Collegedunia NCERT Formula Sheet

The Ultimate Formula Reference for Class 12 (12th) Chemistry — NCERT 2026-27

Chapter 6: Haloalkanes and Haloarenes

Classification · Nomenclature · Preparation · S_N1 & S_N2 · Elimination · Polyhalogens · JEE & NEET

Quick Reference — C–X Bond Data & Symbols (NCERT Table 6.2)

Bond	Length (pm)	Enthalpy (kJ/mol)	Dipole (D)	Symbols used in this sheet
C–F	139	452	1.847	R–X: alkyl halide (R = sp^3 alkyl)
C–Cl	178	351	1.860	Ar–X: aryl halide (X on sp^2 aromatic C)
C–Br	193	293	1.830	α-C bears halogen; β-C adjacent (donates H in E)
C–I	214	234	1.636	Nu^- nucleophile; LG leaving group (I>Br>Cl>F)

1 Classification of Halogenated Compounds

NCERT Section 6.1 groups halogen compounds by (a) the number of halogen atoms (mono-, di-, poly-halogen) and (b) the hybridisation of the carbon bonded to X. The second classification is the more useful one because it directly predicts reactivity.

General molecular formula

Alkyl halide (monohaloalkane): $C_nH_{2n+1}X$, i.e., R–X
Dihaloalkane: $C_nH_{2n}X_2$ **Trihaloalkane**: $C_nH_{2n-1}X_3$
Aryl halide (monohaloarene): $Ar{-}X$ (X on sp^2 aromatic C)
Alkyl halides have halogen on a sp^3 carbon. **Haloalkane** and **haloarene** differ in the hybridisation of the C–X carbon, which controls bond length, polarity, and reactivity.

sp^3 C–X classes (NCERT 6.1.2)

Alkyl halide (R–X): X on a simple sp^3 C; further classified as:
1° (primary): C bearing X has 1 alkyl group
2° (secondary): 2 alkyl groups
3° (tertiary): 3 alkyl groups
Allylic halide: X on sp^3 C *adjacent* to C=C (e.g., $CH_2{=}CH{-}CH_2{-}X$).
Benzylic halide: X on sp^3 C attached to an aromatic ring (e.g., $C_6H_5CH_2Cl$).
Both allylic and benzylic halides ionise easily because the resulting carbocation is **resonance-**

stabilised ⇒ very reactive towards S_N1.

sp^2 C–X classes (NCERT 6.1.3)

Vinylic halide: X on sp^2 C of a C=C (e.g., $CH_2{=}CHCl$, chloroethene).
Aryl halide: X directly on aromatic sp^2 C (e.g., chlorobenzene).
Vinylic and aryl halides are **very unreactive** towards nucleophilic substitution because (i) the C–X bond is **shorter and stronger** (sp^2 C $>$ sp^3 C in s-character) and (ii) lone-pair donation from X into the π system gives partial double-bond character.

Dihalides: gem vs vic

gem-dihalide (alkylidene halide): both X on the *same* C, e.g., CH_3–$CHCl_2$ (1,1-dichloroethane / ethylidene chloride).
vic-dihalide (alkylene halide): X on *adjacent* C, e.g., CH_2Cl–CH_2Cl (1,2-dichloroethane / ethylene dichloride).
vic-dihalides are the standard products of **Br_2/CCl_4 addition to alkenes**, used as a qualitative test for C=C (reddish-brown → colourless).

Why hybridisation matters

A sp^2 C has 33% s-character; a sp^3 C only 25%. The greater s-character pulls bonding electrons closer to the nucleus, so sp^2 C–X bonds are **shorter and stronger** than sp^3 C–X. This single fact explains: aryl/vinyl halides $\gg$ alkyl halides in inertness towards nucleophiles.

2 IUPAC Nomenclature

NCERT Section 6.2 sets nomenclature rules for haloalkanes (treated as halo-substituted hydrocarbons) and haloarenes (where common and IUPAC names usually coincide). Numbering, prefix order, and the di/tri rules for dihalides are the high-yield exam areas.

Naming rules for haloalkanes

(1) Treat halogen as a *halo-* prefix on the parent alkane chain (longest C chain containing C–X).
(2) Number the chain to give the **halogen the lowest locant**; if multiple substituents, use the lowest set of locants.
(3) Prefixes listed **alphabetically** (bromo before chloro before methyl).
(4) For identical halogens: use di-, tri-, tetra-.
Examples: $CH_3CH_2CH_2Br$ → 1-bromopropane; $(CH_3)_2CHBr$ → 2-bromopropane; $(CH_3)_3CBr$ → 2-bromo-2-methylpropane.

Dihaloalkane naming

IUPAC: locants for both halogens, separated by commas.
Common: gem = *alkylidene* halide; vic = *alkylene* halide.
Examples:
CH_3CHCl_2: ethylidene chloride / 1,1-dichloroethane (gem)
CH_2Cl–CH_2Cl: ethylene dichloride / 1,2-dichloroethane (vic)
CH_2Br–CH_2Br: ethylene dibromide / 1,2-dibromoethane (vic)
When the two halogens are different, just list each alphabetically with its locant: CH_2Br–CH_2Cl → 1-bromo-2-chloroethane.

Haloarene naming

Mono-halobenzene: common and IUPAC names *coincide* (chlorobenzene, bromobenzene).
Disubstituted benzene: common uses *o-*, *m-*, *p-*; IUPAC uses 1,2 / 1,3 / 1,4.
o-dichlorobenzene = 1,2-dichlorobenzene
m-dichlorobenzene = 1,3-dichlorobenzene
p-dichlorobenzene = 1,4-dichlorobenzene
Benzyl halide $C_6H_5CH_2Cl$ $\rightarrow$ IUPAC name **(chloromethyl)benzene** or *chlorophenylmethane*. Allyl bromide $CH_2{=}CHCH_2Br$ $\rightarrow$ **3-bromoprop-1-ene**.

Common-name → IUPAC quick map

sec-butyl chloride → 2-chlorobutane tert-butyl bromide → 2-bromo-2-methylpropane
neo-pentyl bromide → 1-bromo-2,2-dimethylpropane
methylene chloride → dichloromethane chloroform → trichloromethane
bromoform → tribromomethane CCl_4 → tetrachloromethane
vinyl chloride → chloroethene allyl bromide → 3-bromoprop-1-ene

3 Nature of the C–X Bond

NCERT Section 6.3 describes the C–X bond as polar covalent (X more electronegative than C). The bond length, bond enthalpy, and dipole moment trends below explain why C–I is most reactive in S_N reactions and why C–F is the strongest C–halogen bond.

Polar C–X bond

$$\overset{\delta+}{C} - \overset{\delta-}{X}$$

C bears **partial positive** charge (electrophilic centre, attacked by nucleophiles); X bears **partial negative** charge.
Polarity *magnitude* of C–X bond (μ in Debye) does **not** follow electronegativity perfectly — C–Cl (1.86 D) $>$ C–F (1.85 D) $>$ C–Br (1.83 D) $>$ C–I (1.64 D). Bond length compensates for electronegativity.

Bond length, enthalpy, reactivity trends

Bond length (F $<$ Cl $<$ Br $<$ I): increases down the group as halogen size grows.
Bond enthalpy (F $>$ Cl $>$ Br $>$ I): decreases (longer bond = weaker).
Reactivity in S_N / elimination:
R–I $>$ R–Br $>$ R–Cl $\gg$ R–F
Same alkyl group, varying halogen: **R–I is most reactive** (weakest bond, best leaving group). R–F barely reacts.

Dipole moment of common halides (NCERT Table 6.2)

$\mu(CH_3F) = 1.847$ D $\mu(CH_3Cl) = 1.860$ D
$\mu(CH_3Br) = 1.830$ D $\mu(CH_3I) = 1.636$ D
Net order: $\mu(CH_3Cl) > \mu(CH_3F) > \mu(CH_3Br) > \mu(CH_3I)$. μ does NOT increase monotonically with electronegativity — the longer C–Cl bond more than compensates for the slightly lower electronegativity of Cl vs F.

μ(chlorobenzene) $<$ μ(cyclohexyl chloride)

NCERT exercise 6.12(i): chlorobenzene has **lower** dipole moment than cyclohexyl chloride even though both have one C–Cl. Reasons — (a) in chlorobenzene the C bearing Cl is sp^2 (s-character 33%) so the C–Cl bond is **shorter** (less $\mu = q \cdot d$); (b) lone-pair donation from Cl into the ring (+M) opposes the C→Cl inductive vector ($-$I), partly cancelling it. In cyclohexyl chloride (sp^3 C) only the

> −I effect operates.

4 Preparation of Haloalkanes (NCERT 6.4)

Three classical routes: (i) from alcohols using HX, PX_3, PX_5, $SOCl_2$ or red P/X_2; (ii) from hydrocarbons by free-radical halogenation of alkanes or addition to alkenes; (iii) halogen exchange (Finkelstein, Swarts).

From alcohols (R–OH → R–X)

Reactivity of alcohols: $3^\circ > 2^\circ > 1^\circ$ (carbocation stability)

Reactivity of HX: HI $>$ HBr $>$ HCl

$R\text{–}OH + HCl \longrightarrow [ZnCl_2]\ R\text{–}Cl + H_2O$ (Lucas test reagent)

$R\text{–}OH + NaBr/H_2SO_4 \rightarrow R\text{–}Br + NaHSO_4 + H_2O$

$3R\text{–}OH + PX_3 \rightarrow 3R\text{–}X + H_3PO_3$ (X = Cl, Br)

$R\text{–}OH + PCl_5 \rightarrow R\text{–}Cl + POCl_3 + HCl$

$R\text{–}OH + SOCl_2 \rightarrow R\text{–}Cl + SO_2\uparrow + HCl\uparrow$

$SOCl_2$ is preferred — gases (SO_2, HCl) escape, giving pure R–Cl. For R–I: heat alcohol with NaI/KI in 95% H_3PO_4 (**not** H_2SO_4, which oxidises HI).

From alkanes: free-radical halogenation

$R\text{–}H + X_2 \longrightarrow [\text{UV / heat}]\ R\text{–}X + HX$

Example: $CH_3CH_2CH_2CH_3 \longrightarrow [Cl_2/h\nu]$ 1-chlorobutane + 2-chlorobutane

Gives a **mixture** of mono- and polyhaloalkanes (poor yield of any single product). Mostly a lab-scale or fluorine-free industrial method.

From alkenes: addition reactions

(i) Addition of HX (Markovnikov on unsymmetrical alkenes):

$CH_3CH{=}CH_2 + HI \rightarrow CH_3CHI\text{–}CH_3$ (major)

(ii) Addition of X_2 (X = Cl, Br) in CCl_4 gives *vic*-dihalides:

$CH_2{=}CH_2 + Br_2 \longrightarrow [CCl_4]\ BrCH_2{-}CH_2Br$

Br_2/CCl_4 test: reddish-brown Br_2 **decolourises** on adding alkene ⇒ test for unsaturation. With **peroxide** (anti-Markovnikov, Kharasch): HBr only — gives the opposite regiochemistry.

Halogen-exchange reactions

Finkelstein: R–X + NaI $\longrightarrow$ [dry acetone] R–I + NaX (X = Cl, Br)

Swarts: R–Cl/Br + AgF (or Hg_2F_2, CoF_2, SbF_3) → R–F + AgCl/Br

Example: $H_3C\text{–}Br + AgF \rightarrow H_3C\text{–}F + AgBr$

Finkelstein works because **NaCl / NaBr are insoluble in dry acetone** while NaI is soluble — Le Chatelier drives the reaction forward. Swarts is the standard route to R–F (free-radical fluorination is too violent).

> **Markovnikov vs peroxide effect**
>
> HCl, HI: always Markovnikov (H to C with more H; X to more-substituted C).
> **HBr only** + ROOR / peroxide ⇒ **anti-Markovnikov** (Kharasch effect).
> Peroxide effect is absent in HCl and HI (bond enthalpies don't allow chain propagation).

5 Preparation of Haloarenes (NCERT 6.5)

NCERT lists two reliable routes: electrophilic halogenation of arenes (gives o/p mixture) and the Sandmeyer / Gattermann sequence on diazonium salts (positional control via the amine precursor).

Electrophilic substitution on arenes

$C_6H_6 + X_2 \longrightarrow$ [Fe or FeX$_3$, dark] C_6H_5–X + HX (X = Cl, Br)

Toluene gives **o-** and **p-halotoluene**; o/p ratio depends on conditions but p-isomer usually dominant in cold/dark.

Iron(III) halide is the Lewis-acid catalyst. Reaction with $\mathbf{I_2}$ is reversible $\Rightarrow$ needs HNO_3 or HIO_4 to oxidise HI. **Fluorine** is too reactive; F-arenes are not made this way (use Schiemann or Swarts).

Sandmeyer & Gattermann reactions

Step 1 — Diazotisation (273–278 K):

Ar–NH_2 + HX + $NaNO_2 \rightarrow$ Ar–$N_2^+X^-$ + NaX + $2H_2O$

Step 2a — **Sandmeyer**: Ar–$N_2^+X^- \longrightarrow$ [Cu_2X_2] Ar–X + $N_2\uparrow$

Step 2b — **Gattermann**: Ar–$N_2^+X^- \longrightarrow$ [Cu / HX] Ar–X + $N_2\uparrow$

For aryl iodide: Ar–$N_2^+X^-$ + KI $\rightarrow$ Ar–I + N_2 + KX (no Cu needed)

Sandmeyer/Gattermann place the halogen at the **exact position** of the original –NH_2 group — crucial when ortho/para electrophilic halogenation would give the wrong isomer.

6 Physical Properties of Haloalkanes

Haloalkanes are polar; their boiling points and densities exceed those of the parent hydrocarbons because of stronger dipole-dipole and van der Waals attractions.

Boiling-point trends

Same alkyl, varying X: R–I $>$ R–Br $>$ R–Cl $>$ R–F (van der Waals $\uparrow$ with molar mass).

Same X, varying chain: b.p. rises with chain length (more electrons $\Rightarrow$ stronger dispersion).

Branching effect (isomeric haloalkanes): more branched $\Rightarrow$ lower b.p. (more spherical, less surface contact).

n-C_4H_9Br = 375 K; sec-C_4H_9Br = 364 K; tert-C_4H_9Br = 346 K.

Methyl chloride, methyl bromide, ethyl chloride are **gases** at RT; higher members are liquids or solids.

Density and solubility

Density (g/mL): bromo-, iodo-, and polychloro derivatives are **heavier than water**; e.g. n-C_3H_7Cl 0.89, n-C_3H_7Br 1.335, n-C_3H_7I 1.747; $CHCl_3$ 1.489, CCl_4 1.595.

Density rises with C count, halogen count, and halogen atomic mass.

Solubility: Haloalkanes are **very slightly soluble in water** — breaking water H-bonds is not compensated by weak haloalkane–water interactions. They dissolve freely in **organic solvents**.

p-dichlorobenzene has **higher m.p.** than o- and m-isomers because its symmetric structure **packs better** in the crystal lattice (NCERT note).

7 Nucleophilic Substitution: General Pattern

Three reaction classes of haloalkanes (NCERT 6.7.1): nucleophilic substitution, β-elimination, and reaction with metals. This section gives the general substitution scheme and the standard nucleophile $\rightarrow$ product map.

General S$_N$ reaction

R–X + $Nu^- \rightarrow$ R–Nu + X^-

where Nu^- = nucleophile (electron-rich); X^- = leaving group (departs with bonding pair).

The C–X carbon is electrophilic (δ^+); Nu^- attacks there and displaces X^-. Reaction rate depends on alkyl class, Nu strength, X (leaving-group ability), and solvent.

Nucleophile → product (NCERT Table 6.4)

Reagent	Nu^-	Product (class)	Reagent	Nu^-	Product (class)
NaOH (aq)	OH^-	R–OH (alcohol)	KCN	$C{\equiv}N^-$	R–CN (nitrile)
H_2O	H_2O	R–OH (alcohol)	AgCN	Ag–CN:	R–NC (isonitrile)
NaOR′	$R'O^-$	R–OR′ (ether)	KNO_2	ONO^-	R–ONO (alkyl nitrite)
NaI	I^-	R–I (Finkelstein)	$AgNO_2$	Ag–O–N=O	R–NO_2 (nitroalkane)
NH_3	NH_3	R–NH_2 (1° amine)	$R'NH_2$	$R'NH_2$	R–NHR′ (2° amine)
R′R″NH	R′R″NH	R–NR′R″ (3° amine)	$LiAlH_4$	H^-	R–H (alkane)
R′COOAg	$R'COO^-$	R′COOR (ester)	R'^-M^+	R'^-	R–R′ (alkane, coupling)
AgF, SbF_3	F^-	R–F (Swarts)			

Ambident nucleophiles (CN^-, NO_2^-): two donor atoms; the product depends on the counter-cation. KCN ionic ⇒ C-attack (R–CN, nitrile). AgCN covalent ⇒ N-attack (R–NC, isonitrile). Ammonolysis with NH_3 gives a **mixture** of 1°/2°/3°/quaternary ammonium salts unless NH_3 is in large excess.

8 S_N2 Mechanism

The bimolecular substitution is a single-step concerted process with a five-coordinate transition state. Rate depends on both R–X and Nu^- concentrations and is strongly slowed by steric bulk on the α-carbon.

S_N2: kinetics & key features

$\text{Rate} = k\,[\text{R–X}][\text{Nu}^-]$ (second-order, **bimolecular**)
One step — no intermediate; Nu attacks α-C *simultaneously* as X leaves.
Transition state: trigonal-bipyramidal $[\text{Nu}\cdots\text{C}\cdots\text{X}]^\ddagger$ with 5 bonds to C.
Inversion of configuration (Walden inversion) at the α-C, like an umbrella turned inside out.
Favoured by: small unhindered alkyl group; strong Nu^-; polar aprotic solvent (DMSO, acetone).
Disfavoured by steric bulk on α-C.

S_N2 reactivity order

$CH_3X > 1°\ \text{R–X} > 2°\ \text{R–X} > 3°\ \text{R–X}$
Relative rates (NCERT Fig. 6.3): Methyl 30 : Ethyl(1°) 1 : Isopropyl(2°) 0.02 : tert-butyl(3°) 0
Bulky groups block backside attack, so 3° halides are virtually inert towards S_N2. For the same alkyl group, R–I > R–Br > R–Cl (leaving-group order).

9 S_N1 Mechanism

The unimolecular substitution proceeds via a planar carbocation intermediate. Rate depends only on [R–X]; the nucleophile enters in a fast second step. The carbocation can be attacked from either face ⇒ racemisation.

S_N1: kinetics & key features

$\text{Rate} = k\,[\text{R–X}]$ (first-order, **unimolecular**)
Step I (slow, rate-determining): $\text{R–X} \rightleftharpoons R^+ + X^-$
Step II (fast): $R^+ + Nu^- \rightarrow \text{R–Nu}$
Example: $(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$

Favoured by: stable carbocation (3°, allylic, benzylic), polar **protic** solvent (water, alcohols, RCOOH) that stabilises ions by H-bonding.

S$_N$1 reactivity order

3° R–X $>$ 2° R–X $>$ 1° R–X $>$ CH_3X

Allylic and **benzylic** halides ionise *very* easily because the resulting cation is **resonance-stabilised**:

$CH_2{=}CH\text{–}CH_2^+ \leftrightarrow {}^+CH_2\text{–}CH{=}CH_2$

Benzyl$^+$ resonance into the ring spreads + charge to o- and p-carbons.

Reactivity in BOTH S$_N$1 and S$_N$2: R–I $>$ R–Br $>$ R–Cl $\gg$ R–F (same alkyl group; leaving-group order is universal).

Stereochemistry: racemisation in S$_N$1

Carbocation R$^+$ is **planar** (sp^2 hybridised) $\Rightarrow$ achiral.

Nu$^-$ can attack from either face with equal probability.

$\Rightarrow$ Equal amounts of two enantiomers $\Rightarrow$ **racemic mixture** ($\pm$ product).

Example: $(-)$-2-bromobutane + H_2O $\longrightarrow$ $(\pm)$-butan-2-ol

Optically active R–X under *S$_N$1 conditions* loses optical activity. Compare: S$_N$2 gives **inversion** (clean, optically active product of opposite sign).

S$_N$1 vs S$_N$2 decision rule

3° R–X, protic solvent, weak Nu $\Rightarrow$ S$_N$1 (racemisation). **1° R–X, aprotic solvent, strong Nu** $\Rightarrow$ S$_N$2 (inversion). **2° R–X**: both compete; depends on Nu strength and solvent. The two reactivity orders are **exactly opposite** — anchor on carbocation stability (S$_N$1) or steric hindrance (S$_N$2).

10 Stereochemistry: Chirality & Optical Activity

NCERT Section 6.7.1(c) defines the stereochemical vocabulary needed to interpret S$_N$1 / S$_N$2 outcomes: optical activity, chirality, enantiomers, retention, inversion, and racemisation.

Chirality & asymmetric carbon

A molecule is **chiral** (handed) if it is **non-superimposable on its mirror image**; otherwise **achiral**. The simplest criterion: a tetrahedral C with **four different groups** (an **asymmetric carbon** or **stereocentre**) makes the molecule chiral. Two non-superimposable mirror images are called **enantiomers**.

Optical activity & specific rotation

Optically active molecules rotate plane-polarised light:

clockwise = **dextrorotatory** (d-, $+$)

anticlockwise = **laevorotatory** (l-, $-$)

A 50:50 mix of enantiomers (**racemic mixture**, $\pm$ or dl-) has **zero net rotation** — the rotations cancel.

Enantiomers have *identical* physical properties (m.p., b.p., density, refractive index) but **opposite signs** of optical rotation. JEE/NEET regulars: only chemical **environment with chiral influence** can distinguish them.

Retention, inversion, racemisation

For replacement of group X by group Y on an asymmetric C:

Retention of configuration: product has *same* spatial arrangement (no bond to stereocentre broken).

Inversion of configuration: product has *mirror-image* arrangement (S_N2 outcome).
Racemisation: 50:50 mix of retention and inversion $\Rightarrow$ optically inactive (S_N1 outcome).
Key result: S_N2 on optically active R–X $\rightarrow$ **inverted** product. S_N1 on optically active R–X $\rightarrow$ **racemic** product.

Sign of rotation $\neq$ absolute configuration

The (+/$-$) sign of optical rotation is an *experimental* property and does **not** fix the absolute (R/S) configuration. A molecule can keep the same configuration during a reaction yet *change* its sign of rotation, because two different compounds with the same configuration may rotate light oppositely.

JEE/NEET Extension: CIP rules for R/S assignment

Step 1. Assign priorities $a > b > c > d$ to the four groups on the stereocentre by atomic number (higher Z = higher priority; tie $\Rightarrow$ go to next atom).
Step 2. Orient the molecule so the lowest-priority group (d) points away from you.
Step 3. Trace $a \rightarrow b \rightarrow c$: clockwise $\Rightarrow$ **R** (rectus); anticlockwise $\Rightarrow$ **S** (sinister).
Halogen priority on a C–X stereocentre: **I** $>$ **Br** $>$ **Cl** $>$ **F** $>$ **O** $>$ **N** $>$ **C** $>$ **H**.

11 Elimination Reactions (β-Elimination)

When a haloalkane with a β-H is heated with alcoholic KOH, a β-H and the halogen are removed to give an alkene. This is dehydrohalogenation. The product is decided by Saitzeff's rule.

β-Elimination: general scheme

$\underset{\beta}{\mathrm{C}}-\underset{\alpha}{\mathrm{C}}-\mathrm{X} \longrightarrow$ [alc. KOH, Δ] C=C $+$ HX($+$KX $+$ H_2O)
α-C: bears the halogen.
β-C: adjacent to α-C; loses the H.
Base (alkoxide RO^- or OH^-) removes β-H; halogen leaves as X^-. **Net loss of HX** (dehydrohalogenation). The C=C forms between the α and β carbons.

Saytzeff (Zaitsev) rule

"In dehydrohalogenation reactions, the preferred product is that alkene which has the **greater number of alkyl groups attached to the doubly bonded carbons**."
Example: 2-bromopentane $\longrightarrow$ [alc. KOH] pent-2-ene (81%, major) $+$ pent-1-ene (19%, minor).
Major alkene = more highly **substituted** (more alkyl groups on C=C). Stability: tetra-substituted $>$ tri- $>$ di- $>$ mono- $>$ unsubstituted.

Substitution vs Elimination competition

Two competing routes for R–X + base/Nu:
S_N favoured by: weak/medium base; primary R–X; aqueous solvent.
E favoured by: **bulky strong base** (e.g., t-BuO^-, OEt^-); higher temperature; tertiary R–X; alcoholic medium.
Quick rule:
1° R–X $+$ alc. KOH $\rightarrow$ S_N2 dominates (some elimination).
2° R–X $+$ alc. KOH $\rightarrow$ E2 / S_N2 mix; bulky base $\rightarrow$ mostly E.
3° R–X $+$ alc. KOH $\rightarrow$ mostly elimination (alkene); S_N1 in water.
NCERT note: **aqueous KOH** $\rightarrow$ **alcohol** (S_N); **alcoholic KOH** $\rightarrow$ **alkene** (E). One reagent, two products, controlled by the solvent.

JEE/NEET Extension: E1 vs E2 & Hofmann

E1: two-step via carbocation (same intermediate as S_N1). Rate $\propto$ [R–X]; favoured by 3° R–X + weak base + protic solvent.
E2: concerted, single-step, **anti-periplanar** H and X. Rate $\propto$ [R–X][base]; favoured by strong base, any R–X with β-H.
Hofmann product (*least*-substituted alkene): bulky base (e.g. t-BuO$^-$, t-BuO$^-$K$^+$) cannot reach the more crowded β-H, so it abstracts the more accessible H $\Rightarrow$ less-substituted alkene becomes major. Default rule = Saytzeff; bulky-base override = Hofmann.

12 Reactions with Metals

Haloalkanes react with active metals to give organo-metallic compounds. The two NCERT-named reactions are Grignard formation (R–MgX) and the Wurtz coupling (2 R–X $\to$ R–R).

Grignard reagent

$\mathrm{R\text{–}X + Mg \longrightarrow [dry\ ether]\ R\text{–}MgX}$
Polarity: $\overset{\delta-}{\mathrm{R}}-\overset{\delta+}{\mathrm{Mg}}-\overset{\delta-}{\mathrm{X}}$; the R–Mg bond is highly polar covalent, Mg–X essentially ionic.
Highly reactive; destroyed by traces of moisture:
$\mathrm{R\text{–}MgX + H_2O \to R\text{–}H + Mg(OH)X}$
Dry ether (anhydrous diethyl ether or THF) is the standard solvent — coordinates Mg and prevents oligomerisation. Grignards add to C=O, C$\equiv$N, epoxides, etc. (Class 12 Aldehydes/Ketones).

Wurtz reaction

$\mathrm{2\,R\text{–}X + 2\,Na \longrightarrow [dry\ ether]\ R\text{–}R + 2\,NaX}$
Example: $\mathrm{2\,CH_3CH_2Br + 2\,Na \to CH_3CH_2CH_2CH_3 + 2\,NaBr}$
Couples two alkyl halides into a **symmetric alkane with double the C count**. Limitation: mixed R–X / R′–X gives a mixture of all three coupling products (RR, RR′, R′R′). Best with **primary** R–X.

Wurtz–Fittig & Fittig reactions

Wurtz–Fittig: alkyl halide + aryl halide + Na/dry ether $\to$ alkylarene.
$\mathrm{Ar\text{–}X + R\text{–}X + 2\,Na \longrightarrow [dry\ ether]\ Ar\text{–}R + 2\,NaX}$
Fittig: two aryl halides + Na/dry ether $\to$ biaryl.
$\mathrm{2\,Ar\text{–}X + 2\,Na \longrightarrow [dry\ ether]\ Ar\text{–}Ar + 2\,NaX}$
e.g., $\mathrm{2\,C_6H_5Br + 2\,Na \to}$ biphenyl $\mathrm{+2\,NaBr}$.
All three coupling reactions need *dry* ether and *anhydrous* conditions. The aryl halide cannot do plain Wurtz (Ar–Ar would compete), so the alkyl partner must be used in excess in Wurtz–Fittig.

13 Reactions of Haloarenes

NCERT Section 6.7.2: aryl halides are very inert towards ordinary S_N but undergo electrophilic substitution on the ring (o-/p-directed by –X). Specific S_NAr (replacement of X by OH) is possible only under harsh conditions or with electron-withdrawing groups at o-/p-.

Why aryl halides are inert to S_N

(i) Resonance / partial double-bond character of C–X (lone pair on X delocalised into ring):
C–Cl in ArCl: 169 pm *vs* 177 pm in alkyl C–Cl $\Rightarrow$ **shorter, stronger**.
(ii) sp^2 C is more electronegative than sp^3 C $\Rightarrow$ holds the C–X bonding pair more tightly.
(iii) Phenyl cation from self-ionisation is **not** resonance-stabilised $\Rightarrow$ S_N1 forbidden.
(iv) Electron-rich ring repels Nu$^-$ approach.
All four effects compound: PhCl + NaOH needs 623 K / 300 atm. Aryl halides essentially do not

react under classical S_N1 / S_N2 conditions.

Replacement of X by OH (S_NAr, Dow process)

$C_6H_5Cl + NaOH \longrightarrow [623\ K,\ 300\ atm]\ C_6H_5ONa \longrightarrow [H^+]\ C_6H_5OH$

Activation by –NO_2 (electron-withdrawing) at *o-/p-*:

p-nitrochlorobenzene + NaOH $\longrightarrow$ $[443\ K]$ *p*-nitrophenol

2,4-dinitrochlorobenzene + NaOH $\longrightarrow$ $[368\ K]$ 2,4-dinitrophenol

2,4,6-trinitrochlorobenzene + warm H_2O → picric acid

–NO_2 at **o-/p-** stabilises the intermediate carbanion (charge sits on C bearing –NO_2). NO_2 at **meta** has *no* activating effect (resonance structures don't place the negative charge on the C bearing NO_2).

Electrophilic substitution on haloarenes

Halogen is **slightly deactivating** but **o-,p-directing** (resonance donation $>$ inductive at o-/p-positions).

Halogenation: C_6H_5Cl + Cl_2 $\longrightarrow$ [anhyd. $FeCl_3$] 1,4-dichlorobenzene (major) + 1,2-dichlorobenzene (minor).

Nitration: C_6H_5Cl + HNO_3/conc. H_2SO_4 → 1-chloro-4-nitrobenzene (major) + 1-chloro-2-nitrobenzene (minor).

Sulphonation: C_6H_5Cl + conc. H_2SO_4/Δ → 4-chlorobenzenesulphonic acid (major) + 2-isomer (minor).

Friedel–Crafts alkylation: C_6H_5Cl + CH_3Cl/anhyd. $AlCl_3$ → 1-chloro-4-methylbenzene (major) + 2-isomer (minor).

Reactivity of haloarene $<$ benzene (net deactivation by –I effect). **Orientation** para $>$ ortho (steric preference) due to resonance donation from X.

"Deactivating but o,p-directing" — halogens are the lone exception

Halogens are unique: –I effect overall **deactivates** the ring (slower than benzene), yet the lone-pair resonance concentrates density at o- and p- ⇒ those positions remain most nucleophilic. All other o,p-directors (–OH, –NH_2, –OR, –R) *activate*; –X alone deactivates while still being o,p-directing.

14 Polyhalogen Compounds (NCERT 6.8)

NCERT Section 6.8 catalogues six industrially relevant polyhalogen compounds. Each has a named structure, a typical use, and a toxicity / environmental issue — standard short-answer territory in CBSE.

Common polyhalogen compounds

Name	Formula	Major Use / Hazard
Dichloromethane (methylene chloride)	CH_2Cl_2	Paint remover, propellant, process solvent
Trichloromethane (chloroform)	$CHCl_3$	Solvent; feedstock for refrigerant R-22
Triiodomethane (iodoform)	CHI_3	Antiseptic (liberates I_2; now obsolete)
Tetrachloromethane (carbon tetrachloride)	CCl_4	Fire extinguisher, CFC feedstock; ozone-depleting
Freon-12	CCl_2F_2	Refrigerant, aerosol propellant; ozone-depleting (Montreal Protocol)
DDT (p, p'-dichlorodiphenyltrichloroethane)	$C_{14}H_9Cl_5$	Insecticide; bioaccumulates in fat; banned in many countries

All NCERT-listed polyhalogens are toxic or environmentally hazardous. CCl_4 and freons deplete stratospheric ozone via Cl· radicals; DDT bioaccumulates in fatty tissues.

Chloroform $\rightarrow$ phosgene (storage hazard)

$2\,CHCl_3 + O_2 \longrightarrow$ [light] $2\,COCl_2 + 2\,HCl$

$COCl_2$ = phosgene (carbonyl chloride), **highly toxic**.

Hence chloroform is stored in **closed, dark-coloured bottles, completely filled** (no air gap, no light) — often with a small amount of ethanol added to consume any phosgene formed.

JEE/NEET Extension: Reimer–Tiemann & haloform

Haloform reaction (Cl_2/NaOH on methyl ketones or ethanol):

$CH_3CHO + 3Cl_2 + 4NaOH \rightarrow CHCl_3 + HCOONa + 3NaCl + 3H_2O$

Gives $CHCl_3$, $CHBr_3$, or CHI_3 from MeC(=O)R or $RCH(OH)CH_3$ (*iodoform test* for ethanol / acetaldehyde / methyl ketones).

Dipole moment: CCl_4 vs $CHCl_3$ vs CH_2Cl_2

$\mu(CCl_4) = 0$ (tetrahedral symmetry cancels all four C–Cl dipoles).

$\mu(CH_2Cl_2) = 1.60$ D $> \mu(CHCl_3) = 1.04$ D — DCM has higher net dipole because the two C–Cl and two C–H dipoles add favourably, whereas in $CHCl_3$ the resultant of three C–Cl dipoles points *opposite* to the C–H dipole, partly cancelling.

Quick Reference — S$_N$1 vs S$_N$2 Comparison & Master Reactions

Comparative Table: S$_N$1 vs S$_N$2

Feature	**S$_N$1 (unimolecular)**	**S$_N$2 (bimolecular)**
Rate law	Rate $= k$[R–X]	Rate $= k$[R–X][Nu$^-$]
Mechanism	Two steps (ionisation + capture)	One step (concerted)
Intermediate	Planar carbocation R$^+$	None; trigonal-bipyramidal TS
R–X reactivity	$3^\circ > 2^\circ > 1^\circ >$ CH$_3$	CH$_3$ $> 1^\circ > 2^\circ > 3^\circ$
Nu dependence	Independent of [Nu]	Strong Nu$^-$ essential
Solvent	Polar protic (H_2O, alcohols)	Polar aprotic (DMSO, acetone)
Stereochemistry	Racemisation	Inversion (Walden)
Rearrangement	Possible (cation shift)	Never
Leaving group	$I^- > Br^- > Cl^- \gg F^-$	$I^- > Br^- > Cl^- \gg F^-$
Favoured for	Allylic, benzylic, 3°	Methyl, 1°, allylic, benzylic