FREE EDITION · NOTES + 3 SAMPLE MCQS

CUET · CHEMISTRY · CLASS XII · CODE 306

Haloalkanes and Haloarenes

CUET unit: Haloalkanes and Haloarenes

By **UniDrill** · NCERT-grounded study material

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📌 Snapshot

- Establishes the chemistry of compounds with C–X bonds where X = F, Cl, Br, I, attached either to sp3 carbon (haloalkanes) or sp2 aromatic carbon (haloarenes).
- Builds the framework for nucleophilic substitution (SN1 vs SN2) and elimination (β-elimination, Saytzeff), the most heavily tested mechanistic topic in organic chemistry.
- Introduces stereochemistry of reactions: inversion of configuration in SN2 and racemisation in SN1 via a planar carbocation.
- Covers preparation routes (from alcohols using PX3/PCl5/SOCl2/HX, from hydrocarbons by free-radical halogenation, from alkenes by Markovnikov/anti-Markovnikov addition, Finkelstein and Swarts halogen exchange, and Sandmeyer for haloarenes).
- Closes with industrially important polyhalogen compounds (CH2Cl2, CHCl3, CHI3, CCl4, freons, DDT) and their environmental impact (ozone depletion, persistence).

📖 Detailed Notes

2.1 Core concepts

- Haloalkanes have X on sp3 carbon of an alkyl group (R–X); haloarenes have X on sp2 carbon of an aryl group; classification is by number of halogens (mono/di/tri/poly) and by carbon hybridisation (NCERT §6.1, p. 159–160).
- Monohalides on sp3 carbon are further split into alkyl halides (1°/2°/3° by the carbon bearing X), allylic halides (X on sp3 C adjacent to C=C), and benzylic halides (X on sp3 C attached to an aromatic ring) (NCERT §6.1.2, p. 160).
- Compounds with C(sp2)–X include vinylic halides (X on sp2 C of C=C) and aryl halides (X on sp2 C of an aromatic ring) (NCERT §6.1.3, p. 161).
- Common names use "alkyl halide"; IUPAC names treat them as halo-substituted hydrocarbons; for benzene derivatives mono-substituted names are common = IUPAC, while o-/m-/p- of common system become 1,2-/1,3-/1,4- in IUPAC (NCERT §6.2, p. 161–162).

- Dihalides with both halogens on the same C are gem-dihalides (alkylidene halides in common name); on adjacent C they are vic-dihalides (alkylene dihalides); IUPAC calls them dihaloalkanes (NCERT §6.2, p. 162).
- Because halogen is more electronegative than C, the C–X bond is polar with $\delta+$ on C and $\delta-$ on X; bond length increases C–F < C–Cl < C–Br < C–I (139, 178, 193, 214 pm) while bond enthalpy falls (452, 351, 293, 234 kJ/mol) (NCERT §6.3 and Table 6.2, p. 163–164).
- Haloalkanes from alcohols: HX (3°>2°>1° reactivity, ZnCl2 catalyst needed for 1° and 2° with HCl; tert-alcohols react with conc. HCl at room temp by shaking; HBr 48% constant-boiling; NaI/KI in 95% H3PO4 for R–I); PCl3, PCl5, PBr3, PI3 (red P + Br2/I2 generated in situ); SOCl2 is preferred because by-products SO2 and HCl escape as gases, leaving pure R–Cl (NCERT §6.4.1, p. 164).
- From hydrocarbons: free-radical chlorination/bromination of alkanes gives a mixture of mono- and polyhaloalkanes, hence low single-product yield (NCERT §6.4.2-I, p. 164–165). From alkenes: addition of HX follows Markovnikov's rule (e.g., propene → 2-halopropane as major), and addition of Br2/CCl4 to a C=C gives vic-dibromides — a test for C=C (NCERT §6.4.2-II, p. 165).
- Halogen exchange: Finkelstein — R–Cl/R–Br + NaI in dry acetone → R–I (NaCl/NaBr precipitates, driving equilibrium forward by Le Chatelier); Swarts — R–Cl/R–Br + AgF/Hg2F2/CoF2/SbF3 → R–F (NCERT §6.4.3, p. 165–166).
- Haloarenes from arenes: electrophilic substitution with Cl2/Br2 in presence of Lewis acid (Fe or FeCl3); iodination needs an oxidising agent (HNO3, HIO4) to remove HI; fluorination not feasible due to fluorine's reactivity (NCERT §6.5-i, p. 166).
- Sandmeyer/Gattermann route: aryl primary amine + NaNO2/cold mineral acid → arene-diazonium salt; with CuCl/CuBr (Sandmeyer) replaces –N2+ by –Cl or –Br; with KI (no Cu halide needed) gives Ar–I (NCERT §6.5-ii, p. 166).
- Physical properties: bromides and iodides develop colour on exposure to light; CH3Cl, CH3Br, C2H5Cl and some chlorofluoromethanes are gases; boiling points of haloalkanes > parent alkanes (greater polarity + mass); for same R, b.p. order is RI > RBr > RCl > RF; b.p. falls with branching; para-dihalobenzenes have higher m.p. than o- and m- because symmetry packs better in the crystal lattice; haloalkanes are slightly soluble in water but soluble in organic solvents (NCERT §6.6, p. 167–169).
- Density: bromo-, iodo- and polychloro derivatives are heavier than water; density rises with C count, halogen count and halogen atomic mass (NCERT Table 6.3, p. 169).
- Three classes of reactions of haloalkanes: nucleophilic substitution, elimination, and reaction with metals (NCERT §6.7.1, p. 169).
- Nucleophilic substitution: a nucleophile replaces the halide (the leaving group); common products include alcohols (with OH–/H2O), ethers (R'O–), R–I (Finkelstein), amines (NH3/R'NH2/R'R''NH), nitriles (KCN → R–CN), isocyanides (AgCN → R–NC),

alkyl nitrites (KNO2) vs nitroalkanes (AgNO2), esters (R'COOAg), hydrocarbons (LiAlH4) (NCERT Table 6.4, p. 170).

- Ambident nucleophiles such as CN– and NO2– have two donor sites; KCN (ionic) attacks via C giving R–CN, while AgCN (covalent) attacks via N giving R–NC; KNO2 → R–O–N=O (alkyl nitrite); AgNO2 → R–NO2 (nitroalkane) (NCERT §6.7.1, p. 170–171).
- SN2 mechanism: single-step, bimolecular, second-order kinetics; nucleophile attacks from the side opposite to the leaving group; transition state has C bonded to 5 atoms with the three other groups coplanar; result is inversion of configuration ("umbrella turning inside out"); reactivity order: methyl > 1° > 2° > 3° (steric hindrance by bulky groups slows the back-side attack); Hughes–Ingold proposed it in 1937 (NCERT §6.7.1-1(a), p. 171–173, Fig. 6.2 and 6.3).
- SN1 mechanism: two-step, unimolecular, first-order kinetics; slow ionisation of R–X gives carbocation (step I, rate-determining), then fast nucleophile attack (step II); favoured by polar protic solvents (water, alcohol, acetic acid); reactivity order: 3° > 2° > 1° > methyl, mirroring carbocation stability; allylic and benzylic halides react fast in SN1 because the resulting carbocation is resonance-stabilised; for the same R, reactivity follows R–I > R–Br > R–Cl >> R–F in both mechanisms (NCERT §6.7.1-1(b), p. 173–174).
- Stereochemistry: SN2 of optically active halides gives 100% inversion of configuration (e.g., (–)-2-bromooctane → (+)-octan-2-ol); SN1 gives racemisation because the sp2 planar carbocation is attacked from either face, yielding equal amounts of two enantiomers (e.g., 2-bromobutane → (±)-butan-2-ol) (NCERT §6.7.1-1(c), p. 175–179).
- Optical activity, chirality, enantiomers, racemic mixture: a carbon with 4 different groups is asymmetric (stereocentre); molecules non-superimposable on their mirror image are chiral and optically active; equal-proportion enantiomer mixture (racemic, dl or ±) shows zero net rotation; "racemisation" is the conversion of a single enantiomer into such a 50:50 mixture (NCERT §6.7.1-1(c), p. 175–178).
- β-Elimination: R–X with β-H heated with alcoholic KOH eliminates H from β-C and X from α-C to give an alkene; when two alkenes are possible, the major product follows Saytzeff (Zaitsev) rule — the alkene with the greater number of alkyl groups on the C=C carbons is preferred (e.g., 2-bromopentane → pent-2-ene as major) (NCERT §6.7.1-2, p. 179–180).
- Substitution vs elimination: 1° R–X favours SN2; 2° R–X gives SN2 or elimination based on base/nucleophile; 3° R–X favours SN1 or elimination; bulky nucleophiles act as bases (eliminate), small/strong nucleophiles substitute (NCERT §6.7.1, p. 180).
- Reaction with metals: Grignard reagents (R–MgX) are formed by R–X + Mg in dry ether; C–Mg bond is covalent but highly polar (δ–C–δ+Mg), Mg–X bond is essentially ionic; they react violently with any proton source (water, alcohols, amines) giving the parent hydrocarbon, hence anhydrous conditions are mandatory (NCERT §6.7.1-3, p. 180–181).

- Wurtz reaction: 2 R–X + 2 Na in dry ether → R–R + 2 NaX, giving an alkane with double the carbon count of the halide (NCERT §6.7.1-3, p. 181).
- Haloarenes are poor substrates for nucleophilic substitution because (i) resonance gives C–X partial double-bond character (shorter, stronger bond — 169 pm vs 177 pm in haloalkane), (ii) the C is sp2 (greater s-character, more electronegative, holds electron pair tighter), (iii) any phenyl cation from ionisation is not resonance-stabilised so SN1 is ruled out, (iv) electron-rich arene repels the electron-rich nucleophile (NCERT §6.7.2-1, p. 181–182).
- Chlorobenzene → phenol on heating with aq. NaOH at 623 K and 300 atm; presence of –NO2 at ortho/para to the halogen activates haloarenes toward nucleophilic substitution because the carbanion intermediate is resonance-stabilised by NO2 at o/p (negative charge appears at the C bearing NO2), but not when NO2 is at meta (NCERT §6.7.2-1, p. 182–183).
- Electrophilic substitution on haloarenes: halogen is slightly deactivating yet o,p-directing — the lone pairs of halogen give resonance structures placing negative charge at o/p (more electron density there); –I effect of X net deactivates the ring (so reactions require more drastic conditions); halogenation, nitration, sulphonation, Friedel-Crafts all give predominantly o- and p-products (NCERT §6.7.2-2, p. 183–185).
- Wurtz-Fittig: alkyl halide + aryl halide + Na in dry ether → alkylarene; Fittig: 2 Ar–X + 2 Na in dry ether → Ar–Ar (biphenyl-type) (NCERT §6.7.2-3, p. 186).
- Polyhalogen compounds — uses and hazards: CH2Cl2 is a paint remover, aerosol propellant, drug-manufacturing solvent, metal cleaner; harms central nervous system, burns skin and cornea (NCERT §6.8.1, p. 187). CHCl3 is a solvent for fats/alkaloids/iodine, feedstock for freon R-22, former anaesthetic now replaced because it depresses CNS and damages liver (via phosgene metabolite) and kidneys; air + light slowly oxidises CHCl3 to phosgene (COCl2) so it is stored in closed dark-coloured bottles completely filled (NCERT §6.8.2, p. 187). CHI3 (iodoform) — antiseptic action is due to free iodine liberated, not iodoform itself; objectionable smell led to its replacement (NCERT §6.8.3, p. 187).
- CCl4 is used for refrigerants, propellants, CFC synthesis, pharma, cleaning, formerly a fire-extinguisher; causes dizziness, nausea, possible liver cancer, irregular heartbeat; in the atmosphere it depletes the ozone layer, raising UV exposure and skin cancer risk (NCERT §6.8.4, p. 187–188). Freons are chlorofluorocarbons of methane/ethane, stable/non-toxic/non-corrosive/easily liquefiable gases; Freon 12 (CCl2F2) is made from CCl4 by Swarts reaction; used as propellants and refrigerants; in stratosphere they trigger radical chain reactions that destroy ozone (NCERT §6.8.5, p. 188). DDT (p,p'-dichlorodiphenyltrichloroethane) was the first chlorinated organic insecticide; Paul Muller (Nobel 1948) showed its insecticidal action; effective vs malaria mosquitoes and typhus lice, but insects developed resistance, it is toxic to fish, fat-soluble, not metabolised so it bioaccumulates; banned in the USA in 1973 (NCERT §6.8.6, p. 188).

2.2 Definitions to memorise

Term	Definition	Page
Haloalkane	A halogen-substituted aliphatic hydrocarbon where X is bonded to an sp3 C of an alkyl group	159
Haloarene	A halogen-substituted aromatic hydrocarbon where X is bonded to an sp2 C of an aryl group	159
Allylic halide	Halogen on sp3 carbon adjacent (allylic) to a C=C double bond	160
Benzylic halide	Halogen on sp3 carbon attached to an aromatic ring	160
Vinylic halide	Halogen on the sp2 carbon of a C=C double bond	161
gem-dihalide	Both halogens on the same carbon (alkylidene halide)	162
vic-dihalide	Halogens on adjacent carbons (alkylene dihalide)	162
Finkelstein reaction	R–Cl/R–Br + NaI in dry acetone → R–I (NaCl/NaBr precipitates)	165
Swarts reaction	R–Cl/R–Br + AgF/Hg2F2/CoF2/SbF3 → R–F	166
Sandmeyer reaction	Ar–N2+X– + CuCl/CuBr → Ar–Cl/Ar–Br	166
Markovnikov's rule	In HX addition to alkene, H attaches to the C with more H	165
Saytzeff (Zaitsev) rule	In dehydrohalogenation, major alkene has more alkyl groups on C=C	180
SN1	Unimolecular, two-step, first-order, via carbocation, racemisation	173
SN2	Bimolecular, single-step, second-order, back-side attack, inversion	171
Inversion of configuration	Spatial arrangement at the stereocentre flips to the mirror image	172
Racemisation	Conversion of a single enantiomer into a 50:50 (±) mixture	178
Ambident nucleophile	Nucleophile with two donor sites (e.g., CN–, NO2–)	170
Grignard reagent	R–MgX prepared from R–X + Mg in dry ether	180
Wurtz reaction	2 R–X + 2 Na in dry ether → R–R + 2 NaX	181
Wurtz-Fittig	R–X + Ar–X + 2 Na (dry ether) → R–Ar	186
Fittig	2 Ar–X + 2 Na (dry ether) → Ar–Ar	186
Freon 12	CCl2F2, made from CCl4 by Swarts; ozone-depleting CFC	188
Phosgene	COCl2 — toxic product of CHCl3 + air + light	187

2.3 Diagrams / processes to remember

- Fig. 6.1 (p. 168): Bar/line chart comparing boiling points of alkyl halides, illustrating RI > RBr > RCl > RF.

- Fig. 6.2 (p. 171): SN2 transition state — incoming nucleophile (red) and outgoing halide (green) on opposite sides; three substituents coplanar at TS; result is inversion.
- Fig. 6.3 (p. 173): Steric effects in SN2 — relative rate falls drastically as substitution at α-C increases (methyl > 1° > 2° > 3°).
- Fig. 6.4–6.7 (p. 176–177): Chirality test — superimposability of mirror images; butan-2-ol vs propan-2-ol; enantiomer pair.
- Two-step SN1 mechanism diagram (p. 173) — slow ionisation forming planar sp2 carbocation, then fast nucleophile attack from either face → racemic product.
- Sandmeyer/Gattermann diazonium → Ar–Cl/Ar–Br/Ar–I scheme (p. 166).
- Resonance structures of haloarene (p. 181, 184) — partial double bond character of C–X explains low SN reactivity and o,p-direction in electrophilic substitution.
- Hydrolysis of chlorobenzene to phenol at 623 K, 300 atm (p. 182).

2.4 Common confusions / NTA trap points

- "Vinyl chloride" ($CH_2=CHCl$) is a vinylic halide with X on sp2 C — it is NOT an alkyl/allylic/benzylic halide, and is very unreactive toward nucleophilic substitution.
- KCN gives R–CN (cyanide via C-attack, ionic) while AgCN gives R–NC (isocyanide via N-attack, covalent) — NTA flips this pair often; same trap with KNO_2 (R–O–N=O alkyl nitrite) vs $AgNO_2$ (R–NO_2 nitroalkane).
- SN1 reactivity order is 3° > 2° > 1° (carbocation stability), but SN2 is exactly the reverse — 1° > 2° > 3° (steric). For the same R, both follow R–I > R–Br > R–Cl >> R–F.
- SN2 gives inversion, SN1 gives racemisation — not "retention". Retention occurs only when no bond to the stereocentre is broken.
- Halogen on benzene ring is deactivating (–I dominates over +R), yet still o,p-directing (because +R places higher electron density only at o,p). Reactivity controlled by –I, orientation by +R.
- Saytzeff's rule applies to elimination products (more substituted alkene); Markovnikov's rule applies to HX addition to alkene (H goes to the C with more H). Anti-Markovnikov requires peroxide and HBr only.
- Freon 12 is made from CCl_4 by Swarts reaction (not from $CHCl_3$ directly); $CHCl_3$ is the feedstock for R-22, a different freon.

🎯 Practice MCQs

Q1. Which of the following compounds is a benzylic halide?

A. $C_6H_5–Cl$

B. $CH_2=CH–Cl$

C. $C_6H_5–CH_2–Cl$

D. $CH_2=CH–CH_2–Cl$

Q2. The IUPAC name of $(CH_3)_3C–Br$ is:

A. tert-Butyl bromide

B. 2-Bromo-2-methylpropane

C. 1-Bromo-2-methylpropane

D. Isobutyl bromide

Q3. Carbon–halogen bond length increases in the order:

A. C–F < C–Br < C–Cl < C–I

B. C–F < C–Cl < C–Br < C–I

C. C–I < C–Br < C–Cl < C–F

D. C–Cl < C–F < C–Br < C–I

📊 PYQ Alignment

This chapter is one of the most reliable score-pickers in CUET Chemistry: roughly 8–12 questions across a CUET paper window touch its topics. Recurring formats include reactivity-order MCQs (SN1 vs SN2 across a set of halides), product-prediction (R–X + KCN/AgCN/KOH-alc/$SOCl_2$), assertion–reason on chirality (inversion vs racemisation), match-the-following for named reactions (Finkelstein, Swarts, Sandmeyer, Wurtz-Fittig), and direct factual recall on polyhalogen compounds (freon synthesis, DDT, CCl4 ozone depletion, CHCl3 → phosgene).

CUET 2025 — Actual PYQs from this chapter

Q.19 (CUET 2025) IUPAC name of $[Pt(NH_3)_2Cl_2]$ is:

- A) Diamminedichloroplatinum (II) B) Diammine dichloroplatinum (IV) C) Dichloro diamminoplatinum (IV) D) Dichloro diamminoplatinum (II)

Tests: IUPAC nomenclature haloalkanes Answer: Not in extracted key

Q.22 (CUET 2025) Optically active alkyl halide undergoing SN2 substitution involves:

- A) retention of configuration B) racemic mixture C) inversion of configuration D) formation of carbocation

Tests: SN1/SN2 mechanism Answer: Not in extracted key

Q.48 (CUET 2025) In Williamson synthesis, the alkoxide ion attacks the alkyl halide via which pathway?

- A) SN2 B) SN1 C) Depends on nature of alkoxide ion D) Depends on nature of alkyl halide

Tests: SN1/SN2 mechanism Answer: Not in extracted key

Q.21 (CUET 2025) Match List-I with List-II: (A) Ambident nucleophiles (B) Plane polarized light (C) Superimposable mirror image (D) β-elimination reaction List-II: Symmetrical object, Saytzeff rule, Cyanides and nitrites, Nicol prism.

- A) — B) — C) — D) —

Tests: Stereochemistry/SN/E reactions — concept matching Answer: Not in extracted key

CUET 2024 — Actual PYQs from this chapter

Q.20 (CUET 2024) In reaction: (CH3)3C–O–CH3+HI(CH_3)_3C–O–CH_3 + HI(CH3)3 C–O–CH3 +HI Products formed are CH_3OH and $(CH_3)_3CI$ because: (A) leaving group forms less stable carbocation (B) leaving group forms more stable carbocation (C) reaction follows SN1 (D) reaction follows SN2 Options given.

- A) — B) — C) — D) —

Tests: SN1/SN2 mechanism Answer: Not in extracted key

Q.31 (CUET 2024) For SN2 reaction, the increasing order of reactivity of the following alkyl halides is: (A) $CH_3CH_2CH_2CH_2Br$ (B) $CH_3CH_2CH(Br)CH_3$ (C) $(CH_3)_3CBr$ (D) $(CH_3)_2CHCH_2Br$ Options:

- A) (A) < (B) < (C) < (D) B) (A) < (C) < (B) < (D) C) (B) < (A) < (D) < (C) D) (C) < (B) < (D) < (A) Passage for Questions 32–35 A fuel cell converts chemical energy into electrical energy. In hydrogen fuel cells: Anode reaction: H2+2OH−→2H2O+2e−H_2 + 2OH^- \rightarrow 2H_2O + 2e^-H2 +2OH−→2H2 O+2e− Cathode reaction: O2+2H2O+4e−→4OH−O_2 + 2H_2O + 4e^- \rightarrow 4OH^-O2 +2H2 O+4e−→4OH− 67.2 L of H_2 at STP reacts in 15 minutes.

Tests: SN1/SN2 mechanism **Answer:** Not in extracted key

CUET 2023 — Actual PYQs from this chapter

Q.5 (CUET 2023) The correct IUPAC name of $CH_3–CH(C_2H_5)–CH_2–Br$ is:

- A) 1-Bromo-2-methylbutane B) 1-Bromo-2-ethylpropane C) 1-Bromo-2-ethyl-2-methyl ethane D) 2-Methyl-1-bromobutane

Tests: IUPAC nomenclature haloalkanes **Answer:** Not in extracted key

Q.16 (CUET 2023) The appropriate reagent for the following conversion (benzene → chlorobenzene) is:

- A) SO_2Cl_2 B) N-Chlorosuccinimide C) $Cl_2/FeCl_3$ D) $SOCl_2$

Tests: Haloalkanes/haloarenes **Answer:** Not in extracted key

Q.26 (CUET 2023) Analytically pure $C_5H_{11}Br$ gives two isomeric alkenes on dehydrohalogenation. Ozonolysis gives CH_3CHO, CH_3COCH_3 and HCHO. Alkyl halide is:

- A) 3-Bromopentane B) 2-Bromo-3-methylbutane C) 2-Bromo-2-methylbutane D) 1-Bromo-2,2-dimethylpropane

Tests: Haloalkanes/haloarenes **Answer:** Not in extracted key