

Chapter 6 · Haloalkanes and Haloarenes

CBSE Class 12 Chemistry (043) · Organic · Unit 6 = 6 marks · Ultimate Revision Sheet

60-SECOND RECALL

Reactivity order	$R-I > R-Br > R-Cl > R-F$ (C-X bond strength decides)
S_N1	$3^\circ > 2^\circ > 1^\circ$ · carbocation intermediate · racemisation · polar protic solvent
S_N2	$1^\circ > 2^\circ > 3^\circ$ · one step · inversion (Walden) · polar aprotic solvent
Haloarenes	Much less reactive — resonance + sp^2 carbon
Saytzeff rule	Elimination gives the more substituted alkene
Finkelstein	$R-Cl + NaI \rightarrow R-I$ (dry acetone)
Swarts	$R-X + AgF \rightarrow R-F$

1. Nature of the C-X Bond

THE BASICS The C-X bond is **polar** because the halogen is more electronegative: carbon carries $\delta+$ and is open to attack by **nucleophiles**.
Bond length increases $C-F < C-Cl < C-Br < C-I$, so **bond strength decreases** in the same order. This is why **iodides are the most reactive** and fluorides the least — the weakest bond breaks most easily.

2. Preparation

THE ROUTES ASKED From alcohols: $R-OH + HX \rightarrow R-X$ (with $ZnCl_2$ for $1^\circ/2^\circ$); better reagents are PCl_5 , PCl_3 or $SOCl_2$.

$SOCl_2$ is preferred because the by-products SO_2 and HCl are **gases that escape**, leaving a pure product. (Darzen's procedure.)

From alkenes: addition of HX follows **Markovnikov's rule**; with **peroxide**, HBr adds **anti-Markovnikov** (Kharasch effect) — **only HBr** , not HCl or HI .

Finkelstein: $R-Cl + NaI \rightarrow R-I + NaCl$, in **dry acetone** ($NaCl$ precipitates, driving it forward).

Swarts: $R-X + AgF / Hg_2F_2 \rightarrow R-F$.

Haloarenes: electrophilic substitution with X_2 and a Lewis acid ($Fe/FeCl_3$), or from a diazonium salt by **Sandmeyer's reaction**.

3. Substitution — S_N1 vs S_N2

THE COMPARISON THAT CARRIES THE MARKS

Basis	S_N1	S_N2
Steps	Two ; slow ionisation first	One , concerted
Intermediate	Carbocation	Transition state only

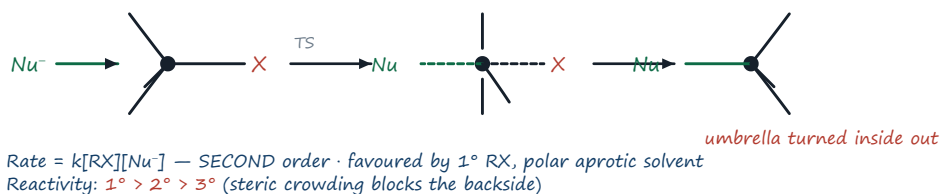
Kinetics	First order — rate = $k[\text{RX}]$	Second order — rate = $k[\text{RX}][\text{Nu}]$
Reactivity	$3^\circ > 2^\circ > 1^\circ > \text{CH}_3\text{X}$	$\text{CH}_3\text{X} > 1^\circ > 2^\circ > 3^\circ$
Stereochemistry	Racemisation (flat carbocation, attack from both sides)	Inversion of configuration (Walden inversion)
Solvent	Polar protic (water, alcohol)	Polar aprotic (acetone, DMSO)

Why 3° favours $\text{S}_\text{N}1$: the carbocation is stabilised by +I and hyperconjugation.

Why 1° favours $\text{S}_\text{N}2$: least steric hindrance to backside attack.

$\text{S}_\text{N}2$ — one step, backside attack, INVERSION

Nu^- comes in as X^- leaves, through a 5-bonded transition state.



$\text{S}_\text{N}1$ — two steps, via a PLANAR carbocation, RACEMISATION



The reactivity orders are **opposite**, and both follow from one idea: $\text{S}_\text{N}2$ is blocked by bulk, $\text{S}_\text{N}1$ is helped by it. Optically pure substrate + inversion $\rightarrow \text{S}_\text{N}2$; + racemic product $\rightarrow \text{S}_\text{N}1$.

4. Elimination and Other Reactions

ELIMINATION With **alcoholic KOH**, a haloalkane gives an **alkene** (dehydrohalogenation). With **aqueous KOH** it gives an **alcohol** instead — that single word decides the product.
Saytzeff's rule: the major alkene is the **more substituted** (more stable) one.

THE NAMED REACTIONS **Wurtz**: $2\text{R-X} + 2\text{Na}$ (dry ether) $\rightarrow \text{R-R}$ — makes a **symmetrical alkane** with double the carbons.

Fittig: two aryl halides + Na $\rightarrow$ biphenyl. **Wurtz-Fittig**: aryl halide + alkyl halide + Na $\rightarrow$ alkylarene.

Grignard reagent: $\text{R-X} + \text{Mg}$ (dry ether) $\rightarrow \text{RMgX}$. Must be prepared in **completely dry** conditions, because even traces of water decompose it to an alkane.

With $\text{AgCN} \rightarrow$ **isocyanide** (ambident nucleophile, N-attack); with $\text{KCN} \rightarrow$ **nitrile** (C-attack).

Same logic: $\text{AgNO}_2 \rightarrow$ **nitroalkane**, $\text{KNO}_2 \rightarrow$ **alkyl nitrite**.

WHY HALOARENES ARE SO UNREACTIVE — the standard 2-marker

1. **Resonance:** the lone pair on the halogen delocalises into the ring, giving the C-X bond **partial double-bond character**, so it is shorter and stronger.
 2. **sp^2 carbon:** the carbon bearing X is sp^2 (more electronegative, holds the bond more tightly) rather than sp^3 .
 3. The ring's π electrons **repel the approaching nucleophile**.
 4. The **phenyl cation** formed on ionisation is very unstable.
- Substitution does occur under **drastic conditions**, and is much easier if **$-NO_2$ groups are present at ortho and para positions**.

POLYHALOGEN COMPOUNDS — quick facts

$CHCl_3$ (chloroform): on standing in air and light it slowly oxidises to poisonous **phosgene ($COCl_2$)**, so it is stored in **dark coloured bottles filled to the brim with 1% ethanol**.

CCl_4 : used as a solvent; depletes the ozone layer. **DDT:** first major synthetic insecticide, now restricted due to persistence. **Freons:** refrigerants, **damage the ozone layer**. **Iodoform CHI_3 :** antiseptic.

5. Question Triggers

what the reagent tells you

Reagent / clue	Product
Aqueous KOH	Alcohol (substitution)
Alcoholic KOH	Alkene (elimination)
KCN vs AgCN	Nitrile vs isocyanide
KNO_2 vs $AgNO_2$	Alkyl nitrite vs nitroalkane
Na / dry ether	Wurtz — symmetrical alkane
Mg / dry ether	Grignard reagent
NaI / dry acetone	Finkelstein → alkyl iodide
"optically active product is racemised"	S_N1 , via carbocation
"configuration is inverted"	S_N2 , Walden inversion

MOST-ASKED BOARD QUESTIONS

1. [3M] Distinguish S_N1 and S_N2 with mechanism, order of reactivity and stereochemistry.
2. [3M] Why are **haloarenes less reactive** than haloalkanes towards nucleophilic substitution?
3. [2M] Convert: alcohol → haloalkane → alkene → alkane (conversion chains).
4. [2M] Explain **Markovnikov** and the **peroxide effect**.
5. [2M] Why is **chloroform stored in dark bottles**?
6. [1M] Which haloalkane is most reactive in S_N1 ? → **Tertiary**

THE HABIT THAT SCORES — In organic chapters the **reagent is the question**. Build the habit of reading the reagent first — aqueous or alcoholic, K or Ag salt, with or without peroxide — because each pair differs by one word and changes the entire product.