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CHAPTER NOTES

Haloalkanes and Haloarenes Class 12 Notes — CBSE Chemistry Chapter 10

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Haloalkanes and Haloarenes Class 12 Notes — CBSE Chemistry Chapter 10

Chapter 10 — **Haloalkanes and Haloarenes** — is the gateway to organic reactions. This chapter introduces substitution and elimination reactions, which form the basis of organic chemistry. It carries **6-8 marks** in Board exams. Master the SN1/SN2 mechanisms and named reactions like Wurtz, Fittig, and Sandmeyer.

Key Concepts

Classification

Type	Structure	Example
Primary (1°)	–CH_2X	CH_3CH_2Cl (ethyl chloride)
Secondary (2°)	–CHX–	$(CH_3)_2CHBr$ (isopropyl bromide)
Tertiary (3°)	–CX–	$(CH_3)_3CCl$ (tert-butyl chloride)
Haloarene	X on benzene ring	C_6H_5Cl (chlorobenzene)

Preparation Methods

1. From Alcohols:

R–OH + HX → R–X + H_2O (reactivity: HI > HBr > HCl)

R–OH + PCl_5 → R–Cl + $POCl_3$ + HCl

3R–OH + PCl_3 → 3R–Cl + H_3PO_3

R–OH + $SOCl_2$ → R–Cl + SO_2↑ + HCl↑ (best method — byproducts are gases!)

2. From Alkenes (Markovnikov's addition):

CH_2=CH_2 + HBr → CH_3CH_2Br

3. Halogenation of Alkanes (free radical):

CH_4 + Cl_2 →(UV/hv) CH_3Cl + HCl

4. Sandmeyer Reaction (for ArX):

$ArN_2^+Cl^- + CuCl/HCl \rightarrow ArCl + N_2$

$ArN_2^+Cl^- + CuBr/HBr \rightarrow ArBr + N_2$

Nucleophilic Substitution Reactions

The C–X bond in haloalkanes is polar (C^δ⁺–X^δ⁻), making carbon susceptible to nucleophilic attack.

SN2 Mechanism (Substitution Nucleophilic Bimolecular)

Rate = k[R–X][Nu⁻] (depends on BOTH reactant and nucleophile)

One-step mechanism: nucleophile attacks from the **back side** (180° to leaving group)

Transition state: pentacoordinate carbon

Result: Walden inversion (configuration inverts — like an umbrella flipping)

Reactivity order: **1° > 2° > 3°** (steric hindrance increases)

SN1 Mechanism (Substitution Nucleophilic Unimolecular)

Rate = k[R–X] (depends only on substrate)

Two steps: (1) Ionisation: R–X → $R^+ + X^-$ (slow, rate-determining)

(2) Nucleophilic attack: $R^+ + Nu^-$ → R–Nu (fast)

Carbocation intermediate: planar → nucleophile attacks from both sides

Result: Racemisation (mixture of d and l forms)

Reactivity order: **3° > 2° > 1°** (more stable carbocation → faster ionisation)

Quick Summary: SN2 = one step, back-side attack, inversion, favoured by 1° substrates and strong nucleophiles. SN1 = two steps, carbocation, racemisation, favoured by 3° substrates and polar protic solvents.

Elimination Reactions

Dehydrohalogenation (β-elimination):

$R–CH_2–CH_2–X + \text{alc. KOH} \rightarrow R–CH=CH_2 + KX + H_2O$

Saytzeff's Rule: The more substituted alkene is the major product

$CH_3CH_2CHBrCH_3 + \text{alc. KOH} \rightarrow CH_3CH=CHCH_3$ (major, more substituted) + $CH_3CH_2CH=CH_2$ (minor)

Reactions of Haloalkanes

Nucleophile	Reagent	Product
OH^-	aq. KOH / NaOH	Alcohol (R–OH)
OR^-	NaOR (Williamson)	Ether (R–O–R')
CN^-	KCN	Nitrile (R–CN) — carbon chain increases by 1!
NC^-	AgCN	Isocyanide (R–NC)
NH_3	excess NH_3	Amines (R–NH_2, R_2NH, R_3N, R_4N^+)
NO_2^-	KNO_2	Nitroalkane (R–NO_2) — via N
NO_2^-	$AgNO_2$	Alkyl nitrite (R–O–N=O) — via O

KCN vs AgCN: KCN is ionic → CN^- attacks through C → cyanide (R–CN). AgCN is covalent → attacks through N → isocyanide (R–NC). Similarly: KNO_2 → nitro, $AgNO_2$ → nitrite.

Important Named Reactions

Wurtz Reaction: $2R–X + 2Na \xrightarrow{\text{(dry ether)}} R–R + 2NaX$

(Used to increase carbon chain — makes symmetric alkanes)

Fittig Reaction: $2ArX + 2Na \rightarrow Ar–Ar + 2NaX$

Wurtz-Fittig: $ArX + RX + 2Na \rightarrow Ar–R + 2NaX$

Finkelstein Reaction: $R–Cl + NaI \xrightarrow{\text{(acetone)}} R–I + NaCl\downarrow$

(NaCl precipitates in acetone → drives reaction forward)

Swarts Reaction: $R–Cl + AgF \rightarrow R–F + AgCl\downarrow$

(Used to prepare fluoroalkanes)

Haloarenes — Why C–X Bond is Less Reactive

Chlorobenzene is much less reactive towards nucleophilic substitution than chloroalkanes because:

1. **Resonance:** Lone pair of Cl delocalises into the ring → C–Cl gets partial double bond character → stronger, shorter bond

2. **sp² carbon:** The carbon attached to Cl is sp² hybridised → more electronegative → holds electrons tighter

3. **Instability of phenyl cation:** $C_6H_5^+$ is very unstable → SN1 doesn't occur easily

Reactions of Haloarenes

- **Electrophilic substitution:** Cl is ortho-para directing (due to +M effect) but deactivating (due to –I effect)
- **Dow process:** $C_6H_5Cl + NaOH \rightarrow$(623 K, 300 atm) $C_6H_5OH + NaCl$
- **Ullmann reaction:** $2C_6H_5Cl + 2Cu \rightarrow(\Delta)\ C_6H_5–C_6H_5$ (biphenyl)

Important Definitions

Term	Definition
Nucleophilic Substitution	Reaction where a nucleophile replaces the leaving group
SN1	Unimolecular nucleophilic substitution — rate depends on substrate only
SN2	Bimolecular nucleophilic substitution — rate depends on both substrate and nucleophile
Walden Inversion	Inversion of configuration at the chiral centre during SN2
Racemisation	Formation of equal amounts of d and l isomers (during SN1)
Elimination	Loss of HX from adjacent carbons to form a double bond

Solved Examples — NCERT Based

Example 1: SN1 vs SN2

Q: Predict the mechanism (SN1 or SN2) for: (a) $CH_3Br + OH^-$ (b) $(CH_3)_3CBr + H_2O$

Solution:

(a) CH_3Br is primary → **SN2** (strong nucleophile OH^-, no steric hindrance)

(b) $(CH_3)_3CBr$ is tertiary → **SN1** (stable 3° carbocation, weak nucleophile H_2O)

Example 2: Wurtz Reaction

Q: How would you prepare butane from ethyl bromide using Wurtz reaction?

Solution:

$2CH_3CH_2Br + 2Na \rightarrow$(dry ether) $CH_3CH_2–CH_2CH_3 + 2NaBr$

Two ethyl groups couple to form **butane** (C_4H_{10}).

Example 3: Reactivity Order

Q: Arrange in decreasing order of SN2 reactivity: CH_3Cl, CH_3Br, CH_3I, CH_3F

Solution:

SN2 reactivity depends on the C–X bond strength (weaker bond = better leaving group):

C–I weakest → C–Br → C–Cl → C–F strongest

Order: **$CH_3I > CH_3Br > CH_3Cl > CH_3F$**

Example 4: Product Prediction

Q: What happens when chlorobenzene is treated with (a) Na in dry ether (b) NaOH at 623 K, 300 atm?

Solution:

(a) **Fittig reaction:** $2C_6H_5Cl + 2Na \rightarrow C_6H_5–C_6H_5$ (biphenyl) + 2NaCl

(b) **Dow process:** $C_6H_5Cl + NaOH \rightarrow C_6H_5OH$ (phenol) + NaCl

Important Questions for Board Exams

1 Mark Questions

1. What is Walden inversion?
2. Which is a better nucleophile: I^- or Cl^-?

3. Write the product of Finkelstein reaction of CH_3Cl with NaI.
4. Why is chlorobenzene less reactive towards nucleophilic substitution?

2 Mark Questions

1. Distinguish between SN1 and SN2 mechanisms (any 4 points).
2. What is Saytzeff's rule? Give an example.
3. Why does KCN give cyanide but AgCN gives isocyanide?
4. Write the Williamson ether synthesis reaction.

3 Mark Questions

1. Explain the SN2 mechanism with an energy diagram. Why does it cause inversion?
2. How do you convert: (a) ethanol to ethyl bromide (b) benzene to chlorobenzene (c) chlorobenzene to phenol?
3. Give reasons: (a) Haloalkanes are more reactive than haloarenes (b) Allyl chloride is more reactive than n-propyl chloride towards SN1

5 Mark Questions

1. Compare SN1 and SN2 reactions. Explain with mechanism, stereochemistry, and examples. What factors favour each?
2. Discuss the preparation, properties and reactions of haloalkanes. Write any 4 nucleophilic substitution reactions with equations.

Quick Revision Points

- 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

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