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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.

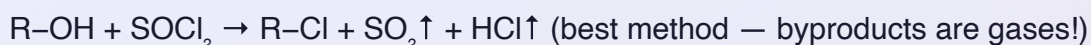
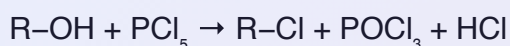
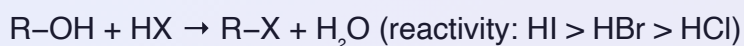
Key Concepts

Classification

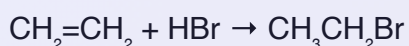
Type	Structure	Example
Primary (1°)	$-\text{CH}_2\text{X}$	$\text{CH}_3\text{CH}_2\text{Cl}$ (ethyl chloride)
Secondary (2°)	$-\text{CHX}-$	$(\text{CH}_3)_2\text{CHBr}$ (isopropyl bromide)
Tertiary (3°)	$-\text{CX}-$	$(\text{CH}_3)_3\text{CCl}$ (tert-butyl chloride)
Haloarene	X on benzene ring	$\text{C}_6\text{H}_5\text{Cl}$ (chlorobenzene)

Preparation Methods

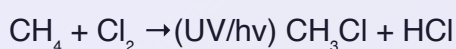
1. From Alcohols:



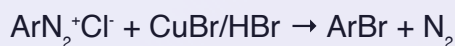
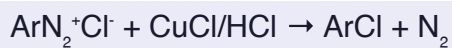
2. From Alkenes (Markovnikov's addition):



3. Halogenation of Alkanes (free radical):



4. Sandmeyer Reaction (for ArX):



Nucleophilic Substitution Reactions

The C–X bond in haloalkanes is polar ($\text{C}^{\delta+}-\text{X}^{\delta-}$), making carbon susceptible to nucleophilic attack.

SN2 Mechanism (Substitution Nucleophilic Bimolecular)

Rate = $k[\text{R-X}][\text{Nu}^-]$ (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: $1^\circ > 2^\circ > 3^\circ$ (steric hindrance increases)

SN1 Mechanism (Substitution Nucleophilic Unimolecular)

Rate = $k[\text{R-X}]$ (depends only on substrate)

Two steps: (1) Ionisation: $\text{R-X} \rightarrow \text{R}^+ + \text{X}^-$ (slow, rate-determining)

(2) Nucleophilic attack: $\text{R}^+ + \text{Nu}^- \rightarrow \text{R-Nu}$ (fast)

Carbocation intermediate: planar $\rightarrow$ nucleophile attacks from both sides

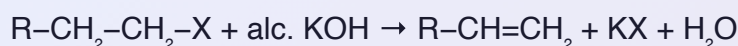
Result: Racemisation (mixture of d and l forms)

Reactivity order: $3^\circ > 2^\circ > 1^\circ$ (more stable carbocation $\rightarrow$ faster ionisation)

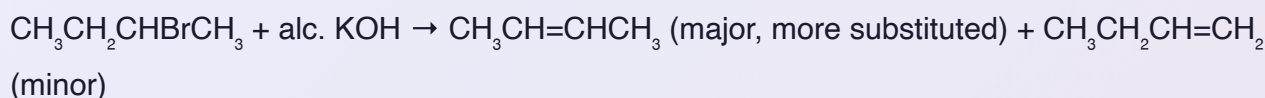
Quick Summary: SN2 = one step, back-side attack, inversion, favoured by 1° substrates and strong nucleophiles. SN1 = two steps, carbocation, racemisation, favoured by 3° substrates and polar protic solvents.

Elimination Reactions

Dehydrohalogenation (β -elimination):



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



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 $\rightarrow \text{CN}^-$ attacks through C $\rightarrow$ cyanide (R-CN). AgCN is covalent $\rightarrow$ attacks through N $\rightarrow$ isocyanide (R-NC). Similarly: $\text{KNO}_2 \rightarrow$ nitro, $\text{AgNO}_2 \rightarrow$ nitrite.

Important Named Reactions

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

(Used to increase carbon chain — makes symmetric alkanes)

Fittig Reaction: $2\text{ArX} + 2\text{Na} \rightarrow \text{Ar-Ar} + 2\text{NaX}$

Wurtz-Fittig: $\text{ArX} + \text{RX} + 2\text{Na} \rightarrow \text{Ar-R} + 2\text{NaX}$

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

(NaCl precipitates in acetone $\rightarrow$ drives reaction forward)

Swarts Reaction: $\text{R-Cl} + \text{AgF} \rightarrow \text{R-F} + \text{AgCl} \downarrow$

(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 $\rightarrow$ C-Cl gets partial double bond character $\rightarrow$ stronger, shorter bond

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

3. **Instability of phenyl cation:** C₆H₅⁺ 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:** C₆H₅Cl + NaOH → (623 K, 300 atm) C₆H₅OH + NaCl
- **Ullmann reaction:** 2C₆H₅Cl + 2Cu → (Δ) C₆H₅-C₆H₅ (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) CH₃Br + OH⁻ (b) (CH₃)₃CBr + H₂O

Solution:

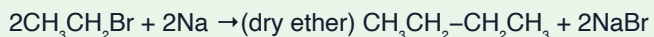
(a) CH₃Br is primary → **SN2** (strong nucleophile OH⁻, no steric hindrance)

(b) (CH₃)₃CBr is tertiary → **SN1** (stable 3° carbocation, weak nucleophile H₂O)

Example 2: Wurtz Reaction

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

Solution:



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

Example 3: Reactivity Order

Q: Arrange in decreasing order of $\text{S}_\text{N}2$ reactivity: CH_3Cl , CH_3Br , CH_3I , CH_3F

Solution:

$\text{S}_\text{N}2$ reactivity depends on the C–X bond strength (weaker bond = better leaving group):

C–I weakest $\rightarrow$ C–Br $\rightarrow$ C–Cl $\rightarrow$ C–F strongest

Order: $\text{CH}_3\text{I} > \text{CH}_3\text{Br} > \text{CH}_3\text{Cl} > \text{CH}_3\text{F}$

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:** $2\text{C}_6\text{H}_5\text{Cl} + 2\text{Na} \rightarrow \text{C}_6\text{H}_5\text{--C}_6\text{H}_5$ (biphenyl) + 2NaCl

(b) **Dow process:** $\text{C}_6\text{H}_5\text{Cl} + \text{NaOH} \rightarrow \text{C}_6\text{H}_5\text{OH}$ (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 SN_1 and SN_2 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 SN_2 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 SN_1

5 Mark Questions

1. Compare SN_1 and SN_2 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 : $\text{R-OH} + \text{SOCl}_2$ (byproducts are gases)
- SN_2 : one step, back-attack, inversion, 1° best, strong nucleophile, aprotic solvent
- SN_1 : two steps, carbocation, racemisation, 3° best, weak nucleophile, protic solvent
- Elimination: alc. $\text{KOH} \rightarrow$ alkene (Saytzeff's rule — more substituted product)
- Substitution: aq. $\text{KOH} \rightarrow$ alcohol
- $\text{KCN} \rightarrow \text{R-CN}$; $\text{AgCN} \rightarrow \text{R-NC}$ (covalent silver salt $\rightarrow$ attacks through N)
- Wurtz: $2\text{RX} + 2\text{Na} \rightarrow \text{R-R}$; Fittig: $2\text{ArX} + 2\text{Na} \rightarrow \text{Ar-Ar}$
- Haloarenes: less reactive due to resonance (C-Cl partial double bond), ortho-para directing
- Finkelstein: $\text{R-Cl} + \text{NaI} \rightarrow \text{R-I}$; Swarts: $\text{R-Cl} + \text{AgF} \rightarrow \text{R-F}$

← Previous: Coordination Compounds

Next: Alcohols, Phenols and Ethers →



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