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CH 07

Alcohols, Phenols & Ethers — Preparation, Acidity & Reactions

Preparation of alcohols and phenols, acidity orders, the Lucas test, dehydration and oxidation, electrophilic substitution of phenol, Kolbe and Reimer–Tiemann reactions, Williamson synthesis and ether cleavage by HI — with an exam trap gallery, graded MCQs and a one-page revision sheet.

WHAT YOU WILL BE ABLE TO DO

- Prepare alcohols from alkenes, carbonyl compounds and Grignard reagents, and phenol by four routes
- Rank the acidity of alcohols and substituted phenols with reasons
- Distinguish 1°, 2° and 3° alcohols by the Lucas test, oxidation and dehydration
- Predict products of electrophilic substitution of phenol, Kolbe and Reimer–Tiemann reactions
- Choose the right Williamson combination and predict products of ether cleavage with HI

INSIDE

A The big picture
B Structure and physical properties
C Preparing alcohols
D Preparing phenol

HOW TO USE THESE NOTES

IN ONE LINE The core idea of a section	**KEY IDEA** The concept to remember	**EXAM TRAP** Where marks are usually lost
SOLVED EXAMPLE Worked step by step	**CHECK YOURSELF** Quick self-test	**MEMORY HOOK** A line that sticks

SECTION A

The big picture

A

Where the oxygen sits decides the chemistry.

IN ONE LINE

Alcohols react at the O–H and the C–O bond; phenols are acidic and their ring is strongly activated toward ortho/para substitution; ethers are unreactive except toward hot HI, which cleaves the C–O bond.

	Alcohol R-OH	Phenol Ar-OH	Ether R-O-R′
Carbon bearing O	sp^3	sp^2 (ring)	sp^3 (or sp^2 in anisole)
Acidity	Very weak (pKa ≈ 16)	Weak acid (pKa ≈ 10)	Not acidic
C–O bond	Breaks easily (with acid)	Partial double bond — hard to break	Breaks only with HI/HBr, heat
Typical reactions	Substitution, dehydration, oxidation	Ring substitution (o/p)	Cleavage, ring substitution (anisole)

THINK OF IT LIKE THIS

Think of the oxygen's lone pair as cash. In an alcohol it stays in the oxygen's pocket, so the O–H holds its hydrogen tightly. In phenol the benzene ring borrows that cash (resonance), the oxygen is left short, and it lets the H^+ go more easily. The ring, now richer, attracts electrophiles.

SECTION B

Structure and physical properties

B

Hydrogen bonding explains almost every physical property.

Feature	Methanol	Phenol	Methoxymethane
Bond angle	C–O–H 108.9°	C–O–H about 109°	C–O–C 111.7°
C–O bond length	142 pm	136 pm (partial double bond)	141 pm

Feature	Methanol	Phenol	Methoxymethane
Why	Lone pairs squeeze the angle below 109.5°	Lone pair conjugated with the ring; sp² carbon	Two bulky alkyl groups repel, opening the angle

Compound	Molar mass	b.p. / K	Reason
Propane	44	231	Only weak van der Waals forces
Methoxymethane	46	248	Dipole–dipole, no H bonding
Ethanol	46	351	Intermolecular H bonding
Butan-1-ol	74	391	Unbranched: largest surface
Butan-2-ol	74	373	Some branching
2-Methylpropan-2-ol	74	355	Most branched: smallest surface

- **Boiling point** rises with molar mass and falls with branching; alcohols boil far above ethers and hydrocarbons of similar mass because of H bonding.
- **Solubility in water** comes from H bonding with water; it falls as the hydrocarbon part grows. Lower alcohols mix in all proportions; ethers are about as soluble as alcohols of similar mass (they accept H bonds from water).
- Phenol is fairly soluble in water and has a much higher b.p. (455 K) than toluene (384 K) of similar mass.

CHECK YOURSELF

C1 Why does ethanol boil 103 K higher than methoxymethane, though both have molar mass 46?

C2 Why is the C–O bond in phenol shorter than in methanol?

Answers at the end of the chapter.

SECTION C

Preparing alcohols

C

Four reliable routes.

Route	Reagent	Product	Note
Acid-catalysed hydration of alkenes	dil. H_2SO_4	Markovnikov alcohol	Via carbocation — can rearrange
Hydroboration–oxidation	(i) B_2H_6 (ii) H_2O_2/NaOH	Anti-Markovnikov alcohol	No rearrangement; syn addition

Route	Reagent	Product	Note
Reduction of carbonyls	$NaBH_4$ or $LiAlH_4$; H_2/Pd	Aldehyde → 1°; ketone → 2°	$LiAlH_4$ also reduces acids and esters to 1° alcohols
Grignard reagent + carbonyl	RMgX, then H_3O^+	HCHO → 1°; RCHO → 2°; R_2CO → 3°	Adds one new C–C bond

SOLVED EXAMPLE 01 — CHOOSING THE GRIGNARD PARTNER

Which carbonyl compound and Grignard reagent give 2-methylbutan-2-ol?

SOLUTION

1. 2-Methylbutan-2-ol is $(CH_3)_2C(OH)CH_2CH_3$ — a 3° alcohol, so start from a ketone.
2. Option 1: acetone + C_2H_5MgBr. Option 2: butan-2-one + CH_3MgBr.

ANSWER Either acetone + ethylmagnesium bromide, or butan-2-one + methylmagnesium bromide (then H_3O^+).

SOLVED EXAMPLE 02 — MARKOVNIKOV OR NOT?

Give the alcohol from propene with (a) dil. H_2SO_4, (b) B_2H_6 then H_2O_2/NaOH.

SOLUTION

1. (a) H^+ adds to C1 to form the 2° carbocation; water attacks C2.
2. (b) Boron adds to the less substituted C1; oxidation replaces B by OH.

ANSWER (a) Propan-2-ol. (b) Propan-1-ol.

Mechanism of acid-catalysed hydration

1. **Protonation:** the alkene's π electrons take H^+ from H_3O^+, giving the more stable carbocation (Markovnikov).
2. **Nucleophilic attack:** water attacks the carbocation, giving a protonated alcohol.
3. **Deprotonation:** water removes H^+, giving the alcohol and regenerating H_3O^+.

Commercial alcohols

- **Methanol (wood spirit):** $CO + 2H_2 \rightarrow CH_3OH$ over $ZnO–Cr_2O_3$ at 573–673 K and 200–300 atm. Highly poisonous — small amounts cause blindness, larger amounts death.
- **Ethanol:** fermentation of molasses or starch. Sucrose → glucose + fructose (enzyme invertase); glucose → $2C_2H_5OH + 2CO_2$ (zymase, from yeast). Air must be kept out, or ethanol is oxidised to ethanoic acid.
- **Denatured alcohol:** ethanol made unfit to drink by adding copper sulphate (colour) and pyridine (smell).

SECTION D

Preparing phenol

D

Four routes, one industrial favourite.

- **Cumene process (industrial):** cumene (isopropylbenzene) + O_2 → cumene hydroperoxide; with dilute acid it rearranges to **phenol + acetone** (a phenyl group migrates to oxygen). Acetone is a valuable by-product.
- **From benzenesulphonic acid:** fuse the sodium salt with NaOH, then acidify.
- **From chlorobenzene (Dow process):** NaOH at 623 K and high pressure, then acidify.
- **From diazonium salts:** warm aqueous $C_6H_5N_2^+Cl^-$ → $C_6H_5OH + N_2 + HCl$.

SECTION E

Acidity

E

Why phenol beats alcohol, and what substituents do.

KEY IDEA

Phenol is acidic because the phenoxide ion is resonance-stabilised: its negative charge spreads over the ring at the ortho and para positions. An alkoxide ion has no such stabilisation. Phenol (pKa ≈ 10) turns blue litmus red only faintly and dissolves in NaOH but **not** in $NaHCO_3$; carboxylic acids (pKa ≈ 4–5) dissolve in both.

- **Alcohols:** acidity 1° > 2° > 3° — alkyl groups push electron density onto O^- and destabilise it (and hinder solvation). Alcohols are weaker acids than water.
- **Electron-withdrawing groups** ($-NO_2$, $-CN$, $-X$) at **ortho/para** stabilise phenoxide strongly by resonance and increase acidity; at meta only by induction.
- **Electron-donating groups** ($-CH_3$, $-OCH_3$) decrease acidity.

Compound	pKa (approx.)
Picric acid (2,4,6-trinitrophenol)	0.4
2,4-Dinitrophenol	4.0
p-Nitrophenol	7.1
o-Nitrophenol	7.2
m-Nitrophenol	8.3
Phenol	10.0
p-Cresol	10.2
Ethanol	15.9

SOLVED EXAMPLE 03 — RANKING ACIDITY

Arrange phenol, p-nitrophenol, m-nitrophenol and p-cresol in decreasing acidity.

SOLUTION

1. p-NO_2 stabilises phenoxide by resonance and induction — strongest.
2. m-NO_2 stabilises by induction only — next.
3. $-CH_3$ is electron-donating — p-cresol is weaker than phenol.

ANSWER p-Nitrophenol > m-nitrophenol > phenol > p-cresol.

CHECK YOURSELF

C3 Why does phenol not dissolve in $NaHCO_3$ solution?

C4 Which is more acidic: ethanol or water?

Answers at the end of the chapter.

SECTION F

F

Reactions of alcohols

Break O–H, break C–O, or oxidise.

Breaking O–H

- **With Na:** $2ROH + 2Na \rightarrow 2RONa + H_2$ (shows alcohols are weak acids).
- **Esterification:** $RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$ (conc. H_2SO_4); with acid chlorides it goes to completion (pyridine removes HCl).

Breaking C–O

- **With HX:** reactivity 3° > 2° > 1° (via carbocation for 3°); HI > HBr > HCl. $ZnCl_2$ catalyses HCl.
- **With PCl_5, PCl_3, $SOCl_2$:** give alkyl chlorides; $SOCl_2$ is best (by-products SO_2 and HCl are gases).
- **Dehydration with conc. H_2SO_4:** ethanol at 443 K → ethene; at 413 K with excess alcohol → diethyl ether. Ease of dehydration: 3° > 2° > 1° (E1 via carbocation, Saytzeff product, rearrangement possible).

Mechanism of dehydration (ethanol → ethene)

1. **Protonation** of –OH: $CH_3CH_2–OH + H^+ \rightarrow CH_3CH_2–OH_2^+$ (fast).
2. **Loss of water** gives a carbocation: $CH_3CH_2^+ + H_2O$ (slow, rate-determining).
3. **Loss of H^+** from the β-carbon gives $CH_2=CH_2$.

At 413 K with excess ethanol, a second ethanol molecule attacks the protonated alcohol instead (SN2), giving diethyl ether: this route works only for primary alcohols — 2° and 3° alcohols dehydrate to alkenes.

Alcohol	Reaction with HX	Mechanism
3°	Fast, even with conc. HCl alone	SN1 via a stable carbocation
2°	Moderate; needs $ZnCl_2$ with HCl	SN1 / SN2
1°	Slow; needs $ZnCl_2$ and heat with HCl	SN2 on $R–OH_2^+$

Oxidation

Alcohol	$KMnO_4$ / $K_2Cr_2O_7$ (acid)	PCC (mild)	Cu at 573 K
1°	Carboxylic acid (via aldehyde)	Aldehyde	Aldehyde (dehydrogenation)
2°	Ketone	Ketone	Ketone
3°	Resists oxidation	No reaction	Alkene (dehydration)

SOLVED EXAMPLE 04 — REARRANGEMENT ON DEHYDRATION

3,3-Dimethylbutan-2-ol is heated with conc. H_2SO_4. Give the major alkene.

SOLUTION

1. Loss of water gives a 2° carbocation next to a tert-butyl carbon.
2. A methyl group shifts to give a more stable 3° carbocation.
3. Loss of H^+ gives the most substituted alkene (Saytzeff).

ANSWER 2,3-Dimethylbut-2-ene (not 3,3-dimethylbut-1-ene).

SOLVED EXAMPLE 05 — OXIDATION AS A TEST OF CLASS

Three isomeric alcohols $C_4H_{10}O$ are treated with acidified $K_2Cr_2O_7$. A gives butanoic acid, B gives butan-2-one, C is not oxidised. Identify A, B and C.

SOLUTION

1. A → acid: a 1° alcohol with an unbranched chain: butan-1-ol.
2. B → ketone: a 2° alcohol: butan-2-ol.
3. C not oxidised: a 3° alcohol: 2-methylpropan-2-ol.

ANSWER A = butan-1-ol; B = butan-2-ol; C = 2-methylpropan-2-ol.

CHECK YOURSELF

C5 Which step is rate-determining in the acid dehydration of ethanol?

C6 Why does 2-methylpropan-2-ol react with conc. HCl at room temperature without $ZnCl_2$?

Answers at the end of the chapter.

SECTION G

Reactions of phenol

G

A strongly activated ring.

The –OH group donates electrons into the ring (+R), so phenol undergoes electrophilic substitution much faster than benzene, at **ortho and para** positions.

Reaction	Conditions	Main product
Bromination	Bromine water	2,4,6-Tribromophenol (white precipitate)
Bromination	Br_2 in CS_2 or $CHCl_3$, low temperature	Mixture of o- and p-bromophenol (para major)
Nitration	Dilute HNO_3, 298 K	o- and p-Nitrophenol (separated by steam distillation)
Nitration	Conc. HNO_3	2,4,6-Trinitrophenol (picric acid)
Kolbe reaction	Sodium phenoxide + CO_2, about 400 K, 4–7 atm; then H^+	Salicylic acid (o-hydroxybenzoic acid)
Reimer–Tiemann	$CHCl_3$ + aq. NaOH, then H^+	Salicylaldehyde (o-hydroxybenzaldehyde); electrophile is dichlorocarbene, $:CCl_2$
Zinc dust distillation	Heat with Zn	Benzene
Oxidation	Air or chromic acid	Benzoquinone

More reactions of phenol

- **With NaOH:** $C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$ (phenol is acidic enough). With Na: $2C_6H_5OH + 2Na \rightarrow 2C_6H_5ONa + H_2$.
- **Esterification (acylation):** phenol + acetyl chloride (or acetic anhydride) in pyridine → phenyl acetate.
- **Aspirin:** salicylic acid + acetic anhydride → acetylsalicylic acid (aspirin) + CH_3COOH.
- **Coupling with diazonium salts:** phenol + $C_6H_5N_2^+Cl^-$ in mild alkali → p-hydroxyazobenzene, an orange dye (azo coupling at the para position).
- **$FeCl_3$ test:** neutral $FeCl_3$ gives a violet colour (iron–phenoxide complex).

SOLVED EXAMPLE 06 — PHENOL TO ASPIRIN

Show how aspirin is made from phenol.

SOLUTION

1. Kolbe reaction: sodium phenoxide + CO_2 (about 400 K, 4–7 atm), then acid → salicylic acid.
2. Acetylation: salicylic acid + $(CH_3CO)_2O$ → acetylsalicylic acid + CH_3COOH.

ANSWER Phenol → (Kolbe) salicylic acid → (acetylation) aspirin.

KEY IDEA

o-Nitrophenol is steam-volatile; p-nitrophenol is not. The ortho isomer forms an intramolecular hydrogen bond, so its molecules do not hold each other; the para isomer forms intermolecular H bonds with other molecules and with water.

CHECK YOURSELF

C7 What is the electrophile in the Reimer–Tiemann reaction?

C8 Why does bromine water give a tribromo product with phenol but not with benzene?

Answers at the end of the chapter.

SECTION H

H

Ethers

Easy to make, hard to break.

- Ethers have a bent C–O–C unit (about 111.7° in methoxymethane) and a small dipole moment.
- No O–H, so no H bonding between ether molecules: b.p. close to alkanes of similar mass, far below alcohols.
- Ethers are good solvents (diethyl ether, THF) because they are unreactive toward most reagents.
- **From alcohols:** $2CH_3CH_2OH \rightarrow CH_3CH_2OCH_2CH_3 + H_2O$ (conc. H_2SO_4, 413 K). Only for **symmetrical ethers of 1° alcohols**: 2° and 3° alcohols give alkenes, and two different alcohols give a mixture of three ethers.

Williamson synthesis

$$R{-}O^{-}Na^{+} + R'{-}X \rightarrow R{-}O{-}R' + NaX$$

An SN2 reaction: the alkyl halide must be methyl or primary

KEY IDEA

Put the bulky group on the alkoxide, never on the halide. For tert-butyl methyl ether use $(CH_3)_3CO^-Na^+ + CH_3Br$. The other pair, $CH_3O^-Na^+ + (CH_3)_3CBr$, gives mainly 2-methylpropene by E2. For aryl ethers, use phenoxide + alkyl halide (an aryl halide will not undergo SN2).

Cleavage with HI

- Ethers are cleaved by hot conc. HI (HI > HBr ≫ HCl).
- **Methyl + 1° or 2° alkyl:** I^- attacks the less hindered carbon by SN2 → CH_3I + ROH.
- **One group 3°:** the C–O bond to the 3° group breaks by SN1 → $(CH_3)_3C–I + CH_3OH$.
- **Alkyl aryl ether (anisole):** gives **phenol + CH_3I** — never iodobenzene, because the aryl C–O bond has partial double-bond character and an sp^2 carbon resists attack.
- With excess HI, the alcohol formed is converted to a second alkyl iodide.

SOLVED EXAMPLE 07 — CLEAVING AN ETHER

Predict the products of (a) $CH_3OC_2H_5$, (b) $CH_3OC(CH_3)_3$, (c) $C_6H_5OCH_3$ with one equivalent of hot HI.

SOLUTION

1. (a) SN2 at the less hindered methyl: $CH_3I + C_2H_5OH$.
2. (b) SN1 at the 3° carbon: $(CH_3)_3CI + CH_3OH$.
3. (c) Aryl C–O does not break: $C_6H_5OH + CH_3I$.

ANSWER (a) CH_3I + ethanol. (b) tert-butyl iodide + methanol. (c) Phenol + CH_3I.

Reaction of anisole	Reagent	Main product
Bromination	Br_2 in ethanoic acid (no catalyst)	p-Bromoanisole (major) + o-bromoanisole
Friedel–Crafts alkylation	CH_3Cl, anhydrous $AlCl_3$	2-Methoxytoluene + 4-methoxytoluene
Friedel–Crafts acylation	CH_3COCl, anhydrous $AlCl_3$	4-Methoxyacetophenone (major) + 2-methoxyacetophenone
Nitration	conc. H_2SO_4 + conc. HNO_3	4-Nitroanisole (major) + 2-nitroanisole

- **Anisole** undergoes electrophilic substitution at ortho/para ($–OCH_3$ activates the ring): bromination in acetic acid gives mainly p-bromoanisole; Friedel–Crafts gives o- and p-products.

SECTION I

Tests and distinctions

I

How to tell them apart in the lab or on paper.

Test	Result	Distinguishes
Lucas reagent (conc. HCl + anhydrous $ZnCl_2$)	3°: turbidity at once; 2°: in about 5 min; 1°: no turbidity at room temperature	1°, 2°, 3° alcohols
Neutral $FeCl_3$	Violet colour	Phenol (and enols) from alcohols
Bromine water	White precipitate	Phenol from alcohols
$NaHCO_3$	No effervescence	Phenol from carboxylic acids
Iodoform (I_2 + NaOH)	Yellow CHI_3	Ethanol and alcohols with $CH_3CH(OH)$– (e.g. propan-2-ol) from methanol, propan-1-ol

SOLVED EXAMPLE 08 — DISTINGUISHING TWO ISOMERS

How would you distinguish propan-1-ol from propan-2-ol?

SOLUTION

1. Iodoform test: propan-2-ol has $CH_3CH(OH)$– and gives yellow CHI_3; propan-1-ol does not.
2. Lucas test: propan-2-ol (2°) turns turbid in about 5 min; propan-1-ol (1°) stays clear.

ANSWER Iodoform test (or Lucas test).

SECTION J

Conversions

J

The step-by-step problems examiners love.

SOLVED EXAMPLE 09 — METHANOL TO ETHANOL

Convert methanol into ethanol.

SOLUTION

1. $CH_3OH + PBr_3 \rightarrow CH_3Br$.
2. CH_3Br + Mg (dry ether) $\rightarrow CH_3MgBr$.
3. CH_3MgBr + HCHO, then $H_3O^+ \rightarrow CH_3CH_2OH$.

ANSWER Methanol → bromomethane → Grignard → (with HCHO) ethanol.

SOLVED EXAMPLE 10 — ETHANOL TO PROPAN-2-OL

Convert ethanol into propan-2-ol.

SOLUTION

1. Oxidise ethanol to ethanal with PCC.
2. Add CH_3MgBr to ethanal; hydrolyse with H_3O^+.

ANSWER $CH_3CH_2OH \rightarrow CH_3CHO \rightarrow (CH_3MgBr, \text{then } H_3O^+)\ CH_3CH(OH)CH_3$.

SOLVED EXAMPLE 11 — BENZENE TO PHENOL

Convert benzene into phenol.

SOLUTION

1. Sulphonate: benzene + conc. H_2SO_4 (oleum) → benzenesulphonic acid.
2. Fuse the sodium salt with NaOH → sodium phenoxide.
3. Acidify → phenol.

ANSWER Benzene → $C_6H_5SO_3H$ → C_6H_5ONa → C_6H_5OH (or via chlorobenzene and the Dow process).

SOLVED EXAMPLE 12 — PROPAN-2-OL TO 2-METHYLPROPAN-2-OL

Convert propan-2-ol into 2-methylpropan-2-ol.

SOLUTION

1. Oxidise to acetone ($K_2Cr_2O_7$ / H^+).
2. Add CH_3MgBr; hydrolyse.

ANSWER Propan-2-ol → acetone → (CH_3MgBr, H_3O^+) 2-methylpropan-2-ol.

SECTION K

Exam trap gallery

K

Where marks are lost in this chapter.

✗ TRAP 01 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Anisole + HI → iodobenzene + methanol.	Phenol + CH_3I.

WHY The aryl C–O bond does not break.

✗ TRAP 02 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
$CH_3ONa + (CH_3)_3CBr$ gives tert-butyl methyl ether.	It gives mainly 2-methylpropene (E2).

WHY Use $(CH_3)_3CONa + CH_3Br$.

✗ TRAP 03 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Phenol dissolves in $NaHCO_3$.	It does not; it dissolves in NaOH.

WHY Phenol (pKa 10) is weaker than H_2CO_3.

✗ TRAP 04 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Ethanol is more acidic than water.	Water is slightly more acidic.

WHY The ethyl group donates electrons to O^-.

✗ TRAP 05 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
3° alcohols are oxidised to ketones by acidified $K_2Cr_2O_7$.	3° alcohols resist oxidation.

WHY No H on the carbon bearing OH.

✗ TRAP 06 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Hydration of propene with dil. H_2SO_4 gives propan-1-ol.	It gives propan-2-ol (Markovnikov); use hydroboration for propan-1-ol.

WHY The 2° carbocation forms.

✗ TRAP 07 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
p-Nitrophenol is steam-volatile.	o-Nitrophenol is steam-volatile.

WHY Intramolecular H bond in the ortho isomer.

✗ TRAP 08 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
m-Nitrophenol is more acidic than p-nitrophenol.	p-Nitrophenol is more acidic.

WHY Para $-NO_2$ stabilises phenoxide by resonance; meta only by induction.

✗ TRAP 09 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Branching raises the boiling point of isomeric alcohols.	Branching lowers it: butan-1-ol 391 K > 2-methylpropan-2-ol 355 K.

WHY Smaller surface area, weaker van der Waals forces.

✗ TRAP 10 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Any two alcohols with conc. H_2SO_4 give a single unsymmetrical ether.	They give a mixture of three ethers (and alkenes).
WHY Use the Williamson synthesis instead.	

✗ TRAP 11 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Phenol + acetyl chloride gives o-hydroxyacetophenone directly.	It gives phenyl acetate (O-acylation).
WHY Acylation occurs at the oxygen first.	

✗ TRAP 12 · WHAT STUDENTS WRITE	✓ WHAT IS ACTUALLY CORRECT
Ethers boil higher than isomeric alcohols.	Alcohols boil much higher.
WHY Ethers have no O–H for H bonding.	

MEMORY HOOK

"Formaldehyde one, aldehyde two, ketone three" — the Grignard alcohol classes.

"Lucas: 3 at once, 2 in five, 1 never."

"Bulky on the oxygen, small on the halide" — Williamson.

"HI never breaks the aryl bond."

SECTION L

Practice MCQs

L

Levels: Easy, Moderate, Tough.

Q01 Phenol is more acidic than ethanol because: [EASY]

(a) phenol is aromatic
(b) phenoxide is resonance-stabilised
(c) ethanol has more H atoms
(d) phenol has a lower molar mass

Q02 HCHO + CH_3MgBr, then H_3O^+, gives: [EASY]

(a) methanol
(b) ethanol
(c) propan-2-ol
(d) acetaldehyde

Q03 Lucas test gives immediate turbidity with: [EASY]

(a) butan-1-ol
(b) butan-2-ol
(c) 2-methylpropan-2-ol
(d) methanol

Q04 Phenol + bromine water gives: [EASY]

(a) o-bromophenol
(b) p-bromophenol
(c) 2,4,6-tribromophenol
(d) bromobenzene

Q05 Cumene process gives phenol and: [EASY]

(a) acetaldehyde (b) acetone
(c) benzene (d) propene

Q06 Most acidic among these: [MODERATE]

(a) phenol (b) p-cresol
(c) p-nitrophenol (d) m-nitrophenol

Q07 Propene + B_2H_6, then H_2O_2/NaOH, gives: [MODERATE]

(a) propan-2-ol (b) propan-1-ol
(c) propanal (d) propane

Q08 Ethanol with conc. H_2SO_4 at 413 K (excess alcohol) gives: [MODERATE]

(a) ethene (b) diethyl ether
(c) ethanal (d) ethyl hydrogen sulphate only

Q09 Kolbe reaction product is: [MODERATE]

(a) salicylaldehyde (b) salicylic acid
(c) benzoic acid (d) picric acid

Q10 The electrophile in Reimer–Tiemann reaction is: [MODERATE]

(a) $CHCl_3$ (b) $:CCl_2$
(c) CCl_3^+ (d) Cl^+

Q11 Best synthesis of tert-butyl ethyl ether: [MODERATE]

(a) $C_2H_5ONa + (CH_3)_3CBr$ (b) $(CH_3)_3CONa + C_2H_5Br$
(c) $C_2H_5OH + (CH_3)_3COH$, heat (d) $(CH_3)_3CBr + C_2H_5Br + Na$

Q12 Which alcohol gives an alkene with Cu at 573 K? [MODERATE]

(a) ethanol (b) propan-2-ol
(c) 2-methylpropan-2-ol (d) methanol

Q13 $CH_3–O–C(CH_3)_3$ + HI (1 equivalent) gives: [TOUGH]

(a) $CH_3I + (CH_3)_3COH$ (b) $CH_3OH + (CH_3)_3Cl$
(c) $CH_4 + (CH_3)_3COI$ (d) $CH_3OH + (CH_3)_2C{=}CH_2$ only

Q14 3,3-Dimethylbutan-2-ol with conc. H_2SO_4, heat, gives mainly: [TOUGH]

(a) 3,3-dimethylbut-1-ene (b) 2,3-dimethylbut-2-ene
(c) 2,3-dimethylbut-1-ene (d) 2,2-dimethylbutane

Q15 A compound C_3H_8O gives a positive iodoform test. It is: [TOUGH]

(a) propan-1-ol (b) propan-2-ol
(c) methoxyethane (d) propanal

Q16 Wood spirit is: [EASY]

(a) ethanol (b) methanol
(c) propanol (d) glycerol

Q17 Phenol gives a violet colour with: [EASY]

(a) Br_2 water (b) neutral $FeCl_3$
(c) $NaHCO_3$ (d) Tollens' reagent

Q18 The enzyme converting glucose to ethanol is: [EASY]

(a) invertase (b) zymase
(c) diastase (d) maltase

Q19 Highest boiling point: [MODERATE]

(a) butan-1-ol (b) butan-2-ol
(c) 2-methylpropan-2-ol (d) ethoxyethane

Q20 Rate-determining step of acid dehydration of ethanol: [MODERATE]

(a) protonation of OH (b) loss of water to form the carbocation
(c) loss of H^+ (d) attack of water

Q21 Phenol + benzenediazonium chloride in mild alkali gives: [MODERATE]

(a) aniline (b) p-hydroxyazobenzene
(c) chlorobenzene (d) benzene

Q22 Anisole + CH_3COCl / $AlCl_3$ gives mainly: [MODERATE]

(a) phenyl acetate (b) 4-methoxyacetophenone
(c) acetophenone (d) methyl benzoate

Q23 Salicylic acid + acetic anhydride gives: [MODERATE]

(a) methyl salicylate (b) aspirin
(c) phenyl acetate (d) salicylaldehyde

Q24 C–O–C bond angle in methoxymethane is about: [TOUGH]

(a) 104.5° (b) 109.5°
(c) 111.7° (d) 120°

Q25 CH_3MgBr + ethanal, then H_3O^+, gives: [TOUGH]

(a) ethanol (b) propan-1-ol
(c) propan-2-ol (d) 2-methylpropan-2-ol

Answer key with explanations

Q01 **(b) phenoxide is resonance-stabilised** — Charge spreads into the ring.

Q02 **(b) ethanol** — Formaldehyde → 1° alcohol.

Q03 **(c) 2-methylpropan-2-ol** — 3° alcohol.

Q04 (c) **2,4,6-tribromophenol** — Highly activated ring.

Q05 (b) **acetone** — By-product.

Q06 (c) **p-nitrophenol** — Para $-NO_2$, resonance.

Q07 (b) **propan-1-ol** — Anti-Markovnikov.

Q08 (b) **diethyl ether** — Lower temperature → ether.

Q09 (b) **salicylic acid** — Phenoxide + CO_2.

Q10 (b) **:CCl_2** — Dichlorocarbene.

Q11 (b) **$(CH_3)_3CONa + C_2H_5Br$** — SN2 on a 1° halide.

Q12 (c) **2-methylpropan-2-ol** — 3° alcohols dehydrate.

Q13 (b) **$CH_3OH + (CH_3)_3Cl$** — SN1 at the 3° carbon.

Q14 (b) **2,3-dimethylbut-2-ene** — Methyl shift, then Saytzeff.

Q15 (b) **propan-2-ol** — Has $CH_3CH(OH)–$.

Q16 (b) **methanol** — Methanol.

Q17 (b) **neutral $FeCl_3$** — Iron–phenoxide complex.

Q18 (b) **zymase** — From yeast.

Q19 (a) **butan-1-ol** — Unbranched alcohol.

Q20 (b) **loss of water to form the carbocation** — Slow step.

Q21 (b) **p-hydroxyazobenzene** — Azo coupling.

Q22 (b) **4-methoxyacetophenone** — o/p director, para major.

Q23 (b) **aspirin** — Acetylation of –OH.

Q24 (c) **111.7°** — Repulsion between methyl groups.

Q25 (c) **propan-2-ol** — Aldehyde (not HCHO) → 2° alcohol.

SECTION M

Advanced problems

M

Each needs two ideas from the chapter.

SOLVED EXAMPLE 13 IDENTIFY THE COMPOUND

Compound A ($C_4H_{10}O$) reacts with Na to give H_2, gives turbidity with Lucas reagent at once, and does not decolourise acidified $K_2Cr_2O_7$. Identify A.

SOLUTION

1. Na → H_2: it is an alcohol (not an ether).
2. Instant Lucas turbidity and resistance to oxidation: 3° alcohol.
3. The only 3° C_4 alcohol is $(CH_3)_3COH$.

ANSWER A is 2-methylpropan-2-ol.

SOLVED EXAMPLE 14 — SEPARATING NITROPHENOLS

Nitration of phenol gives a mixture of o- and p-nitrophenol. How are they separated, and why does the method work?

SOLUTION

1. Steam distil the mixture.
2. o-Nitrophenol has an intramolecular H bond, is less associated, more volatile and passes over with steam.
3. p-Nitrophenol is H-bonded to other molecules and to water, and stays behind.

ANSWER Steam distillation: o-nitrophenol distils over; p-nitrophenol remains.

Check-yourself answers

C1 Ethanol molecules are linked by intermolecular hydrogen bonds; methoxymethane has no O–H.

C2 The oxygen lone pair is conjugated with the ring, giving the C–O bond partial double-bond character, and the carbon is sp^2 (more s character).

C3 Phenol (pKa 10) is a weaker acid than carbonic acid (pKa 6.4), so it cannot displace CO_2 from bicarbonate.

C4 Water (pKa 15.7) is slightly more acidic than ethanol (pKa ≈ 15.9).

C5 Loss of water from the protonated alcohol to form the carbocation.

C6 It forms a stable 3° carbocation easily, so the SN1 reaction is fast without a catalyst.

C7 Dichlorocarbene, $:CCl_2$ (formed from $CHCl_3$ and OH^-).

C8 The –OH group strongly activates the ring by donating its lone pair, so even the weak electrophile in bromine water substitutes all three o/p positions; benzene needs a Lewis acid catalyst.

QUICK REVISION

One-page revision

Read this page the night before the exam.

Making alcohols

- dil. H_2SO_4: Markovnikov (may rearrange)
- B_2H_6/H_2O_2: anti-Markovnikov
- $NaBH_4$: aldehyde → 1°, ketone → 2°
- RMgX: HCHO 1°, RCHO 2°, R_2CO 3°

Making phenol

- Cumene → phenol + acetone
- Benzenesulphonate + NaOH fusion
- Dow: C_6H_5Cl + NaOH, 623 K
- Diazonium salt + warm water

Acidity

- Phenol pKa 10; ethanol ≈ 16
- Alcohols: 1° > 2° > 3°; water > ethanol
- o/p $-NO_2$ ↑ acidity; $-CH_3$ ↓
- Phenol: dissolves in NaOH, not $NaHCO_3$

Alcohol reactions

- Lucas: 3° at once, 2° 5 min, 1° none
- H_2SO_4: 443 K ethene; 413 K ether
- 1° → acid / aldehyde (PCC); 2° → ketone; 3° resists
- Cu, 573 K: 3° → alkene

Phenol reactions

- Br_2 water → 2,4,6-tribromophenol
- dil. HNO_3 → o + p; conc. → picric acid
- Kolbe → salicylic acid
- Reimer–Tiemann ($:CCl_2$) → salicylaldehyde

Ethers

- Williamson: SN2, 1° halide
- Bulky group on the alkoxide
- HI: SN2 at methyl; SN1 at 3°
- Anisole + HI → phenol + CH_3I

END OF NOTES · RAMGOVINDYADAV.COM