FREE NOTES · NCERT + JEE/NEET LEVEL

Haloalkanes & Haloarenes

Classification and naming, C–X bond, preparation, physical properties, SN1 and SN2 mechanisms, stereochemistry, elimination, reactions with metals, reactions of haloarenes and important polyhalogen compounds.

01 Classification & nature of the C–X bond
02 Preparation
03 Physical properties
04 Nucleophilic substitution
05 SN1 vs SN2
06 Stereochemistry basics
07 Elimination & reaction with metals
08 Haloarenes
09 Polyhalogen compounds
10 JEE Extra + Tricks
11 Solved questions, mistakes & practice
12 Quick revision

01 Classification & nature of the C–X bond

- Mono-, di-, poly-halo compounds. By carbon type: **1°, 2°, 3°** alkyl halides; **allylic** (X on C next to C=C), **benzylic** (X on C next to ring), **vinylic** (X on C=C), **aryl** (X on ring).
- C–X is polar (C δ+, X δ−). Bond length C–F < C–Cl < C–Br < C–I; bond strength in the reverse order ⇒ **reactivity R–I > R–Br > R–Cl > R–F**.
- Naming: halogen is a prefix (2-bromobutane, 1-chloro-2-methylpropane). Common names: CH_2Cl_2 methylene chloride, $CHCl_3$ chloroform, CHI_3 iodoform, CCl_4 carbon tetrachloride.

02 Preparation

From	Reagent	Note
Alcohol	HX + $ZnCl_2$ (Lucas, for 1°/2°), PCl_3, PCl_5, **$SOCl_2$**	$SOCl_2$ best: by-products SO_2, HCl are gases
Alkane	Cl_2 / hv (free radical)	Mixture of products
Alkene	HX (Markovnikov); HBr + peroxide (anti-Markovnikov)	X_2 gives vic-dihalide
Halide exchange	**Finkelstein:** R–Cl + NaI (acetone) → R–I; **Swarts:** R–Br + AgF/Hg_2F_2 → R–F	NaCl precipitates in acetone, drives reaction
Arene	X_2 + Fe/$FeCl_3$ (dark); ortho + para	Electrophilic substitution
Aniline	**Sandmeyer:** $ArN_2^+Cl^-$ + CuCl/HCl or CuBr/HBr; KI for ArI	Via diazonium salt

03 Physical properties

- Boiling point: higher than parent alkane (polarity, bigger mass). For the same alkyl group: RI > RBr > RCl > RF. For isomers, more branching ⇒ lower b.p.
- Density: bromo, iodo and polychloro compounds are denser than water.
- Slightly soluble in water (can't form strong H-bonds), soluble in organic solvents.
- p-Dichlorobenzene has a higher m.p. than o- and m- (symmetry, fits better in the crystal).

04 Nucleophilic substitution

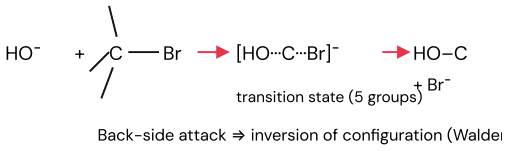
A nucleophile (Nu^-) replaces X^-. $R–X + Nu^- \rightarrow R–Nu + X^-$.

Reagent	Product
aq. KOH / NaOH	Alcohol R–OH
NaOR′	Ether R–O–R′ (Williamson)
KCN (ionic)	Alkyl cyanide R–CN (attacks through C)
AgCN (covalent)	Isocyanide R–NC (attacks through N)
KNO_2	Alkyl nitrite R–O–N=O
$AgNO_2$	Nitroalkane R–NO_2
NH_3	Amines (mixture)
$LiAlH_4$	Alkane R–H
R′COOAg	Ester

CN^- and NO_2^- are **ambident** nucleophiles: they can attack through two different atoms.

05 SN1 vs SN2

	SN2	SN1
Steps	One step, concerted	Two steps via **carbocation**
Rate law	k[RX][Nu^-] (second order)	k[RX] (first order)
Reactivity	CH_3X > 1° > 2° > 3° (crowding blocks attack)	3° > 2° > 1° > CH_3X (carbocation stability)
Stereo	**Inversion**	**Racemisation** (attack from both faces)
Solvent	Polar aprotic (acetone, DMSO)	Polar protic (water, alcohol)
Also fast		Allylic and benzylic halides (resonance-stabilised cation)



SN2: nucleophile enters from the back while the leaving group departs

06 Stereochemistry basics

- **Chiral carbon:** carbon with four different groups (2-bromobutane). Such molecules are **optically active**.
- **Enantiomers:** non-superimposable mirror images; rotate plane-polarised light equally but in opposite directions (d/+ and l/-).
- **Racemic mixture:** 50:50 of both enantiomers, optically inactive (external compensation).
- **Retention** = same spatial arrangement after reaction; **inversion** = flipped.

07 Elimination & reaction with metals

Dehydrohalogenation: alc. KOH removes HX ⇒ alkene. **Saytzeff (Zaitsev) rule:** the more substituted alkene is the major product. 2-bromobutane → but-2-ene (major) + but-1-ene.

SUBSTITUTION VS ELIMINATION

Aqueous KOH ⇒ substitution (alcohol). Alcoholic KOH ⇒ elimination (alkene). Bulky strong base and 3° halide favour elimination.

- **Grignard reagent:** R–X + Mg (dry ether) → RMgX. Very reactive; reacts with water: RMgX + H_2O → R–H, so must be kept dry.
- **Wurtz reaction:** 2R–X + 2Na (dry ether) → R–R. **Wurtz-Fittig:** ArX + RX + Na → Ar–R. **Fittig:** 2ArX + 2Na → Ar–Ar.

08 Haloarenes

Haloarenes are much **less reactive** to nucleophilic substitution because:

1. **Resonance**: C–X gets partial double bond character.
2. C is **sp^2** (more s character) ⇒ shorter, stronger C–X bond.
3. Phenyl cation is unstable (no SN1).
4. Electron-rich ring repels the nucleophile.

Conversion needs harsh conditions: chlorobenzene + NaOH at 623 K, 300 atm → phenol (Dow process). **–NO_2 at ortho/para** makes it easier (2,4,6-trinitrochlorobenzene reacts with warm water).

ELECTROPHILIC SUBSTITUTION

Halogen is **deactivating** (–I effect) but **ortho/para directing** (+R effect). Chlorobenzene gives o- and p- products in halogenation, nitration, sulphonation, Friedel-Crafts (para major).

09 Polyhalogen compounds

Compound	Use / effect
CH_2Cl_2	Solvent, paint remover; affects nervous system
$CHCl_3$	Solvent; old anaesthetic. In light + air forms poisonous **phosgene** $COCl_2$, so stored in dark bottles filled to the top with 1% ethanol
CHI_3 (iodoform)	Antiseptic (releases I_2), yellow
CCl_4	Solvent, refrigerants; damages ozone and liver
Freons (CCl_2F_2)	Refrigerants, aerosols; release Cl radicals that destroy ozone
DDT	First chlorinated insecticide (malaria mosquitoes); not biodegradable, builds up in food chain

10 JEE Extra + Tricks

JEE LEVEL

- S_N2: one step, inversion (Walden), rate ∝ [RX][Nu]; order CH_3X > 1° > 2° > 3°. S_N1: carbocation, racemisation, rate ∝ [RX]; 3° > 2° > 1°.
- Polar aprotic solvents (DMSO, acetone) favour S_N2; polar protic (water, alcohol) favour S_N1.
- Saytzeff (Zaitsev) rule: elimination gives more substituted alkene; alcoholic KOH ⇒ elimination, aqueous KOH ⇒ substitution.
- Aryl halides resist nucleophilic substitution (partial double bond, sp^2 C); $-NO_2$ at o/p activates (Meisenheimer complex).
- KCN gives nitrile (C attacks); AgCN gives isocyanide (N attacks). KNO_2 ⇒ nitrite; $AgNO_2$ ⇒ nitroalkane.
- Named: Finkelstein (NaI in acetone), Swarts (AgF/Hg_2F_2), Wurtz–Fittig, Fittig, Sandmeyer.

11 Solved questions, mistakes & practice

Q1. Which reacts faster by SN2: 1-bromobutane or 2-bromobutane?

1-bromobutane (1°, less crowded).

Q2. Arrange for SN1: CH_3CH_2Br, $(CH_3)_2CHBr$, $(CH_3)_3CBr$.

$(CH_3)_3CBr$ > $(CH_3)_2CHBr$ > CH_3CH_2Br (3° > 2° > 1° carbocation stability).

Q3. Give the product: CH_3CH_2Br + KCN and CH_3CH_2Br + AgCN.

CH_3CH_2CN (propanenitrile) and CH_3CH_2NC (ethyl isocyanide).

- Mixing up KCN (cyanide) and AgCN (isocyanide).
- Writing retention for SN2 (it's inversion).
- Calling chlorine an activating group (it deactivates but directs o/p).
- Using aqueous KOH when the question wants an alkene.

1. Name the reaction: R–Br + NaI in acetone.
2. Why is chloroform kept in dark bottles?
3. Major product of 2-bromopentane with alc. KOH?
4. Which is optically active: 1-bromobutane or 2-bromobutane?

ANSWERS

1) Finkelstein · 2) Light + air convert it to phosgene · 3) Pent-2-ene · 4) 2-bromobutane

12 Quick revision: 5 minutes before the exam

PREPARATION

- $SOCl_2$ best for alcohols.
- Finkelstein (I), Swarts (F).
- Sandmeyer: ArN_2^+ + CuX.

MECHANISM

- SN2: 1° fast, inversion.
- SN1: 3° fast, racemisation.
- Alc. KOH ⇒ alkene (Saytzeff).

REAGENTS

- KCN → RCN; AgCN → RNC.
- KNO_2 → R–ONO; $AgNO_2$ → RNO_2.
- Wurtz: 2RX + 2Na → R–R.

HALOARENES

- Low reactivity: resonance, sp^2 C.
- X: deactivating, o/p directing.
- $CHCl_3$ → phosgene in light.

Have a doubt? Ask the AI Doubt Solver at padhaiadda.netlify.app, or take the mock test on this chapter.