Unit 8 · Haloalkanes

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Organic Chemistry (Units 8–17 together): 33 of 75 marks; 2 MCQs, 3 short and 2 long questions
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** short: P, C_3H_7Br, from a secondary alcohol T (C_3H_8O); P to Q, C_6H_{14} with methyls on neighboring carbons (Wurtz, 2,3-dimethylbutane); P to R and S, CH_2O and C_2H_4O (propene by alcoholic KOH, then ozonolysis)
- **MCQ (1 mark)**
  - $C_nH_{2n+1}X$; the polar C–X bond; IUPAC name; 4 isomers of C_4H_9Cl, the chiral one; why b.p. higher than alkanes
  - fastest hydrolyzed; SN1 or SN2 for 1° and 3°; aqueous vs alcoholic KOH; Saytzeff product of 2-bromobutane; R–I > R–Br > R–Cl
  - reducing agent; Wurtz (ethyl bromide → butane); $CHCl_3$ + Ag powder → ethyne
- **Short (5 marks, in parts)**
  - C–X bond polarity; isomers of C_4H_9Cl, $C_5H_{11}Cl$; 1°, 2°, 3°; preparations with reagents; b.p. factors
  - SN1 vs SN2 (mechanisms, rate laws, stereochemistry); SN2 order of CH_3Cl, C_2H_5Cl, $(CH_3)_2CHCl$; chloroethane with aq. KOH, KCN, AgCN, NH_3, $AgNO_2$, KNO_2
  - Saytzeff; Markovnikov and the peroxide effect; Wurtz and dry ether; chloroform: why not an anesthetic now, its storage, its reactions
- **Long (8 marks)**: bromoethane with aq. NaOH (SN2, test for Br^-); alcohol X → Y (Lucas) → Z (alc. KOH) → ozonolysis; 2-bromopropane with aq. and alc. KOH, Baeyer's test; chloroform from ethanol and bleaching powder; conversions

Key terms

Haloalkane (alkyl halide): halogen on an sp^3 carbon, R–X, $C_nH_{2n+1}X$; **haloarene**: on an aromatic ring.

Vicinal dihalide: X on neighboring carbons ($BrCH_2CH_2Br$); **geminal**: both on one carbon (CH_3CHBr_2, CH_2Cl_2).

1°, 2°, 3° haloalkane: X on a carbon joined to one, two, three other carbons.

Chiral carbon: four different groups; **enantiomers**: non-superimposable mirror images.

Nucleophile: gives a lone pair to a $\delta+$ carbon (OH^-, CN^-, RO^-, NH_3); **leaving group**: X^-.

SN1: two steps through a carbocation, rate = k[RX]; **SN2**: one step, backside attack, rate = k[RX][Nu^-].

Racemization: both enantiomers equally (SN1); **Walden inversion**: configuration turned inside out (SN2).

Ambident nucleophile: can bond through two atoms: CN^- (C or N), NO_2^- (N or O).

Dehydrohalogenation: loss of HX from α and β carbons, giving an alkene (β-elimination).

Saytzeff's rule: the more substituted alkene (fewer H on the double bond) is the major product.

Markovnikov's rule: H goes to the carbon of C=C that has more H; **Kharasch effect**: with peroxide, HBr adds the other way.

Grignard reagent: R–Mg–X, carbon $\delta-$, made in dry ether.

Haloform reaction: CH_3–C=O (or $CH_3CH(OH)$–) with X_2 and alkali gives CHX_3.

C–X bond, classes, names (8.1–8.2)

- C–X polar, C $\delta+$: electronegativity F 3.98, Cl 3.16, Br 2.96, I 2.66 against C 2.55
- bond enthalpy C–F 452, C–Cl 351, C–Br 293, C–I 234 kJ/mol; length 139 → 214 pm
- reactivity **R–I > R–Br > R–Cl > R–F**: the weakest bond breaks first, not the most polar
- C_4H_9Cl: 1-chlorobutane, 2-chlorobutane (chiral), 1-chloro-2-methylpropane, 2-chloro-2-methylpropane; chain and position isomers
- common name: alkyl + halide, two words; IUPAC: prefix, one word; lowest numbers; alphabetical (bromo, chloro, methyl)

- $CHCl_3$ **trichloromethane** (no numbers); $(CH_3)_3CCl$ 2-chloro-2-methylpropane, *tert*-butyl chloride; $(CH_3)_2CHBr$ 2-bromopropane

Preparation (8.3)

From	Reagent	Product, note
alkane	Cl_2 or Br_2, light	mixture: $CH_3Cl \rightarrow CH_2Cl_2 \rightarrow CHCl_3 \rightarrow CCl_4$
alkane	I_2 + HIO_3 (or HgO)	removes HI, which reverses it
alkene	HX (HI > HBr > HCl)	Markovnikov: propene → 2-bromopropane
alkene	HBr + peroxide	anti-Markovnikov: 1-bromopropane
alcohol	conc. HCl + anhyd. $ZnCl_2$ (Lucas)	3° at once, 2° in ~5 min, 1° only hot
alcohol	NaBr + conc. H_2SO_4	HBr made in the flask
alcohol	PCl_3, PBr_3 ($P + I_2$)	$3ROH + PX_3 \rightarrow 3RX + H_3PO_3$
alcohol	PCl_5 (cold)	$RCl + POCl_3 + HCl$
alcohol	$SOCl_2$, pyridine	$RCl + SO_2\uparrow + HCl\uparrow$: purest

- peroxide effect only with HBr: H–Cl too strong, I atoms too unreactive

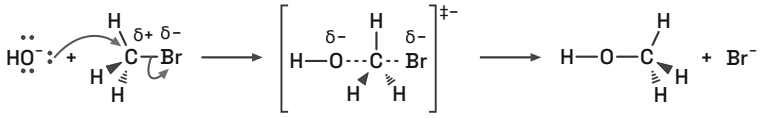
Physical properties (8.4)

- CH_3Cl, CH_3Br, C_2H_5Cl gases; b.p. well above alkanes (dipole + London): bromoethane 38 °C, ethane −89 °C
- b.p. RF < RCl < RBr < RI; rises with chain (CH_3Cl −24, C_2H_5Cl 12, C_3H_7Cl 47, C_4H_9Cl 78 °C)
- branching lowers b.p.: C_4H_9Cl isomers 78, 69, 68, 51 °C (2-chloro-2-methylpropane lowest)
- density: bromo-, iodo- and polyhalo- denser than water (CH_3I 2.28, $CHCl_3$ 1.48); falls up a series as b.p. rises
- insoluble in water (can't H-bond with it); soluble in organic solvents

Substitution: SN1 and SN2 (8.5)

	SN1	SN2
steps	two: ionize (slow), then attack	one, concerted
intermediate	flat carbocation	transition state only
rate	k[RX], first order	$k[RX][Nu^-]$, second order
reactivity	3° > 2° > 1° > CH_3	CH_3 > 1° > 2° > 3°
why	carbocation stability (+I)	steric hindrance
product	racemic (mostly)	inverted
solvent	polar protic (water)	polar aprotic (acetone)

- $(CH_3)_3CBr + H_2O$: SN1, rate unchanged by $[OH^-]$; $CH_3Br + OH^-$: SN2; CH_3Br ~30× faster than C_2H_5Br
- (R)-2-bromobutane → (S)-butan-2-ol by SN2; 3-bromo-3-methylhexane → racemic alcohol by SN1



SN2: OH^- attacks from the back, Br^- leaves, the carbon turns inside out.

Products from R–X (8.6)

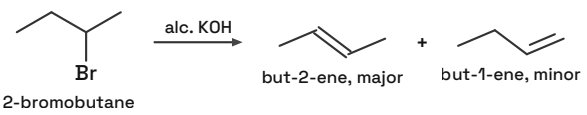
Reagent	Product
aq. KOH, or moist Ag_2O	alcohol R–OH
alc. KCN	nitrile R–C≡N (one C more)
AgCN	isocyanide R–N≡C
NH_3 (alc., sealed tube)	1°, 2°, 3° amines, $R_4N^+X^-$
R′ONa (Williamson)	ether R–O–R′
Na_2S	thioether R–S–R (2RX)
$AgNO_2$	nitroalkane R–NO_2
KNO_2	alkyl nitrite R–O–N=O

- KCN ionic: free CN^- bonds through C; AgCN covalent Ag–C: N attacks; $AgNO_2$ through N, KNO_2 through O
- nitrile: conc. HCl → amide; $RCN + 2\,H_2O + HCl \longrightarrow RCOOH + NH_4Cl$; $LiAlH_4$ → RCH_2NH_2 (propanenitrile → propan-1-amine)
- excess NH_3 for the 1° amine; excess RX for the quaternary salt
- $C_2H_5Br + CH_3ONa$ → methoxyethane; + C_2H_5ONa → ethoxyethane

Elimination, reduction, Wurtz, Grignard (8.7)

- **alcoholic** KOH → alkene: 1-bromopropane → $CH_3CH{=}CH_2 + KBr + H_2O$; **aqueous** KOH → alcohol
- E2 one step (strong base); E1 via carbocation (3°, weak base)

- 2-bromobutane → but-2-ene (~80%) + but-1-ene (~20%); 2-bromo-2-methylbutane → 2-methylbut-2-ene
- reduction: Zn/HCl, Na/C_2H_5OH, $LiAlH_4$ or H_2/Ni: R–X → R–H (bromoethane → ethane)
- **Wurtz**: $2\,RX + 2\,Na \longrightarrow R{-}R + 2\,NaX$ in dry ether; CH_3Br → ethane, C_2H_5I → butane; symmetrical only (mixed RX give three alkanes); dry: Na + water → H_2
- model paper: 2-bromopropane + Na → $(CH_3)_2CH{-}CH(CH_3)_2$, 2,3-dimethylbutane; P from propan-2-ol + PBr_3; propene + O_3, Zn/H_2O → HCHO + CH_3CHO
- **Grignard**: RX + Mg ⟶ RMgX in dry ether; with HCHO → 1° alcohol, RCHO → 2°, ketone → 3°, then H_2O (Mg(OH)X)
- HCHO + CH_3MgBr → ethanol; CH_3CHO → propan-2-ol; propanone → 2-methylpropan-2-ol
- RX + 2 Li ⟶ RLi + LiX: even more reactive



2-Bromobutane + alcoholic KOH: mostly but-2-ene (Saytzeff).

Chloroform and iodoform (8.8–8.9)

- **preparation** (bleaching powder: Cl_2 oxidizes, chlorinates; $Ca(OH)_2$ hydrolyzes)
  - ethanol: $CH_3CH_2OH + Cl_2 \longrightarrow CH_3CHO + 2\,HCl$; $CH_3CHO + 3\,Cl_2 \longrightarrow CCl_3CHO + 3\,HCl$; $2\,CCl_3CHO + Ca(OH)_2 \longrightarrow 2\,CHCl_3 + (HCOO)_2Ca$
  - acetone: $CH_3COCH_3 + 3\,Cl_2 \longrightarrow CCl_3COCH_3 + 3\,HCl$; with $Ca(OH)_2$ → $CHCl_3$ + calcium ethanoate
  - purify: separating funnel, dil. NaOH, water, anhyd. $CaCl_2$, redistil at 61 °C
- colorless, sweet smell, b.p. 61 °C, 1.48 g/mL; old anesthetic, dropped: harms the liver, stops the heart
- light + air: $2\,CHCl_3 + O_2 \longrightarrow 2\,COCl_2 + 2\,HCl$ (phosgene): brown bottles, full, ~1% ethanol ($COCl_2 + 2\,C_2H_5OH \longrightarrow (C_2H_5O)_2CO + 2\,HCl$)

Reagent	Product
Zn/HCl; Zn/H_2O	CH_2Cl_2; CH_4
Ag powder, heat	$2\,CHCl_3 + 6\,Ag \longrightarrow HC{\equiv}CH + 6\,AgCl$
conc. HNO_3	chloropicrin CCl_3NO_2 (tear gas)
propanone + KOH	chloretone (hypnotic)
aq. KOH	$CHCl_3 + 4\,KOH \longrightarrow HCOOK + 3\,KCl + 2\,H_2O$
RNH_2 + alc. KOH	isocyanide R–NC, foul smell (1° amines only)
phenol + NaOH, 70 °C	salicylaldehyde (Reimer–Tiemann)

- **iodoform** CHI_3: yellow, m.p. 119 °C, antiseptic smell; from CH_3CO– or $CH_3CH(OH)$– with I_2 + NaOH
- iodoform test: ethanol, ethanal, propanone, propan-2-ol give it; methanol, propanal, propan-1-ol don't

COMMON MISTAKES

✗ CH_2Cl_2 is a vicinal dihalide
✓ geminal (both Cl on one carbon).

✗ $CHCl_3$ is methyl chloride, 1,1,1-trichloromethane
✓ trichloromethane; CH_3Cl is methyl chloride.

✗ the halogen is attached as a nucleophile
✓ it is the leaving group.

✗ chloroethane + KOH gives KBr
✓ KCl: the halide comes from the haloalkane.

✗ carbylamine with aqueous alkali
✓ alcoholic KOH.

✗ density rises up a series with b.p.
✓ it falls.

✗ Grignard + water gives $Mg^{2+} + X^-$
✓ Mg(OH)X.

✗ aqueous and alcoholic KOH do the same
✓ substitution vs elimination.