



Collegedunia NCERT Notes

The Ultimate NCERT Revision Guide for Class 12 Chemistry (Part II)

12th Chemistry — Syllabus 2026-27 (New NCERT)

Chapter 6: Haloalkanes and Haloarenes

Why this chapter matters

Haloalkanes and haloarenes lie at the heart of organic synthesis — they are the practical bridge between alkanes/arenes and almost every other functional group (alcohols, ethers, amines, nitriles, esters, hydrocarbons). For JEE/NEET, this chapter delivers 2–3 direct questions on **S_N1 vs S_N2 reactivity ordering, stereochemistry of substitution** (inversion / racemisation / retention), **Zaitsev's rule in elimination, Sandmeyer / Wurtz / Wurtz-Fittig sequences**, and **nomenclature + isomer counting**. Expect mechanism-write questions on benzyne-style aromatic substitution and short numerical-style ordering of reactivity.

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1 Classification and Nomenclature

Halogen-substituted hydrocarbons fall into two broad families: **haloalkanes** (the halogen sits on an sp^3 carbon of an aliphatic chain) and **haloarenes** (the halogen sits on an sp^2 carbon of an aromatic ring). Their reactivity, physical properties and synthetic utility differ sharply — and that difference is the central theme of the entire chapter.

1.1 Classification by Number and Hybridisation

Two orthogonal axes of classification

By number of halogen atoms: mono-, di-, tri-, tetra-, polyhalogen compounds.

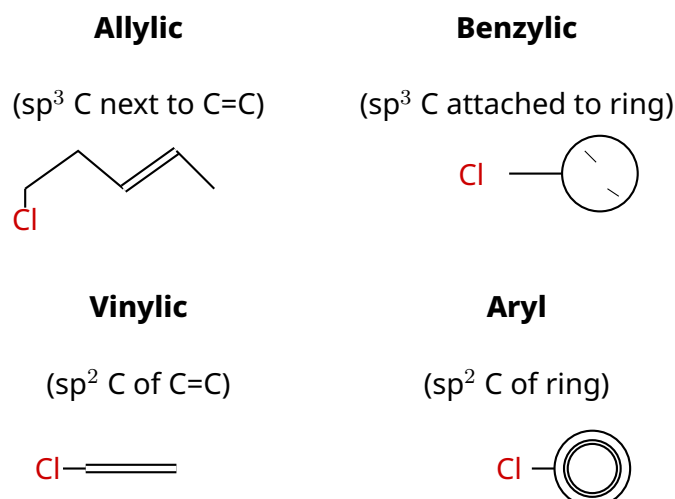
By hybridisation of the carbon bearing X:

- **sp^3 C-X:** alkyl halides (R-X), **allylic** halides (X on sp^3 C next to C=C), **benzylic** halides (X on sp^3 C attached to an aryl ring).
- **sp^2 C-X:** **vinyllic** halides (X on sp^2 C of C=C), **aryl** halides (X on sp^2 C of an aromatic ring).

Alkyl halides are further classified by the *degree* of the carbon bearing X:

- **Primary (1°):** C-X carbon bonded to one other carbon. *Ex:* $\text{CH}_3\text{CH}_2\text{Br}$.
- **Secondary (2°):** bonded to two other carbons. *Ex:* $(\text{CH}_3)_2\text{CHBr}$.
- **Tertiary (3°):** bonded to three other carbons. *Ex:* $(\text{CH}_3)_3\text{CBr}$.

Dihalides have two further sub-types. **Gem-dihalides** (geminal) carry both halogens on the same carbon; in common names they are alkylidene halides (e.g. ethylidene chloride for CH_3CHCl_2). **Vic-dihalides** (vicinal) carry the halogens on adjacent carbons; common names are alkylene dihalides (e.g. ethylene dichloride for $\text{CH}_2\text{ClCH}_2\text{Cl}$).



Hybridisation map of common haloalkane/haloarene sub-classes. The vinyl and aryl halides have the halogen on an sp² carbon and behave very differently from the rest.

Allyl vs Vinyl — where is the double bond?

Allyl = halogen is *one carbon away* from C=C (on sp³ C). Sp³ halides are reactive.

Vinyl = halogen is *directly on* the C=C carbon (on sp² C). Sp² halides are unreactive.

Think '**V**inyl is right **V**-on the double bond'.

1.2 IUPAC Nomenclature

The IUPAC system names alkyl halides as *halosubstituted hydrocarbons*. The longest carbon chain containing the halogen is the parent; the halogen is a prefix (chloro-, bromo-, iodo-, fluoro-); the locant is the lowest possible. For aromatic compounds, monohalogen benzenes share their common and IUPAC names (e.g. chlorobenzene); for dihalobenzenes the IUPAC numerals (1,2-; 1,3-; 1,4-) replace the common o-, m-, p- prefixes.

Structure	Common name	IUPAC name
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$	sec-Butyl chloride	2-Chlorobutane
$(\text{CH}_3)_3\text{CBr}$	tert-Butyl bromide	2-Bromo-2-methylpropane
$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	neo-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$\text{CH}_2=\text{CHCl}$	Vinyl chloride	Chloroethene
$\text{CH}_2=\text{CHCH}_2\text{Br}$	Allyl bromide	3-Bromopropene
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	Benzyl chloride	(Chloromethyl)benzene
CH_2Cl_2	Methylene chloride	Dichloromethane
CHCl_3	Chloroform	Trichloromethane
CCl_4	Carbon tetrachloride	Tetrachloromethane

Quick Tip

For dihalides, decide gem vs vic at a glance: **same carbon = gem, different carbon = vic**. In common names, gem \rightarrow alkylidene halide, vic \rightarrow alkylene dihalide. In IUPAC, both are simply dihaloalkanes with two locants.

1.3 Worked Example — 8 Isomers of $\text{C}_5\text{H}_{11}\text{Br}$

The eight structural isomers of pentyl bromide show how the primary, secondary and tertiary classification interlocks with branching.

Structure	IUPAC name	Class
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	1-Bromopentane	1°
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$	2-Bromopentane	2°
$\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$	3-Bromopentane	2°
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Br}$	1-Bromo-3-methylbutane	1°
$(\text{CH}_3)_2\text{CHCHBrCH}_3$	2-Bromo-3-methylbutane	2°
$(\text{CH}_3)_2\text{CBrCH}_2\text{CH}_3$	2-Bromo-2-methylbutane	3°
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$	1-Bromo-2-methylbutane	1°
$(\text{CH}_3)_3\text{CCH}_2\text{Br}$	1-Bromo-2,2-dimethylpropane	1°

Common Mistake

Students often miscount the carbons in branched isomers — always pick the *longest chain that includes the C-X carbon*, even if a shorter chain has more substituents. For $(\text{CH}_3)_3\text{CCH}_2\text{Br}$, the longest chain through the CBr is propane

(not butane), giving 1-bromo-2,2-dimethylpropane (*not* “neopentyl bromide” in IUPAC).

2 Nature of the C–X Bond

The chemistry of haloalkanes hinges on a single structural feature: the polar C–X bond. Because halogens are more electronegative than carbon, the carbon bears a partial positive charge (δ^+) and the halogen a partial negative charge (δ^-) — the carbon is the site of nucleophilic attack, the halogen is the leaving group.

2.1 Bond Length, Bond Enthalpy and Dipole Moment

Down the halogen group (F \rightarrow I), atomic size rises sharply. The C–X bond therefore lengthens, and because the orbital overlap between carbon ($2sp^3$) and the halogen valence shell weakens, the bond enthalpy falls.

Bond	Bond length / pm	Bond enthalpy / kJ mol^{-1}	Dipole moment / D
CH ₃ –F	139	452	1.847
CH ₃ –Cl	178	351	1.860
CH ₃ –Br	193	293	1.830
CH ₃ –I	214	234	1.636

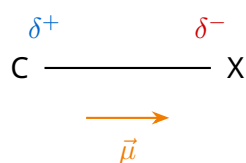
Two competing trends on dipole moment

Dipole moment $\mu = q \times d$ where q is the partial charge and d is the bond length.

Going F \rightarrow I: q decreases (electronegativity drops), d increases. The two effects partly cancel, but the drop in q wins from Cl onwards. That is why $\mu(\text{CH}_3\text{Cl}) \approx \mu(\text{CH}_3\text{F})$ but $\mu(\text{CH}_3\text{I})$ is markedly lower.

Quick Tip

A common JEE/NEET MCQ: “Which methyl halide has the largest dipole moment?” Answer: CH₃Cl ($\mu = 1.86$ D), *not* CH₃F. Bond length effects matter.

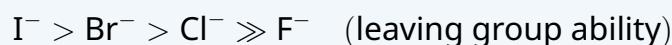
Polar C-X bond**Down the group**

- > size ↑
- > length ↑
- > energy ↓
- > polarity ↓

The polarity of the C-X bond drives nucleophilic substitution; the lower enthalpy of weaker C-X bonds makes them faster leaving groups.

Leaving group ability

A halide's ability to leave correlates with the stability of X^- in solution. Bigger, more polarisable anions stabilise the negative charge better, so:



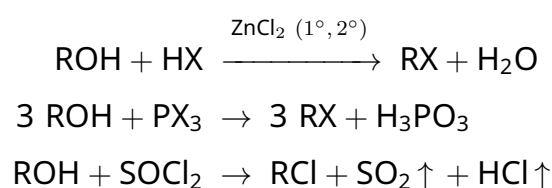
This is exactly the reverse of bond strength: weaker bonds break more easily. R-I reacts fastest, R-F essentially does not react under typical S_N conditions.

3 Methods of Preparation

Haloalkanes are most commonly synthesised from *alcohols* (the workhorse), from *hydrocarbons* (alkanes via radical halogenation, alkenes via HX/X_2 addition), and by *halogen exchange* (interconversion between R-X and R-X'). Haloarenes come from a different toolbox: *electrophilic substitution* of arenes and the *Sandmeyer reaction* from amines.

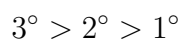
3.1 From Alcohols

The hydroxyl group of an alcohol is replaced by a halogen on reaction with concentrated halogen acids, phosphorus halides (PCl_3 , PCl_5 , PBr_3 , PI_3 — the last two generated *in situ* from red P + Br_2/I_2), or thionyl chloride ($SOCl_2$).

Three classical conversions

Thionyl chloride is the cleanest of the three because both by-products (SO_2 and HCl) escape as gases, leaving the pure alkyl chloride behind. The reactivity of al-

cohols with a given haloacid follows:



which mirrors carbocation stability. The reaction proceeds via an S_N1 -like pathway for tertiary alcohols (no $ZnCl_2$ needed — just shake with conc. HCl at room temperature) and an S_N2 -like pathway for primary alcohols (Lucas catalyst $ZnCl_2$ required).

Alkyl iodides from alcohols: heat ROH with NaI or KI in 95% orthophosphoric acid. **Alkyl bromides** from constant-boiling 48% HBr.

Quick Tip

The **Lucas test** for distinguishing 1° , 2° and 3° alcohols uses Lucas reagent (conc. HCl + $ZnCl_2$). $3^\circ \rightarrow$ cloudiness in seconds, $2^\circ \rightarrow$ 5 min, $1^\circ \rightarrow$ no reaction at room temperature. This directly mirrors carbocation stability.

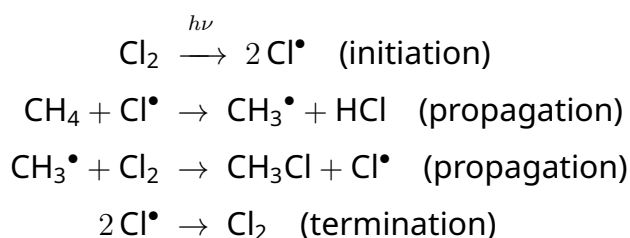
Common Mistake

The C–OH bond of a phenol is partly double-bond in character (resonance with the ring), and stronger than an aliphatic C–OH. *Aryl halides cannot* be made from phenols by this route — a frequent student error.

3.2 From Hydrocarbons — Alkanes

Free-radical chlorination or bromination of an alkane with Cl_2/Br_2 in UV light gives a mixture of mono- and polyhaloalkanes. Yields are low for any single isomer; the method is rarely used preparatively but is foundational for understanding radical mechanisms.

Free-radical chlorination of methane



The hydrogen abstracted preferentially is the one that gives the most stable radical: $3^\circ > 2^\circ > 1^\circ$. Hence isobutane chlorinates mostly at the tertiary carbon ('Markovnikov for radicals').

3.3 From Hydrocarbons — Alkenes

(a) Addition of hydrogen halides. An alkene + HX \rightarrow alkyl halide. Markovnikov's rule (Class XI) predicts that H goes to the carbon already bearing more H's, so the

halogen ends up on the more substituted carbon (the more stable carbocation):



(b) Addition of halogens. Bromine in CCl_4 adds across a $\text{C}=\text{C}$ double bond to give a *vic*-dibromide; the discharge of the reddish-brown bromine colour is the classic visual test for unsaturation.

Markovnikov vs anti-Markovnikov

Markovnikov (ionic HBr, no peroxide): H to the C with more H's.

Anti-Markovnikov (peroxide effect, only HBr): Free-radical chain reverses the selectivity. Halide goes to the less substituted carbon.

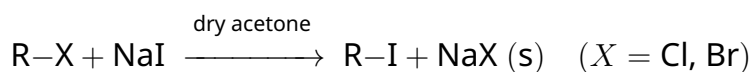
Anti-Markovnikov works only for HBr — not for HCl (Cl atom adds too slowly) or HI (I-I bond too weak to propagate the chain).

Quick Tip

“Peroxide effect = HBr only” is a high-yield JEE/NEET MCQ. Memorise it as a hard rule.

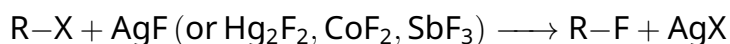
3.4 Halogen Exchange — Finkelstein and Swarts

Finkelstein reaction: alkyl iodide from alkyl chloride/bromide.



NaI is soluble in acetone but NaCl and NaBr are not. Precipitation of NaCl/NaBr removes them from the equilibrium, pulling the reaction to the right by Le Chatelier's principle.

Swarts reaction: alkyl fluoride from alkyl chloride/bromide using a metal fluoride.



Direct fluorination is too violent; Swarts is the practical route to alkyl fluorides.

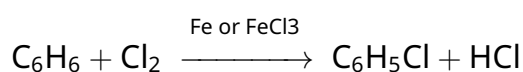
Finkelstein vs Swarts

Finkelstein: F-inkelstein gives “I” (Iodide) — the F is a decoy. Reagent is **NaI / acetone**.

Swarts: S-warts gives “F” (Fluoride). Reagent is a **metal fluoride** like AgF / SbF_3 .

3.5 Preparation of Haloarenes

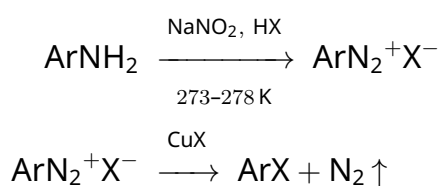
(i) Electrophilic substitution. Cl_2 or Br_2 with a Lewis acid catalyst (Fe or FeX_3) gives a mixture of o- and p-haloarenes, separable by their melting-point difference (para usually crystallises higher — see Physical Properties).



Iodination is reversible and needs an oxidising agent (HNO_3 or HIO_4) to oxidise the HI by-product. Fluorination by this method is impractical — too violent.

(ii) Sandmeyer's reaction. A primary aromatic amine in cold dilute mineral acid + NaNO_2 ($0-5^\circ\text{C}$) gives a diazonium salt; this is then treated with CuCl/CuBr to replace $-\text{N}_2^+$ by $-\text{Cl}/-\text{Br}$.

Sandmeyer sequence



For iodine, CuI is not needed — the diazonium salt + KI gives the aryl iodide directly (with N_2 evolution). For fluorine, the related **Balz-Schiemann reaction** uses HBF_4 to give $\text{ArF} + \text{N}_2 + \text{BF}_3$.

Real-World Application

The Sandmeyer reaction is the standard industrial route to many aryl halides used in dye, pharmaceutical and agrochemical synthesis — for example, in making the antimalarial chloroquine and the herbicide 2,4-D, both of which start from aniline.

Quick Tip

[JEE/NEET extension] For preparing ArI , skip the CuI — just shake the diazonium salt with KI . For ArF , use HBF_4 (Balz-Schiemann), *not* CuF .

4 Physical Properties

Three properties dominate exam questions: boiling point, density and solubility.

4.1 Melting and Boiling Points

Methyl chloride, methyl bromide, ethyl chloride and some chlorofluoromethanes are **gases** at room temperature; higher members are liquids or low-melting solids. Boiling points rise sharply with the size of the alkyl group and the halogen, because of stronger dipole-dipole and van der Waals interactions.

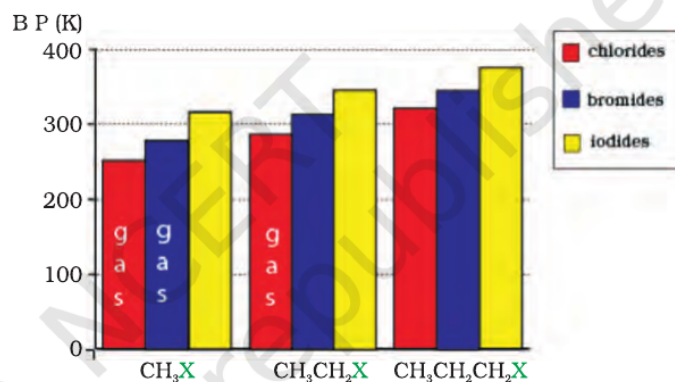


Fig. 6.1: Comparison of boiling points of some alkyl halides

The boiling points of isomeric haloalkanes decrease with increase in branching. For example, 2-bromo-2-methylpropane has the lowest boiling point among the isomers of C₄H₉Br.

Source: NCERT Class 12 Chemistry Part II, Chapter 6 — Fig. 6.1: Comparison of boiling points of alkyl chlorides, bromides and iodides for CH₃X, CH₃CH₂X and CH₃CH₂CH₂X.

Two boiling-point rules

Rule 1 — For the same alkyl group, halogen size wins:



Bigger, more polarisable halogens have stronger London (dispersion) forces.

Rule 2 — For isomers, more branching = lower BP:

n-BuBr (375 K) > sec-BuBr (364 K) > tert-BuBr (346 K).

Branching reduces the surface area for van der Waals contacts.

For isomeric dihalobenzenes: boiling points are nearly identical (similar dipoles cancel/add in symmetric ways). However, the **para isomer is markedly higher melting** than ortho or meta because the symmetric para shape packs more tightly into the crystal lattice.

Common Mistake

“Same boiling point, different melting point.” Students often try to use BP to distinguish o-/m-/p-dichlorobenzene — it does not work. Use *melting point* (para ≫ ortho ≈ meta).

4.2 Density

Density rises with (i) the atomic mass of the halogen, (ii) the number of halogens and (iii) the carbon count.

Compound	Density (g/mL)	Compound	Density (g/mL)
n-C ₃ H ₇ Cl	0.89	CH ₂ Cl ₂	1.336
n-C ₃ H ₇ Br	1.335	CHCl ₃	1.489
n-C ₃ H ₇ I	1.747	CCl ₄	1.595

Bromo-, iodo- and polychloro derivatives are heavier than water — chloroform and carbon tetrachloride therefore sink and form the bottom layer when shaken with water. (Compare: most hydrocarbons float.)

4.3 Solubility

Haloalkanes are *slightly* soluble in water but freely soluble in organic solvents. The reason is energetic balance: dissolving a haloalkane in water requires breaking strong H-bonds in water, but the new water-haloalkane dipole-dipole interactions formed are weaker. Net ΔH is unfavourable, so solubility is low.

In an organic solvent, the new solvent interactions are similar in strength to the ones being broken: $\Delta H \approx 0$, and entropy drives dissolution.

Real-World Application

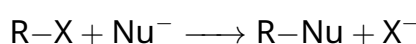
This is why halogenated solvents (CH₂Cl₂, CHCl₃, CCl₄) are so common in industry: they dissolve oils, fats, resins and many organic compounds but form a clean separate phase from water — ideal for liquid-liquid extraction.

5 Chemical Reactions of Haloalkanes

The reactivity of alkyl halides clusters into three families: **nucleophilic substitution**, **elimination**, and **reactions with metals** (Grignard / Wurtz / Wurtz-Fittig). Each is worth mastering — they dominate the chapter in exams.

5.1 Nucleophilic Substitution — Overview

A nucleophile (electron-pair donor) attacks the δ^+ carbon of an alkyl halide; the halogen leaves as a halide ion.



The huge variety of nucleophiles is what makes haloalkanes the synthetic linchpin: each Nu⁻ converts R-X into a different functional class.

Reagent	Nucleophile	Product R-Nu	Class
NaOH / KOH (aq)	OH ⁻	ROH	Alcohol
H ₂ O	H ₂ O	ROH	Alcohol
NaOR'	R'O ⁻	ROR'	Ether (Williamson)
NaI / dry acetone	I ⁻	RI	Alkyl iodide (Finkelstein)
NH ₃	NH ₃	RNH ₂	1° amine
R'NH ₂	R'NH ₂	RNHR'	2° amine
R'R''NH	R'R''NH	RNR'R''	3° amine
KCN	C≡N ⁻	RCN	Nitrile
AgCN	:N≡C-Ag	RNC	Isonitrile
KNO ₂	ONO ⁻	R-O-N=O	Alkyl nitrite
AgNO ₂	Ag-O-N=O	R-NO ₂	Nitroalkane
R'COOAg	R'COO ⁻	R'COOR	Ester
LiAlH ₄	H ⁻	RH	Hydrocarbon
R'M (R'Li, R' ₂ CuLi)	R' ⁻	R-R'	Alkane (coupling)

Ambident nucleophiles. CN⁻ and NO₂⁻ have two reactive sites:

- **CN⁻:** ionic KCN attacks through C (stronger C-C bond) → R-C≡N (nitrile); covalent AgCN attacks through N → R-N≡C (isocyanide).
- **NO₂⁻:** ionic KNO₂ attacks through O → R-O-N=O (alkyl nitrite); covalent AgNO₂ attacks through N → R-NO₂ (nitroalkane).

Why KCN gives nitrile but AgCN gives isocyanide

KCN is predominantly *ionic*: it provides a free CN⁻ in solution. Both C and N can donate, but the C-C bond formed is stronger than C-N, so attack from C predominates — the nitrile is the product.

AgCN is predominantly *covalent*: only the nitrogen lone pair is free to attack, so the product is the isocyanide R-N≡C.

Ambident pairs — silver loves nitrogen

KCN → nitrile (C-bonded); AgCN → isocyanide (N-bonded).

KNO₂ → alkyl nitrite (O-bonded); AgNO₂ → nitroalkane (N-bonded).

Silver salts always direct the attack to nitrogen.

5.2 S_N2 Mechanism — Bimolecular

When CH₃Cl reacts with OH⁻, the kinetics is **second order**: rate = *k*[CH₃Cl][OH⁻]. The mechanism is concerted: nucleophile attacks from the back-side as the leaving group departs, in a single step through a five-coordinate transition state.

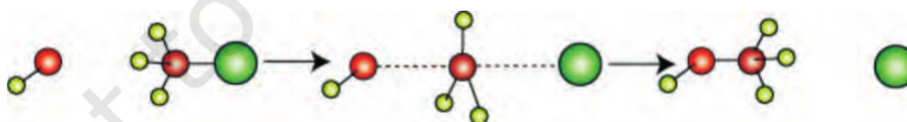


Fig. 6.2: Red ball represents the incoming hydroxide ion and green ball represents the outgoing halide ion

In the year 1937, Edward Davies Hughes and Sir Christopher Ingold proposed the S_N2 mechanism. It depicts a bimolecular nucleophilic substitution (S_N2) reaction; the incoming nucleophile interacts with alkyl halide causing the carbon-halide bond to break and a new bond is formed between the nucleophile and the carbon atom. The three C-H bonds invert through the plane like an umbrella turning inside out.

Source: NCERT Class 12 Chemistry Part II, Chapter 6 — Fig. 6.2: The S_N2 reaction shown as a ball-and-stick trajectory. Red ball = incoming hydroxide; green ball = outgoing halide. The three C-H bonds invert through the plane like an umbrella turning inside out.

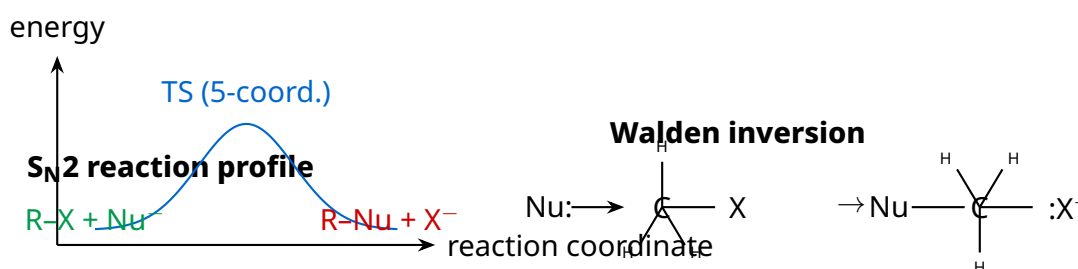
S_N2 : rate law and stereochemistry

$$\text{rate} = k [\text{R-X}] [\text{Nu}^-]$$

Mechanism: single step, no intermediate.

Transition state: five groups around the central carbon — the three substituents lie in a plane while Nu and X are partially bonded on opposite sides.

Stereochemistry: complete inversion of configuration at the chiral carbon ("Walden inversion").



Left: a single-barrier energy profile, no intermediate. Right: the umbrella inverts as Nu attaches and X departs.

Steric effects: bulky substituents on or next to the C-X carbon block back-side attack. Methyl halides react fastest, tertiary halides essentially do not react by S_N2 .

Primary halide > Secondary halide > Tertiary halide.

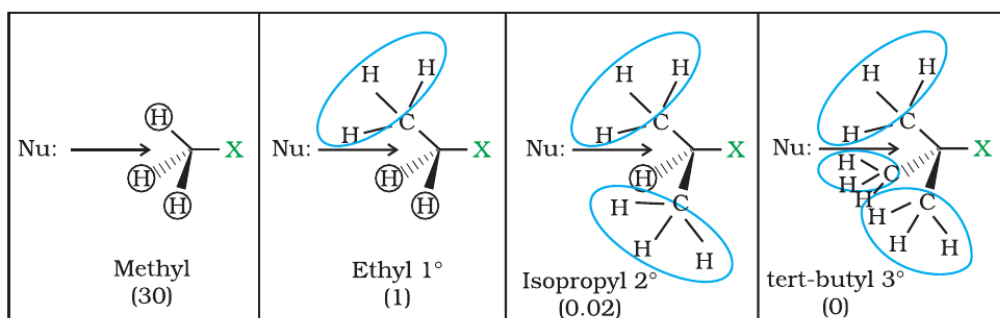
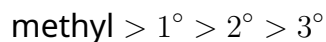


Fig.6.3: Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis

Source: NCERT Class 12 Chemistry Part II, Chapter 6 — Fig. 6.3: Steric crowding around the S_N2 carbon. Relative rate in parenthesis: methyl (30), ethyl (1), isopropyl (0.02), tert-butyl (~ 0).

S_N2 reactivity order

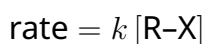


For a given alkyl group: $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$ (better leaving group = faster).

5.3 S_N1 Mechanism — Unimolecular

When tert-butyl bromide is hydrolysed by aqueous NaOH, the kinetics is **first order**: $\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$ (no dependence on $[\text{OH}^-]$). The mechanism is a two-step process going through a carbocation.

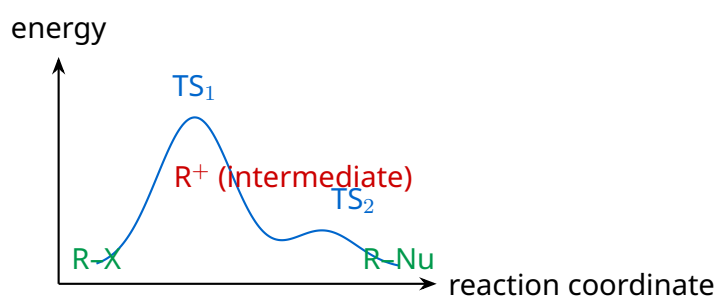
S_N1 : rate law and mechanism



Step 1 (slow, rate-determining): $\text{R-X} \rightarrow \text{R}^+ + \text{X}^-$. The C-X bond ionises heterolytically.

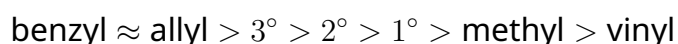
Step 2 (fast): $\text{R}^+ + \text{Nu}^- \rightarrow \text{R-Nu}$. The planar (sp^2) cation is attacked from either face.

Stereochemistry: *racemisation* (50:50 mixture of inverted and retained product).

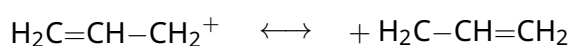


S_N1 has a two-barrier profile with a discrete carbocation intermediate at the well between them.

Reactivity in S_N1 is governed by carbocation stability:



Allylic and benzylic halides react especially fast in S_N1 because the carbocation intermediate is stabilised by resonance:



resonance delocalisation of allyl cation

Quick Tip

For SAME alkyl group, both S_N1 and S_N2 follow $R-I > R-Br > R-Cl > R-F$. But for DIFFERENT alkyl groups:

- S_N1 : $3^\circ > 2^\circ > 1^\circ > \text{methyl}$ (carbocation stability).
- S_N2 : $\text{methyl} > 1^\circ > 2^\circ > 3^\circ$ (steric).

This neat reverse ordering is a guaranteed JEE/NEET MCQ.

5.4 Solvent and Nucleophile Effects**Solvent choice**

Polar protic solvents (H_2O , alcohol, acetic acid) stabilise both the carbocation and the leaving anion — they *favour* S_N1 .

Polar aprotic solvents (acetone, DMSO, DMF) do not solvate Nu^- effectively — the naked nucleophile is more reactive — they *favour* S_N2 .

Common Mistake

“Methanol favours S_N2 because it is polar.” *False* — methanol is polar but *protic*; it stabilises ions and favours S_N1 . The polar-*aprotic* ones are acetone, DMSO, DMF, HMPA.

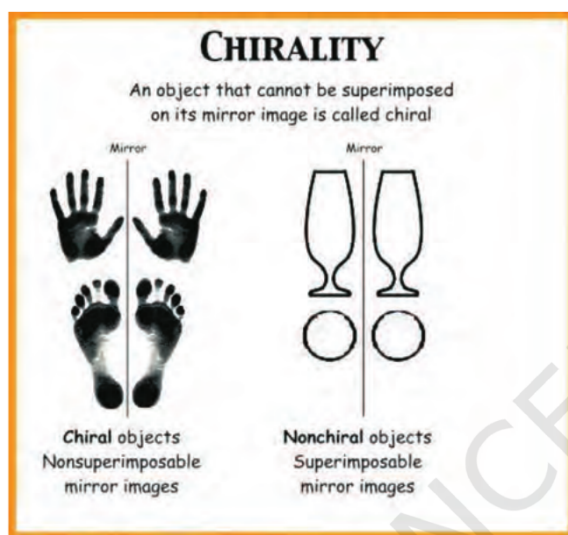
5.5 Comparison: S_N1 vs S_N2

Feature	S_N1	S_N2
Molecularity	1	2
Order of kinetics	First (only R-X)	Second (R-X and Nu)
Number of steps	Two	One (concerted)
Intermediate	Carbocation (sp^2 , planar)	None (5-coord TS only)
Substrate preference	$3^\circ > \text{benzyl, allyl}$	$\text{methyl} > 1^\circ$
Solvent preference	Polar protic	Polar aprotic
Stereochemistry	Racemisation	Inversion (Walden)
Rearrangement	Possible (carbocation)	Not possible

5.6 Stereochemistry — Optical Activity, Chirality, Enantiomers

A compound that rotates the plane of plane-polarised light is **optically active**. Clockwise rotation → dextrorotatory (+); anti-clockwise → laevorotatory (–). The angle is measured in a polarimeter.

Chirality = non-superimposability on the mirror image. A carbon bonded to four different groups is an **asymmetric (stereo) centre**; molecules with such a centre are typically chiral and optically active. A mixture of equal (+) and (–) enantiomers (a **racemic mixture**, \pm) is optically inactive.



Source: NCERT Class 12 Chemistry Part II, Chapter 6 — Fig. 6.4: Chiral (hand, foot — non-superimposable on mirror image) and achiral (cone, sphere — superimposable) objects.

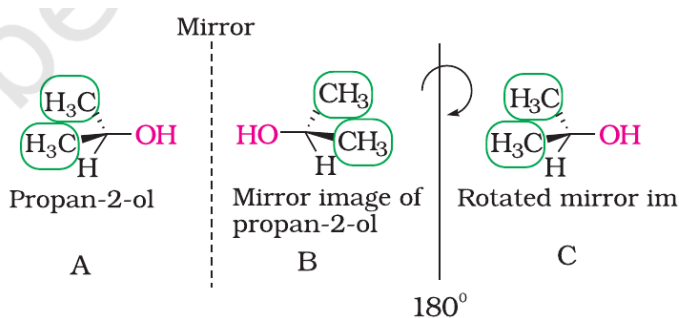


Fig 6.5: B is mirror image of A; B is rotated by 180° a obtained; C is superimposable on A.

Source: NCERT Class 12 Chemistry Part II, Chapter 6 — Fig. 6.5: Propan-2-ol is achiral. Mirror image B is rotated 180° to give C, which is superimposable on A.

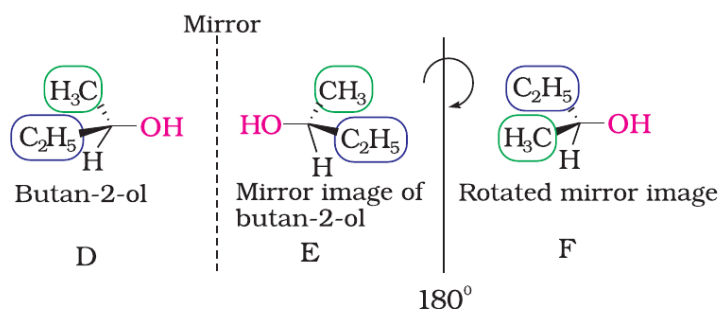


Fig 6.6: E is mirror image of D; E is rotated by 180° to get F and non superimposable on its mirror image D.

Source: NCERT Class 12 Chemistry Part II, Chapter 6 — Fig. 6.6: Butan-2-ol is chiral. Mirror image *E* rotated to *F* is not superimposable on *D* — *D* and *F* are enantiomers.

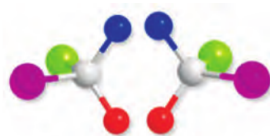


Fig. 6.7: A chiral molecule and its mirror image

Source: NCERT Class 12 Chemistry Part II, Chapter 6 — Fig. 6.7: A chiral molecule and its non-superimposable mirror image (enantiomer pair).

Three outcomes for the chiral carbon

After a reaction at an asymmetric centre where a bond to the centre is broken, three stereochemical outcomes are possible:

- **Retention:** same configuration (no bond to stereocentre broken, or broken-then-reformed on the same face).
- **Inversion:** opposite configuration (S_N2 -type back-side attack).
- **Racemisation:** 50:50 inverted + retained, optically inactive (S_N1 attack on planar carbocation from either face).

In summary:

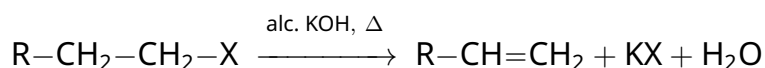
- S_N2 on a chiral $R-X \rightarrow$ inversion of configuration (Walden inversion). Optically active product, opposite sign.
- S_N1 on a chiral $R-X \rightarrow$ racemisation. Optically inactive product.

'Walden = wall' — Nu hits the back wall

The S_N2 Nu attacks from the back (opposite the leaving group). The carbon flips like an umbrella in a storm — the configuration *inverts*. "Walden = back-wall inversion."

5.7 Elimination Reactions

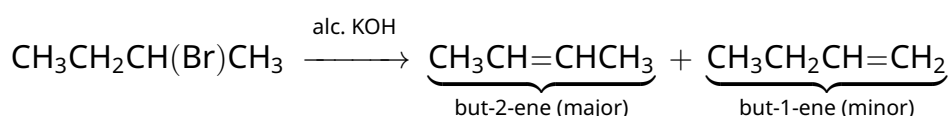
When a haloalkane bearing a β -hydrogen is heated with *alcoholic* KOH (NOT aqueous), an H from the β -carbon and X from the α -carbon are removed to give an alkene. This is β -**elimination** (also called dehydrohalogenation, or $E2$ mechanism).

E2 dehydrohalogenation

Both H and X are lost *anti-periplanar* (180° apart) in a single concerted step.

Rate = $k[\text{R-X}][\text{base}]$.

Zaitsev's rule. When more than one β -H is available, the major product is the *more substituted (more stable) alkene*.



The more substituted alkene is thermodynamically more stable because of hyper-conjugation (n α -C-H bonds donating into the π^*).

Quick Tip

Aqueous KOH \rightarrow **alcohol (substitution).** **Alcoholic KOH** \rightarrow **alkene (elimination).**

The same nucleophile/base; the solvent switches the pathway. Aqueous solvation slows down deprotonation; alcoholic medium does not solvate OH^- as well, so OH^- acts as a base.

Substitution vs Elimination — a competition

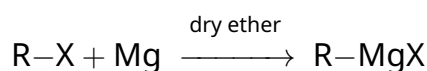
The two pathways race against each other. Factors that favour elimination:

- **Substrate:** tertiary halides (steric block of $\text{S}_{\text{N}}2$; also lots of β -H's).
- **Base:** strong, bulky bases ($t\text{-BuO}^-$ rather than CH_3O^-).
- **Solvent:** less polar / less nucleophile-solvating.
- **Temperature:** higher T favours elimination (entropy).

A primary halide with NaCN /acetone gives substitution; a tertiary halide with alc. KOH gives elimination.

5.8 Reactions with Metals — Grignard and Wurtz

Grignard reagent. Haloalkanes react with magnesium turnings in dry ether to form alkyl magnesium halides (R-MgX), discovered by Victor Grignard (Nobel Prize, 1912).



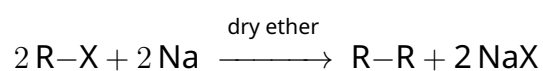
The C-Mg bond is highly polar with carbon as the nucleophile (carbanion character); the Mg-X bond is essentially ionic. Grignard reagents are *the workhorse* for

forming new C–C bonds in organic chemistry — they react with carbonyls (C=O), CO₂, epoxides, esters and many more.

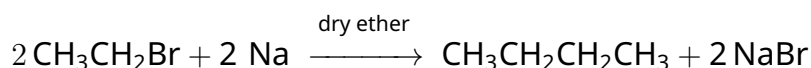
Common Mistake

Grignard reagents are destroyed instantly by any source of a proton — water, alcohol, amines, even moist air. “Dry ether” is non-negotiable. A common exam line: “Why is dry ether used?” — to keep H₂O and other protic species away from R–MgX.

Wurtz reaction. Two molecules of R–X plus 2 Na in dry ether give an alkane with double the carbon count.



Wurtz couples *identical* alkyl halides cleanly. For example,



Mixed reactions give a statistical mixture of three possible products and are therefore preparatively unimportant.

Real-World Application

The Grignard reaction is still in routine industrial use — synthesis of tamoxifen (breast-cancer drug), naproxen, and countless agrochemicals all hinge on a Grignard step somewhere in the route. Despite being 120+ years old, it has not been replaced.

6 Chemical Reactions of Haloarenes

Aryl halides are sluggish where alkyl halides are active. The reasons — resonance, sp² hybridisation and electronic repulsion — explain why a single C–Cl bond on benzene can be inert under conditions that hydrolyse R–Cl in seconds.

6.1 Why Haloarenes Resist Nucleophilic Substitution

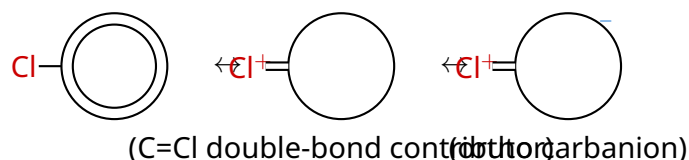
Four reasons haloarenes resist S_N1/S_N2

(i) Resonance. The halogen lone pair conjugates with the π system of the ring; the C–X bond acquires partial double-bond character (167–169 pm, vs 177 pm in CH₃Cl). Shorter, stronger bonds are harder to break.

(ii) Hybridisation. The C of an aryl halide is sp² (33% s-character); the C in R–Cl is sp³ (25% s). More s-character → more electronegative C → holds the bonding pair more tightly.

(iii) Carbocation instability. A phenyl cation (after C–X ionisation) cannot be stabilised by resonance — the empty orbital lies in the ring plane, not in the π system. S_N1 is ruled out.

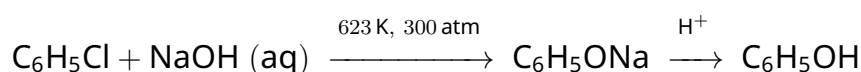
(iv) Electron-electron repulsion. An electron-rich nucleophile is repelled by the π -cloud of the ring; back-side approach is impossible (geometry of the ring).



The halogen lone pair donates into the ring; the resulting C=X partial double-bond shortens and strengthens C–X. Aryl halides are not amenable to ordinary S_N pathways.

6.2 Replacement by Hydroxyl — Forcing Conditions

Chlorobenzene + NaOH (aq) requires harsh conditions — **623 K and 300 atm** — to give phenol.



Effect of electron-withdrawing groups. A nitro group at *ortho* or *para* (**not** meta) hugely accelerates the substitution. The carbanion intermediate has the negative charge stabilised by the $-\text{NO}_2$ via resonance only at o-/p-:

- p-Nitrochlorobenzene + NaOH (dilute) \rightarrow p-nitrophenol at 443 K (much milder than 623 K).
- 2,4-Dinitrochlorobenzene + warm NaOH \rightarrow 2,4-dinitrophenol at \sim 370 K.
- 2,4,6-Trinitrochlorobenzene (picryl chloride) + H_2O \rightarrow picric acid at room temperature.

Why ortho/para, not meta

The carbanion intermediate (formed after Nu addition) places a negative charge on the ortho and para carbons relative to the leaving group. A nitro group at ortho or para can absorb this negative charge by resonance into its oxygens. A nitro group at meta has no resonance contributor that places the negative charge on the C bearing NO_2 , so it cannot stabilise the intermediate.

Activation by EWG is ortho/para specific.

Quick Tip

[JEE/NEET extension] Activated nucleophilic aromatic substitution proceeds

via the **Addition-Elimination (S_NAr)** mechanism through a Meisenheimer complex. Rate is highest with strongly EWG ($-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$) at o/p positions. The reactivity order: trinitro > dinitro > mononitro \gg none.

Common Mistake

The harsh-conditions hydrolysis of chlorobenzene (623 K, 300 atm) is mechanistically different — it goes through a **benzyne intermediate** (Elimination-Addition or S_N1Ar pathway), *not* the Meisenheimer complex. The reaction with EWG-activated aryl halides at mild T goes through Meisenheimer (Addition-Elimination). Two different mechanisms, two different sets of conditions.

6.3 Electrophilic Substitution on Haloarenes

Halogen on a benzene ring is *deactivating but ortho/para-directing*. The two effects — inductive ($-I$) and mesomeric ($+M$) — pull in opposite directions:

- $-I$ effect dominates the *reactivity*: halogen withdraws electron density overall, so the ring is less reactive than benzene.
- $+M$ effect dominates the *orientation*: lone-pair donation increases electron density at ortho/para, so EAS prefers those positions.

The four standard EAS on chlorobenzene

Halogenation: $\text{Cl}_2/\text{FeCl}_3 \rightarrow$ o- and p-dichlorobenzene.

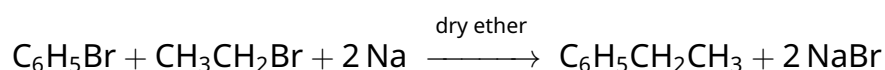
Nitration: conc. $\text{HNO}_3/\text{conc. H}_2\text{SO}_4 \rightarrow$ o- and p-chloronitrobenzene.

Sulphonation: conc. H_2SO_4 / oleum \rightarrow o- and p-chlorobenzenesulphonic acid.

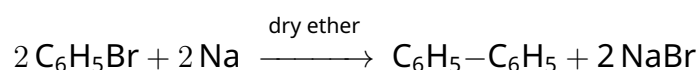
Friedel-Crafts alkylation: $\text{RCl}/\text{AlCl}_3 \rightarrow$ o- and p-substituted product.
(All slower than the corresponding benzene reactions.)

6.4 Reactions of Haloarenes with Metals — Wurtz-Fittig and Fittig

Wurtz-Fittig reaction: alkyl halide + aryl halide + Na in dry ether \rightarrow alkylarene.



Fittig reaction: 2 aryl halides + Na in dry ether \rightarrow biaryl.



Wurtz family

Wurtz: 2 alkyl halides → alkane (R-R).

Wurtz-Fittig: alkyl + aryl → alkylarene (R-Ar).

Fittig: 2 aryl halides → biaryl (Ar-Ar).

Each adds an aryl ring to the recipe.

7 Polyhalogen Compounds

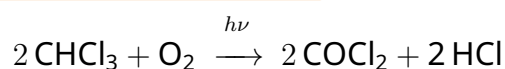
Compounds with two or more halogens on the same molecule have distinctive properties and uses. The NCERT focuses on six classics: dichloromethane, chloroform, iodoform, carbon tetrachloride, freons and DDT.

7.1 Dichloromethane (CH₂Cl₂, Methylene Chloride)

A widely used industrial solvent — paint remover, aerosol propellant, drug manufacturing process solvent and metal degreaser. Toxicological hazards: depresses the CNS, mild skin burns on direct contact, corneal burns on eye contact. Higher airborne levels cause dizziness, nausea, tingling and numbness in fingers and toes.

7.2 Trichloromethane (CHCl₃, Chloroform)

Used industrially as a solvent for fats, alkaloids and iodine. The dominant modern use is as a feedstock for freon R-22. Historically used as a general anaesthetic but has been replaced by safer agents (e.g. halothane, sevoflurane). Chronic exposure damages liver (chloroform is metabolised to phosgene there) and kidneys.

The chloroform → phosgene problem

Phosgene (COCl₂, carbonyl chloride) is a deadly poison. Chloroform is stored in dark-coloured bottles, completely filled (to exclude air), to prevent this slow photo-oxidation.

7.3 Triiodomethane (CHI₃, Iodoform)

A yellow crystalline solid with a characteristic medicinal smell. Once used as an antiseptic — the actual antiseptic activity is from *free I₂ liberated* on the skin, not from CHI₃ itself. Replaced by iodine-based modern antiseptics.

Iodoform test: compounds with the structural element CH₃CO- (methyl ketone) or CH₃CH(OH)- (secondary alcohol on a methyl carbon) give a positive iodoform test — yellow precipitate of CHI₃ on treatment with I₂ + NaOH.

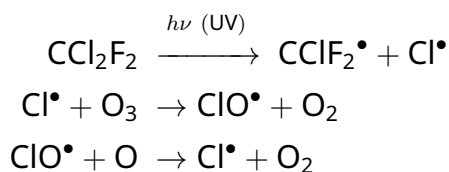
7.4 Tetrachloromethane (CCl₄, Carbon Tetrachloride)

Was widely used as a cleaning fluid, degreaser, spot remover and fire extinguisher; almost all of these uses are now banned because of (i) liver toxicity in humans and (ii) stratospheric ozone depletion (long-lived, drifts up, releases Cl radicals). Symptoms: dizziness, light-headedness, nausea, vomiting; severe cases lead to coma and death. Cardiac arrhythmias also possible.

7.5 Freons (CFCs)

Chlorofluorocarbons of methane and ethane are collectively called freons. The classic example is **Freon-12 (CCl₂F₂)** — the workhorse refrigerant before the Montreal Protocol. It is made by the Swarts reaction from CCl₄. Freons are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefied — exactly the properties that make them accumulate in the stratosphere and damage the ozone layer.

Ozone destruction by CFCs (Class XI revision)



One Cl radical destroys $\sim 10^5$ ozone molecules before being scavenged.

7.6 DDT (p,p'-Dichlorodiphenyltrichloroethane)

(ClC₆H₄)₂CHCCl₃. The first major synthetic insecticide. Effective against malaria-carrying mosquitoes and typhus-carrying lice; Paul Müller won the Nobel Prize in 1948 for this discovery. However, DDT is fat-soluble, persists in the food chain (bioaccumulation), and is highly toxic to fish and birds. Banned in the United States in 1973 and many countries since.

Real-World Application

DDT, freons and CCl₄ illustrate a recurring lesson: the same chemical stability that makes a compound industrially attractive (long shelf life, predictable behaviour) often makes it an environmental persistent — it does not biodegrade. “Useful and persistent” is a warning signal, not a virtue.

8 Quick Reference Summary

8.1 Reactivity Orders — Master These Cold

Cheat-sheet of orderings

Boiling point (for same R): $R-I > R-Br > R-Cl > R-F$.

Boiling point (for isomers): $n- > sec- > tert-$ (less branching, more BP).

Dipole moment of methyl halides: $CH_3Cl > CH_3F > CH_3Br > CH_3I$.

Bond enthalpy of C-X: $C-F > C-Cl > C-Br > C-I$.

Bond length of C-X: $C-I > C-Br > C-Cl > C-F$.

Leaving group ability: $I^- > Br^- > Cl^- > F^-$.

Reactivity of alcohols with HX: $3^\circ > 2^\circ > 1^\circ$.

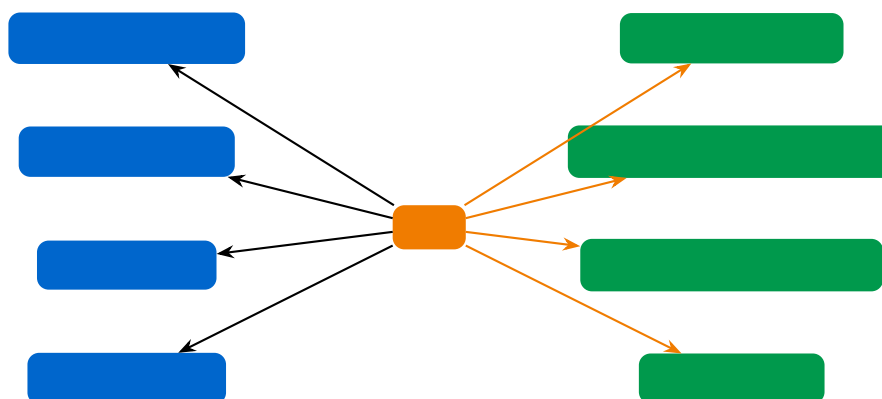
S_N2 reactivity (alkyl): $CH_3X > 1^\circ > 2^\circ > 3^\circ$.

S_N1 reactivity (alkyl): $benzyl \approx allyl > 3^\circ > 2^\circ > 1^\circ > CH_3X$.

Carbocation stability: $benzyl \approx allyl > 3^\circ > 2^\circ > 1^\circ > CH_3^+ > vinyl$.

Zaitsev (alkene stability): most substituted $>$ less substituted.

8.2 Master Reaction Map of R-X



Blue arrows (left): nucleophilic substitution products. Orange arrows (right): elimination, metals and reduction.

8.3 Named Reactions in This Chapter

Name	One-line summary
Finkelstein	$R-Cl/Br + NaI / \text{dry acetone} \rightarrow R-I$ (NaCl/NaBr precipitates).
Swarts	$R-Cl/Br + AgF / Hg_2F_2 / SbF_3 \rightarrow R-F$.
Sandmeyer	$ArN_2^+ + CuX (X=Cl, Br) \rightarrow ArX + N_2$.
Balz-Schiemann	$ArN_2^+BF_4^- \xrightarrow{\Delta} ArF + N_2 + BF_3$.
Wurtz	$2 R-X + 2 Na / \text{dry ether} \rightarrow R-R$.
Wurtz-Fittig	$R-X + Ar-X + 2 Na / \text{dry ether} \rightarrow R-Ar$.
Fittig	$2 Ar-X + 2 Na / \text{dry ether} \rightarrow Ar-Ar$.
Grignard	$R-X + Mg / \text{dry ether} \rightarrow R-MgX$.
Zaitsev rule	In dehydrohalogenation, the more substituted alkene is the major product.
Markovnikov	HX adds to alkene with H on the C bearing more H (ionic).
Anti-Markovnikov	HBr + peroxide adds Br to less substituted C (radical, HBr only).

8.4 Distinguishing Tests — Mini Catalogue

- **Beilstein test:** hot Cu wire + organic halide \rightarrow green flame (Cu halide).
- **Silver nitrate test (after fusion or for active halides):** $RX + AgNO_3/EtOH \rightarrow AgX$ precipitate. R-I gives yellow AgI; R-Br gives pale yellow AgBr; R-Cl gives white AgCl. Rate: R-I > R-Br > R-Cl. Aryl halides give no precipitate under these conditions.
- **Iodoform test:** compounds with CH_3CO- or $CH_3CH(OH)-$ \rightarrow yellow CHI_3 with $I_2/NaOH$.
- **Bromine water test:** alkenes/alkynes (and good electron donors) decolourise Br_2/H_2O ; alkyl halides do not.

8.5 Final Checklist Before the Exam

Quick Tip

1. **Nomenclature:** Longest chain through C-X, lowest locant, alphabetical substituent order.
2. **S_N2:** bimolecular, single step, back-side attack, inversion. Methyl best; tert worst.
3. **S_N1:** unimolecular, two steps via planar carbocation, racemisation. Tert best; methyl worst.

4. **Aqueous KOH** → **substitution**; **alcoholic KOH** → **elimination**.
5. **Zaitsev**: more substituted alkene wins.
6. **Haloarenes are unreactive** towards S_N unless activated by $-\text{NO}_2$ at o/p.
7. **Halogens on rings are deactivating but o/p-directing** in EAS.
8. **Grignard / Wurtz / Wurtz-Fittig / Fittig** all require dry ether and Na/Mg.
9. **Sandmeyer (CuX)** for ArCl/ArBr; **KI alone** for ArI; **HBF_4** for ArF.
10. **Polyhalogen compounds**: chloroform forms phosgene; freons deplete ozone; DDT bioaccumulates.