Unit 9 · Haloarenes

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:** short (OR): A, a chlorine on a benzene ring, with chloral and conc. H_2SO_4 gives the insecticide B (DDT), with CH_3COCl and anhyd. $AlCl_3$ gives C (4-chloroacetophenone); why aq. NaOH reacts with A harder than with chloroethane; A from benzenediazonium chloride
- **MCQ (1 mark)**
  - b.p. above benzene; order of the dichlorobenzenes' b.p.; reagent for the diazonium route; which halide resists nucleophiles, and why
  - +M and −I: o, p director yet deactivating; DDT's two reactants; poor Friedel–Crafts yield; Fittig product; major nitration product
- **Short (5 marks, in parts)**
  - isomers of $C_6H_4Cl_2$; methods of making chlorobenzene; resonance and the C–Cl bond; nucleophilic substitution (Dow, NH_3, CuCN)
  - electrophilic substitution (complete, major product); Fittig and Wurtz–Fittig, dry ether; DDT; why PCBs are banned
- **Long (8 marks)**: chlorobenzene vs benzyl chloride with aq. NaOH; chlorobenzene vs $CHCl_3$ with Zn/HCl; conversions

Key terms

Haloarene (aryl halide): X joined **directly to an sp^2 carbon of an aromatic ring**, Ar–X; on a side chain ($C_6H_5CH_2Cl$, benzyl chloride) it is a haloalkane.

o-, m-, p-: two groups at 1,2, 1,3 and 1,4 on the ring.

Halogen carrier: anhydrous $FeCl_3$ ($FeBr_3$, $AlCl_3$), which makes the electrophile Cl^+.

Diazotization: aniline + $NaNO_2$ + HCl at 0–5 °C → benzenediazonium chloride, $C_6H_5N_2^+Cl^-$.

Sandmeyer reaction: diazonium salt + CuCl/HCl (CuBr/HBr), warm → ArCl (ArBr) + N_2.

Gattermann reaction: the same with copper powder and HCl (HBr).

+M (+R) effect: a halogen's lone pair pushed into the ring by resonance, onto o and p.

−I effect: electrons pulled out of the ring along the σ bond.

Dow's process: chlorobenzene + NaOH, 623 K, 300 atm → phenol.

Fittig reaction: 2ArX + 2Na → Ar–Ar; **Wurtz–Fittig**: ArX + RX + 2Na → Ar–R.

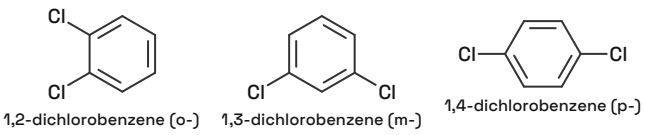
DDT: p,p′-dichlorodiphenyltrichloroethane, 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane.

Names and isomers (9.1–9.2)

- prefix + arene: chlorobenzene, bromobenzene; $C_6H_4Cl_2$: 1,2- (o), 1,3- (m), 1,4- (p)
- named from a parent with its own name: 2-chlorotoluene (o), 3- (m), 4- (p); 1-bromo-4-chlorobenzene
- 2 and 6 both ortho, 3 and 5 both meta: number for the lowest set

Preparation (9.3)

- direct: $C_6H_6 + Cl_2 \longrightarrow C_6H_5Cl + HCl$ with $FeCl_3$ in the dark, electrophilic substitution
- in sunlight, no carrier: Cl_2 **adds** → $C_6H_6Cl_6$ (BHC), not a haloarene
- aniline + $NaNO_2$ + 2HCl at 0–5 °C → $C_6H_5N_2^+Cl^-$ + NaCl + $2H_2O$; used cold: above 5 °C it gives phenol + N_2
- Sandmeyer: $C_6H_5N_2^+Cl^- \longrightarrow C_6H_5Cl + N_2$ with CuCl/HCl; Gattermann: Cu powder + HCl
- with KI, warm: iodobenzene; the diazonium route puts X exactly where $-NH_2$ was



The three dichlorobenzenes: 1,2- (o), 1,3- (m), 1,4- (p).

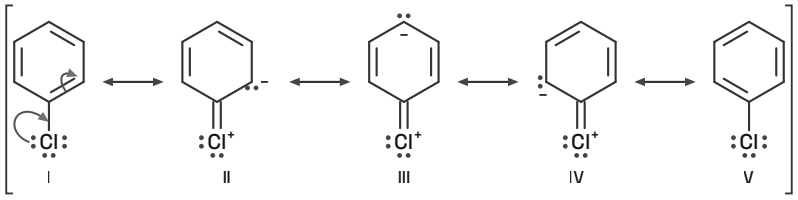
Physical properties (9.4)

- colorless liquid, b.p. 132 °C (benzene 80 °C: heavier, polar), density 1.11 g/cm^3 (sinks); insoluble in water
- b.p. rises from F to I with molar mass
- dichlorobenzenes: m.p. o −17, m −25, **p 53 °C** (symmetry, packs well); b.p. o 180, p 174, m 173 °C; μ o 2.50, m 1.72, p 0 D

Nucleophilic substitution: very hard (9.5.1)

	CH_3–Cl	C_6H_5–Cl
carbon	sp^3 (25% s)	sp^2 (33% s)
C–Cl length	177 pm	169 pm
bond energy	~350 kJ/mol	~400 kJ/mol
dipole moment	1.89 D	1.69 D
hot aq. NaOH	methanol	no reaction

- why: (1) **resonance**: a Cl lone pair into the ring, C–Cl partly double (five structures, three with $C{=}Cl^+$); (2) sp^2 carbon holds the pair closer; (3) the π cloud repels the nucleophile; (4) no SN2 (back of C–Cl inside the ring), no SN1 (phenyl cation unstable)



Chlorobenzene's five resonance structures: three put $C{=}Cl^+$ in the ring.

- special conditions:
  - Dow, 623 K, 300 atm: $C_6H_5Cl + 2\,NaOH \longrightarrow C_6H_5ONa + NaCl + H_2O$; then HCl → phenol
  - Cu_2O, 200 °C, 60 atm: $C_6H_5Cl + 2\,NH_3 \longrightarrow C_6H_5NH_2 + NH_4Cl$ (aniline)
  - pyridine, 200 °C: $C_6H_5Cl + CuCN \longrightarrow C_6H_5CN + CuCl$ (benzonitrile)
- $-NO_2$ at **o, p** makes it easier: one, NaOH at 443 K; two (2,4-), 368 K; three (2,4,6-), warm water; meta $-NO_2$ doesn't help
- benzyl chloride, chloroethane: sp^3 C–Cl, plain single bond, open to backside attack → substituted easily

Reduction, electrophilic substitution (9.5.2–9.5.3)

- Ni–Al alloy, NaOH: $C_6H_5Cl + 2\,[H] \longrightarrow C_6H_6 + HCl$; $CHCl_3$ with Zn/HCl → CH_2Cl_2, but chlorobenzene's stronger C–Cl isn't touched
- halogen: **o, p director** (+M puts more on o, p than on m) but **deactivating** (−I stronger): slower than benzene
- para major (ortho crowded, one para to two ortho):

Reagent	Major (para) product
Cl_2, $FeCl_3$	1,4-dichlorobenzene (+ 1,2-)
Br_2, $FeBr_3$	1-bromo-4-chlorobenzene
conc. HNO_3 + conc. H_2SO_4	1-chloro-4-nitrobenzene
conc. H_2SO_4, heat	4-chlorobenzenesulphonic acid
CH_3Cl, anhyd. $AlCl_3$	4-chlorotoluene
CH_3COCl, anhyd. $AlCl_3$	4-chloroacetophenone

- Friedel–Crafts slow, poor yields: the ring is deactivated

Sodium, chloral, uses (9.5.4–9.6)

- **Fittig**: $2\,C_6H_5Cl + 2\,Na \longrightarrow C_6H_5{-}C_6H_5 + 2\,NaCl$ (biphenyl)
- **Wurtz–Fittig**: $C_6H_5Cl + CH_3Cl + 2\,Na \longrightarrow C_6H_5CH_3 + 2\,NaCl$; side products biphenyl and ethane, distilled apart
- both in dry ether: Na + water → NaOH + H_2 (fire), wasting the sodium
- **DDT**: conc. H_2SO_4: $2\,C_6H_5Cl + CCl_3CHO \longrightarrow (ClC_6H_4)_2CH{-}CCl_3 + H_2O$; each ring joins at para; H_2SO_4 makes the electrophile and takes up water
- DDT: insect nerve poison (keeps Na^+ channels open); persistent, fat-soluble, builds up in food chains; malaria campaign in Nepal from 1958; banned in Nepal 2001
- uses: nitrochlorobenzenes → dyes, paracetamol; solvents (chlorobenzene, o-dichlorobenzene); p-dichlorobenzene moth balls, toilet blocks; C_6H_5MgBr; drugs (diclofenac, chloroquine)
- **PCBs**: transformer and capacitor oils (don't burn or conduct); persistent, toxic, build up in fat → banned

COMMON MISTAKES

✗ benzyl chloride is a haloarene
✓ Cl on the side chain: a haloalkane.

✗ chlorination in sunlight gives chlorobenzene
✓ addition, $C_6H_6Cl_6$; use $FeCl_3$ in the dark.

✗ b.p. ortho > meta > para
✓ o 180 > p 174 ≈ m 173 °C.

✗ Dow's process at 300 °C and 200 atm
✓ 623 K (350 °C), 300 atm.

✗ $C_6H_5Cl + NH_3 \longrightarrow C_6H_5NH_2 + HCl$
✓ $2NH_3$, NH_4Cl.

✗ the halogen raises the ring's electron density at o and p
✓ lowers it everywhere, least at o and p.

✗ chlorine is o, p directing so it activates
✓ it deactivates.