Unit 6 : Haloalkanes & Haloarenes

हैलोऐल्केन एवं हैलोऐरीन — Class 12 Chemistry (NCERT) · Bilingual Notes

Haloalkane (alkyl halide, R–X): halogen on sp^3 carbon of an alkyl group. **Haloarene (aryl halide, Ar–X):** halogen on sp^2 carbon of an aryl ring.

हैलोऐल्केन: हैलोजन ऐल्किल समूह के sp^3 कार्बन पर; हैलोऐरीन: हैलोजन ऐरिल वलय के sp^2 कार्बन पर।

Uses: **chloramphenicol** (Cl-antibiotic) — typhoid; **thyroxine** (I-hormone) — deficiency causes goitre; **chloroquine** — malaria; **halothane** — anaesthetic; fully fluorinated compounds — possible blood substitutes.

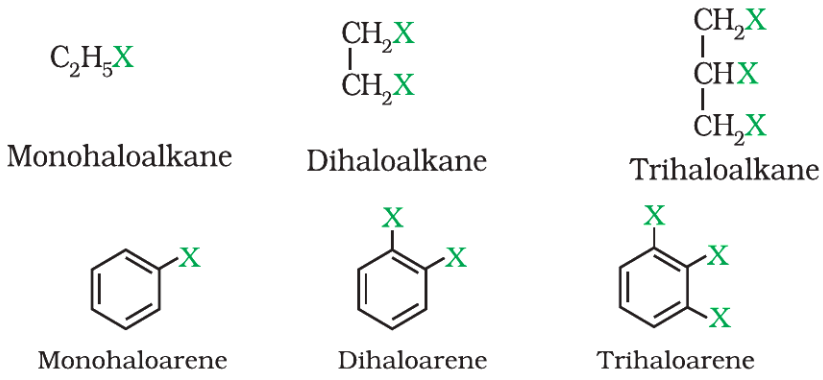
क्लोरैम्फ़ेनिकॉल — टाइफ़ॉइड; थायरॉक्सिन (आयोडीन) — कमी से घेंघा; क्लोरोक्विन — मलेरिया; हैलोथेन — निश्चेतक।

Memory trick: "**Chloramphenicol–Typhoid, Chloroquine–Quinine-like (Malaria), Halothane–Hospital (anaesthesia), Thyroxine–Thyroid (I)**".
क्लोरोक्विन = मलेरिया; हैलोथेन = ऑपरेशन; थायरॉक्सिन = थायरॉइड।

6.1 Classification (वर्गीकरण)

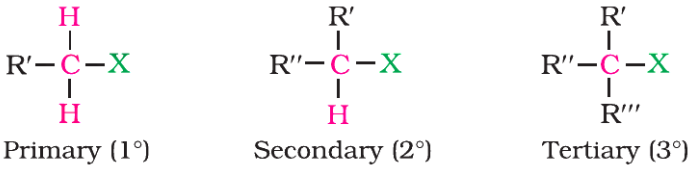
6.1.1 By number of halogen atoms / हैलोजन परमाणुओं की संख्या से

Mono-, di-, poly- (tri-, tetra-) halogen compounds. — एक, दो या अधिक हैलोजन।



6.1.2 Compounds with sp^3 C–X bond

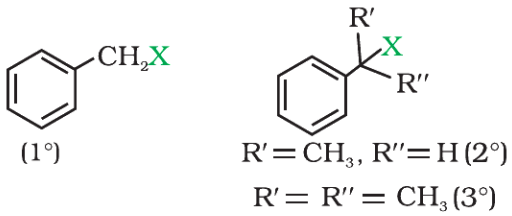
(a) Alkyl halides (R–X): homologous series $C_nH_{2n+1}X$; 1°, 2°, 3° by the carbon bearing X. — हैलोजन जिस कार्बन पर है, उसी के अनुसार 1°, 2°, 3°।



(b) Allylic halides: X on sp^3 C **next to C=C.** — द्विबंध के बगल वाले sp^3 कार्बन पर X।



(c) Benzylic halides: X on sp^3 C **attached to an aromatic ring.** — ऐरोमैटिक वलय से जुड़े sp^3 कार्बन पर X।

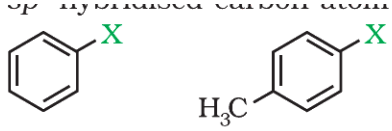


6.1.3 Compounds with sp^2 C–X bond

(a) Vinylic halides: X directly on a C=C carbon. — द्विबंध वाले कार्बन पर ही X।



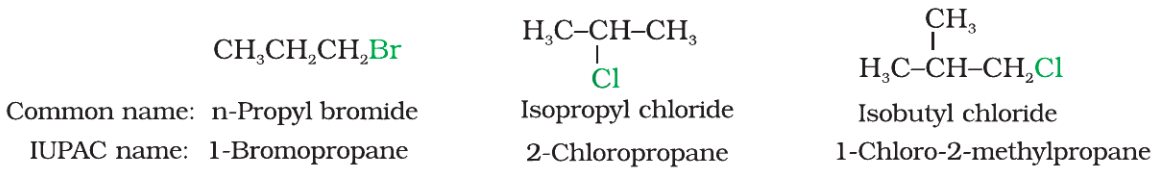
(b) Aryl halides: X directly on a ring carbon. — वलय के कार्बन पर सीधे X।

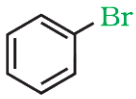
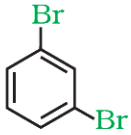
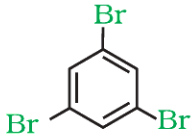


Trick: "**Allylic/Benzylic = Bagal mein (next to, sp^3); Vinylic/Aryl = Upar hi (on it, sp^2)**".
ऐलिलिक/बेंज़िलिक = बगल में (sp^3); वाइनिलिक/ऐरिल = उसी पर (sp^2)।

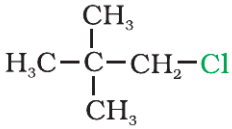
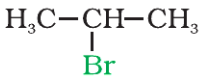
6.2 Nomenclature (नामकरण)

- **Common:** alkyl group + halide (n-propyl bromide). **IUPAC:** halo-substituted hydrocarbon (1-bromopropane). — सामान्य: ऐल्किल + हैलाइड; IUPAC: हैलो + ऐल्केन।
- Benzene derivatives: common names use **o-, m-, p-**; IUPAC uses **1,2-; 1,3-; 1,4-**. — ऑर्थो/मेटा/पैरा बनाम 1,2/1,3/1,4।



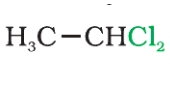
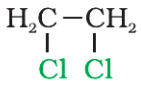
Common name:	Bromobenzene	*m*-Dibromobenzene	*sym*-Tribromobenzene
IUPAC name:	Bromobenzene	1,3-Dibromobenzene	1,3,5-Tribromobenzene

IUPAC name:	1-Chloro-2,2-dimethylpropane	2-Bromopropane

***Dihalides: gem-dihalide** (both X on same C) = **alkylidene halide**; **vic-dihalide** (X on adjacent C) = **alkylene dihalide**. IUPAC: dihaloalkanes.*

जेम-डाइहैलाइड (एक ही कार्बन पर दोनों X) = ऐल्किलिडीन हैलाइड; विसिनल (पास-पास के कार्बनों पर) = ऐल्किलीन डाइहैलाइड।

Common name:	Ethylidene chloride (gem-dihalide)	Ethylene dichloride (vic-dihalide)
IUPAC name:	1, 1-Dichloroethane	1, 2-Dichloroethane

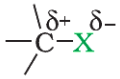
***Trick:** "**GEMini = twins on SAME carbon → alkyliDENE; VICinal = VICinity (neighbours) → alkyLENE**".*

जेम = जुड़वाँ एक ही कार्बन पर; विक = पड़ोसी कार्बनों पर।

Structure	Common name	IUPAC name
$CH_3CH_2CH(Cl)CH_3$	*sec*-Butyl chloride	2-Chlorobutane
$(CH_3)_3CCH_2Br$	*neo*-Pentyl bromide	1-Bromo-2,2-dimethylpropane
$(CH_3)_3CBr$	*tert*-Butyl bromide	2-Bromo-2-methylpropane
$CH_2=CHCl$	Vinyl chloride	Chloroethene
$CH_2=CHCH_2Br$	Allyl bromide	3-Bromopropene
$o\text{-}ClC_6H_4CH_3$	*o*-Chlorotoluene	1-Chloro-2-methylbenzene
$C_6H_5CH_2Cl$	Benzyl chloride	Chlorophenylmethane
CH_2Cl_2	Methylene chloride	Dichloromethane
$CHCl_3$ / $CHBr_3$	Chloroform / Bromoform	Trichloromethane / Tribromomethane
CCl_4	Carbon tetrachloride	Tetrachloromethane
$CH_3CH_2CH_2F$	*n*-Propyl fluoride	1-Fluoropropane

Example 6.1 — 8 isomers of $C_5H_{11}Br$: 1-bromopentane (1°), 2-bromopentane (2°), 3-bromopentane (2°), 1-bromo-3-methylbutane (1°), 2-bromo-3-methylbutane (2°), 2-bromo-2-methylbutane (3°), 1-bromo-2-methylbutane (1°), 1-bromo-2,2-dimethylpropane (1°).

6.3 Nature of C–X Bond (C–X बंध की प्रकृति)



X more electronegative than C → **polar bond**: C gets **δ+**, X gets **δ−**. Down the group, halogen size ↑ → **C–X bond length** ↑ (C–F shortest, C–I longest), bond enthalpy ↓.

X अधिक विद्युतऋणी → C पर δ+, X पर δ−। समूह में नीचे जाने पर बंध लंबाई बढ़ती, बंध ऊर्जा घटती है।

Bond	Bond length/pm	C-X Bond enthalpies/ kJmol^{-1}	Dipole moment/Debye
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

Trick: "**F se I tak — Lamba hota jaata (length ↑), Kamzor hota jaata (enthalpy ↓)**". Dipole moment max at **C–Cl (1.860 D)**.
F से I तक: बंध लंबा और कमज़ोर; द्विध्रुव आघूर्ण C–Cl में सबसे अधिक।

6.4 Preparation of Haloalkanes (हैलोऐल्केन बनाने की विधियाँ)

6.4.1 From alcohols / ऐल्कोहॉल से

–OH replaced by X using conc. HX, phosphorus halides or $SOCl_2$.

$$R\text{–}OH + HCl \xrightarrow{ZnCl_2} R\text{–}Cl + H_2O$$

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

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

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

$$R\text{–}OH \xrightarrow[X_2=Br_2,I_2]{\text{red P}/X_2} R\text{–}X$$

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

- **$SOCl_2$ preferred** — by-products SO_2 + HCl are gases → **pure** alkyl halide. — उपोत्पाद गैसें, शुद्ध उत्पाद।
- 1° & 2° alcohols + HCl need **$ZnCl_2$**; 3° just shaken with conc. HCl at room temp. — 1°/2° के लिए $ZnCl_2$; 3° के लिए केवल सान्द्र HCl।
- R–Br: constant-boiling **48% HBr**; R–I: heat with **NaI/KI in 95% H_3PO_4**. — आयोडाइड के लिए ऑर्थोफ़ॉस्फ़ोरिक अम्ल।
- Reactivity of alcohols with HX: **3° > 2° > 1°**. — अभिक्रियाशीलता क्रम।
- PBr_3, PI_3 made ***in situ*** from red P + Br_2/I_2.
- **Not used for aryl halides** — phenol C–O has partial double bond character. — फ़ीनॉल का C–O बंध आंशिक द्विबंध, टूटता नहीं।

Trick: "**$SOCl_2$ = So Clean**" (gases fly away). "**KI ke saath H_3PO_4, H_2SO_4 nahi**" — H_2SO_4 oxidises HI to I_2 (Intext 6.2).
KI के साथ H_2SO_4 नहीं — वह HI को I_2 में ऑक्सीकृत कर देता है।

6.4.2 From hydrocarbons / हाइड्रोकार्बन से

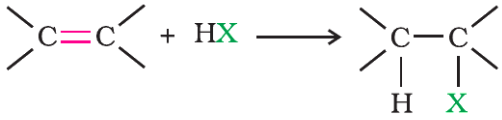
(I) Free radical halogenation of alkanes (Cl_2/UV or heat) → complex mixture of isomers → low yield of any one. — मुक्त मूलक हैलोजनीकरण: समावयवों का मिश्रण, कम लब्धि।

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

Example 6.3: $(CH_3)_2CHCH_2CH_3$ has 4 types of H → 4 monochloro isomers: $(CH_3)_2CHCH_2CH_2Cl$, $(CH_3)_2CHCH(Cl)CH_3$, $(CH_3)_2C(Cl)CH_2CH_3$, $CH_3CH(CH_2Cl)CH_2CH_3$.

(II) From alkenes:

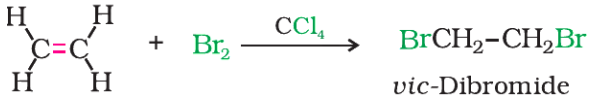
(i) **Addition of HX** (HCl, HBr, HI); unsymmetrical alkenes follow **Markovnikov's rule**. — मार्कोनीकॉफ़ नियम।



$$CH_3CH=CH_2 + H\text{–}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$$

(ii) **Addition of Br_2 in CCl_4** → colourless **vic-dibromide**; discharge of reddish-brown colour = **test for C=C**.

Br_2/CCl_4 का लाल-भूरा रंग उड़ जाना — द्विबंध का परीक्षण।



Trick: "**Bromine ka laal rang gaya = Double bond mila**".
ब्रोमीन का लाल रंग गया = द्विबंध मिला।

6.4.3 Halogen exchange / हैलोजन विनिमय

Finkelstein reaction: R–Cl / R–Br + **NaI in dry acetone** → R–I. NaCl/NaBr precipitates in dry acetone → pushes reaction forward (**Le Chatelier**).

फ़िंकेलस्टाइन: शुष्क ऐसीटोन में NaI से ऐल्किल आयोडाइड; NaCl/NaBr अवक्षेपित होकर अभिक्रिया आगे बढ़ाते हैं।

$$R\text{–}X + NaI \longrightarrow R\text{–}I + NaX$$

X=Cl, Br

Swarts reaction: R–Cl / R–Br + metallic fluoride (**AgF, Hg_2F_2, CoF_2, SbF_3**) → **R–F**.

स्वार्ट्स: धात्विक फ़्लुओराइड से ऐल्किल फ़्लुओराइड।

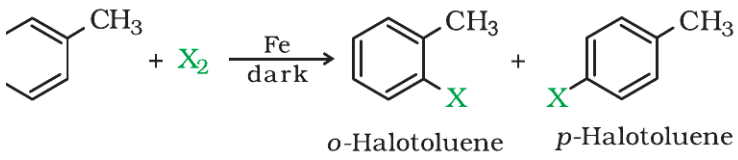
$$H_3C\text{–}Br + AgF \longrightarrow H_3C\text{–}F + AgBr$$

Trick: "**Finkelstein = Iodine (F-I: 'Find I'); Swarts = Fluorine (S-F: 'Super Fluoride')**". Finkelstein needs **dry acetone**; Swarts needs **metal fluorides**.
फ़िंकेलस्टाइन → आयोडाइड (NaI + शुष्क ऐसीटोन); स्वार्ट्स → फ़्लुओराइड (AgF आदि)।

6.5 Preparation of Haloarenes (हैलोऐरीन बनाना)

(i) Electrophilic substitution: arene + Cl_2/Br_2, Lewis acid (**Fe / $FeCl_3$**), dark → o- + p-isomers (separated by large m.p. difference).

इलेक्ट्रॉनस्नेही प्रतिस्थापन: Fe/$FeCl_3$ उत्प्रेरक; ऑर्थो व पैरा का पृथक्करण गलनांक अंतर से।

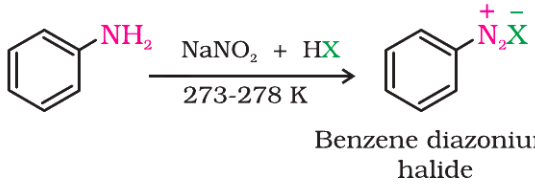


o-Halotoluene *p*-Halotoluene

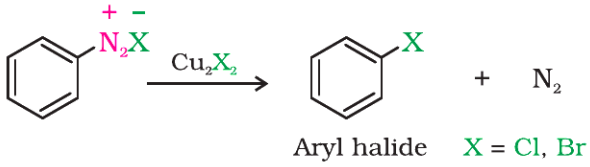
- Iodination is **reversible** → needs oxidising agent (HNO_3, HIO_4) to remove HI. — आयोडीनीकरण उत्क्रमणीय, ऑक्सीकारक चाहिए।
- **Fluoro compounds not made this way** (F too reactive). — फ़्लुओरीन अति क्रियाशील।

(ii) Sandmeyer's reaction: $ArNH_2$ + $NaNO_2$/HX (273–278 K) → diazonium salt → **Cu_2Cl_2 / Cu_2Br_2** → ArCl / ArBr.

सैंडमेयर: डाइऐज़ोनियम लवण + क्यूप्रस हैलाइड → ऐरिल हैलाइड।

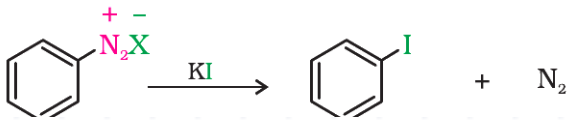


Benzene diazonium halide



Aryl halide X = Cl, Br

Iodine: just shake diazonium salt with **KI** (no cuprous halide). — आयोडीन के लिए केवल KI।



Trick: "**Sandmeyer = Salt of Cu(I)**"; "**Iodine ko Cu nahi chahiye, sirf KI**".
सैंडमेयर = Cu(I) लवण; आयोडीन के लिए केवल KI।

6.6 Physical Properties (भौतिक गुण)

- Colourless when pure; bromides & iodides **develop colour in light**. Volatile ones smell sweet. — प्रकाश में ब्रोमाइड/आयोडाइड रंगीन।
- CH_3Cl, CH_3Br, C_2H_5Cl, some CFCs = gases; higher = liquids/solids.

Melting & boiling points / गलनांक व क्वथनांक

b.p. of halides ≫ parent hydrocarbons (polarity + higher mass → stronger dipole–dipole & van der Waals).

ध्रुवता व अधिक द्रव्यमान के कारण हाइड्रोकार्बन से अधिक क्वथनांक।

Same alkyl group: RI > RBr > RCl > RF

हैलोजन का आकार बढ़ने पर वान्डरवाल्स बल बढ़ता है।

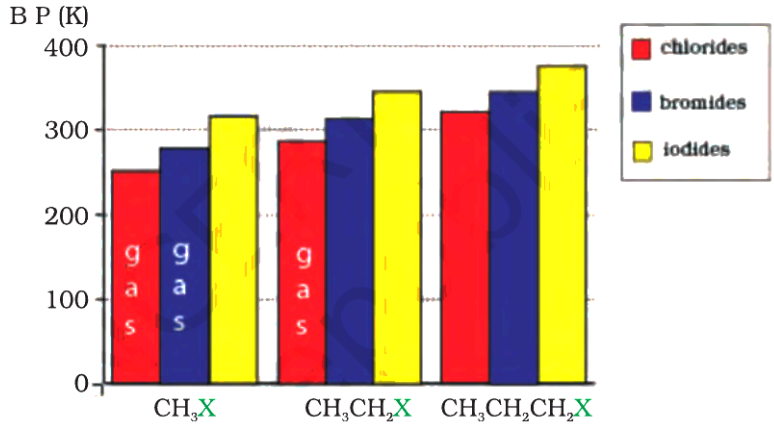


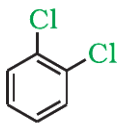
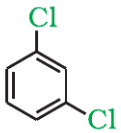
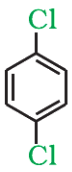
Fig. 6.1: *Comparison of boiling points of some alkyl halides*

Isomeric haloalkanes: b.p. ***decreases with branching****. — शाखन बढ़ने पर क्वथनांक घटता है।*

	$CH_3CH_2CH_2CH_2Br$	$CH_3CH_2\underset{\displaystyle Br}{\underset{\vert}{C}}HCH_3$	$H_3C-\underset{\displaystyle Br}{\underset{\vert}{\overset{\displaystyle CH_3}{\overset{\vert}{C}}}}-CH_3$
b.p./K	375	364	346

Dihalobenzenes: b.p. nearly same, but ***para has highest m.p.*** *(symmetry → fits crystal lattice better).*

पैरा-समावयव सममित — क्रिस्टल जालक में अच्छी तरह फ़िट → सबसे अधिक गलनांक।

			
b.p / K	453	446	448
m.p/K	256	249	323

Trick: "***Para = Perfect fit — Pighalna mushkil (high m.p.)***". "***Branch badhe, Boiling ghate***".

पैरा = पूरी तरह फ़िट, पिघलना मुश्किल; शाखा बढ़े, क्वथनांक घटे।

Density / घनत्व

Bromo, iodo, polychloro compounds are ***heavier than water****. Density ↑ with no. of C, no. of X, and atomic mass of X.*

Compound	Density (g/mL)	Compound	Density (g/mL)
$n\text{-}C_3H_7Cl$	0.89	CH_2Cl_2	1.336
$n\text{-}C_3H_7Br$	1.335	$CHCl_3$	1.489
$n\text{-}C_3H_7I$	1.747	CCl_4	1.595

Solubility / विलेयता

Very slightly soluble in water — energy released by new haloalkane–water attractions is less than energy needed to break water's H-bonds. **Soluble in organic solvents** (similar strength of attractions).

जल में बहुत कम विलेय — नए आकर्षण, जल के H-बंधों जितने प्रबल नहीं; कार्बनिक विलायकों में विलेय।

Intext 6.6: (i) chloromethane < bromomethane < dibromomethane < bromoform (ii) isopropyl chloride < 1-chloropropane < 1-chlorobutane

6.7 Chemical Reactions (रासायनिक अभिक्रियाएँ)

6.7.1 Haloalkanes — three types / हैलोऐल्केन — तीन प्रकार

(1) Nucleophilic substitution (2) Elimination (3) Reaction with metals.

(1) Nucleophilic substitution / नाभिकस्नेही प्रतिस्थापन

Electron-rich nucleophile attacks δ+ carbon; halogen leaves as halide (**leaving group**).

नाभिकस्नेही, δ+ कार्बन पर आक्रमण करता है; हैलोजन हैलाइड आयन के रूप में निकलता है (अवशिष्ट समूह)।

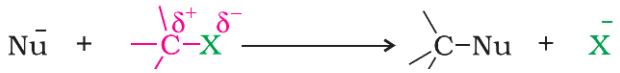


Table 6.4: Nucleophilic Substitution of Alkyl Halides (R–X)

$$R - X + Nu^- \rightarrow R - Nu + X^-$$

Reagent	Nucleophile (Nu^-)	Substitution product R–Nu	Class of main product
NaOH (KOH)	HO^-	ROH	Alcohol
H_2O	H_2O	ROH	Alcohol
NaOR′	$R'O^-$	ROR′	Ether
NaI	I^-	R—I	Alkyl iodide
NH_3	NH_3	RNH_2	Primary amine
$R'NH_2$	$R'NH_2$	RNHR′	Sec. amine
R′R″NH	R′R″NH	RNR′R″	Tert. amine
KCN	$\bar{C}\equiv N:$	RCN	Nitrile (cyanide)
AgCN	Ag-CN:	RNC (isocyanide)	Isonitrile
KNO_2	O=N—O	R—O—N=O	Alkyl nitrite
$AgNO_2$	Ag—Ö—N=O	$R—NO_2$	Nitroalkane
R′COOAg	$R'COO^-$	R′COOR	Ester
$LiAlH_4$	H	RH	Hydrocarbon
R'^-M^+	R'^-	RR′	Alkane

Ambident nucleophiles — *two nucleophilic centres: CN^- (C or N), NO_2^- (O or N).*

उभयदंती नाभिकस्नेही: दो आक्रमण केंद्र — सायनाइड (C या N), नाइट्राइट (O या N)।

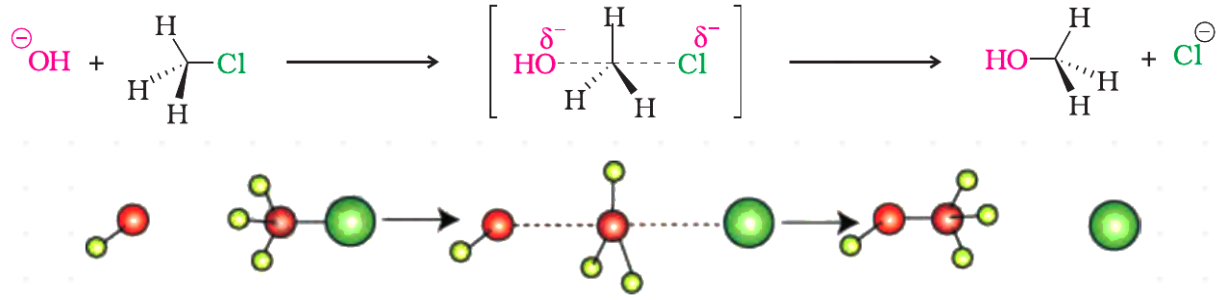
Reagent	Nature	Attacks via	Product
KCN	Ionic	C	**Alkyl cyanide (R–CN)**
AgCN	Covalent	N	**Isocyanide (R–NC)**
KNO_2	Ionic	O	**Alkyl nitrite (R–O–N=O)**
$AgNO_2$	Covalent	N	**Nitroalkane ($R–NO_2$)**

Ambident trick: "K = Kuchh normal (cyanide, nitrite); Ag = Alag (iso-cyanide, nitro)".
KCN ionic → C attacks (C–C bond more stable); AgCN covalent → N free to attack.
K से सामान्य उत्पाद (सायनाइड, नाइट्राइट), Ag से अलग (आइसोसायनाइड, नाइट्रो)।

(a) S_N2 — bimolecular / द्वि-आण्विक

$CH_3Cl + OH^- \rightarrow CH_3OH$: ***second order*** *(rate ∝ $[RX][OH^-]$).* ***One step****, no intermediate; Nu attacks from the side* ***opposite*** *to X; transition state — C bonded to* ***5 atoms****;* ***inversion of configuration*** *(like an umbrella turned inside out). (Hughes & Ingold, 1937)*

S_N2: द्वितीय कोटि, एक चरण, कोई मध्यवर्ती नहीं; नाभिकस्नेही पीछे से आक्रमण करता है; संक्रमण अवस्था में C पाँच परमाणुओं से जुड़ा; विन्यास का प्रतीपन (छाता उलटने जैसा)।



Steric effect: *bulky groups block Nu →* ***CH_3X > 1° > 2° > 3°*** *(relative rates 30 : 1 : 0.02 : 0).*

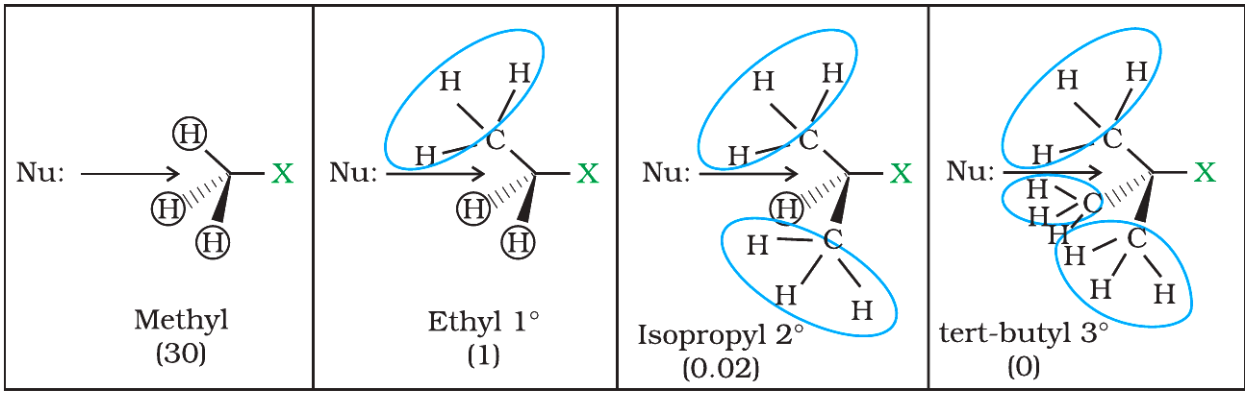


Fig.6.3: *Steric effects in S_N2 reaction. The relative rate of S_N2 reaction is given in parenthesis*

S_N2 trick: "2 = Do log ek saath (bimolecular), Ek hi kadam (one step), Peeche se vaar (backside attack), Chhata ulta (inversion)". "Chhota sabse tez — Methyl wins".

S_N2 = दो अणु एक साथ, एक कदम, पीछे से वार, छाता उलटा; मेथिल सबसे तेज़।

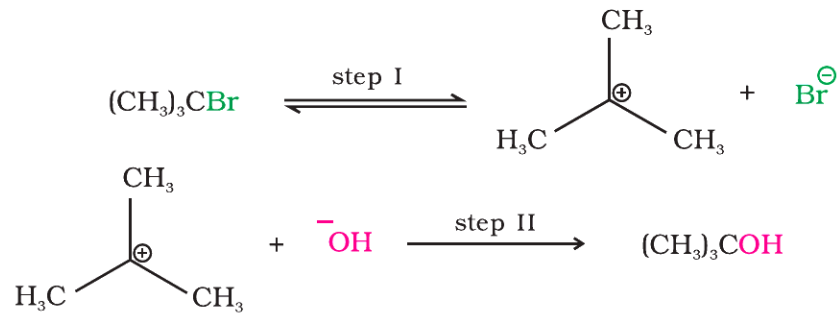
(b) S_N1 — unimolecular / एक-आण्विक

In ***polar protic solvents*** *(water, alcohol, acetic acid). $(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH$:* ***first order*** *(rate ∝ [RX] only).*



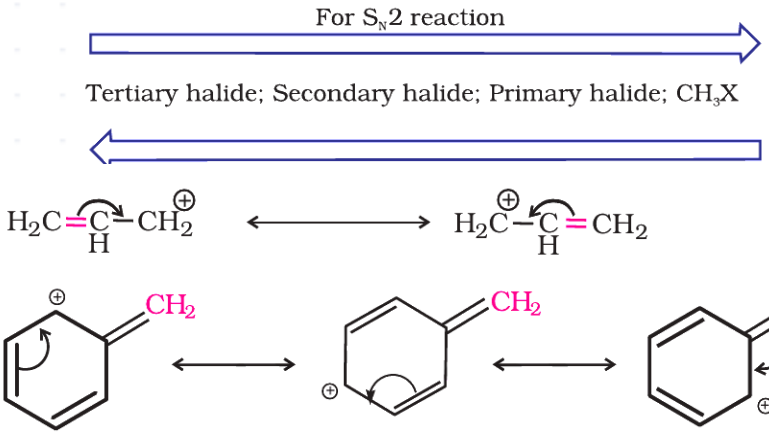
Two steps: *Step I — slow, reversible C–Br cleavage →* ***carbocation*** *(rate-determining; energy from solvation of halide by protic solvent). Step II — Nu attacks carbocation (fast).*

दो चरण: I — धीमा, कार्बोधनायन बनना (दर-निर्धारक); II — नाभिकस्नेही का तेज़ आक्रमण।



More stable carbocation → faster: ***3° > 2° > 1° > CH_3X.*** ***Allylic & benzylic*** *halides very reactive in S_N1 (resonance-stabilised carbocation).*

कार्बोधनायन जितना स्थायी, S_N1 उतना तेज़; ऐलिलिक व बेंज़िलिक अनुनाद से स्थायी।



For a given R: ***R–I > R–Br > R–Cl >> R–F*** *in* ***both*** *mechanisms (I^- = best leaving group). — दोनों में आयोडाइड सबसे तेज़।*

Feature	S_N1	S_N2
Order / molecularity	1st order, unimolecular	2nd order, bimolecular
Steps	2 (via carbocation)	1 (transition state)
Reactivity	3° > 2° > 1° > CH_3	CH_3 > 1° > 2° > 3°
Solvent	Polar protic	(Polar aprotic favoured)
Stereochemistry	**Racemisation**	**Inversion**

S_N1 vs S_N2 trick: *"**S_N1 = Teesra Tez (3° fast), Racemic (Rasgulla — dono taraf se); S_N2 = Methyl Mast, Inversion**". The two orders are* ***exactly reverse.***

S_N1 में तृतीयक तेज़ और रेसिमीकरण; S_N2 में मेथिल तेज़ और प्रतीपन — दोनों क्रम उलटे।

Example 6.7: *(i) S_N1: 1-bromobutane < 1-bromo-2-methylpropane < 2-bromobutane < 2-bromo-2-methylpropane; S_N2 reverse. (ii) S_N1: $C_6H_5C(CH_3)(C_6H_5)Br$ > $C_6H_5CH(C_6H_5)Br$ > $C_6H_5CH(CH_3)Br$ > $C_6H_5CH_2Br$; S_N2 reverse.*

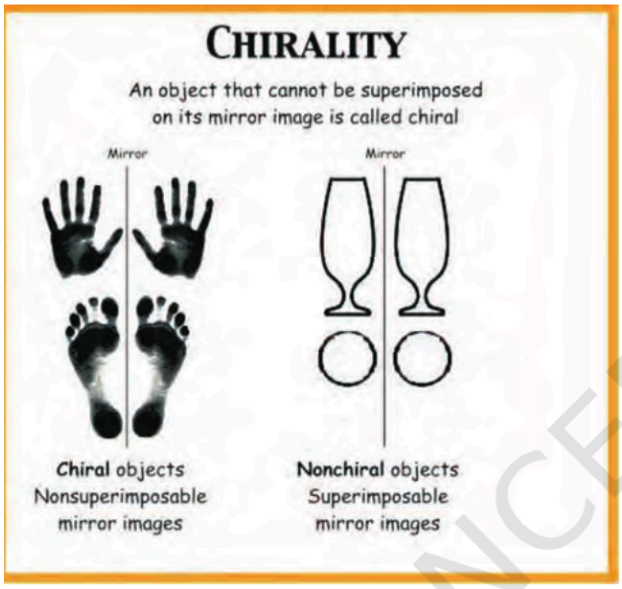
(c) Stereochemistry / त्रिविम रसायन

(i) Optical activity: rotation of **plane polarised light** (from **Nicol prism**), measured by **polarimeter**. Clockwise = **dextrorotatory (d, +)**; anticlockwise = **laevorotatory (l, –)**. (+) and (–) forms = **optical isomers**.

ध्रुवित प्रकाश के तल को घुमाने वाले = प्रकाशिक सक्रिय; दाईं ओर = दक्षिणध्रुवण घूर्णक (+), बाईं ओर = वामध्रुवण घूर्णक (–)।

(ii) Chirality: Pasteur (1848) — mirror-image crystals. **Van't Hoff & Le Bel (1874)** — tetrahedral C with 4 different groups → mirror image **not superimposable** → **asymmetric carbon / stereocentre**. Objects non-superimposable on mirror image (like hands) = **chiral** (optically active); superimposable = **achiral** (inactive).

काइरल: दर्पण प्रतिबिंब पर अध्यारोपित न हो (जैसे हाथ) — प्रकाशिक सक्रिय; अकाइरल: अध्यारोपित — निष्क्रिय। चार भिन्न समूहों वाला कार्बन = असममित कार्बन।



Propan-2-ol — achiral (two CH_3 same):

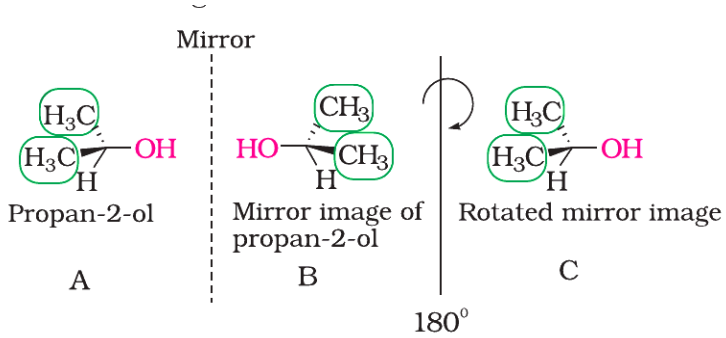
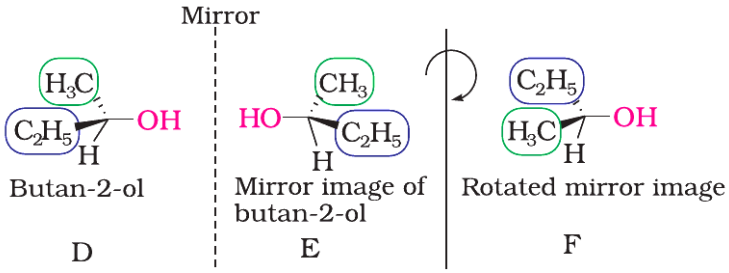


Fig 6.5: *B is mirror image of A; B is rotated by 180° and C is obtained; C is superimposable on A*

Butan-2-ol — chiral (4 different groups):

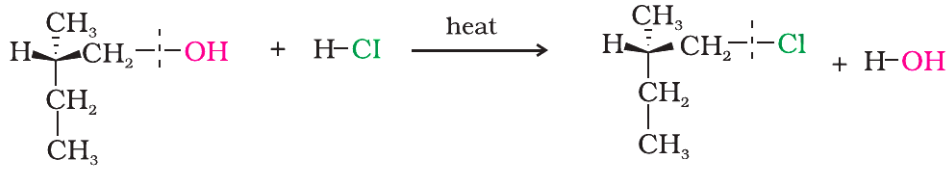


Other chiral examples: 2-chlorobutane, 2,3-dihydroxypropanal, BrClCHI, 2-bromopropanoic acid.

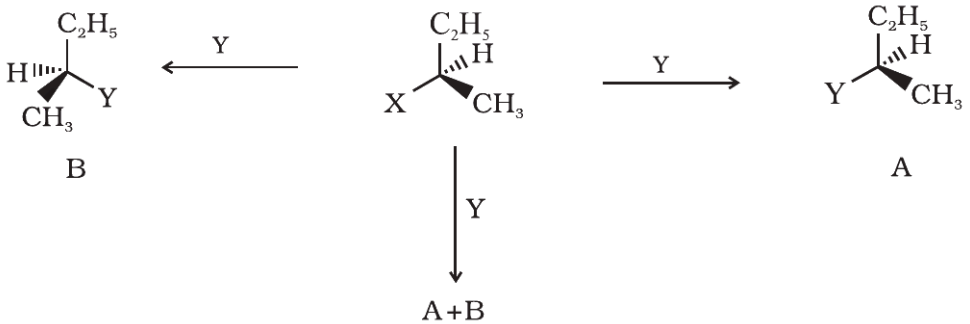
- ***Enantiomers:*** *non-superimposable mirror images; identical physical properties (m.p., b.p., refractive index); differ only in* ***direction*** *of rotation. Sign of rotation is* ***not*** *related to absolute configuration. — प्रतिबिंबरूपी समावयव: भौतिक गुण समान, केवल घूर्णन की दिशा भिन्न।*
- ***Racemic mixture:*** *50:50 enantiomers → **zero rotation**; written **dl** or **(±)**. Converting an enantiomer into racemic mixture = **racemisation**. — रेसेमिक मिश्रण: घूर्णन शून्य।*

Chirality trick: *"**Char alag dost = Chiral (4 different groups)**"; "**Haath = Chiral, Gend (ball) = Achiral**"; "**Racemic = Rasta band (zero rotation)**".*
चार अलग दोस्त = काइरल; हाथ काइरल, गेंद अकाइरल; रेसेमिक = घूर्णन शून्य।

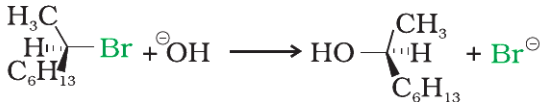
(iii) Retention: *spatial arrangement around stereocentre preserved (no bond to stereocentre broken). E.g. (–)-2-methylbutan-1-ol + HCl → (+)-1-chloro-2-methylbutane — **same configuration, but sign changed**.*
प्रतिधारण: विन्यास वही रहता है, पर घूर्णन का चिह्न बदल सकता है।



(iv) Inversion, retention, racemisation *— when a bond to the stereocentre breaks: only A → retention; only B → inversion; 50:50 → racemisation.*

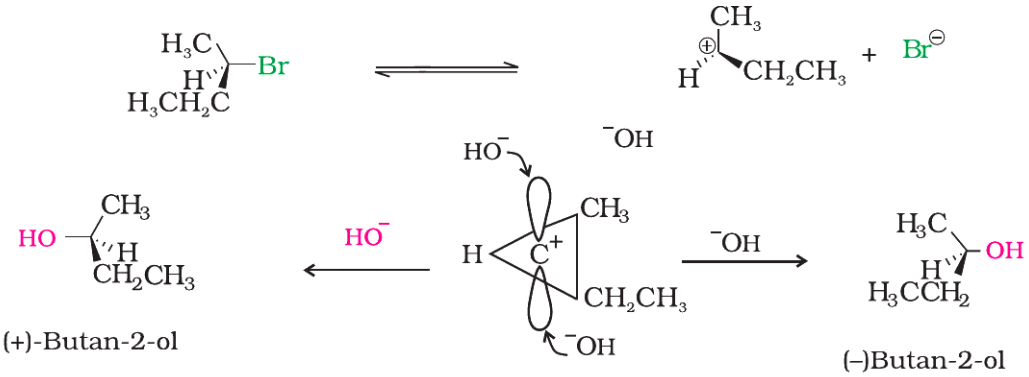


S_N2 → inversion: *Nu attaches opposite to X. (–)-2-bromooctane + NaOH → (+)-octan-2-ol.*



S_N1 → racemisation: *carbocation is* **sp^2, planar (achiral)**; *Nu attacks from* **either face** → *mixture. Optically active 2-bromobutane → (±)-butan-2-ol.*

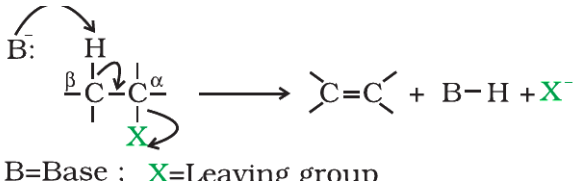
S_N1 में कार्बोधनायन समतलीय — दोनों ओर से आक्रमण → रेसेमिक मिश्रण।



(2) Elimination — dehydrohalogenation / विलोपन

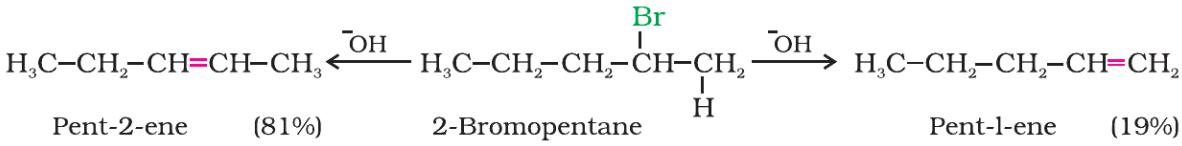
Haloalkane with **β-H + alcoholic KOH**, *heat → alkene. H removed from* **β-carbon**, *X from* **α-carbon** → **β-elimination.**

ऐल्कोहॉली KOH के साथ गरम करने पर β-कार्बन से H और α-कार्बन से X निकलकर ऐल्कीन — β-विलोपन।



Zaitsev (Saytzeff) rule: *the preferred alkene is the one with* **more alkyl groups on the double-bonded carbons** *(more substituted). 2-Bromopentane →* **pent-2-ene (81%)** *+ pent-1-ene (19%).*

ज़ैतसेव नियम: अधिक प्रतिस्थापित ऐल्कीन (द्विबंध वाले कार्बनों पर अधिक ऐल्किल समूह) मुख्य उत्पाद।

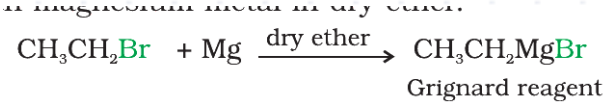


Trick: "**Aqueous KOH → Alcohol (substitution); Alcoholic KOH → Alkene (elimination)**" — "**Paani mein Pratisthapan, Alcohol mein Alkene**".
Zaitsev: "**Zyada substituted = Zaitsev ka favourite**" (poor get poorer — H leaves from the carbon with fewer H).
जलीय KOH = प्रतिस्थापन (ऐल्कोहॉल), ऐल्कोहॉली KOH = विलोपन (ऐल्कीन)।

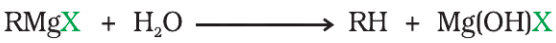
Elimination vs substitution: bulky Nu acts as a base (elimination). 1° → S_N2; 2° → S_N2 or elimination (depends on base strength); 3° → S_N1 or elimination (carbocation stability / more substituted alkene).
भारी नाभिकस्नेही क्षारक बनकर विलोपन कराता है।

(3) Reaction with metals / धातुओं से अभिक्रिया

Grignard reagent (RMgX): R–X + **Mg in dry ether** (Victor Grignard, 1900; Nobel 1912 with Sabatier). C–Mg bond covalent but highly polar ($C^{\delta-}$); Mg–X ionic.
ग्रिन्यार अभिकर्मक: शुष्क ईथर में R–X + Mg; C–Mg बंध सहसंयोजी पर अत्यधिक ध्रुवीय।



Very reactive with **any proton source** (water, alcohol, amine) → hydrocarbon. So **no moisture** — use dry ether. (Also a way to convert RX → RH.)
जल, ऐल्कोहॉल, ऐमीन से भी अभिक्रिया करके हाइड्रोकार्बन — इसलिए नमी बिल्कुल नहीं; शुष्क ईथर।



Wurtz reaction: 2R–X + 2Na (**dry ether**) → R–R (**double** the carbons) + 2NaX.
वुट्ज़ अभिक्रिया: Na + शुष्क ईथर → कार्बन संख्या दोगुनी।

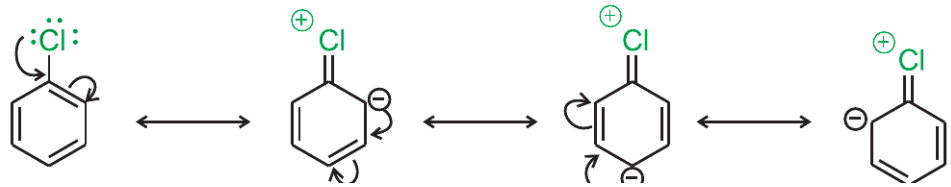


Trick: "**Grignard = Mg (Magnesium = Magic reagent), Paani se Dushmani**"; "**Wurtz = Na, Double karo**".
ग्रिन्यार = Mg, पानी से दुश्मनी; वुट्ज़ = Na, कार्बन दोगुने।

6.7.2 Reactions of Haloarenes / हैलोऐरीन की अभिक्रियाएँ

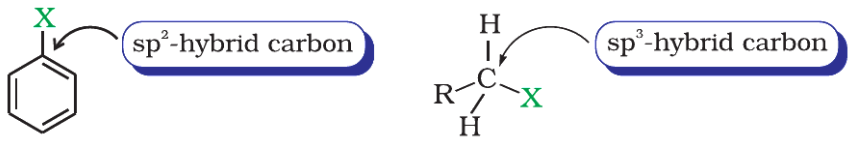
1. Nucleophilic substitution — very difficult. Reasons:

(i) Resonance: lone pair of X conjugates with ring → C–Cl gets **partial double bond** character → harder to break.
(i) अनुनाद: C–Cl बंध में आंशिक द्विबंध गुण, तोड़ना कठिन।



(ii) Hybridisation: C is **sp^2** (more s-character, more electronegative) → holds bond pair tighter → C–Cl shorter (**169 pm** vs 177 pm in haloalkane).

(ii) sp^2 कार्बन अधिक विद्युतऋणी — बंध छोटा (169 pm) और मज़बूत।

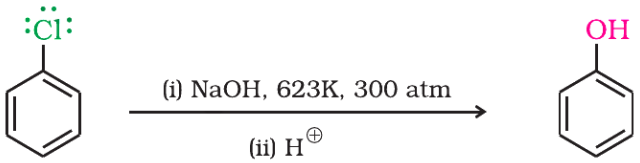


(iii) Phenyl cation unstable (no resonance) → S_N1 ruled out. **(iv) Repulsion** between electron-rich Nu and electron-rich ring.

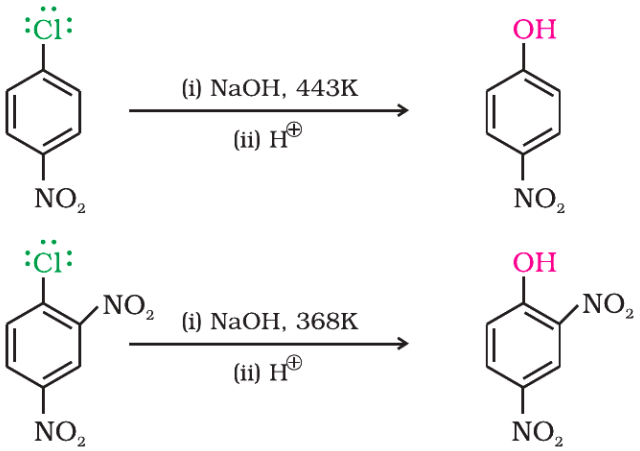
(iii) फ़ेनिल धनायन अस्थायी — S_N1 नहीं; (iv) इलेक्ट्रॉन-धनी नाभिकस्नेही व इलेक्ट्रॉन-धनी वलय में प्रतिकर्षण।

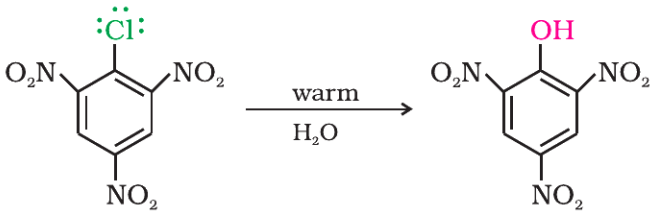
4 reasons trick — "RHIR" → "Ram Hamesha Inko Rokta": **R**esonance, **H**ybridisation (sp^2), **I**nstability of phenyl cation, **R**epulsion.
"राम हमेशा इनको रोकता" — अनुनाद, संकरण, अस्थायी फ़ेनिल धनायन, प्रतिकर्षण।

Replacement by –OH (Dow's process): chlorobenzene + NaOH, **623 K, 300 atm** → phenol.



$-NO_2$ at o/p increases reactivity (no effect at meta). More NO_2 → milder conditions:

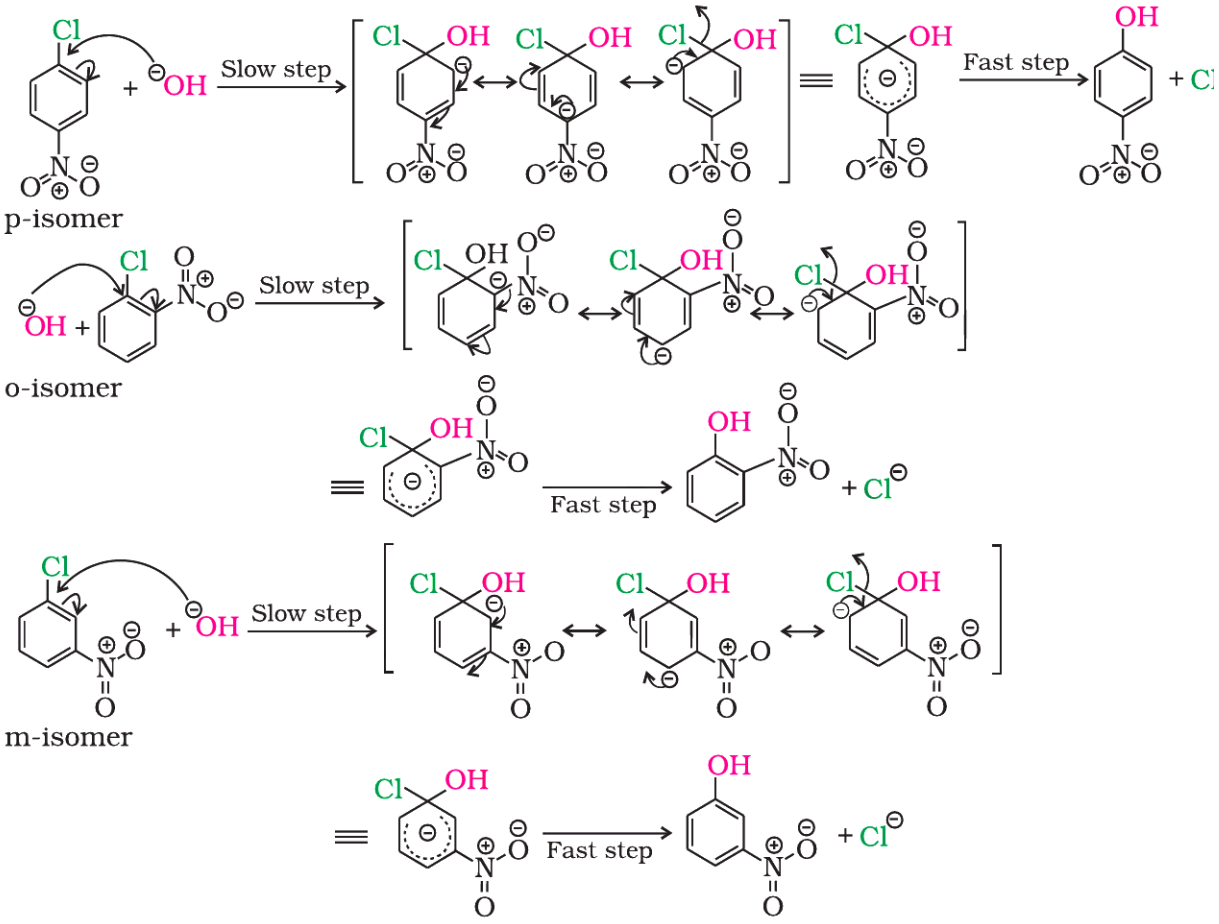




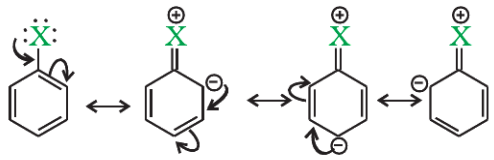
Compound	Condition
Chlorobenzene	NaOH, **623 K, 300 atm**
4-Nitrochlorobenzene	NaOH, **443 K**
2,4-Dinitrochlorobenzene	NaOH, **368 K**
2,4,6-Trinitrochlorobenzene	**Warm water**

Trick: "**Jitne Nitro (o/p par), utni Aasaani**" — 623 → 443 → 368 K → warm water.
जितने नाइट्रो (ऑर्थो/पैरा पर), उतनी आसानी।

Mechanism: Nu adds → carbanion (slow) → Cl^- leaves (fast). With NO_2 at o/p, the negative charge reaches the C bearing NO_2 and is stabilised; at meta it never does.
ऑर्थो/पैरा पर NO_2 ऋणावेश को अनुनाद से स्थायी करता है; मेटा पर ऋणावेश NO_2 वाले कार्बन तक नहीं पहुँचता।

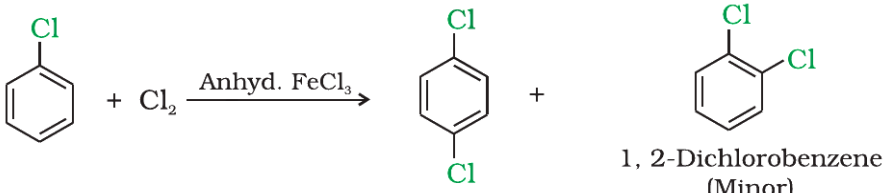


2. Electrophilic substitution: halogen is **slightly deactivating** (−I effect) but **o/p-directing** (resonance raises electron density at o/p). Reactions are slower than benzene.
हैलोजन: −I प्रभाव से हल्का निष्क्रियक, पर अनुनाद से ऑर्थो/पैरा निर्देशक।



I II III IV

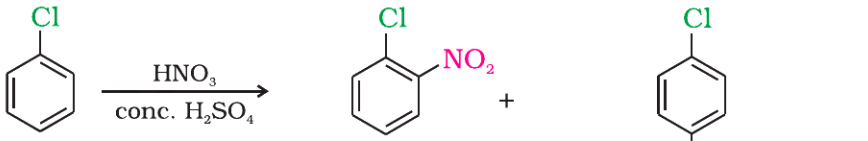
(i) Halogenation (Cl_2, anhyd. $FeCl_3$) → 1,4-dichlorobenzene (major) + 1,2 (minor)



1, 4-Dichlorobenzene

1, 2-Dichlorobenzene (Minor)

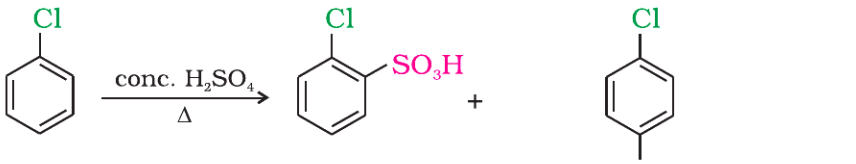
(ii) Nitration (conc. HNO_3 + H_2SO_4) → 1-chloro-4-nitrobenzene (major)



1-Chloro-2-nitrobenzene (Minor)

1-Chloro-4-nitrobenzene

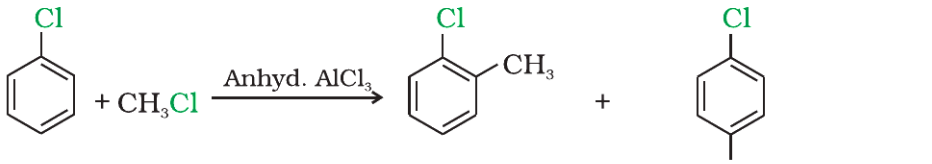
(iii) Sulphonation (conc. H_2SO_4, Δ) → 4-chlorobenzenesulphonic acid (major)



2-Chlorobenzenesulfonic acid (Minor)

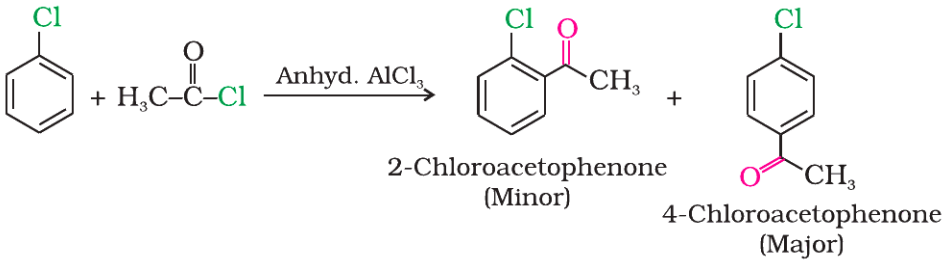
4-Chlorobenzenesulfonic acid (Major)

(iv) Friedel–Crafts (CH_3Cl or CH_3COCl, anhyd. $AlCl_3$) → para major



1-Chloro-2-methylbenzene (Minor)

1-Chloro-4-methylbenzene (Major)

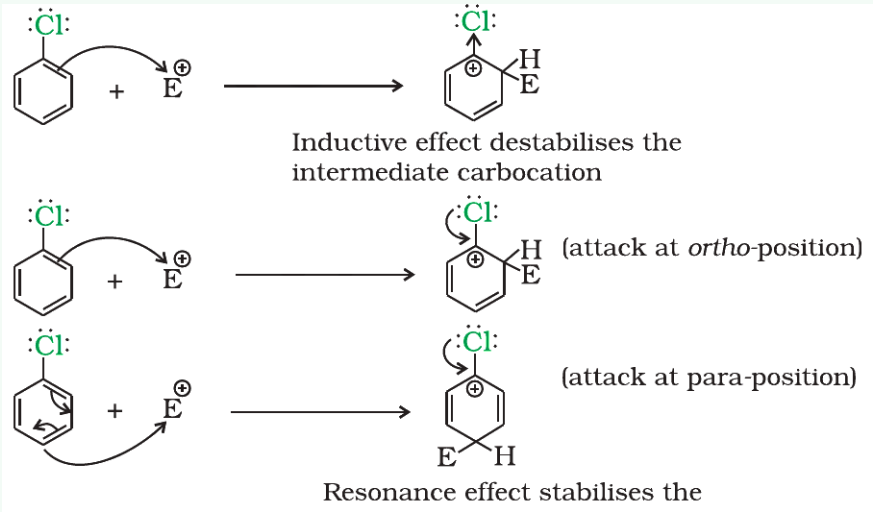


2-Chloroacetophenone (Minor)

4-Chloroacetophenone (Major)

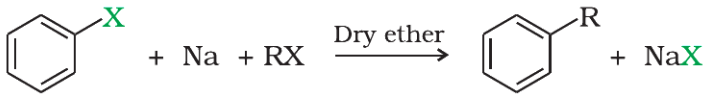
Trick: "**Halogen = Ulta insaan — I-effect se rokta (deactivate), Resonance se rasta dikhata (o/p)**". *In every case* **para = major** *(less crowded).*
हैलोजन: −I से रोकता, अनुनाद से ऑर्थो/पैरा का रास्ता दिखाता; हमेशा पैरा मुख्य।

Example 6.9: *Cl withdraws by −I (destabilises carbocation → net deactivation) but donates by resonance, stabilising the carbocation for o/p attack →* **reactivity controlled by −I, orientation by resonance.**

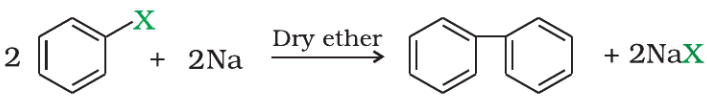


3. Reaction with metals:

Wurtz–Fittig: *alkyl halide + aryl halide + Na (dry ether) →* **alkylarene.**



Fittig: *2 aryl halides + 2Na (dry ether) →* **diphenyl.**



Diphenyl

Trick: "**Wurtz = R + R; Fittig = Ar + Ar; Wurtz–Fittig = R + Ar**" — *all with* **Na + dry ether.**
वुट्ज़ = ऐल्किल+ऐल्किल; फ़िटिग = ऐरिल+ऐरिल; वुट्ज़-फ़िटिग = ऐल्किल+ऐरिल।

6.8 Polyhalogen Compounds (बहुहैलोजन यौगिक)

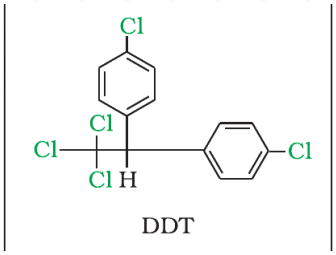
Compound	Uses	Harmful effects
Dichloromethane (CH_2Cl_2)	Solvent, paint remover, aerosol propellant, drug manufacture, metal cleaning	Harms CNS; impaired hearing/vision; dizziness, nausea, numbness; burns skin & cornea
Chloroform ($CHCl_3$)	Solvent (fats, alkaloids, I_2); mainly to make **freon R-22**; once an anaesthetic	Depresses CNS; 900 ppm → dizziness, fatigue, headache; liver & kidney damage
Iodoform (CHI_3)	Earlier antiseptic (due to **free iodine** released)	Objectionable smell → replaced
CCl_4	Refrigerants, aerosol propellants, CFC feedstock, solvent; earlier fire extinguisher, spot remover	Liver cancer (evidence), dizziness, nausea, nerve damage, irregular heartbeat; **depletes ozone**
Freons (CFCs, e.g. Freon-12 = CCl_2F_2)	Aerosol propellants, refrigeration, AC; stable, non-toxic, easily liquefied; made by **Swarts reaction** from CCl_4	Reach stratosphere → radical chain reactions → **ozone depletion**
DDT (p,p'-dichlorodiphenyltrichloroethane)	First chlorinated insecticide; against malaria mosquito, typhus lice (Paul Müller, Nobel 1948)	Insect resistance; toxic to fish; **stable, fat-soluble → stored in fatty tissue**; banned in USA 1973

Chloroform storage: slowly oxidised by air in light to **phosgene ($COCl_2$)**, extremely poisonous → stored in **closed, dark-coloured bottles, completely filled**.

क्लोरोफ़ॉर्म प्रकाश व वायु में विषैली फ़ॉस्जीन गैस बनाता है — इसलिए गहरे रंग की, पूरी भरी, बंद बोतलों में रखते हैं।

$$2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl$$

Phosgene



DDT

Ozone depletion → more UV → skin cancer, eye diseases, immune disruption. — ओज़ोन क्षय से त्वचा कैंसर, नेत्र रोग।

Trick: "**Chloroform + Light + Air = Phosgene (Poison) → Dark bottle, full bhari**"; "**Iodoform ka kaam Iodine karta**"; "**CCl_4 & Freon = Ozone ke dushman**"; "**DDT = Charbi mein jama (fat-soluble)**".

Master Sheet — Named Reactions (सारांश)

Reaction	Reactants → Product	Reagent / condition
Alcohol → RX	ROH → RCl	$SOCl_2$ (best), PCl_5, HCl/$ZnCl_2$
Finkelstein	RCl/RBr → RI	NaI, dry acetone
Swarts	RCl/RBr → RF	AgF, Hg_2F_2, CoF_2, SbF_3
Sandmeyer	ArN_2^+ → ArCl/ArBr	Cu_2Cl_2/Cu_2Br_2
Markovnikov addition	Alkene + HX → RX	H to C with more H
β-Elimination (Zaitsev)	RX → alkene	Alcoholic KOH, heat
Grignard	RX → RMgX	Mg, dry ether
Wurtz	2RX → R–R	Na, dry ether
Wurtz–Fittig	ArX + RX → Ar–R	Na, dry ether
Fittig	2ArX → Ar–Ar	Na, dry ether
Dow's process	C_6H_5Cl → C_6H_5OH	NaOH, 623 K, 300 atm; H^+
KCN / AgCN	RX → RCN / RNC	Ambident CN^-
KNO_2 / $AgNO_2$	RX → R–ONO / R–NO_2	Ambident NO_2^-

Quick Revision / त्वरित दोहराव

- b.p.: RI > RBr > RCl > RF; branching ↓ b.p.; para-dihalobenzene highest m.p. — क्वथनांक/गलनांक।
- S_N2: CH_3 > 1° > 2° > 3°, inversion; S_N1: 3° > 2° > 1°, racemisation. — क्रियाविधि।
- Leaving group: I^- > Br^- > Cl^- >> F^-. — अवशिष्ट समूह।
- Aq. KOH → substitution; alc. KOH → elimination. — जलीय बनाम ऐल्कोहॉली KOH।
- Haloarenes: inert to S_N (resonance, sp^2, phenyl cation, repulsion); o/p-NO_2 activates; ring X deactivating but o/p-directing. — हैलोऐरीन। **All the best! शुभकामनाएँ!**