

Haloalkanes and Haloarenes: one-page cheat sheet

NEET Chemistry · Unit 16 · Organic Chemistry

1 · Classification & C-X bond

sp^3 C-X alkyl, **allylic** (next to C=C), **benzylic** (next to ring)

sp^2 C-X **vinyllic** and **aryl** halides

Bond	Length (pm)	Enthalpy (kJ)
C-F	139	452
C-Cl	178	351
C-Br	193	293
C-I	214	234

Dipole $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$

b.p. $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$; branching lowers b.p.; para isomer: highest m.p.

2 · Preparation

SOCl₂ best lab route; SO₂ and HCl escape

PCl₅ / PBr₃ give POCl₃ / H₃PO₃ as by-products

Lucas HCl / ZnCl₂: 3° fastest

Finkelstein RCl or RBr + NaI (dry acetone) → RI

Swarts RBr + AgF (or Hg₂F₂) → RF

Sandmeyer $\text{ArN}_2^+ + \text{Cu}_2\text{X}_2 \rightarrow \text{ArX}$

Arl $\text{ArN}_2^+ + \text{KI}$, no copper needed

Balz-Schiemann $\text{ArN}_2^+ \text{BF}_4^- (\Delta) \rightarrow \text{ArF}$

3 · S_N1 vs S_N2

	S _N 2	S _N 1
Rate	$k[\text{RX}][\text{Nu}]$	$k[\text{RX}]$
Steps	one, concerted	two, via cation
Substrate	$\text{CH}_3 > 1^\circ > 2^\circ > 3^\circ$	$3^\circ > \text{benzyl, allyl} > 2^\circ$
Product	inversion	racemisation
Solvent	polar aprotic	polar protic
Nucleophile	strong	weak is enough

Leaving group $\text{I}^- > \text{Br}^- > \text{Cl}^- \gg \text{F}^-$ (both)

4 · Stereochemistry

Chiral four different groups; mirror image not superimposable

Enantiomers equal and opposite rotation; same m.p. and b.p.

Racemic 1:1 mixture, net rotation zero

Meso chiral centres plus a mirror plane; inactive

Diastereomers not mirror images; different properties

5 · Elimination & metals

alc. KOH β-elimination: **Saytzeff** (more substituted alkene)

aq. KOH substitution gives the alcohol

Grignard $\text{RX} + \text{Mg}$ (dry ether) → RMgX; water gives RH

Wurtz-Fittig $\text{ArX} + \text{RX} + 2\text{Na} \rightarrow \text{ArR}$

Ambident KCN gives RCN; **AgCN** gives RNC (isocyanide); AgNO₂ gives RNO₂

6 · Haloarenes

Why unreactive resonance (C-Cl 169 pm), sp^2 carbon, unstable phenyl cation, π repulsion

Dow process $\text{PhCl} + \text{aq. NaOH}$, 623 K, 300 atm

Substrate	NaOH temp.
4-nitrochlorobenzene	443 K
2,4-dinitrochlorobenzene	368 K
2,4,6-trinitrochlorobenzene	warm water

EAS weakly deactivating (−I), ortho/para-directing (+M)

7 · Polyhalogenes

CHCl₃ air and light give **phosgene** COCl₂; store in full, dark bottles with 1% ethanol

CHI₃ yellow antiseptic

CCl₄ fire extinguisher; phosgene with hot steam

Freon-12 CCl₂F₂ (Swarts); Cl radicals deplete ozone

DDT chlorobenzene + chloral; persistent, biomagnified

8 · Reagents on RX

Reagent	Product
aq. KOH	ROH
alc. KOH	alkene
KCN / AgCN	RCN / RNC
KNO ₂ / AgNO ₂	R-ONO / R-NO ₂
NH ₃	RNH ₂
Na, dry ether	R-R
Mg, dry ether	RMgX

Seen in NEET 2024

Fastest S_N1: bromobenzene, 1-bromo-1-phenylethane, (bromomethyl)cyclohexane, bromocyclohexane.

1-Bromo-1-phenylethane: it gives a resonance-stabilised benzylic cation.

Seen in NEET 2025, 2021

1-Iodobutane is faster in S_N2 than 1-chlorobutane: I[−] is the better leaving group.

Bond enthalpy: $\text{CH}_3\text{F} > \text{CH}_3\text{Cl} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$.

Seen in NEET 2020, 2022, 2023

Aryl halides resist S_N: resonance, sp^2 carbon and phenyl cation instability, **all** together.

Enantiomers are **non-superimposable** mirror images.

$\text{CH}_3\text{CH}=\text{CHCH}(\text{Cl})\text{CH}_2\text{CH}_3$ is an **allylic** halide.

Seen in NEET 2026

Propan-1-ol + PCl₅ gives 1-chloropropane, POCl₃ and HCl.

$\text{C}_2\text{H}_5\text{Cl} + \text{AgCN}$ gives ethyl isocyanide, $\text{C}_2\text{H}_5\text{NC}$.

Six traps to remember

- SOCl₂ is the best route from alcohols: both by-products are gases.
- S_N2 inverts the configuration; S_N1 racemises it.
- Alc. KOH eliminates; aq. KOH substitutes.
- AgCN gives the isocyanide, KCN gives the cyanide.
- Haloarenes resist nucleophiles; ortho/para nitro groups activate them.
- Chloroform is stored in dark, full bottles to avoid phosgene.