Unit 12 · Ethers

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:** no question from this unit; ethers come into the alcohol and haloalkane chains ($C_4H_{10}O$ from ethanol at 413 K)
- **MCQ (1 mark)**
  - CH_3OCH_3 + excess HI → CH_3I; ether + cold conc. HCl → oxonium salt; $FeSO_4$ detects peroxides
  - dehydration at 413 K → ethoxyethane; bulky groups don't give ethers; tert-butyl chloride + $NaOC_2H_5$ → 2-methylpropene
  - Williamson products; ethers boil lower than alcohols; functional isomer butan-1-ol; least reactive: ethers
  - anisole: Friedel–Crafts acylation → 4-methoxyacetophenone; mixed acid → 4-nitroanisole
- **Short (5 marks, in parts)**
  - prepare methoxypropane, ethoxyethane (Williamson), anisole, iodoethane from ether
  - what happens: ethanol at 140 °C; excess HI; air; Cl_2 in sunlight; Williamson
  - identify Z ($C_8H_{10}O$) or X ($C_4H_{10}O$) from HI products; ether vs butan-1-ol b.p. and solubility
  - reasons: iron in ether bottles; old ether dangerous to boil; functional isomers of alcohols
- **Long (8 marks)**: identify P–T (ethanol: Na, iodoform, 140 °C, HI, Williamson); a reaction table A–E; formula from 65% C, 13% H, 22% O ($C_4H_{10}O$), its oxonium salt, storing it

Key terms

Ether: O bonded to **two alkyl or aryl groups**, **R–O–R′**; –O– is the **ether linkage**; open-chain saturated: $C_nH_{2n+2}O$ (same as alcohols).

Simple (symmetrical): R–O–R; **mixed (unsymmetrical)**: R–O–R′; **aliphatic**: both alkyl; **aromatic**: one or both aryl.

Functional isomers: same formula, different group: ethers and alcohols (methoxyethane, propan-1-ol: C_3H_8O).

Metamerism: same group, different groups either side: ethoxyethane and 1-methoxypropane; also position and chain isomers.

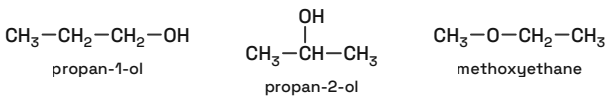
Williamson's synthesis: haloalkane + sodium alkoxide, heat → ether + NaX (SN2).

Oxonium salt: ether protonated by cold conc. acid (three groups on O^+).

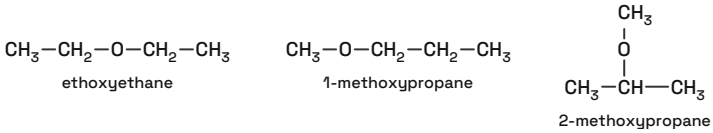
Naming

- common: the two groups **alphabetically** + ether; same groups **di**: ethyl methyl ether, diethyl ether
- IUPAC **alkoxyalkane**: larger group the parent, smaller + O the **alkoxy** prefix (methoxy, ethoxy, phenoxy)

Formula	IUPAC	Common
CH_3OCH_3	methoxymethane	dimethyl ether
$C_2H_5OCH_3$	methoxyethane	ethyl methyl ether
$C_2H_5OC_2H_5$	ethoxyethane	diethyl ether
$C_2H_5OCH_2CH_2CH_3$	1-ethoxypropane	ethyl propyl ether
$(CH_3)_2CHOCH_3$	2-methoxypropane	isopropyl methyl ether
$(CH_3)_3COCH_3$	2-methoxy-2-methylpropane	tert-butyl methyl ether (MTBE)
$C_6H_5OCH_3$	methoxybenzene	anisole
$C_6H_5OC_2H_5$	ethoxybenzene	phenetole
$C_6H_5OC_6H_5$	phenoxybenzene	diphenyl ether



C_3H_8O: two alcohols and an ether.



The three ethers $C_4H_{10}O$.

Preparation

Williamson's synthesis:

$R{-}X + R'ONa \xrightarrow{\Delta} R{-}O{-}R' + NaX$

- $C_2H_5Cl + C_2H_5ONa \xrightarrow[\text{heat}]{\text{dry ether}} C_2H_5OC_2H_5 + NaCl$
- $C_2H_5Cl + CH_3ONa \longrightarrow C_2H_5OCH_3 + NaCl$ (methoxyethane)
- $CH_3Br + (CH_3)_2CHONa \longrightarrow (CH_3)_2CHOCH_3 + NaBr$ (2-methoxypropane)
- alkoxide (strong nucleophile) attacks C–X from the **back**: **SN2**

Haloalkane must be primary

- 3° (2° mostly) with alkoxide → **alkene** by E2: steric hindrance blocks the back; alkoxide a strong base takes a β-H; heat favors elimination

- $(CH_3)_3CCl + CH_3ONa \xrightarrow{heat} (CH_3)_2C{=}CH_2 + CH_3OH + NaCl$ (2-methylpropene)
- 2-chloro-2-methylbutane + $C_2H_5ONa \rightarrow$ 2-methylbut-2-ene (major, Saytzeff) + 2-methylbut-1-ene; 2-chloro-2-methylpentane $\rightarrow$ 2-methylpent-2-ene
- tertiary ether: 3° group on the **alkoxide**: $(CH_3)_3CONa + CH_3I \longrightarrow (CH_3)_3COCH_3 + NaI$

Aromatic ethers

- $C_6H_5OH \xrightarrow{NaOH} C_6H_5ONa \xrightarrow{CH_3I} C_6H_5OCH_3$ (anisole)
- halogen must be on the **alkyl** group: chlorobenzene + CH_3ONa gives no anisole (C–Cl partly double)

Dehydration (primary alcohols; excess alcohol)

- $2\,C_2H_5OH \xrightarrow[413\,K]{conc.\ H_2SO_4} C_2H_5OC_2H_5 + H_2O$
- at **443 K** (170 °C): mainly **ethene**; 2°, 3° alcohols give alkenes

Physical properties

- methoxymethane (b.p. −24 °C), methoxyethane (7 °C) gases; ethoxyethane (35 °C) on: colorless, sweet liquids
- ethoxyethane very **volatile, flammable**: vapor heavier than air, ignites at 160 °C on a hot surface
- **lighter than water** (0.71 g/cm^3): **upper** layer in a separating funnel (extraction)
- **slightly polar** (bent C–O–C, about 110–112°; 1.2 D); about 6 g/100 mL water: O **accepts** H bonds from water, gives none
- **no O–H group** $\rightarrow$ no H bonds between ether molecules $\rightarrow$ b.p. far below alcohols, near alkanes

Compound	M (g/mol)	b.p. (°C)
pentane	72	36.1
ethoxyethane	74	34.6
butan-1-ol	74	117.7

Chemical properties

- **least reactive**: not attacked by bases, dilute acids, Na, oxidizing agents (cold) $\rightarrow$ solvent for Grignard and Wurtz; reactions start at O's **lone pairs**

HI (hot, conc.): O protonated, I^- attacks

- $C_2H_5OC_2H_5 + HI \xrightarrow{heat} C_2H_5OH + C_2H_5I$
- excess HI: $C_2H_5OC_2H_5 + 2\,HI \longrightarrow 2\,C_2H_5I + H_2O$ (2 R–X from one ether)
- unsymmetrical, 1°/2°: **SN2** at the **less crowded** C: smaller group $\rightarrow$ iodide; $CH_3OC_2H_5 \rightarrow CH_3I + C_2H_5OH$; 2-methoxypropane $\rightarrow CH_3I$ + propan-2-ol
- tertiary group: **SN1**, the 3° group $\rightarrow$ iodide: $(CH_3)_3COCH_3 \rightarrow (CH_3)_3CI + CH_3OH$
- aryl alkyl: ring–O never breaks: $C_6H_5OCH_3 + HI \longrightarrow C_6H_5OH + CH_3I$

Cold conc. acids (ether a weak base): oxonium salts; dissolves, unlike alkanes; water gives back the ether

- $C_2H_5OC_2H_5 + H_2SO_4 \longrightarrow [(C_2H_5)_2OH]^+\,HSO_4^-$
- $C_2H_5OC_2H_5 + HCl \longrightarrow [(C_2H_5)_2OH]^+\,Cl^-$

Air and light: $C_2H_5OC_2H_5 + O_2 \longrightarrow CH_3CH(OOH)OC_2H_5$ (1-ethoxyethyl hydroperoxide, on the α-carbon)

- peroxides **explode** on heating; left concentrated when old ether is distilled
- test: $FeSO_4 + KSCN \rightarrow$ **blood-red**: $2\,Fe^{2+} + ROOH + 2\,H^+ \longrightarrow 2\,Fe^{3+} + ROH + H_2O$; $Fe^{3+} + SCN^- \longrightarrow [Fe(SCN)]^{2+}$
- prevent: dark, closed bottles; **iron wire** or copper inside; shake with $FeSO_4$; BHT

Chlorine

- dark (α-H first): $C_2H_5OC_2H_5 + 2\,Cl_2 \longrightarrow CH_3CHClOCHClCH_3 + 2\,HCl$ (α,α'-dichlorodiethyl ether)
- sunlight: $C_2H_5OC_2H_5 + 10\,Cl_2 \longrightarrow C_2Cl_5OC_2Cl_5 + 10\,HCl$ (perchlorodiethyl ether)

Anisole's ring: $-OCH_3$ +R $\rightarrow$ activated, **o, p** director, para major

- conc. HNO_3 + conc. $H_2SO_4 \rightarrow$ 4-nitroanisole (major) + 2-nitroanisole
- CH_3COCl, anhyd. $AlCl_3 \rightarrow$ 4-methoxyacetophenone (major) + 2-
- Br_2 in ethanoic acid, no catalyst $\rightarrow$ 4-bromoanisole (major) + 2-

Uses

- **solvent**: oils, fats, waxes, resins; Grignard reagents, Wurtz; extraction
- **anesthetic**: ether first; now halogenated ethers (isoflurane, sevoflurane, desflurane), non-flammable
- **perfumes, flavors**: anisole, diphenyl ether, anethole (saunf)
- **fuel**: MTBE in petrol; dimethyl ether as diesel, in LPG
- dimethyl ether: refrigerant, aerosol propellant

Conversions (exercise chains)

- $C_2H_5OH \xrightarrow{conc.\ H_2SO_4} C_2H_5OC_2H_5 \xrightarrow{excess\ HI} C_2H_5I$ (ether at 140 °C)
- back: $C_2H_5I \xrightarrow{C_2H_5ONa} C_2H_5OC_2H_5$
- $CH_3OCH_3 \xrightarrow[heat]{excess\ HI} CH_3I \xrightarrow{C_6H_5ONa} C_6H_5OCH_3$
- 65% C, 13% H, 22% O $\rightarrow C_4H_{10}O$, symmetrical: **ethoxyethane**

COMMON MISTAKES

✗ ethers show only functional isomerism and metamerism
✓ also **position** and **chain** isomers.

✗ HI cleavage by +I of the larger group
✓ **steric**: SN2 at the less crowded C; a 3° group goes SN1 and becomes the iodide.

✗ 2-chloro-2-methylpentane $\rightarrow$ 2-methylbut-2-ene
✓ **2-methylpent-2-ene** (no carbon lost).

✗ anisole + HI $\rightarrow$ iodobenzene + methanol
✓ **phenol + iodomethane**.

✗ ether peroxide $R_2O{\rightarrow}O$
✓ **hydroperoxide** on the α-carbon, $CH_3CH(OOH)OC_2H_5$.

✗ chlorination without HCl
✓ + 2HCl (dark), + **10**HCl (light).

✗ ether as solvent of Friedel–Crafts
✓ of **Grignard** and **Wurtz** (it ties up $AlCl_3$).

✗ C–O–C angle exactly 110°
✓ about **110–112**°.