Unit 10 · Alcohols

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: the isomeric alcohols of C_3H_8O with IUPAC names; tell them apart by Victor Meyer's method; long: a primary alcohol of molar mass 46 (ethanol) with I_2 and NaOH (iodoform), with ethanoic acid and conc. H_2SO_4 (an ester), with conc. H_2SO_4 alone; telling it from methanol
- **MCQ (1 mark)**
  - $C_nH_{2^n+1}OH$; IUPAC name; absolute alcohol; b.p. above alkenes, solubility (H-bonds); Lucas to tell 1°, 2°, 3°; $FeCl_3$ (phenols only)
  - ethene → ethanol; iodoform-positive alcohol; zymase; dehydrating agent; which gives a ketone; stopping at the aldehyde; denaturing; esterification; methanol's poison; optical activity
- **Short (5 marks, in parts)**
  - isomers of $C_4H_{10}O$; why lower alcohols are liquids; Victor Meyer's steps; fermentation in Nepal; hydration and hydroboration–oxidation
  - Lucas and $KMnO_4$ tests; complete reactions; why 3° dehydrate most easily; heated copper with 1°, 2°, 3°
- **Long (8 marks)**: identify A ($C_4H_{10}O$) → B (PCl_5) → C (alc. KOH); M (C_3H_8O) → aldehyde N; X ($C_5H_{12}O$, Lucas in 5 min); A → ketone B, iodoform; A (C_2H_6O) with Na

Key terms

Alcohol: –OH on an sp^3 carbon, R–OH; monohydric $C_nH_{2^n+1}OH$; on a ring carbon it is a **phenol**.

Mono-, di-, trihydric: one, two, three –OH, each on its own carbon (ethanol, ethane-1,2-diol, glycerol).

1°, 2°, 3° alcohol: –OH carbon joined to one ($–CH_2OH$), two (>CHOH), three other carbons (no H on it).

α-hydrogen: H on the carbon carrying –OH; needed for oxidation and dehydrogenation.

Fermentation: enzymes of living cells (yeast) break sugars and starch into ethanol and CO_2.

Rectified spirit: 95.6% ethanol, an azeotrope that distillation can't pass.

Absolute alcohol: ≥ 99.5% ethanol, by azeotropic distillation or drying (CaO, molecular sieves).

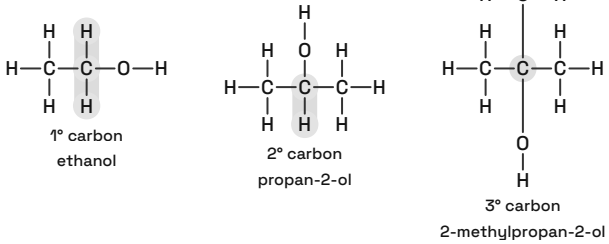
Power alcohol (gasohol): absolute ethanol in petrol (E10, E20); anti-knock, octane above 100.

Denatured alcohol: made unfit to drink (methylated spirit: methanol, pyridine, dye).

Alcoholic beverage: undistilled 4–15% (jaand, beer, wine); distilled 20–50% (raksi, whisky); % by volume.

Esterification: acid + alcohol ⇌ ester + water (conc. H_2SO_4).

Dehydrogenation: H_2 removed over hot copper (300 °C).



1°, 2°, 3°: count the carbons on the C–OH carbon.

Names, isomers (10.1–10.2)

- longest chain with –OH, numbered from the end nearer it, -e → **-ol**; -diol, -triol keep the -e
- propan-1-ol (*n*-propyl), propan-2-ol (isopropyl), butan-2-ol (*sec*-butyl), 2-methylpropan-1-ol (isobutyl), 2-methylpropan-2-ol (*tert*-butyl), 2,2-dimethylpropan-1-ol (neopentyl)
- chain (from C_4), position (from C_3), functional with ethers (C_2H_6O: ethanol 78 °C, methoxymethane −24 °C)
- C_3H_8O: propan-1-ol, propan-2-ol, methoxyethane; $C_4H_{10}O$: four alcohols, butan-2-ol chiral (enantiomers)

Victor Meyer's method (10.3)

- R–OH → R–I (red P + I_2) → R–NO_2 ($AgNO_2$) → HNO_2 ($NaNO_2$ + HCl) → KOH

Alcohol	H on C–NO_2	With HNO_2	Color in KOH
1°, RCH_2OH	2	nitrolic acid $RC(=NOH)NO_2$	**red**
2°, R_2CHOH	1	pseudonitrol $R_2C(NO)NO_2$	**blue**
3°, R_3COH	0	no reaction	**colorless**

- model paper: propan-1-ol red, propan-2-ol blue; methanol red
- C_4H_9OH: colorless = 2-methylpropan-2-ol; red = butan-1-ol or 2-methylpropan-1-ol; blue = butan-2-ol

Preparation (10.4–10.5)

From	Reagent	Gives
R–X	**aqueous** NaOH/KOH, boil	R–OH (alcoholic KOH: alkene)
RCOOR′	$H_2O + H^+$, or NaOH	RCOOH (or salt) + R′OH
RCOOR′	$LiAlH_4$ or Na/C_2H_5OH	$RCH_2OH + R'OH$
RCHO, RCOR′, RCOOH	$LiAlH_4$ ($NaBH_4$ not acids, esters)	1°, 2°, 1°
RNH_2	HNO_2, 0–5 °C	R–OH + N_2 (a test, poor yield)
HCHO / R′CHO / ketone	RMgX, then H_2O/H^+	1° / 2° / 3°

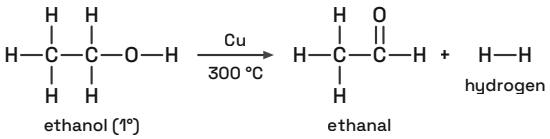
- methyl propanoate + 4[H] → propan-1-ol + methanol; ethyl ethanoate → 2 ethanol
- Grignard: HCHO + CH_3MgBr → ethanol; CH_3CHO → propan-2-ol; propanone → 2-methylpropan-2-ol; CO_2 → acid
- **oxo process**: alkene + CO + H_2, $[Co(CO)_4]_2$, heat, pressure → aldehyde, then H_2/Ni: ethene → propanal → propan-1-ol
- **hydroboration–oxidation**: $6\,CH_2{=}CH_2 + B_2H_6 \longrightarrow 2\,(C_2H_5)_3B$; with NaOH, $(C_2H_5)_3B + 3\,H_2O_2 \longrightarrow 3\,C_2H_5OH + B(OH)_3$; propene → **propan-1-ol** (anti-Markovnikov)
- hydration (H_3PO_4, 300 °C, 60–70 atm): $CH_2{=}CH_2 + H_2O \rightleftharpoons C_2H_5OH$; dil. H_2SO_4, Markovnikov: propene → propan-2-ol
- **molasses**: invertase, $C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$; zymase, $C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2$; 30–35 °C, stops at 10–15%
- **starch**: diastase (malt) → maltose; maltase → glucose; zymase → ethanol; jaand, tongba: **marcha** starter
- methanol poison: → HCHO → HCOOH; optic nerve, blindness, death

Physical properties (10.7)

- H-bonds: ethanol 78 °C, methoxymethane −24 °C, propane −42 °C (all ~45 g/mol)
- b.p. rises up the series: methanol 65, ethanol 78, propan-1-ol 97, butan-1-ol 118 °C; branching lowers b.p.: butan-1-ol 118 > 2-methylpropan-1-ol 108 > butan-2-ol 100 > 2-methylpropan-2-ol 82 °C
- C_1–C_3 mix with water (H-bonds with it); longer hydrophobic chain, less soluble; branched more soluble
- up to ~C_{11} liquids with a spirit smell; higher ones waxy solids

Reactions (10.8)

- C–OH broken by HX (3° > 2° > 1°; HI > HBr > HCl), PX_3 ($3ROH \rightarrow 3RX + H_3PO_3$), PCl_5 ($RCl + POCl_3 + HCl$, white fumes: test for –OH), $SOCl_2$ + pyridine (gases escape)
- **Lucas** (conc. HCl + anhyd. $ZnCl_2$): 3° cloudy at once, 2° in ~5 min, 1° clear (only hot); carbocation stability
- Na: $2\,C_2H_5OH + 2\,Na \longrightarrow 2\,C_2H_5ONa + H_2$ (gentler than water); very weak acid (methanol pKa ~15.5); weak base, $R{-}OH_2^+$
- **dehydration** with conc. H_2SO_4:
  - below 100 °C: $C_2H_5OSO_3H$; **140 °C (413 K)**, excess ethanol: $2\,C_2H_5OH \longrightarrow C_2H_5OC_2H_5 + H_2O$
  - **170 °C (443 K)**, excess acid: $C_2H_5OH \longrightarrow CH_2{=}CH_2 + H_2O$; propan-2-ol → propene; butan-1-ol → mainly but-2-ene (the cation rearranges)
  - Al_2O_3: ether at 250 °C, alkene at 350 °C; ease 3° > 2° > 1° (carbocation); Saytzeff: more substituted alkene
- **oxidation** ([O]: $K_2Cr_2O_7/H^+$, $KMnO_4$; PCC stops at the aldehyde)
  - 1° → aldehyde → acid (distill ethanal off at 20 °C); 2° → ketone; 3° resists (drastic: smaller acids, ketones)
- hot Cu, 300 °C: 1° → aldehyde + H_2; 2° → ketone + H_2; 3° → alkene + H_2O: $(CH_3)_3COH \longrightarrow (CH_3)_2C{=}CH_2 + H_2O$; 2,2-dimethylpropan-1-ol is 1°: → 2,2-dimethylpropanal



Ethanol over hot copper: H_2 leaves, ethanal forms.

- **esterification**: conc. H_2SO_4, $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$, ~⅔ at equilibrium; fruity smells
- dichromate test, orange → green (1°, 2°; 3° stays orange):

$$3\,C_2H_5OH + K_2Cr_2O_7 + 4\,H_2SO_4$$

$$\longrightarrow 3\,CH_3CHO + K_2SO_4 + Cr_2(SO_4)_3 + 7\,H_2O$$

- **iodoform** test, yellow CHI_3 from $CH_3CH(OH)$–; ethanol yes, methanol no (model paper):

$$C_2H_5OH + 4\,I_2 + 6\,NaOH$$

$$\longrightarrow CHI_3 + HCOONa + 5\,NaI + 5\,H_2O$$

- ceric ammonium nitrate: red with any alcohol; neutral $FeCl_3$ violet only with phenols

COMMON MISTAKES

✗ dihydric = one –OH; tertiary = –OH on a carbon with two carbons
✓ two –OH; three carbons.

✗ amine + HNO_2 is a test for alcohols
✓ for primary amines (N_2).

✗ $LiAlH_4$ gives nascent hydrogen
✓ it hands over hydride ions, H^-.

✗ invertase turns glucose into ethanol
✓ zymase; invertase only splits sucrose.

✗ absolute alcohol is in beverages
✓ ≥ 99.5%, not drunk.

✗ 3° > 2° > 1° for oxidation
✓ for dehydration; 3° resist oxidation.

✗ $KMnO_4$, $K_2Cr_2O_7$ are mild
✓ strong; PCC is mild.

✗ $2ROH + Na \rightarrow RONa + H_2$
✓ 2Na, 2RONa.