid gives **p-aminophenol**; long: oil of mirbane: what it is, its electrolytic reduction in acid, its conversion to a yellow dye (aniline → diazonium → coupled with aniline)
- **MCQ (1 mark)**
  - ambident: the nitrite ion; 1- and 2-nitrobutane: position isomers; ethane + HNO_3 vapor at about 430 °C → nitroethane
  - $C_2H_5I + AgNO_2 \rightarrow C_2H_5NO_2$; secondary nitroalkane; nitroethane → ethanamine (Sn/HCl, H_2/Ni, $LiAlH_4$)
  - nitration; sulphonation conditions (fuming H_2SO_4, heat); $-NO_2$ deactivating, meta; $Br_2/FeBr_3$ → m-bromonitrobenzene
  - products of each medium: Sn/HCl → aniline, Zn/NaOH(aq) → hydrazobenzene, Zn/NH_4Cl → N-phenylhydroxylamine
- **Short (5 marks, in parts)**: role of conc. H_2SO_4 in the nitrating mixture; phenol vs nitrobenzene nitration; $C_4H_9NO_2$ insoluble in NaOH (the 3° one)
- **Long (8 marks)**: benzene → P → Q → R ($CHCl_3$/KOH) → S; aniline → A … E; nitrobenzene → phenol, then $FeCl_3$; reagents and products table

Key terms

Nitro compound: $-NO_2$ bonded to carbon **through N**; nitroalkanes $R-NO_2$, aromatic $Ar-NO_2$.

Nitro group: N^+ with one N=O and one $N-O^-$; the two N–O equal (about 122 pm), a resonance hybrid; strongly electron-withdrawing (−I, −R).

Ambident nucleophile: attacks through two atoms: NO_2^- by N (nitroalkane) or O (alkyl nitrite).

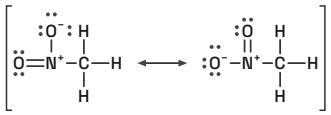
α-hydrogen: on the C carrying $-NO_2$: acidic (nitromethane pKa about 10).

Nitrating mixture: conc. HNO_3 + conc. H_2SO_4, gives $\mathbf{NO_2^+}$.

Oil of mirbane: nitrobenzene (almond smell).

Nitroalkanes

- IUPAC: **nitro always a prefix**; lowest number; prefixes alphabetical: $CH_3C(CH_3)(NO_2)CH_2CH_3$ **2-methyl-2-nitrobutane**; $(CH_3)_3CNO_2$ 2-methyl-2-nitropropane
- **1°** $R-CH_2NO_2$ (and CH_3NO_2), **2°** R_2CH-NO_2, **3°** R_3C-NO_2 (no α-H)
- isomers: **chain** (1-nitrobutane, 2-methyl-2-nitropropane), **position** (1-, 2-nitropropane), **functional** with alkyl **nitrites** R–O–N=O (CH_3NO_2, CH_3ONO); $C_3H_7NO_2$: 1-, 2-nitropropane, propyl and propan-2-yl nitrite



Nitromethane: two resonance structures.

Preparation

- **$AgNO_2$** (ethanol, heat): $C_2H_5Br + AgNO_2 \longrightarrow C_2H_5NO_2 + AgBr$, some ethyl nitrite; $NaNO_2/KNO_2$ (ionic) give much more nitrite
- **vapor-phase nitration**, about 400–450 °C, by radicals: $C_2H_6 + HNO_3 \longrightarrow C_2H_5NO_2 + H_2O$; propane → 1-, 2-nitropropane + nitroethane + nitromethane (chains broken)
- not by the nitrating mixture (no π electrons)

Physical: colorless liquids (CH_3NO_2 b.p. 101 °C, butane −0.5 °C); very **polar** (3.5 D); sparingly soluble; denser than water (1.14 g/cm^3); 1°, 2° **dissolve in NaOH**: $CH_3NO_2 + NaOH \longrightarrow Na^+[CH_2NO_2]^- + H_2O$

Reduction

- **H_2/Ni** (Pt, Pd) → 1° amine: $C_2H_5NO_2 + 3\,H_2 \longrightarrow C_2H_5NH_2 + 2\,H_2O$
- **Sn** (Fe, Zn) + conc. HCl, or $LiAlH_4$ → 1° amine: $C_2H_5NO_2 + 6\,[H] \longrightarrow C_2H_5NH_2 + 2\,H_2O$
- **Zn dust + NH_4Cl(aq)**, warm → N-alkylhydroxylamine: $CH_3NO_2 + 4\,[H] \longrightarrow CH_3NHOH + H_2O$
- in acid the amine comes out as its salt: $RNH_3^+Cl^- + NaOH \longrightarrow RNH_2 + NaCl + H_2O$

Nitrobenzene

Preparation: $C_6H_6 + HNO_3 \xrightarrow[50\text{-}60\ ^\circ C]{\text{conc. } H_2SO_4} C_6H_5NO_2 + H_2O$ (above 60 °C, 1,3-dinitrobenzene)

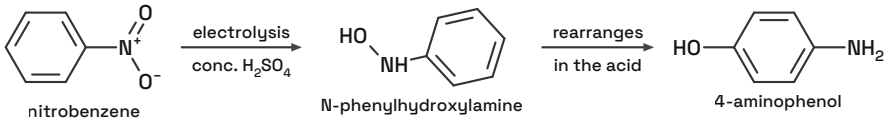
- $HNO_3 + 2\,H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2\,HSO_4^-$: H_2SO_4 the stronger acid protonates HNO_3, which loses water
- ring attacks NO_2^+ (slow) → arenium ion (σ complex); HSO_4^- takes H^+ (fast), ring aromatic again

Physical: pale yellow oily liquid, **oil of mirbane**; b.p. 211 °C, f.p. 6 °C; insoluble in water, denser (1.20 g/cm^3, **lower** layer); bitter almonds; toxic, through the skin (methemoglobin, blue lips)

Reduction: the medium decides

Medium, reagent	Product
acid: Sn or Fe + conc. HCl (then NaOH)	aniline, $C_6H_5NH_2$
neutral: Zn + NH_4Cl(aq), warm	N-phenylhydroxylamine, C_6H_5NHOH
alkaline: Na_3AsO_3 or glucose, NaOH	azoxybenzene (pale yellow)
alkaline: Zn, NaOH, methanol (or $LiAlH_4$)	azobenzene (orange-red)
alkaline: Zn, NaOH(aq)	hydrazobenzene (colorless)
electrolytic, conc. H_2SO_4	**4-aminophenol** (p-aminophenol)
catalytic: H_2, Ni (Pt, Pd)	aniline

- $C_6H_5NO_2 + 6\,[H] \xrightarrow{Sn,\ conc.\ HCl} C_6H_5NH_2 + 2\,H_2O$
- $C_6H_5NO_2 + 4\,[H] \xrightarrow{Zn,\ NH_4Cl} C_6H_5NHOH + H_2O$
- $2\,C_6H_5NO_2 + 6\,[H] \longrightarrow C_6H_5N(O)=NC_6H_5 + 3\,H_2O$
- $2\,C_6H_5NO_2 + 8\,[H] \longrightarrow C_6H_5N=NC_6H_5 + 4\,H_2O$
- $2\,C_6H_5NO_2 + 10\,[H] \longrightarrow C_6H_5NH{-}NHC_6H_5 + 4\,H_2O$
- electrolytic: $C_6H_5NO_2 + 4\,[H] \longrightarrow C_6H_5NHOH + H_2O$, then in acid the OH moves to the **para** C: $HO{-}C_6H_4{-}NH_2$
- alkaline: nitrosobenzene and phenylhydroxylamine join through N: two rings; each step 2 [H] more



Electrolytic reduction in strong acid: N-phenylhydroxylamine rearranges to 4-aminophenol.

Ring substitution: $-NO_2$ $-I$, $-R$ → + on o, p carbons: **deactivating, meta**; attack o/p puts + on C-1 beside N^+; no Friedel–Crafts (used as its solvent)

- nitration: fuming HNO_3 + conc. H_2SO_4, about **100 °C** → **1,3-dinitrobenzene**; very harsh → 1,3,5-trinitrobenzene
- $C_6H_5NO_2 + Br_2 \xrightarrow[heat]{FeBr_3} BrC_6H_4NO_2 + HBr$ (1-bromo-3-nitrobenzene); $Cl_2/FeCl_3$ the same
- $C_6H_5NO_2 + H_2SO_4 \xrightarrow{fuming,\ heat} O_2NC_6H_4SO_3H + H_2O$ (3-nitrobenzenesulphonic acid)
- compare phenol: activated, dilute HNO_3, room temperature, o and p



Nitrobenzene: + on carbons 2, 4 and 6, so meta is attacked.

Model paper chains

- yellow dye: $C_6H_5NO_2 \xrightarrow{Sn/HCl} C_6H_5NH_2 \xrightarrow[0\text{-}5\ °C]{NaNO_2,\ HCl} C_6H_5N_2Cl$; + aniline → **p-aminoazobenzene** (yellow)
- $C_6H_6 \longrightarrow C_6H_5NO_2 \longrightarrow C_6H_5NH_2 \xrightarrow{CHCl_3/alc.\ KOH} C_6H_5NC \xrightarrow{H_2,\ Pd} C_6H_5NHCH_3$ (phenyl isocyanide, N-methylaniline)
- nitrobenzene → phenol: Sn/HCl → aniline → diazonium (0–5 °C) → warm water → phenol; with neutral $FeCl_3$, **violet**

Uses

- solvents; **aniline** (95% of nitrobenzene: dyes, paracetamol via 4-aminophenol, rubber chemicals, foam)
- nitromethane racing fuel (carries its own oxygen); medicines (metronidazole, chloramphenicol); chloropicrin
- mild oxidizing agent; once in polishes and soap; explosives: **TNT**, picric acid
- nitroglycerin is a **nitrate ester** (C–O–NO_2), not a nitro compound

COMMON MISTAKES

✗ 2-nitro-2-methylpropane for $CH_3C(CH_3)(NO_2)CH_2CH_3$
✓ **2-methyl-2-nitrobutane** (four-C chain, alphabetical).

✗ isomers of $C_3H_5NO_2$
✓ **$C_3H_7NO_2$**.

✗ alkanes nitrated by the nitrating mixture
✓ HNO_3 **vapor**, 400–450 °C, radicals, a mixture.

✗ nitrobenzene + 4[H] (neutral) → C_6H_5NHOH + $2H_2O$
✓ + **H_2O**.

✗ oil of mirabane
✓ **mirbane**.

✗ "ambient" group
✓ **ambident**.

✗ $LiAlH_4$ reduces nitrobenzene to aniline
✓ to **azobenzene**.

✗ nitrobenzene + $NaNO_2$/HCl
✓ no reaction: **aniline** is diazotized.

✗ Zn in methanol alone → azobenzene
✓ **Zn/NaOH** in methanol.