

Chapter 7 · Alcohols, Phenols and Ethers

CBSE Class 12 Chemistry (043) · Organic · Unit 7 = 6 marks · Ultimate Revision Sheet

60-SECOND RECALL

Acidity order	Phenol > water > alcohol · among alcohols $1^\circ > 2^\circ > 3^\circ$
Why phenol is acidic	Phenoxide ion is resonance stabilised
Lucas test	3° immediate turbidity · 2° in 5 min · 1° on heating
Victor Meyer	1° red · 2° blue · 3° colourless
Phenol test	Neutral $\text{FeCl}_3 \rightarrow$ violet colour
Williamson	$\text{R-X} + \text{R'ONa} \rightarrow$ ether — use primary halide
Kolbe	Phenol + $\text{CO}_2/\text{NaOH} \rightarrow$ salicylic acid
Reimer-Tiemann	Phenol + $\text{CHCl}_3/\text{NaOH} \rightarrow$ salicylaldehyde

1. Preparation

ALCOHOLS From alkenes: acid-catalysed hydration (Markovnikov); hydroboration-oxidation with $\text{B}_2\text{H}_6/\text{H}_2\text{O}_2$, OH^- gives the anti-Markovnikov alcohol.

From carbonyls: reduction with NaBH_4 or LiAlH_4 — aldehyde $\rightarrow 1^\circ$ alcohol, ketone $\rightarrow 2^\circ$ alcohol.

From Grignard reagents: $\text{HCHO} \rightarrow 1^\circ$, any other aldehyde $\rightarrow 2^\circ$, ketone $\rightarrow 3^\circ$ alcohol. This pattern is asked constantly.

PHENOLS From cumene (the industrial route): cumene + $\text{O}_2 \rightarrow$ cumene hydroperoxide $\rightarrow$ with dilute acid gives phenol + acetone.

From haloarenes: chlorobenzene + NaOH at 623 K, 300 atm (Dow's process).

From diazonium salts: warm with water.

From benzene sulphonic acid: fuse with NaOH .

2. Acidity — the central idea of the chapter

WHY PHENOL IS MORE ACIDIC THAN AN ALCOHOL On losing H^+ , phenol gives the phenoxide ion, whose negative charge is delocalised over the ring by resonance — so it is stable.

An alkoxide ion has no such delocalisation, and the +I effect of the alkyl group actually intensifies the negative charge, destabilising it.

Among alcohols, acidity falls $1^\circ > 2^\circ > 3^\circ$, because more alkyl groups mean more +I effect.

SUBSTITUENT EFFECT ON PHENOL Electron-withdrawing groups ($-\text{NO}_2$, $-\text{X}$) INCREASE acidity — they spread the negative charge further. Order: picric acid (2,4,6-trinitrophenol) > nitrophenol > phenol.

Electron-donating groups ($-\text{CH}_3$, $-\text{OCH}_3$) **DECREASE** acidity — cresol is a weaker acid than phenol.

3. Reactions of Alcohols

THE KEY REACTIONS With Na: gives alkoxide + H_2 — shows the acidic hydrogen.

Esterification: alcohol + carboxylic acid / acid chloride / anhydride $\rightarrow$ ester. The reaction with an acid chloride is faster and is called **acetylation**.

Dehydration with conc. H_2SO_4 : at 443 K $\rightarrow$ alkene; at 413 K $\rightarrow$ ether. The temperature is the whole question. Ease of dehydration: $3^\circ > 2^\circ > 1^\circ$.

Oxidation: $1^\circ \rightarrow$ aldehyde $\rightarrow$ carboxylic acid; PCC stops at the aldehyde. $2^\circ \rightarrow$ ketone. 3° resists oxidation (no α -H on the carbinol carbon).

THE THREE DISTINGUISHING TESTS

Test	1°	2°	3°
Lucas (conc. $\text{HCl} + \text{ZnCl}_2$)	Turbidity only on heating	Turbidity in ~5 min	Immediate turbidity
Victor Meyer	Red	Blue	Colourless
Oxidation	Aldehyde then acid	Ketone	No reaction

4. Reactions of Phenol

THE NAMED REACTIONS Kolbe's reaction: sodium phenoxide + CO_2 (400 K, 4–7 atm), then $\text{H}^+ \rightarrow$ salicylic acid (2-hydroxybenzoic acid) — the precursor of aspirin.

Reimer-Tiemann: phenol + $\text{CHCl}_3 + \text{NaOH}$, then $\text{H}^+ \rightarrow$ salicylaldehyde (2-hydroxybenzaldehyde).

The attacking species is dichlorocarbene, $:\text{CCl}_2$.

Bromination: with bromine water phenol gives an immediate white precipitate of 2,4,6-tribromophenol; in CS_2 at low temperature it gives mainly the para monobromo product.

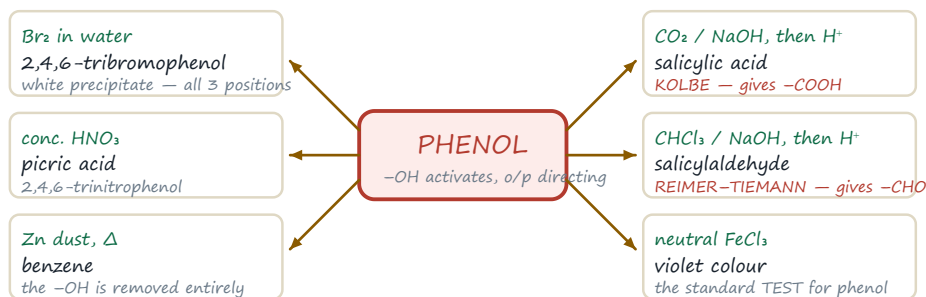
With neutral FeCl_3 : a violet colour — the standard test for phenol.

Nitration: dilute HNO_3 gives o- and p-nitrophenol; conc. HNO_3 gives picric acid.

TRAP The $-\text{OH}$ group is strongly activating and ortho/para directing, which is why phenol reacts with bromine water without any catalyst while benzene needs a Lewis acid.

Phenol does not undergo the Friedel-Crafts reaction well with AlCl_3 , because the Lewis acid bonds to the $-\text{OH}$ oxygen.

Phenol — the six reactions worth memorising as a map



Acidity: *picric acid* > *nitrophenol* > *phenol* > *ethanol* — phenol beats alcohol because the phenoxide ion is resonance stabilised; $-\text{NO}_2$ groups stabilise it further, $-\text{CH}_3$ groups do the opposite. But phenol does NOT react with NaHCO_3 — a carboxylic acid does. That is how you tell them apart.

Kolbe gives **-COOH**, Reimer-Tiemann gives **-CHO**. Both attach at the ortho position, and mixing up which reagent gives which is the usual lost mark.

5. Ethers

PREPARATION AND REACTIONS

Williamson synthesis: $\text{R-X} + \text{R}'\text{O}^-\text{Na}^+ \rightarrow \text{ether}$. It is an $\text{S}_{\text{N}}2$ reaction, so the halide **must be primary** — a tertiary halide gives the **alkene** by elimination instead. This is a favourite trap.

Cleavage by HX: the halide attacks the **smaller alkyl group** ($\text{S}_{\text{N}}2$), giving an alkyl halide plus an alcohol. If one group is **tertiary**, it goes by $\text{S}_{\text{N}}1$ and the **tertiary halide** forms.

Anisole (methoxybenzene) with HI gives **phenol + methyl iodide**, never iodobenzene, because the C-O bond to the ring has partial double bond character.

6. Question Triggers

what the reagent tells you

Reagent / clue	Product or answer
Conc. H_2SO_4 , 443 K	Alkene
Conc. H_2SO_4 , 413 K	Ether
PCC	1° alcohol → aldehyde (stops there)
$\text{CHCl}_3 + \text{NaOH}$ on phenol	Salicylaldehyde (Reimer-Tiemann)
$\text{CO}_2 + \text{NaOH}$ on phenol	Salicylic acid (Kolbe)
Neutral $\text{FeCl}_3 \rightarrow$ violet	Phenol present
Bromine water → white ppt	2,4,6-tribromophenol
B_2H_6 then $\text{H}_2\text{O}_2/\text{OH}^-$	Anti-Markovnikov alcohol
"distinguish 1°, 2°, 3° alcohol"	Lucas or Victor Meyer test

MOST-ASKED BOARD QUESTIONS

- [3M] Why is **phenol** more acidic than **ethanol**? Explain using resonance, and order substituted phenols by acidity.
- [3M] Write the **Kolbe** and **Reimer-Tiemann** reactions with equations.

3. [2M] Explain the **Williamson synthesis** and why a tertiary halide fails.
4. [2M] How will you distinguish between **1°, 2° and 3°** alcohols?
5. [2M] Conversion chains: propene → propan-2-ol, phenol → aspirin, etc.
6. [1M] What does phenol give with **neutral FeCl₃**? → **Violet colour**

THE HABIT THAT SCORES — Nearly every "explain the order" question in this chapter is answered by **resonance stabilisation of the anion** or the **+I / -I effect**. Name the effect, then say whether it stabilises or destabilises the conjugate base — that two-step sentence is the full mark.