Unit 15 · Aromatic Hydrocarbons

STUDY NOTES

WHAT NEB'S GRADE 11 EXAM ASKS

- **CDC's grid (2077):** Organic Chemistry (Units 12–15 together): 18 of 75 marks
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** no question from this unit; its reactions come into the organic conversions
- **MCQ (1 mark)**: benzene 78 u; nitration set-up gives nitrobenzene; phenol + Zn → C_6H_6; $AlCl_3$ for Friedel–Crafts; nitration is electrophilic substitution; sodium benzoate + soda lime gives Na_2CO_3 too; arenes; anthracene 14 π electrons; sp^2
- **Short (5 marks, in parts)**
  - physical and chemical properties of benzene; ethyne → benzene → nitrobenzene with conditions
  - aromatic or not by Hückel's rule
  - products: Cl_2 in sunlight; sodium benzoate + soda lime; benzene + ethanoyl chloride ($AlCl_3$)
  - aliphatic vs aromatic; alkylation vs acylation; sooty vs non-sooty flame
- **Long (8 marks)**: C : H bars (C_6H_6 the aromatic), Cl_2 in the dark, ethyne in a red-hot tube; phenol → X → Y; addition vs substitution; A (78) → B (nitration), C (acylation); benzoic acid → sodium benzoate → benzene → toluene; a cycle M → N → O → M; resonance of benzene; burning

Key terms

Aromatic compounds (arenes): flat rings whose π electrons are **delocalized** round the ring; stable, prefer **substitution** to addition; first named for their smell.

Hückel's rule: a ring is aromatic if it is **cyclic**, **flat**, has a **p orbital on every ring atom** and **(4n + 2) π electrons** (n = 0, 1, 2…).

Resonance: one molecule drawn by structures differing only in where π electrons are (↔); the real one is a **hybrid**, more stable than any.

Electrophilic substitution: an electrophile (NO_2^+, Cl^+, R^+, RCO^+, SO_3) replaces an H of the ring; the ring stays aromatic.

ortho, meta, para (o, m, p): positions 2 and 6, 3 and 5, 4, counted from the group already there.

Friedel–Crafts: alkylation (RCl) or acylation (RCOCl) of the ring with **anhydrous $AlCl_3$**.

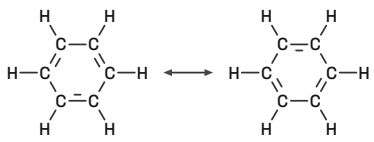
Aromaticity

- sooty flame: high **carbon to hydrogen ratio** (C_6H_6 1 : 1; hexane C_6H_{14} more than 1 : 2), carbon left unburnt as soot
- 4n + 2: benzene **6** (n = 1); naphthalene **10** (n = 2); anthracene **14** (n = 3); pyridine, furan, thiophene, pyrrole 6
- not aromatic: cyclopentadiene (sp^3 CH_2 breaks the ring of p orbitals; 4 π electrons); cycloheptatriene (sp^3 CH_2, though 6 π); cyclohexane (none)

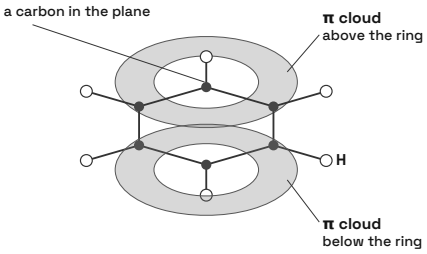
	Aliphatic	Aromatic
chain	open, or rings like alicyclics	flat ring, delocalized π
C : H	lower	high
flame	non-sooty (alkanes)	sooty, yellow
typical reaction	addition (alkenes) or substitution (alkanes)	electrophilic substitution
Br_2 water, Baeyer	alkenes decolorize	no change

Structure of benzene

- C_6H_6 (empirical CH, mass 78): 8 H fewer than hexane, so unsaturated or cyclic
- **Kekulé** (1865): ring of six C, alternate single and double bonds
- **supports**: only **one** monosubstituted product (C_6H_5Cl); adds **3 H_2** → cyclohexane (ring + three double bonds)
- **objections**: doesn't add easily or decolorize Br_2 water, Baeyer; all six C–C bonds **equal, 139 pm** (C–C 154, C=C 134); only **one** 1,2-dibromobenzene, not two
- answer: **resonance**; the hybrid's six π electrons spread round the ring



Benzene's two Kekulé structures, joined by the resonance arrow ↔: same atoms, π electrons placed differently.



Six sp^2 carbons, each with an upright 2p orbital; they overlap all round into two rings of π cloud above and below.

- orbital structure: each C **sp^2**, 120°, flat; σ bonds C–C, C–H; six 2p orbitals overlap sideways → delocalized π cloud above and below the ring
- resonance energy: hydrogenation gives out 208 kJ/mol, not $3 \times 120 = 360$: about **150 kJ/mol** more stable
- isomers: one C_6H_5X; **three** $C_6H_4X_2$ (1,2-ortho, 1,3-meta, 1,4-para); three trisubstituted (1,2,3- vicinal, 1,2,4-unsymmetrical, 1,3,5- symmetrical)

Preparation

- **decarboxylation**: $C_6H_5COONa + NaOH \xrightarrow[\Delta]{CaO} C_6H_6 + Na_2CO_3$
- **phenol + zinc dust**: $C_6H_5OH + Zn \xrightarrow{\Delta} C_6H_6 + ZnO$
- **ethyne**, red-hot iron or copper tube, about 500 °C: $3\,C_2H_2 \longrightarrow C_6H_6$
- reducing chlorobenzene: $C_6H_5Cl + 2\,[H] \xrightarrow{Ni-Al,\ NaOH} C_6H_6 + HCl$
- benzoic acid ($C_7H_6O_2$) + NaOH → sodium benzoate → benzene → toluene (CH_3Cl, $AlCl_3$)

Properties

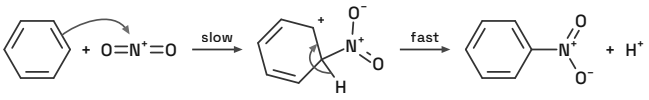
- colorless, sweet-smelling, volatile liquid; b.p. **80.1 °C**, m.p. 5.5 °C; density 0.877 g/cm^3 (floats on water, doesn't mix); dissolves fats, iodine, rubber; burns with a sooty flame
- **toxic, carcinogenic** (leukemia); petrol limited to 1%

Addition (hard conditions)

- $C_6H_6 + 3\,H_2 \xrightarrow[200\text{-}250\ °C]{Ni} C_6H_{12}$ (cyclohexane, for nylon)
- $C_6H_6 + 3\,Cl_2 \xrightarrow{sunlight} C_6H_6Cl_6$ (BHC, 1,2,3,4,5,6-hexachlorocyclohexane; no catalyst)

Electrophilic substitution

- **nitration**: conc. HNO_3 + conc. H_2SO_4, **50–60 °C**: $C_6H_6 + HNO_3 \longrightarrow C_6H_5NO_2 + H_2O$; electrophile $HNO_3 + 2\,H_2SO_4 \longrightarrow NO_2^+ + H_3O^+ + 2\,HSO_4^-$; at 100 °C → 1,3-dinitrobenzene
- **sulphonation**: $C_6H_6 + H_2SO_4 \xrightarrow{\Delta} C_6H_5SO_3H + H_2O$ (fuming acid: $C_6H_6 + SO_3 \longrightarrow C_6H_5SO_3H$)
- **halogenation**, $FeCl_3$ (or Fe), **dark**: $C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$; $Cl_2 + FeCl_3 \longrightarrow Cl^+ + FeCl_4^-$
- **Friedel–Crafts alkylation**: $C_6H_6 + CH_3Cl \xrightarrow{anhyd.\ AlCl_3} C_6H_5CH_3 + HCl$ (toluene); C_2H_5Cl → ethylbenzene
- **acylation**: $C_6H_6 + CH_3COCl \xrightarrow{anhyd.\ AlCl_3} C_6H_5COCH_3 + HCl$ (acetophenone); with $(CH_3CO)_2O$ → acetophenone + CH_3COOH
- **combustion**: $2\,C_6H_6 + 15\,O_2 \longrightarrow 12\,CO_2 + 6\,H_2O$, sooty



Nitration's mechanism: the ring's π electrons attack NO_2^+ (slow), giving the arenium ion; it loses H^+ (fast) and the ring is aromatic again.

	Alkylation	Acylation
reagent	R–Cl (CH_3Cl)	RCOCl or $(RCO)_2O$
electrophile	R^+	RCO^+
product	alkylbenzene (toluene)	ketone (acetophenone)
more substitution	yes (ring activated)	stops at one (C=O deactivates)

Addition	Substitution
ring's aromaticity lost (cyclohexane, BHC)	ring kept
sunlight, or catalyst + heat + pressure	electrophile, catalyst
H_2, Cl_2 (3 molecules)	one H replaced

Directing groups (the group already there decides)

- **o, p directors** (activate, push electrons in, +R): –OH, –NH_2, –OR, –CH_3; halogens **o, p but deactivate**
- **m directors** (deactivate, pull out, −R): –NO_2, –CN, –SO_3H, –COOH, –CHO, –COR
- why: aniline's lone pair puts − charge on C-2, 4, 6; nitrobenzene's NO_2 leaves + on C-2, 4, 6, so meta is least poor

Uses: making ethylbenzene (styrene, polystyrene), cumene (phenol, acetone), cyclohexane (nylon), nitrobenzene (aniline, dyes, drugs); formerly solvent, dry cleaning, fuel

COMMON MISTAKES

✗ sooty flame from high unsaturation
✓ from the high **C : H ratio**.

✗ Hückel by counting π electrons only
✓ also **flat** with a **p orbital on every ring atom**: cyclopentadiene, cycloheptatriene fail.

✗ Kekulé structures joined by ⇌
✓ ↔; resonance is not an equilibrium.

✗ benzene a pale yellow liquid
✓ **colorless**.

✗ halogens are meta directors
✓ **ortho, para** directors that deactivate.

✗ Friedel–Craft's, acylation in ether
✓ **Friedel–Crafts**; anhydrous $AlCl_3$, no ether.

✗ $C_6H_5OH + Zn \rightarrow C_6H_6 + Zn$
✓ + **ZnO**.