Haloalkanes and Haloarenes Class 12 Key Points

CBSE Class 12 Chemistry · NCERT · for boards, NEET and JEE revision

ChapterNotes

Classification & Nomenclature

$(CH_3)_3CBr$ = 2-bromo-2-methylpropane

Halogen is a 'halo-' prefix; number the chain for the lowest locant set.

- By carbon type: 1°, 2°, 3° (X on C bonded to 1, 2, 3 other carbons)
- Allylic/benzylic = X next to C=C / benzene → very reactive
- Vinylic/aryl = X on sp^2 C → unreactive; this split drives the chapter

The Polar C–X Bond

C^δ⁺–X^δ⁻ · bond strength: C–F > C–Cl > C–Br > C–I

Down the group bond length increases and strength decreases; C–I breaks easiest.

- C–I weakest → iodides are the most reactive
- Insoluble in water (no strong H-bonds), soluble in organic solvents
- Same R: b.p. R–I > R–Br > R–Cl > R–F; branching lowers b.p.

Making Haloalkanes

$ROH + SOCl_2 \rightarrow RCl + SO_2\uparrow + HCl\uparrow$

$SOCl_2$ is best - by-products escape as gases, giving pure RCl.

- With HX: reactivity HI > HBr > HCl (HCl needs $ZnCl_2$ / Lucas reagent)
- Also PCl_3 and PCl_5 convert ROH to RCl
- Alkene + HX follows Markovnikov; HBr + peroxide → anti-Markovnikov (Kharasch)

Finkelstein & Swarts

$R–Cl + NaI \rightarrow_{\text{(dry acetone)}} R–I + NaCl\downarrow$

NaCl precipitates in acetone, pulling Finkelstein forward.

- Finkelstein: R–Cl/R–Br + NaI in dry acetone → R–I
- Swarts: R–Br + AgF → R–F + AgBr (route to fluorides)
- Haloarenes: arene + Cl_2/Br_2 with anhydrous $FeCl_3$ (Lewis acid)

SN2 Substitution

rate = k[RX][Nu] (second order)

Back-side attack flips the centre → inversion (Walden inversion).

- Reactivity 1° > 2° > 3° (least steric hindrance wins)
- Gives complete inversion of configuration
- Favoured by strong nucleophiles and polar aprotic solvents

SN1 Substitution

rate = k[RX] (first order, Nu-independent)

Planar carbocation is attacked from both faces → racemic mixture.

- Reactivity 3° > 2° > 1° (more stable carbocation wins)
- Gives partial racemisation, not clean inversion
- Favoured by polar protic solvents; allylic/benzylic react fast

Elimination (β-Elimination)

alcoholic KOH → alkene · aqueous KOH → alcohol

The favourite NEET trap: 'alcoholic = alkene', 'aqueous = substitution'.

- Saytzeff (Zaitsev): more substituted, more stable alkene is the major product
- 2-bromobutane + alc. KOH → mainly but-2-ene
- Reactivity 3° > 2° > 1°; bulky base + 3° + heat favours elimination

Haloarenes: Low Reactivity

Resonance → partial C=X double-bond → short, strong C–X

Phenol from chlorobenzene needs ~623 K and 300 atm (forcing conditions).

- Resonance + sp^2 carbon hold the C–X bond tighter (stronger, shorter)
- In EAS, halogen is deactivating but o,p-directing
- $–NO_2$ at ortho/para boosts reactivity (addition-elimination)

Quick revision

- Best prep of R–Cl: R–OH + $SOCl_2$ (byproducts are gases)
- SN2: one step, back-attack, inversion, 1° best, strong nucleophile, aprotic solvent
- SN1: two steps, carbocation, racemisation, 3° best, weak nucleophile, protic solvent
- Elimination: alc. KOH → alkene (Saytzeff's rule - more substituted product)
- Substitution: aq. KOH → alcohol
- KCN → R–CN; AgCN → R–NC (covalent silver salt → attacks through N)
- Wurtz: 2RX + 2Na → R–R; Fittig: 2ArX + 2Na → Ar–Ar
- Haloarenes: less reactive due to resonance (C–Cl partial double bond), ortho-para directing
- Finkelstein: R–Cl + NaI → R–I; Swarts: R–Cl + AgF → R–F

Full chapter notes with solved examples and practice questions: https://chapternotes.in/cbse/class-12-chemistry/haloalkanes-and-haloarenes-class-12-notes/