

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-, polyhalogen) 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 \Rightarrow 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., $\text{CH}_2=\text{CHCl}$, 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., $\text{CH}_3\text{-CHCl}_2$ (1,1-dichloroethane / ethylidene chloride).

vic-dihalide (alkylene halide): X on *adjacent* C, e.g., $\text{CH}_2\text{Cl-CH}_2\text{Cl}$ (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 \rightarrow 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: $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \rightarrow$ 1-bromopropane; $(\text{CH}_3)_2\text{CHBr} \rightarrow$ 2-bromopropane; $(\text{CH}_3)_3\text{CBr} \rightarrow$ 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)

$\text{CH}_2\text{Cl-CH}_2\text{Cl}$: ethylene dichloride / 1,2-dichloroethane (vic)

$\text{CH}_2\text{Br-CH}_2\text{Br}$: ethylene dibromide / 1,2-dibromoethane (vic)

When the two halogens are different, just list each alphabetically with its locant: $\text{CH}_2\text{Br-CH}_2\text{Cl} \rightarrow$ 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 $C_6H_5CH_2Cl$ → IUPAC name **(chloromethyl)benzene** or *chlorophenylmethane*. Allyl bromide $CH_2=CHCH_2Br$ → **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

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.

$\mu(\text{chlorobenzene}) < \mu(\text{cyclohexyl chloride})$

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: $HI > HBr > HCl$

$R-OH + HCl \rightarrow [ZnCl_2] R-Cl + H_2O$ (Lucas test reagent)

$R-OH + NaBr/H_2SO_4 \rightarrow R-Br + NaHSO_4 + H_2O$

$3R-OH + PX_3 \rightarrow 3R-X + H_3PO_3$ (X = Cl, Br)

$R-OH + PCl_5 \rightarrow R-Cl + POCl_3 + HCl$

$R-OH + SOCl_2 \rightarrow R-Cl + SO_2\uparrow + HCl\uparrow$

$SOCl_2$ 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

$R-H + X_2 \rightarrow [UV / heat] R-X + HX$

Example: $CH_3CH_2CH_2CH_3 \rightarrow [Cl_2/h\nu]$ 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):

$CH_3CH=CH_2 + HI \rightarrow CH_3CHI-CH_3$ (major)

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

$CH_2=CH_2 + Br_2 \rightarrow [CCl_4] BrCH_2-CH_2Br$

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

Halogen-exchange reactions

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

Swarts: $R-Cl/Br + AgF$ (or Hg_2F_2 , CoF_2 , SbF_3) $\rightarrow R-F + AgCl/Br$

Example: $H_3C-Br + AgF \rightarrow H_3C-F + AgBr$

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 \Rightarrow **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).

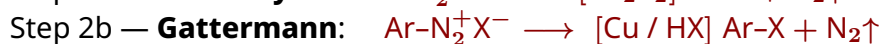
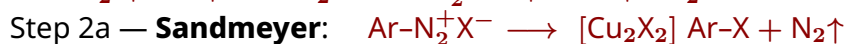
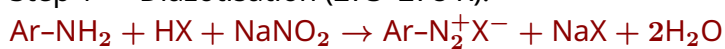
Electrophilic substitution on arenes

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 **I₂** is reversible \Rightarrow needs **HNO₃** or **HIO₄** 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):



Sandmeyer/Gattermann place the halogen at the **exact position** of the original $-\text{NH}_2$ 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: $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$ (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).

$n\text{-C}_4\text{H}_9\text{Br} = 375 \text{ K}$; $\text{sec-C}_4\text{H}_9\text{Br} = 364 \text{ K}$; $\text{tert-C}_4\text{H}_9\text{Br} = 346 \text{ K}$.

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. $n\text{-C}_3\text{H}_7\text{Cl}$ 0.89, $n\text{-C}_3\text{H}_7\text{Br}$ 1.335, $n\text{-C}_3\text{H}_7\text{I}$ 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

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≡N ⁻ | R-CN (nitrile) |
| H ₂ O | H ₂ O | 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⁻, NO₂⁻): 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 NH₃ gives a **mixture** of 1°/2°/3°/quaternary ammonium salts unless NH₃ 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

Rate = $k [R-X][Nu^-]$ (second-order, **bimolecular**)

One step — no intermediate; Nu attacks α-C *simultaneously* as X leaves.

Transition state: trigonal-bipyramidal [Nu...C...X][‡] 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

CH₃X > 1° R-X > 2° R-X > 3° 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

Rate = $k [R-X]$ (first-order, **unimolecular**)

Step I (slow, rate-determining): R-X ⇌ R⁺ + X⁻

Step II (fast): R⁺ + Nu⁻ → R-Nu

Example: (CH₃)₃CBr + OH⁻ → (CH₃)₃COH + Br⁻

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

S_N1 reactivity order



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



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

Reactivity in BOTH S_N1 and S_N2 : $\text{R-I} > \text{R-Br} > \text{R-Cl} \gg \text{R-F}$ (same alkyl group; leaving-group order is universal).

Stereochemistry: racemisation in S_N1

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 + $\text{H}_2\text{O} \rightarrow (\pm)$ -butan-2-ol

Optically active R-X under S_N1 conditions loses optical activity. Compare: S_N2 gives **inversion** (clean, optically active product of opposite sign).

S_N1 vs S_N2 decision rule

3°R-X , protic solvent, weak Nu $\Rightarrow S_N1$ (racemisation). **1°R-X , aprotic solvent, strong Nu** $\Rightarrow S_N2$ (inversion). **2°R-X** : both compete; depends on Nu strength and solvent. The two reactivity orders are **exactly opposite** — anchor on carbocation stability (S_N1) or steric hindrance (S_N2).

10 Stereochemistry: Chirality & Optical Activity

NCERT Section 6.7.1(c) defines the stereochemical vocabulary needed to interpret S_N1 / S_N2 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 Saytzeff's rule.

β -Elimination: general scheme



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 \rightarrow [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., $t\text{-BuO}^-$, 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 $\propto [R-X][\text{base}]$; favoured by strong base, any R-X with β -H.

Hofmann product (*least*-substituted alkene): bulky base (e.g. $t\text{-BuO}^-$, $t\text{-BuO}^-\text{K}^+$) 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.

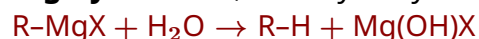
12 Reactions with Metals

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

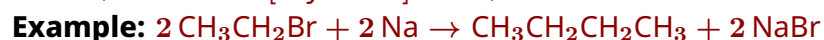
Grignard reagent

Polarity: $R^{\delta-}-Mg^{\delta+}-X^{\delta-}$; the R-Mg bond is highly polar covalent, Mg-X essentially ionic.

Highly reactive; destroyed by traces of moisture:



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

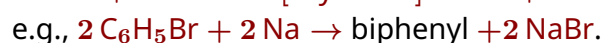
Couples two alkyl halides into a **symmetric alkane with double the C count**. Limitation: mixed $R-X / R'-X$ gives a mixture of all three coupling products (RR , RR' , $R'R'$). Best with **primary** R-X.

Wurtz-Fittig & Fittig reactions

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



Fittig: two aryl halides + Na/dry ether \rightarrow biaryl.



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.

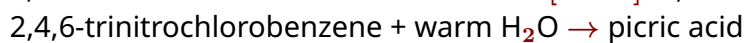
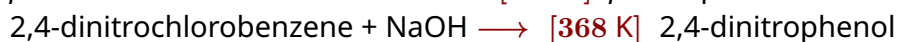
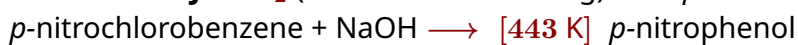
All four effects compound: $PhCl + NaOH$ needs 623 K / 300 atm. Aryl halides essentially do not

react under classical S_N1 / S_N2 conditions.

Replacement of X by OH (S_NAr , Dow process)



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



$-NO_2$ 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: $C_6H_5Cl + HNO_3/conc. H_2SO_4 \longrightarrow$ 1-chloro-4-nitrobenzene (major) + 1-chloro-2-nitrobenzene (minor).

Sulphonation: $C_6H_5Cl + conc. H_2SO_4/\Delta \longrightarrow$ 4-chlorobenzenesulphonic acid (major) + 2-isomer (minor).

Friedel-Crafts alkylation: $C_6H_5Cl + CH_3Cl/anhyd. AlCl_3 \longrightarrow$ 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*- \Rightarrow 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 ₂ Cl 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 ₂ F ₂ | Refrigerant, aerosol propellant; ozone-depleting (Montreal Protocol) |
| DDT (<i>p, p'</i> -dichlorodiphenyltrichloroethane) | C ₁₄ H ₉ Cl ₅ | Insecticide; bioaccumulates in fat; banned in many countries |

All NCERT-listed polyhalogens are toxic or environmentally hazardous. CCl₄ and freons deplete stratospheric ozone via Cl· radicals; DDT bioaccumulates in fatty tissues.

Chloroform → phosgene (storage hazard)

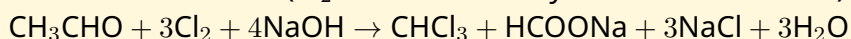


COCl₂ = phosgene (carbonyl chloride), **highly toxic**.

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 (Cl₂/NaOH on methyl ketones or ethanol):



Gives CHCl₃, CHBr₃, or CHI₃ from MeC(=O)R or RCH(OH)CH₃ (*iodoform test* for ethanol / acetaldehyde / methyl ketones).

Dipole moment: CCl₄ vs CHCl₃ vs CH₂Cl₂

$\mu(\text{CCl}_4) = 0$ (tetrahedral symmetry cancels all four C–Cl dipoles).

$\mu(\text{CH}_2\text{Cl}_2) = 1.60 \text{ D} > \mu(\text{CHCl}_3) = 1.04 \text{ D}$ — DCM has higher net dipole because the two C–Cl and two C–H dipoles add favourably, whereas in CHCl₃ the resultant of three C–Cl dipoles points *opposite* to the C–H dipole, partly cancelling.

Quick Reference — S_N1 vs S_N2 Comparison & Master Reactions

Comparative Table: S_N1 vs S_N2

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