FSc / ICS Part-II Chemistry — Punjab Board

CHAPTER 11
Alcohols, Phenols and Ethers

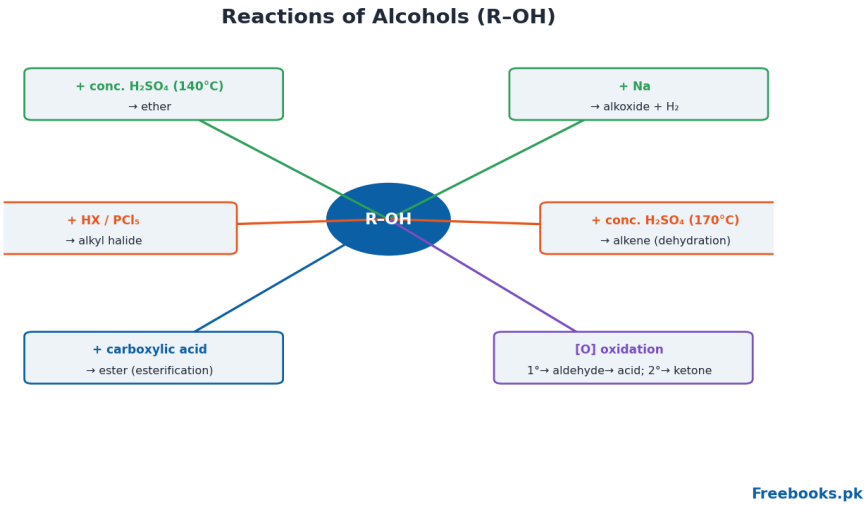

Figure 11.1 — The versatile reactions of alcohols (R–OH).

1. Chapter Overview

This chapter deals with three related families of oxygen-containing organic compounds. Alcohols (R–OH) have a hydroxyl group attached to a carbon chain; phenols (C_6H_5–OH) have a hydroxyl group attached directly to a benzene ring; and ethers (R–O–R′) have an oxygen atom joining two carbon groups. Alcohols such as ethanol are among the most useful of all organic compounds — as solvents, fuels, antiseptics and starting materials — so most of the chapter focuses on their preparation, properties and reactions, followed by the special behaviour of phenols and ethers.

2. Learning Objectives

- Define and classify alcohols as primary, secondary and tertiary.
- Describe the preparation of alcohols, including fermentation.
- Describe the important reactions of alcohols.
- Distinguish 1°, 2° and 3° alcohols by oxidation and the Lucas test.
- Explain why phenol is acidic and describe its reactions.
- Describe the preparation (Williamson synthesis) and properties of ethers.

3. Key Concepts

3.1 Alcohols and Their Classification

An alcohol contains the hydroxyl (–OH) functional group. Alcohols are classified by the carbon that carries the –OH group: in a primary (1°) alcohol that carbon is joined to one other carbon, in a secondary (2°) alcohol to two, and in a tertiary (3°) alcohol to three. This classification controls how the alcohol behaves on oxidation and in the Lucas test.

3.2 Preparation — Including Fermentation

Alcohols can be prepared by hydration of alkenes (H_2O/H^+), by reduction of aldehydes and ketones, and by the hydrolysis of alkyl halides. Ethanol is also made on a large scale by fermentation, in which enzymes (zymase) in yeast convert sugars into ethanol and carbon dioxide: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$. This is the basis of the alcoholic-drinks industry and of bio-ethanol fuel.

3.3 Reactions of Alcohols

The –OH group makes alcohols react in several ways. With sodium they release hydrogen and form alkoxides. With concentrated sulphuric acid they undergo dehydration — at about 170 °C to give an alkene, or at about 140 °C to give an ether. With hydrogen halides or PCl_5 the –OH is replaced by a halogen to give an alkyl halide. With carboxylic acids they form sweet-smelling esters (esterification). And they can be oxidised, which distinguishes the three classes.

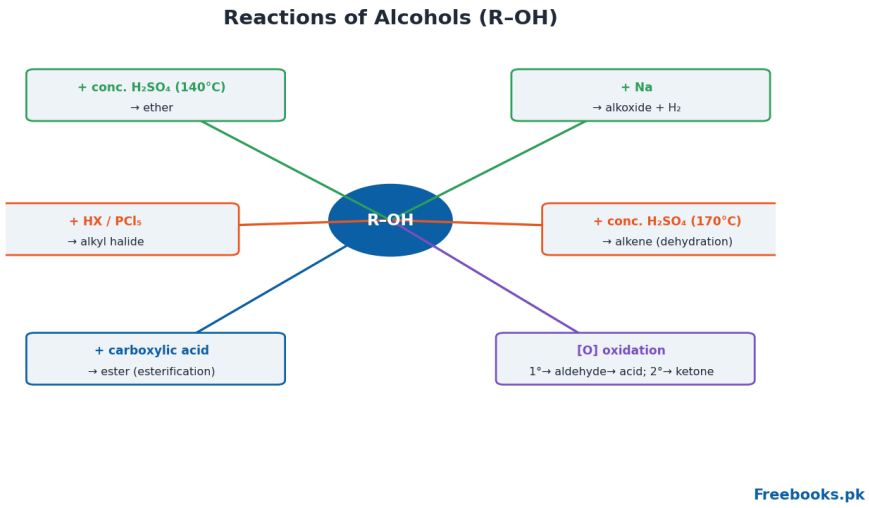

Figure 11.2 — Summary of alcohol reactions.

Distinguishing 1°, 2° and 3° Alcohols

On oxidation, a primary alcohol first gives an aldehyde and then a carboxylic acid; a secondary alcohol gives a ketone; and a tertiary alcohol is not easily oxidised, because the carbon bearing the –OH has no hydrogen to remove. The Lucas test (with anhydrous $ZnCl_2$ and concentrated HCl) also distinguishes them: tertiary alcohols react at once (immediate turbidity), secondary alcohols react within a few minutes, and primary alcohols do not react at room temperature.

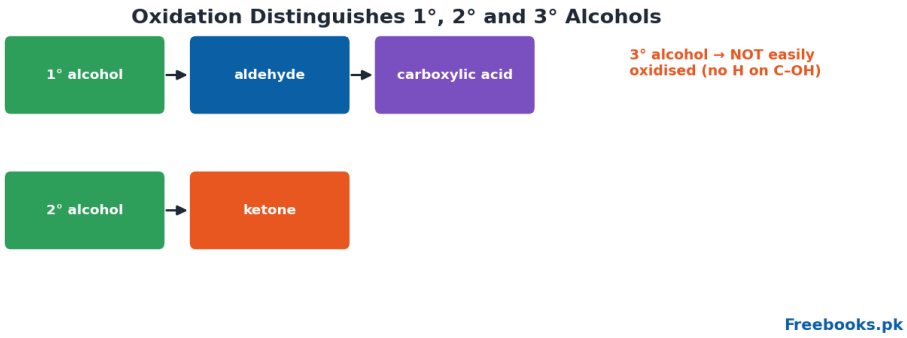

Figure 11.3 — Oxidation products distinguish 1°, 2° and 3° alcohols.

> **Memory Trick**
> **Oxidation shortcut:** 1° → aldehyde → acid; 2° → ketone; 3° → no reaction (no H on the C–OH).

3.4 Phenols

In phenol (C_6H_5OH) the –OH group is attached directly to the benzene ring. Unlike ordinary alcohols, phenol is weakly acidic: it reacts with sodium hydroxide to form sodium phenoxide and water, because the ring stabilises the phenoxide ion by delocalising its negative charge. Phenol also undergoes electrophilic substitution on the ring very readily (for example bromination), and it is used to make plastics (Bakelite), antiseptics and dyes.

Teacher's Note

A key comparison for exams: ordinary alcohols are neutral, but phenol is weakly acidic because the benzene ring delocalises the negative charge of the phenoxide ion. Emphasise this difference.

3.5 Ethers

Ethers have the general formula R–O–R′. They are fairly unreactive and are widely used as solvents (for example diethyl ether). A common laboratory method of making them is the Williamson synthesis, in which a sodium alkoxide reacts with an alkyl halide: R–ONa + R′–X → R–O–R′ + NaX.

4. Important Definitions

Term	Definition
Alcohol	An organic compound containing the –OH group attached to a carbon chain.
Phenol	A compound with –OH attached directly to a benzene ring.
Ether	A compound of the type R–O–R′ with oxygen joining two carbon groups.
Fermentation	Enzyme-catalysed conversion of sugars into ethanol and CO_2.
Esterification	Reaction of an alcohol with a carboxylic acid to form an ester and water.
Williamson synthesis	Preparation of an ether from a sodium alkoxide and an alkyl halide.

5. Formulas / Rules

Must-Know Facts

Classes: 1°, 2°, 3° alcohols by the carbon bearing –OH.
Dehydration: conc. H_2SO_4 at 170 °C → alkene; at 140 °C → ether.
Oxidation: 1° → aldehyde → acid; 2° → ketone; 3° → no easy oxidation.
Lucas test: 3° immediate, 2° in minutes, 1° no reaction (cold).
Fermentation: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ (zymase).
Phenol is weakly acidic; reacts with NaOH → sodium phenoxide.

6. Diagrams / Illustrations

Key diagrams for revision:

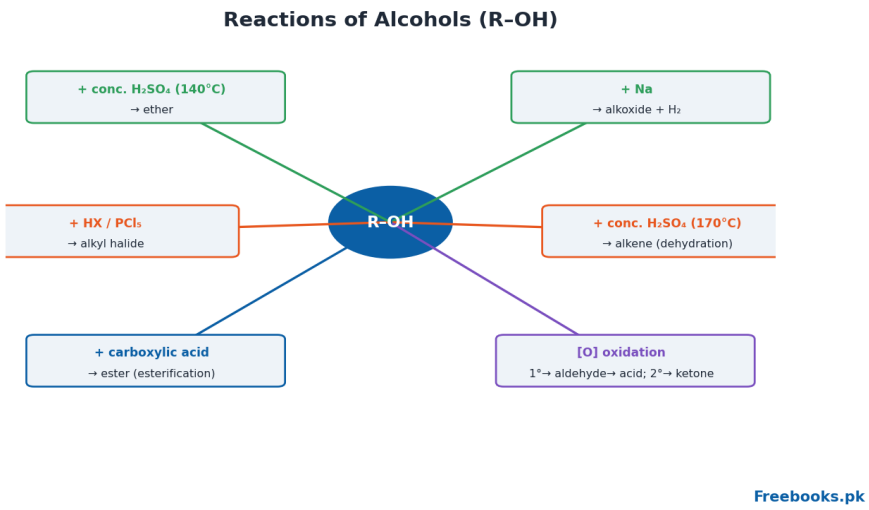

Diagram 1 — Reactions of alcohols.

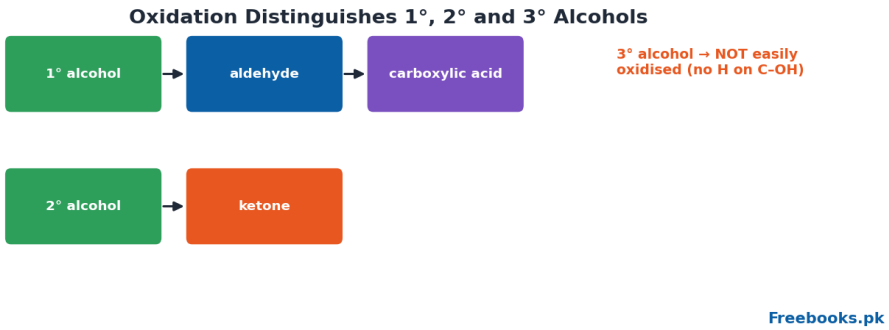

Diagram 2 — Oxidation distinguishes alcohol classes.

7. Solved Examples

Example 1 — Oxidation

Q: What is formed when ethanol (a 1° alcohol) is oxidised?

Solution: It is first oxidised to ethanal (an aldehyde) and then to ethanoic acid (a carboxylic acid).

Example 2 — Distinguishing alcohols

Q: How can you distinguish a tertiary alcohol from a primary alcohol?

Solution: Use the Lucas test ($ZnCl_2$ + conc. HCl). A tertiary alcohol gives immediate turbidity; a primary alcohol does not react at room temperature. Alternatively, on oxidation the tertiary alcohol resists oxidation while the primary gives an aldehyde/acid.

Example 3 — Acidity of phenol

Q: Why is phenol acidic while ethanol is neutral?

Solution: When phenol loses H^+, the benzene ring delocalises the negative charge of the phenoxide ion, stabilising it. Ethanol's alkoxide has no such stabilisation, so ethanol is neutral.

8. Short Questions

Q1. What is the functional group of alcohols?
Ans. The hydroxyl group, –OH.

Q2. How are alcohols classified?
Ans. As primary, secondary or tertiary, depending on the number of carbons attached to the carbon bearing –OH.

Q3. What is fermentation?
Ans. The enzyme-catalysed conversion of sugars into ethanol and CO_2 by yeast.

Q4. What forms when a 2° alcohol is oxidised?
Ans. A ketone.

Q5. Why can a tertiary alcohol not be easily oxidised?
Ans. The carbon bearing –OH has no hydrogen atom to be removed during oxidation.

Q6. What is the Lucas test used for?
Ans. To distinguish 1°, 2° and 3° alcohols by how fast they react with $ZnCl_2$/conc. HCl.

Q7. Why is phenol acidic?
Ans. The phenoxide ion is stabilised by delocalisation of its charge over the benzene ring.

Q8. Name a method to prepare ethers.
Ans. The Williamson synthesis (sodium alkoxide + alkyl halide).

9. Long Questions

Q1. Describe the important reactions of alcohols.

The hydroxyl group makes alcohols react in several characteristic ways. With active metals such as sodium they release hydrogen gas and form alkoxides, showing that the O–H bond is weakly acidic. With concentrated sulphuric acid they undergo dehydration: at about 170 °C an alcohol loses water to form an alkene, while at about 140 °C two molecules combine with loss of water to give an ether. With hydrogen halides, PCl_5 or PCl_3 the –OH group is replaced by a halogen atom to give an alkyl halide. With carboxylic acids, in the presence of a little acid catalyst, alcohols form sweet-smelling esters (esterification), the reverse being hydrolysis. Finally, alcohols can be oxidised: a primary alcohol gives first an aldehyde and then a carboxylic acid, a secondary alcohol gives a ketone, and a tertiary alcohol resists oxidation. These reactions make alcohols central to organic synthesis.

Q2. How are primary, secondary and tertiary alcohols distinguished?

Primary, secondary and tertiary alcohols can be told apart by two simple methods. The first is oxidation: when treated with an oxidising agent such as acidified potassium dichromate, a primary alcohol is oxidised first to an aldehyde and then to a carboxylic acid, a secondary alcohol is oxidised to a ketone, and a tertiary alcohol is not oxidised under ordinary conditions because the carbon carrying the –OH group has no hydrogen atom to be removed. The second method is the Lucas test, in which the alcohol is shaken with the Lucas reagent (anhydrous zinc chloride dissolved in concentrated hydrochloric acid): a tertiary alcohol produces cloudiness (turbidity) immediately, a secondary alcohol produces it within about five minutes, and a primary alcohol

produces no turbidity at room temperature. Together these tests give a reliable way of classifying an unknown alcohol.

Q3. Compare alcohols and phenols.

Alcohols and phenols both contain the hydroxyl group, but they differ in where it is attached and in how it behaves. In an alcohol the –OH is joined to a saturated carbon of a chain, whereas in a phenol it is joined directly to a benzene ring. This difference gives them different acidity: ordinary alcohols are essentially neutral and do not react with sodium hydroxide, while phenol is weakly acidic and does react with sodium hydroxide to form sodium phenoxide, because the benzene ring can delocalise and stabilise the negative charge of the phenoxide ion. Phenols also undergo electrophilic substitution on the ring much more readily than benzene itself, and they give a characteristic violet colour with neutral ferric chloride, a test that alcohols do not give. Thus, although related, alcohols and phenols show clearly different chemistry.

10. Multiple Choice Questions (MCQs)

1. The functional group of alcohols is:
(A) –CHO (B) –OH (C) –COOH (D) –O–

2. Oxidation of a primary alcohol first gives:
(A) ketone (B) aldehyde (C) ether (D) ester

3. Oxidation of a secondary alcohol gives:
(A) aldehyde (B) ketone (C) acid (D) alkene

4. Which alcohol resists easy oxidation?
(A) primary (B) secondary (C) tertiary (D) all equally

5. Fermentation of glucose gives ethanol and:
(A) O_2 (B) CO_2 (C) H_2 (D) CH_4

6. Dehydration of ethanol at 170 °C gives:
(A) ether (B) ethene (C) ethane (D) ethanal

7. The Lucas test distinguishes:
(A) acids (B) alcohols (1°,2°,3°) (C) ethers (D) esters

8. Phenol reacting with NaOH shows it is:
(A) basic (B) neutral (C) weakly acidic (D) amphoteric

9. Ethers are prepared by the:
(A) Wurtz reaction (B) Williamson synthesis (C) Kolbe reaction (D) Cannizzaro reaction

10. Alcohol + carboxylic acid gives:
(A) ether (B) ester (C) ketone (D) amide

MCQ Answer Key

1-B 2-B 3-B 4-C 5-B 6-B 7-B 8-C 9-B 10-B

11. Quick Revision / Summary

- Alcohol R–OH; classify 1°, 2°, 3° by carbon bearing –OH.
- Prepared by hydration of alkenes, reduction, and fermentation (sugar → ethanol + CO_2).

- Reactions: with Na (H_2), dehydration (alkene/ether), with HX/PCl_5 (halide), esterification, oxidation.
- Oxidation: 1° → aldehyde → acid; 2° → ketone; 3° → resists.
- Lucas test: 3° immediate, 2° minutes, 1° no reaction cold.
- Phenol is weakly acidic; ethers (R–O–R′) made by Williamson synthesis.

12. Exam Tips

Teacher's Note

Draw the alcohol-reactions map and label conditions (140 °C vs 170 °C for H_2SO_4).

Learn oxidation products for each class — 1°→aldehyde→acid, 2°→ketone, 3°→no reaction.

Lucas test order (3° > 2° > 1°) is a favourite short question.

Explain phenol's acidity via delocalisation of the phenoxide charge.

Remember fermentation equation and the enzyme (zymase in yeast).