Collegedunia NCERT Notes

The Ultimate NCERT Revision Guide for Class 12 Chemistry (2026-27 / New NCERT)

Chapter 7: Alcohols, Phenols and Ethers

Class 12th Chemistry — Organic Chemistry — Functional Group Family

What you will master in this chapter

The trio of **alcohols, phenols and ethers** forms the backbone of oxygen-containing organic chemistry. You will learn to (i) name and classify them by IUPAC rules, (ii) prepare them by half a dozen industrial and laboratory routes, (iii) explain their physical behaviour through hydrogen bonding, (iv) work through every chemical reaction the syllabus demands — with mechanisms for the high-yield ones, and (v) handle the pH/acidity arguments that JEE and NEET ask every year.

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1 Classification and IUPAC Nomenclature

Alcohols, phenols and ethers are all derivatives of water in which one or both hydrogens of H_2O are replaced by carbon-containing groups. Substitute one H of water by an alkyl group and you get an alcohol R – OH; replace it by an aryl group and you get a phenol Ar – OH; replace both H's by alkyl/aryl groups and you get an ether R$-$O$-$R′. The hydroxyl in alcohols sits on an sp^3 **carbon**, the hydroxyl in phenols sits on an sp^2 **carbon of an aromatic ring**, and ethers carry no O–H bond at all — this single structural distinction drives every chemical difference that follows.

1.1 Classification of Alcohols

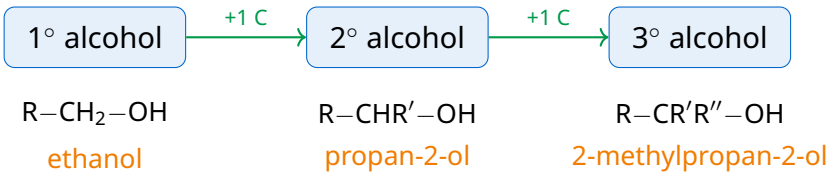
Monohydric alcohols (one –OH group) are split by the hybridisation of the carbon attached to oxygen.

(i) C(sp^3) – OH alcohols — the –OH is on an sp^3 carbon. These are further classified as:

- **Primary (1°)**: –OH on a carbon attached to only one other carbon (e.g. ethanol, CH_3CH_2OH).
- **Secondary (2°)**: –OH on a carbon attached to two carbons (e.g. propan-2-ol, $(CH_3)_2CHOH$).
- **Tertiary (3°)**: –OH on a carbon attached to three carbons (e.g. 2-methylpropan-2-ol, $(CH_3)_3COH$).
- **Allylic**: –OH on the sp^3 carbon adjacent to a C = C bond (e.g. $CH_2 = CH - CH_2 - OH$).
- **Benzylic**: –OH on the sp^3 carbon adjacent to an aromatic ring (e.g. $C_6H_5 - CH_2 - OH$).

(ii) C(sp^2) – OH alcohols (vinyl alcohols) — the –OH sits on a C = C carbon, e.g. $CH_2 = CH - OH$. These are unstable and tautomerise to the carbonyl form.

Polyhydric alcohols carry two (**diols** like ethane-1,2-diol), three (**triols** like glycerol — propane-1,2,3-triol), or more –OH groups.



Why classification matters

The 1°/2°/3° label is the single best predictor of how an alcohol will behave. It governs the speed of dehydration (3° fastest), the speed of the Lucas test ($HCl/ZnCl_2$, 3° turbid instantly), the oxidation product (1° →aldehyde→acid, 2° →ketone, 3° →no reaction), and the mechanism with HX (3° via S_N1, 1° via S_N2).

1.2 Classification of Phenols and Ethers

Phenols carry –OH directly on an aromatic ring. They are mono-, di- or trihydric depending on how many –OH groups the ring carries (e.g. phenol, catechol, pyrogallol).

Ethers carry the C – O – C link. They are **symmetrical (simple)** if the two carbon-containing groups are identical — diethyl ether $C_2H_5 - O - C_2H_5$ — and **unsymmetrical (mixed)** otherwise — ethyl methyl ether $C_2H_5 - O - CH_3$, anisole $C_6H_5 - O - CH_3$.

1.3 IUPAC Nomenclature

The IUPAC rules for the three families are summarised below.

IUPAC Naming Rules

Alcohols: Drop *-e* of the parent alkane, add *-ol*. Number the chain so –OH gets the lowest locant.

Polyhydric alcohols: Keep the *-e* of alkane, add *-diol/-triol* with locants.

Phenols: The trivial name "phenol" is itself an accepted IUPAC name. Substituents are numbered with –OH on C-1.

Ethers (IUPAC): Treat the smaller –OR group as an **alkoxy** substituent on the longer parent chain. Example: $CH_3-O-CH_2CH_2CH_3$ is 1-methoxypropane.

Structure	Common name	IUPAC name
CH_3OH	Methyl alcohol	Methanol
$CH_3CH_2CH_2OH$	n-Propyl alcohol	Propan-1-ol
$(CH_3)_2CHOH$	Isopropyl alcohol	Propan-2-ol
$(CH_3)_3COH$	$tert$-Butyl alcohol	2-Methylpropan-2-ol
$HOCH_2CH_2OH$	Ethylene glycol	Ethane-1,2-diol
$HOCH_2CH(OH)CH_2OH$	Glycerol	Propane-1,2,3-triol
C_6H_5OH	Phenol / carbolic acid	Phenol
ortho-$CH_3C_6H_4OH$	o-Cresol	2-Methylphenol
1,4-$C_6H_4(OH)_2$	Hydroquinone / quinol	Benzene-1,4-diol
$C_2H_5OC_2H_5$	Diethyl ether	Ethoxyethane
$CH_3OC_6H_5$	Anisole / methyl phenyl ether	Methoxybenzene

Naming shortcut for ethers

For an ether R−O−R′, identify the larger group — this becomes the parent. The smaller group plus the oxygen becomes the **alkoxy** prefix (-OCH_3 = methoxy, -OC_2H_5 = ethoxy, -OC_6H_5 = phenoxy). One-second naming: $CH_3-O-CH_2CH_2CH_3$ → propane parent, methoxy substituent → **1-methoxypropane**.

Cresol positions

For methylphenols: **2-methylphenol** = o-cresol (**o**rtho, next door), **3-methylphenol** = m-cresol (**m**eta, one seat over), **4-methylphenol** = p-cresol (**p**ara, across the ring). Mnemonic: **O**-M-**P** read as the seats 2-3-4.

2 Structure of the Functional Groups

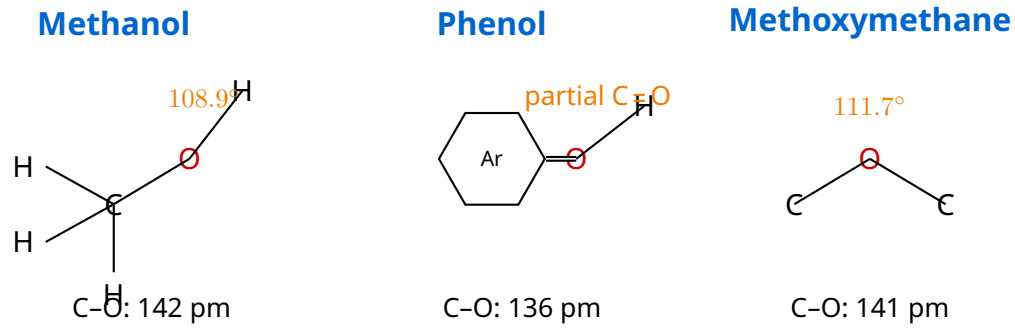
The hydroxyl and ether oxygens are tetrahedrally hybridised, but small angle and bond-length differences across the three families produce dramatically different chemistry. Understanding these geometric facts up front saves a lot of confusion later.

2.1 Geometry around oxygen

In **methanol**, oxygen is sp^3. It uses two of its four sp^3 orbitals to form a sigma bond to carbon and a sigma bond to hydrogen; the other two carry lone pairs. The C–O–H angle is about $108.9°$, slightly less than the ideal tetrahedral $109.5°$ because the two lone pairs squeeze the bonding orbitals together.

In **phenol**, the carbon attached to oxygen is now sp^2 (it belongs to the aromatic ring). The C–O bond length shrinks to about **136 pm** from **142 pm** in methanol. Two reasons: (i) the sp^2 carbon is smaller than an sp^3 carbon, and (ii) the lone pair on oxygen conjugates with the aromatic π system, giving the C–O bond partial double-bond character.

In **ethers** (e.g. methoxymethane), the oxygen carries two bulky alkyl groups; the C–O–C angle widens to about $111.7°$ because of the steric repulsion between them. C–O bond length is roughly 141 pm, very close to that of alcohols.



Caption: Comparison of bond geometry. The aromatic ring in phenol shortens the C–O bond via p–π conjugation; the two bulky R groups in an ether open the C–O–C angle above tetrahedral.

Take-away on geometry

The shorter, partially-double C–O bond in phenols means the oxygen lone pair is partially delocalised into the ring. This single fact explains why phenols are millions of times more acidic than alcohols (Section 4) and why their ring is so reactive towards electrophilic aromatic substitution (Section 5).

3 Preparation of Alcohols, Phenols and Ethers

This section gathers every preparation route the NCERT syllabus expects. Group them mentally: alcohols are made from alkenes and carbonyls; phenols are made from aromatics; ethers come from alcohols (dehydration) or from alkoxides (Williamson).

3.1 Alcohols from alkenes

(i) Acid-catalysed hydration. Alkenes pick up water in the presence of dilute H_2SO_4 (or H_3PO_4) following **Markovnikov's rule** — the proton attaches to the carbon already carrying more hydrogens.

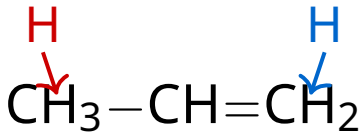
$$CH_3-CH=CH_2 + H_2O \xrightarrow{H+} CH_3-CHOH-CH_3$$

Mechanism (three steps):

1. **Protonation of the alkene** forms a carbocation: $H^+ + H_2O \longrightarrow H_3O^+$, then H_3O^+ delivers H^+ to the alkene to make the more stable carbocation (Markovnikov).
2. **Nucleophilic attack of water** on the carbocation gives a protonated alcohol $R-OH_2^+$.
3. **Deprotonation** by another water molecule yields the alcohol $R-OH$.

(ii) Hydroboration–oxidation. Diborane $(BH_3)_2$ adds across the double bond. Boron settles on the **less substituted** (more-H) carbon, giving a trialkyl borane. Alkaline H_2O_2 then replaces boron with –OH, retaining the position. Overall the OH ends up on the less substituted carbon — **anti-Markovnikov addition** — in excellent yield.

$$6\,RCH=CH_2 + (BH_3)_2 \longrightarrow 2\,(RCH_2-CH_2)_3B \xrightarrow{H_2O_2,\ OH^-} 6\,RCH_2-CH_2-OH + 2\,B(OH)_3$$



Markovnikov: H^+/H_2O

anti-Mark.: $(BH_3)_2 / H_2O_2$

OH (anti-Mark.) OH (Mark.)

Markovnikov vs anti-Markovnikov in 5 seconds

If the reagent is H^+/H_2O (acid + water), –OH goes to the more substituted carbon — think "rich get richer". If the reagent is diborane followed by H_2O_2/OH^-, the –OH goes to the less substituted carbon — the boron pre-empts the favoured position.

3.2 Alcohols from carbonyl compounds

(i) Reduction of aldehydes and ketones. Aldehydes give primary alcohols; ketones give secondary alcohols. Reagents commonly used are H_2/Pt or Pd or Ni (catalytic hydrogenation), $NaBH_4$, or $LiAlH_4$.

$$R{-}CHO \xrightarrow{NaBH_4} R{-}CH_2OH \qquad R{-}CO{-}R' \xrightarrow{NaBH_4} R{-}CHOH{-}R'$$

(ii) Reduction of carboxylic acids and esters. Strong reagent $LiAlH_4$ reduces –COOH all the way to $-CH_2OH$ in excellent yield.

$$R{-}COOH \xrightarrow[(ii)\ H2O]{(i)\ LiAlH4} R{-}CH_2OH$$

Commercially, the cheaper route is to convert the acid to its ester, then hydrogenate the ester catalytically.

3.3 Alcohols from Grignard reagents

Grignard reagents R – MgX are powerful carbon nucleophiles. They add across the polarised C = O of an aldehyde or ketone to form a magnesium alkoxide adduct, which is then hydrolysed to the alcohol.

$$R{-}MgX + R'_2C{=}O \longrightarrow R'_2C(OMgX){-}R \xrightarrow{H2O} R'_2C(OH){-}R + Mg(OH)X$$

The carbonyl substrate dictates which class of alcohol you obtain:

Carbonyl substrate	Class of alcohol	Example product (with CH_3MgBr)
Methanal (HCHO)	Primary (1°)	Ethanol
Any other aldehyde R – CHO	Secondary (2°)	e.g. propan-2-ol from CH_3CHO
Any ketone R–CO–R′	Tertiary (3°)	e.g. 2-methylpropan-2-ol from $(CH_3)_2CO$

Grignards are intolerant

Grignard reagents are destroyed by anything with an acidic O–H or N–H bond: water, alcohols, phenols, carboxylic acids, amines all kill the reagent before it can attack the carbonyl. Substrate purity matters, and the carbonyl substrate itself must be free of –OH groups (otherwise you waste one equivalent of RMgX on a proton transfer).

3.4 Preparation of Phenols

1. From haloarenes (Dow process). Chlorobenzene fused with molten NaOH at **623 K and 320 atm** gives sodium phenoxide, acidified to phenol.

$$C_6H_5{-}Cl + 2\,NaOH \xrightarrow[320\,atm]{623\,K} C_6H_5{-}ONa + NaCl + H_2O \xrightarrow{H+} C_6H_5{-}OH$$

2. From benzene sulphonic acid. Sulphonate benzene with oleum, fuse the sulphonic acid with molten NaOH, acidify.

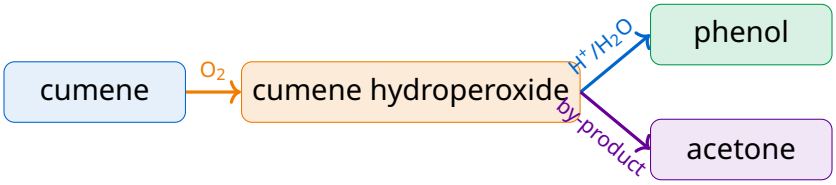
$$C_6H_6 \xrightarrow{H2SO4(oleum)} C_6H_5{-}SO_3H \xrightarrow{NaOH,\ \Delta} C_6H_5{-}ONa \xrightarrow{H+} C_6H_5{-}OH$$

3. From diazonium salts. A primary aromatic amine is diazotised with $NaNO_2$/HCl at 273–278 K, then the diazonium salt is hydrolysed in warm water to give phenol.

$$C_6H_5{-}NH_2 \xrightarrow[273-278\,K]{NaNO2,\ HCl} C_6H_5{-}N_2{}^{+}Cl^{-} \xrightarrow{H2O,\ warm} C_6H_5{-}OH + N_2 + HCl$$

4. From cumene (industrial route). This is the dominant route worldwide. Cumene (isopropylbenzene) is oxidised in air to cumene hydroperoxide; dilute acid then cleaves the peroxide into phenol and acetone.

$$C_6H_5{-}CH(CH_3)_2 \xrightarrow{O2(air)} C_6H_5{-}C(CH_3)_2{-}OOH \xrightarrow{H+,H2O} C_6H_5{-}OH + (CH_3)_2C{=}O$$



The cumene process pays twice

The cumene process is the most economically important phenol synthesis because it co-produces acetone, an enormously useful solvent. Industries

that need either phenol or acetone — nylon-66 (from phenol), polycarbonate plastics (from phenol via bisphenol-A), and methyl methacrylate (Plexiglas, from acetone) — can absorb both streams. Over 95% of the world's phenol comes from this one route.

3.5 Preparation of Ethers

1. Acid dehydration of alcohols. Two molecules of a primary alcohol lose one molecule of water to form an ether. The mechanism is S_N2 — one protonated alcohol is attacked by a second alcohol.

$$2\,C_2H_5OH \xrightarrow[413\,K]{H2SO4} C_2H_5{-}O{-}C_2H_5 + H_2O$$

At **443 K** the same alcohol gives ethene (elimination wins); at **413 K** the ether wins. The method works only for **primary alcohols with unhindered carbon**; with 2°/3° alcohols, S_N1 takes over and elimination dominates so you get the alkene, not the ether.

2. Williamson synthesis. The most reliable lab method. A sodium alkoxide attacks a primary alkyl halide by S_N2.

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

The alkyl halide must be primary; with 3° alkyl halides, the alkoxide acts as a strong base and elimination dominates, giving an alkene exclusively. Phenoxides also work (so anisole is made from $C_6H_5 - O^-Na^+ + CH_3 - Br$).

Pick the right disconnection

For an unsymmetrical ether $R{-}O{-}R'$, always disconnect so the **primary alkyl halide** is on the side of the leaving group and the bulkier group is on the alkoxide side. To make t-butyl ethyl ether, use $(CH_3)_3C - O^-Na^+ + CH_3CH_2 - Br$, never the reverse — (CH3)3C-Br would just eliminate to isobutylene.

Williamson with a tertiary halide fails

A common exam trap: writing $(CH_3)_3C - Br + CH_3CH_2 - O^-Na^+ \longrightarrow (CH_3)_3C - O - C_2H_5$. The actual product is $(CH_3)_2C = CH_2 + C_2H_5OH + NaBr$. Ethoxide is a strong base; it attacks the β-hydrogen of the tertiary halide and gives an E2 alkene, not the ether.

4 Physical Properties of Alcohols, Phenols and Ethers

The physical properties of the three families track directly to the presence or absence of an O–H bond and the resulting hydrogen-bonding ability.

4.1 Boiling points

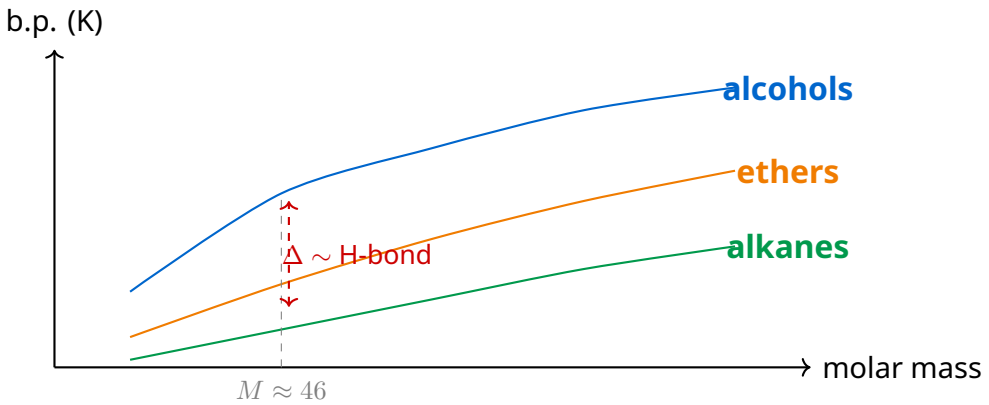
Alcohols and phenols boil much higher than alkanes, ethers, or haloalkanes of comparable molar mass, purely because of **intermolecular hydrogen bonding**. The energy cost of disrupting an H-bonded liquid network is what shows up as elevated boiling point.

Compound	Formula	M (g mol^{-1})	b.p. / K
n-Pentane	C_5H_{12}	72	309
Ethoxyethane	$C_4H_{10}O$	74	308
Butan-1-ol	$C_4H_{10}O$	74	390
Ethanol	C_2H_6O	46	351
Methoxymethane	C_2H_6O	46	248
Propane	C_3H_8	44	231

Observe: ethanol (351 K), methoxymethane (248 K), and propane (231 K) all have the same molar mass region, yet ethanol boils dramatically higher because only ethanol can H-bond.

Two extra trends within alcohols themselves:

- **Boiling point rises with chain length** (larger van der Waals contact area).
- **Boiling point falls with branching**: compact molecules have less surface for van der Waals contact. So b.p. of butan-1-ol (390 K) $>$ 2-methylpropan-1-ol $>$ 2-methylpropan-2-ol.

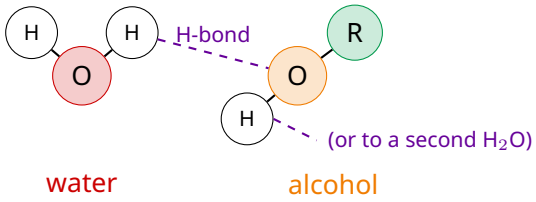


4.2 Solubility in water

Lower alcohols and phenol are appreciably water-soluble because the –OH group H-bonds to water. Solubility falls steeply as the carbon chain grows — the hydro-

carbon tail is hydrophobic, and at C_4/C_5 the tail wins. Methanol, ethanol, propan-1-ol are infinitely miscible; butan-1-ol is partially miscible; pentan-1-ol onwards is nearly immiscible.

Ethers are surprisingly water-soluble at low molar mass — the lone pair on oxygen accepts H-bonds from water (even though ethers cannot donate H-bonds). Ethoxyethane (7.5 g per 100 mL water) is soluble to roughly the same extent as butan-1-ol (9 g per 100 mL water).



Solubility heuristic

Up to 3 carbons, all alcohols are infinitely water-miscible. From 4 to 5 carbons, partial miscibility. From 6 carbons onwards, treat the alcohol as practically insoluble. Mnemonic: **"3 in, 5 borderline, 6 out".**

5 Chemical Reactions of Alcohols and Phenols

Alcohols and phenols behave both as nucleophiles (the lone pair on oxygen attacks) and as electrophiles after protonation (the carbon now bears the leaving group $-OH_2^+$). Cleavage either at the **O–H** or at the **C–O** bond defines two big families of reactions.

5.1 Reactions involving O–H cleavage — acidity

(i) Reaction with active metals. Both alcohols and phenols release H_2 on contact with Na, K, or Al, producing the corresponding alkoxide or phenoxide.

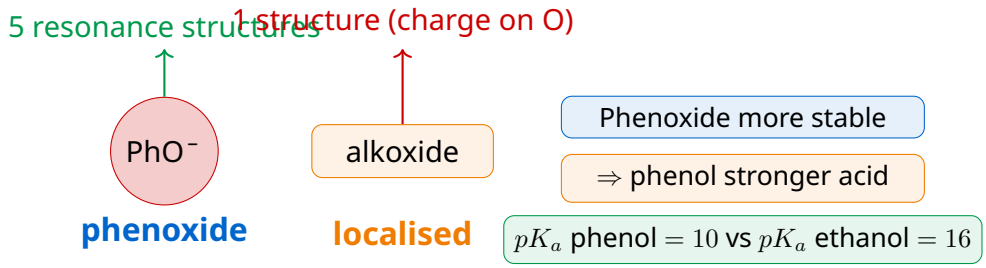
$$2\,R{-}OH + 2\,Na \longrightarrow 2\,R{-}O^-Na^+ + H_2 \qquad 2\,C_6H_5{-}OH + 2\,Na \longrightarrow 2\,C_6H_5{-}O^-Na^+ + H_2$$

Phenols additionally react with **aqueous NaOH**, which alcohols do *not*:

$$C_6H_5{-}OH + NaOH \longrightarrow C_6H_5{-}O^-Na^+ + H_2O$$

This single fact establishes that phenols are stronger acids than alcohols — strong enough to be deprotonated by an aqueous base, whereas alcohols are not.

(ii) Why phenols are millions of times more acidic. The decisive factor is the stability of the conjugate base, the **phenoxide ion**. The negative charge on phenoxide is delocalised onto the ring through five resonance structures.



In an alkoxide R – O^-, the negative charge sits stubbornly on a single oxygen — no delocalisation, no stabilisation. So phenol gives up its H much more readily.

Compound	Formula	pK_a
p-Nitrophenol	p-$O_2N-C_6H_4-OH$	7.1
o-Nitrophenol	o-$O_2N-C_6H_4-OH$	7.2
m-Nitrophenol	m-$O_2N-C_6H_4-OH$	8.3
Phenol	C_6H_5-OH	10.0
o-Cresol / m-Cresol / p-Cresol	methylphenols	10.1–10.2
Ethanol	C_2H_5-OH	15.9

The lower the pK_a, the stronger the acid. **Phenol is roughly 10^6 times more acidic than ethanol.**

(iii) Substituent effects on phenol acidity.

- **Electron-withdrawing groups** (e.g. $-NO_2$, $-Cl$, $-CN$) at $ortho$ or $para$ stabilise the negative charge on phenoxide $\rightarrow$ **stronger acid**. Resonance delocalisation onto the substituent only operates from o or p.
- **Electron-donating groups** ($-CH_3$, $-OCH_3$, $-NH_2$) at $ortho$ or $para$ destabilise the negative charge $\rightarrow$ **weaker acid**.
- $meta$-substituents lack the through-resonance pathway, so their effect is weaker (mostly inductive).

Acid-strength order example: C_3H_7OH < p-cresol < phenol < m-nitrophenol < 3,5-dinitrophenol < 2,4,6-trinitrophenol (picric acid).

Acidity of phenols

EWG win, EDG sin. Electron-Withdrawing Groups Win the negative charge $\rightarrow$ acid stronger. Electron-Donating Groups Sin (destabilise) $\rightarrow$ acid weaker. And only o/p positions feed resonance into the charge — m-substituents only push or pull inductively.

(iv) Esterification. Alcohols and phenols react with carboxylic acids (using catalytic conc. H_2SO_4), acid chlorides (using pyridine as HCl scavenger), or acid anhydrides to give esters.

$$R-OH + R'-COOH \xrightarrow[\Delta]{conc.\ H2SO4} R'-COO-R + H_2O$$

$$\text{R/Ar}-\text{OH} + \text{R}'-\text{COCl} \xrightarrow{pyridine} \text{R}'-\text{COO}-\text{R/Ar} + \text{HCl}$$

Acetylation of salicylic acid with acetic anhydride produces **aspirin**.

Aspirin: the everyday acetylation

The acetylation of salicylic acid (2-hydroxybenzoic acid) by acetic anhydride is one of the most-run reactions on Earth — aspirin is produced by the tens of thousands of tonnes annually. Pharmaceutical aspirin tablets are this very acetyl ester, sold for analgesic, anti-inflammatory and antipyretic action.

5.2 Reactions involving C–O cleavage (alcohols only)

This family shows up only with alcohols — phenols don't undergo C–O cleavage (the sp^2 Ar – O bond is too strong) except in the very specific case of distillation over Zn.

1. Reaction with hydrogen halides.

$$\text{R}-\text{OH} + \text{HX} \longrightarrow \text{R}-\text{X} + \text{H}_2\text{O}$$

Lucas test distinguishes 1°, 2°, 3° alcohols. The Lucas reagent (conc. HCl + anhydrous $ZnCl_2$) reacts with alcohols to form the alkyl chloride, which is insoluble in the reagent and produces a turbid layer.

Alcohol	Mechanism	Time to turbidity
Tertiary (3°)	S_N1 via stable 3° carbocation	immediate at room temp
Secondary (2°)	S_N1 via 2° carbocation	5–10 minutes
Primary (1°)	S_N2 (no carbocation)	no turbidity at room temp; needs heating

2. Reaction with phosphorus trihalides. Bromides and iodides from PBr_3 or red P + I_2; chlorides from PCl_5 or $SOCl_2$. $SOCl_2$ is the cleanest — the by-products (SO_2, HCl) are gases that leave the reaction vessel.

$$3\,\text{R}-\text{OH} + \text{PBr}_3 \longrightarrow 3\,\text{R}-\text{Br} + \text{H}_3\text{PO}_3 \qquad \text{R}-\text{OH} + \text{SOCl}_2 \longrightarrow \text{R}-\text{Cl} + \text{SO}_2\uparrow + \text{HCl}\uparrow$$

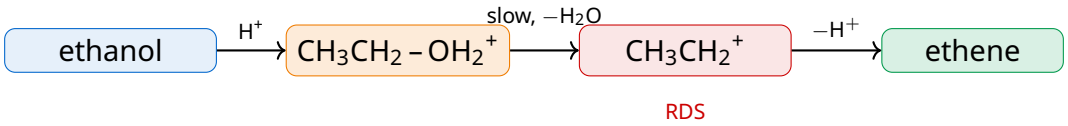
3. Dehydration to alkenes. Alcohols lose water to alkenes when heated with conc. H_2SO_4 or H_3PO_4, or with anhydrous $ZnCl_2$ or Al_2O_3.

$$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[443\,K]{conc.\ H2SO4} \text{CH}_2{=}\text{CH}_2 + \text{H}_2\text{O}$$

The relative ease of dehydration is **3**$^\circ > $ **2**$^\circ > $ **1**$^\circ$, because the rate-determining step is formation of a carbocation, and tertiary cations are the most stable.

Mechanism of ethanol dehydration ($E1$):

1. **Protonation of the –OH** by H_2SO_4 forms an oxonium ion $CH_3CH_2-OH_2^+$.
2. **Loss of water** (slow, rate-determining) gives an ethyl carbocation $CH_3CH_2^+$.
3. **Loss of β-proton** to a base (water/bisulphate) gives ethene; the catalyst H^+ is regenerated.



4. Oxidation. Oxidation builds a C = O from C – OH by removing two H atoms (one from O, one from C). Tertiary alcohols, having no α-H on the carbinol carbon, resist oxidation.

Alcohol	**Mild oxidant** (e.g. PCC, CrO_3)	**Strong oxidant** (e.g. acidified $KMnO_4$, $K_2Cr_2O_7$)
Primary (1°)	Aldehyde (R – CHO)	Carboxylic acid (R – COOH)
Secondary (2°)	Ketone (R$-$CO$-$R′)	Ketone (further oxidation breaks C–C bonds, gives shorter acids)
Tertiary (3°)	No reaction	Cleavage of C–C bonds gives mixture of shorter carboxylic acids

PCC (pyridinium chlorochromate) = CrO_3 + pyridine + HCl. It is the reagent of choice when you want to stop at the aldehyde stage and not over-oxidise to the carboxylic acid.

$$\mathrm{R{-}CH_2OH} \xrightarrow{PCC} \mathrm{R{-}CHO} \qquad \mathrm{R{-}CHOH{-}R'} \xrightarrow{CrO3} \mathrm{R{-}CO{-}R'}$$

Catalytic dehydrogenation on heated Cu at 573 K: 1° $\rightarrow$aldehyde, 2° $\rightarrow$ketone, but 3° alcohols (no α-H to lose) undergo *dehydration* instead of dehydrogenation, giving an alkene.

The two confusable Cr reagents

$K_2Cr_2O_7/H_2SO_4$ takes a primary alcohol all the way to the carboxylic acid. **PCC** stops at the aldehyde. If an exam question asks you to make an aldehyde from a primary alcohol and you reach for acidified $K_2Cr_2O_7$, you have over-oxidised. Use PCC or anhydrous CrO_3.

Oxidation outcomes

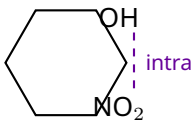
1° goes to A or AC — 2° stops at K — 3° *stops, period.* (Aldehyde or Acid — Ketone — No reaction.) Tertiary alcohols cannot oxidise because the carbinol carbon has no C–H to lose.

5.3 Reactions unique to phenols

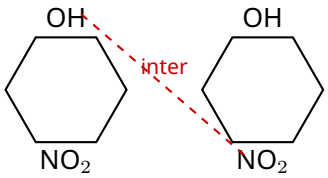
1. Electrophilic aromatic substitution. The lone pair on the phenolic –OH conjugates into the ring, raising electron density at **ortho and para** positions. So phenol undergoes EAS far more readily than benzene, and the products are ortho/para-directed.

(i) Nitration.

- **Dilute HNO_3 at 298 K:** mixture of o- and p-nitrophenol. The two are separated by steam distillation: o-nitrophenol is steam-volatile (intramolecular H-bond, chelated, no association), p-nitrophenol is not (intermolecular H-bond, associated).
- **Concentrated HNO_3:** introduces three nitro groups to give **2,4,6-trinitrophenol (picric acid)**. Yield is poor, so industrially phenol is first sulphonated with conc. H_2SO_4, then nitrated with conc. HNO_3.



o-nitrophenol (volatile)



p-nitrophenol (not volatile)

(ii) Halogenation.

- In a **non-polar solvent** ($CHCl_3$ or CS_2) at low temperature: monobromophenols (mostly p, some o). No Lewis acid catalyst needed — the –OH on phenol is so activating it polarises Br_2 directly.
- In **aqueous bromine** (bromine water): **2,4,6-tribromophenol** precipitates as a white solid. Used as a qualitative test for phenol.

2. Kolbe's reaction. Sodium phenoxide is even more electron-rich than phenol. It picks up CO_2 (a weak electrophile) at the $ortho$ position; acid workup gives **salicylic acid** (2-hydroxybenzoic acid).

$$C_6H_5{-}O^-Na^+ + CO_2 \xrightarrow[(ii)\ H+]{(i)\ 400\,K,\ 4{-}7\,atm} 2\text{-HO-}C_6H_4\text{-COOH}$$

This is the industrial route to salicylic acid — the precursor to aspirin.

3. Reimer–Tiemann reaction. Phenol + $CHCl_3$ + aqueous NaOH gives **salicylaldehyde** (2-hydroxybenzaldehyde) after acid workup. The mechanism goes through a dichlorocarbene $:CCl_2$ intermediate that attacks the ortho position; alkali then hydrolyses the resulting $-CHCl_2$ group to $-CHO$.

$$C_6H_5-OH \xrightarrow[aq.]{CHCl3,NaOH} 2\text{-HO-}C_6H_4\text{-CHO}$$

4. Reaction with zinc dust. Distillation of phenol over zinc dust converts the C – OH bond to C – H — you recover benzene. (This is one of the rare phenol reactions in which the Ar – O bond is cleaved.)

$$C_6H_5-OH + Zn \xrightarrow{\Delta} C_6H_6 + ZnO$$

5. Oxidation. Phenol oxidised by chromic acid gives **benzoquinone**, a conjugated diketone. In the open air phenols slowly oxidise to coloured quinone mixtures — which is why bottled phenol turns pink-brown after exposure to air.

Phenol-only reactions to memorise

Five reactions are unique to phenol, not seen with simple alcohols: (i) reacts with NaOH (aq), (ii) Kolbe's — gives salicylic acid, (iii) Reimer–Tiemann — gives salicylaldehyde, (iv) reaction with Zn dust — gives benzene, (v) $FeCl_3$ test (gives violet colour). Pattern: anything involving the aromatic ring or its enhanced acidity is phenol-only.

Antiseptics and aspirin from phenol

Phenol itself (carbolic acid) was the first antiseptic — Joseph Lister introduced it in surgical wards in 1865, dramatically cutting post-operative deaths. Today, phenol derivatives such as Dettol (chloroxylenol), TCP (trichlorophenol), and hexachlorophene are mainstays of household antiseptics. And the Kolbe reaction product, salicylic acid, is the parent of aspirin, methyl salicylate (Iodex/Moov), and salicylanilide.

6 Commercially Important Alcohols

The two alcohols every Class 12 student must know in industrial detail are methanol and ethanol — both produced at the multi-million-tonne scale annually.

6.1 Methanol (wood spirit)

Formerly produced by **destructive distillation of wood**, hence the name "wood spirit". The modern industrial route is catalytic hydrogenation of carbon monoxide:

$$CO + 2\,H_2 \xrightarrow[200-300\,atm,\ 573-673\,K]{ZnO-Cr2O3} CH_3OH$$

Methanol is a colourless liquid (b.p. 337 K). It is **highly poisonous** — 10 mL can cause blindness, 30 mL can be fatal. Used as a solvent, antifreeze and fuel additive, and as a precursor to formaldehyde, MTBE and biodiesel.

6.2 Ethanol

The oldest fermentation reaction known to humans. Sugars in molasses, sugarcane juice or fruit are converted to glucose/fructose by **invertase**, then to ethanol by **zymase**, both enzymes produced by yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow{zymase} 2\,C_2H_5OH + 2\,CO_2$$

Fermentation is anaerobic. Zymase is inhibited once ethanol exceeds 14%, which is why naturally fermented wines top out around that strength. Above 14% requires distillation. Modern industrial ethanol is also made by acid-catalysed hydration of ethene (Section 3.1).

Commercial alcohol is rendered unfit for drinking by adding pyridine (foul-smelling) and copper sulphate (turns it blue); methanol is sometimes added too. This is called **denaturation**, and it lets industrial ethanol escape the high alcohol-beverage taxes.

> **Methanol poisoning treatment**
>
> Methanol is converted by liver enzymes to methanal (formaldehyde) and then methanoic acid (formic acid) — the formic acid is what causes blindness and death. Treatment: intravenous ethanol. Ethanol competes for the same enzyme (alcohol dehydrogenase), saturating it so methanol is excreted by the kidneys before it gets oxidised. Strange but life-saving.

7 Chemical Reactions of Ethers

Ethers are the least reactive functional group in this chapter. They have no O–H bond (so no acidity, no esterification, no metal reactions), and the C – O – C link is hard to cleave because oxygen is a poor leaving group. The two reactions you must know are (a) C–O cleavage with HX and (b) electrophilic substitution on the aromatic ring of an aryl ether.

7.1 Cleavage of the C–O bond by HX

Concentrated HI (or HBr) at high temperature cleaves dialkyl ethers into an alkyl halide and an alcohol; with excess HI, the alcohol itself reacts further to give a second alkyl halide.

$$R{-}O{-}R' + HI \xrightarrow{\Delta} R{-}I + R'{-}OH$$

Reactivity order: HI $>$ HBr $>$ HCl. HCl is too weakly acidic to protonate the ether oxygen.

Mechanism with HI:

1. **Protonation** of ether: $R{-}O{-}R' + HI \longrightarrow R{-}O^{+}H{-}R' + I^{-}$, creating an oxonium ion.
2. S_N2 **attack of** I^- at the less substituted carbon of the oxonium ion. The alcohol $R'{-}OH$ leaves and R – I forms.
3. **If excess HI present:** the alcohol reacts further — $R'{-}OH + HI \longrightarrow R'{-}I + H_2O$.

Which side of an unsymmetrical ether gives R – I? For two primary or secondary alkyl groups, I^- attacks the **less hindered (smaller)** carbon by S_N2. So with methyl ethyl ether + HI, CH_3I forms (and C_2H_5OH).

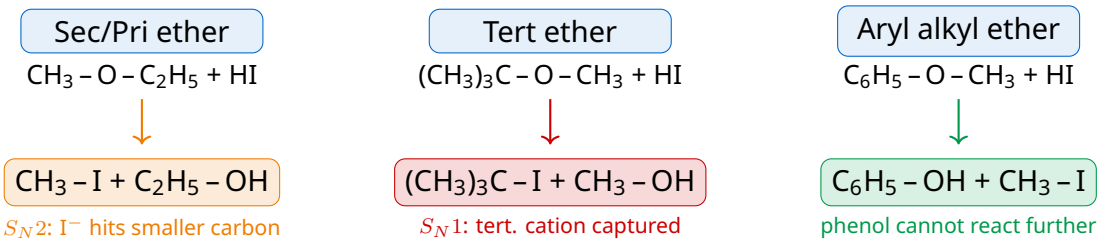
Tertiary case (S_N1 takes over). When one group is tertiary, e.g. t-butyl methyl ether, protonation is followed by **ionisation** to a stable tertiary carbocation. I^- then captures the tertiary cation:

$$(CH_3)_3C{-}O{-}CH_3 + HI \longrightarrow (CH_3)_3C{-}I + CH_3{-}OH$$

So with a tertiary alkyl group, the tertiary side becomes the alkyl iodide — the opposite of the primary/secondary case.

Anisole + HI. The methylphenyl oxonium ion $C_6H_5 - O^+(H) - CH_3$ can only be attacked at the methyl carbon, because the phenyl carbon is sp^2 and cannot undergo S_N2 from the back side. Result: methyl iodide and **phenol** — the phenol is not further attacked by HI.

$$C_6H_5{-}O{-}CH_3 + HI \longrightarrow C_6H_5{-}OH + CH_3{-}I$$



Why phenol survives, methanol doesn't

For a dialkyl ether in excess HI, the alcohol byproduct R – OH reacts further with HI to give R – I + H_2O — so eventually both alkyl groups end up as alkyl iodides. But with an aryl alkyl ether, the phenolic product has the –OH on an sp^2 carbon; phenols cannot undergo S_N2 at the ring carbon (back-side attack on sp^2 aromatic is impossible). So phenol is the final product and survives intact.

7.2 Electrophilic substitution on the aromatic ring

In aryl alkyl ethers like anisole, the alkoxy group – OR donates electrons by resonance, just like – OH in phenol. The ring is activated towards electrophilic substitution, and the incoming electrophile goes to $ortho$ and $para$.

(i) Halogenation. Anisole + Br_2 in ethanoic acid gives **p-bromoanisole (90%)** as the major product. No $FeBr_3$ catalyst is needed — the ring is already activated.

(ii) Friedel–Crafts alkylation and acylation. Anisole + R – X (or R – COCl) with anhydrous $AlCl_3$ introduces R (or RCO) at $ortho$ and $para$.

(iii) Nitration. Anisole + dilute HNO_3/H_2SO_4 mixture gives o- and p-nitroanisole.

$ortho/para$ direction in anisole

The methoxy group is a stronger activator than even an alkyl group. The $para$ product dominates in halogenation because of steric crowding at $ortho$ next to the bulky – OCH_3 substituent. Free-running rule: if the substituent has a lone pair to donate (– OH, – OR, – NH_2, – NHR), expect strong o/p activation.

8 JEE/NEET Extensions

A handful of topics appear regularly in JEE/NEET papers that are either touched only briefly by NCERT or extend its scope. Master these to clear the cut-off questions.

8.1 Carbocation rearrangements [JEE extension]

When an alcohol dehydrates via a 2° carbocation that is one hydride-shift away from a 3° cation, the cation *will* rearrange. Example: 3-methylbutan-2-ol with HBr forms a 2° cation at C-2, which undergoes a **1,2-hydride shift** from C-3 to give a more stable 3° cation; bromide captures the 3° centre. Product: 2-bromo-2-methylbutane, not 2-bromo-3-methylbutane.

$$(CH_3)_2CH{-}CHOH{-}CH_3 \xrightarrow{H+} (CH_3)_2CH{-}{}^{+}CH{-}CH_3 \xrightarrow[\text{1,2-H shift}]{} (CH_3)_2C^{+}{-}CH_2{-}CH_3 \xrightarrow{Br-} (CH_3)_2CBr{-}CH_2{-}CH_3$$

8.2 Saytzeff vs Hofmann in dehydration [JEE extension]

Acid dehydration of an alcohol that can give two regioisomeric alkenes follows the **Saytzeff rule**: the more substituted (more stable) alkene predominates. So butan-2-ol dehydrates mainly to but-2-ene, not but-1-ene.

8.3 Pinacol-pinacolone rearrangement [JEE extension]

Vicinal diols (1,2-diols) heated with acid undergo a backbone reshuffle: a hydride or alkyl group migrates to the carbocation generated by losing the first –OH; the second –OH then loses a proton to give a ketone. Pinacol (2,3-dimethylbutane-2,3-diol) gives pinacolone (3,3-dimethylbutan-2-one). Not in NCERT, but a perennial JEE single-correct question.

8.4 Mechanism of Reimer–Tiemann [JEE extension]

The reactive electrophile in Reimer–Tiemann is the singlet carbene $:CCl_2$ (dichlorocarbene), generated when NaOH deprotonates $CHCl_3$:

$$CHCl_3 \xrightarrow{OH-} {}^{-}CCl_3 \longrightarrow :CCl_2 + Cl^{-}$$

The phenoxide ring attacks the carbene at $ortho$, forming an aryl dichloromethyl species which alkali then hydrolyses to –CHO. Examiners love asking for the role of each reagent.

8.5 Williamson with both alkoxide and halide options [JEE extension]

To make 2-ethoxy-3-methylpentane, you can disconnect at either C–O bond. The correct disconnection uses ethoxide + 3-methylpentan-2-yl bromide — but the alkyl halide here is secondary, so yields are modest. The reverse disconnection (2-methylpent-3-yl alkoxide + ethyl bromide) uses a primary halide — much cleaner S_N2, higher yield. Always pick the disconnection that puts the leaving group on the **less hindered carbon**.

9 Quick Reference Summary

A one-page condensed checklist for revision the night before the exam.

Key reactions to memorise

Alcohol preparation:

$R-CH=CH_2 \xrightarrow{H+,\,H2O} R-CHOH-CH_3$ — Markovnikov

$R-CH=CH_2 \xrightarrow[(ii)\ H2O2,\,OH-]{(i)\ (BH3)2} R-CH_2-CH_2OH$ — anti-Mark.

$R-COOH \xrightarrow{LiAlH4} R-CH_2OH$ — reduction

$R-CHO + R'-MgX \longrightarrow R-CHOH-R'$ — Grignard

Phenol preparation:

$C_6H_5Cl \xrightarrow[623\,K,\,320\,atm]{NaOH} C_6H_5OH$ — Dow

$C_6H_5-CH(CH_3)_2 \xrightarrow{O2,\,H+} C_6H_5OH + (CH_3)_2CO$ — cumene route

Ether preparation:

$R-O^-Na^+ + R'-X \longrightarrow R-O-R' + NaX$ — Williamson

Alcohol reactions:

$R-OH + HX \longrightarrow R-X + H_2O$ — 3° fastest (Lucas)

$R-CH_2OH \xrightarrow{PCC} R-CHO$ — stop at aldehyde

$R-CH_2OH \xrightarrow{K2Cr2O7,\,H+} R-COOH$ — to the acid

$R-OH \xrightarrow[443\,K]{conc.\ H2SO4}$ alkene — 3° >2° >1°

Phenol reactions:

$C_6H_5O^-Na^+ + CO_2 \longrightarrow$ 2-OH-C_6H_4-COOH — Kolbe

$C_6H_5OH + CHCl_3/NaOH \longrightarrow$ 2-OH-C_6H_4-CHO — Reimer–Tiemann

$C_6H_5OH + Br_2(H_2O) \longrightarrow$ 2,4,6-Br_3-C_6H_2-OH — white ppt

Ether cleavage:

$R-O-R' + HI \longrightarrow R-I + R'-OH$ — smaller R gets I (1°/2°)

$(CH_3)_3C-O-R + HI \longrightarrow (CH_3)_3C-I + R-OH$ — tert. side gets I (S_N1)

$Ar-O-R + HI \longrightarrow Ar-OH + R-I$ — phenol survives

Acidity ranking (pK_a values)

- Picric acid (2,4,6-trinitrophenol) $pK_a \approx 0.4$
- p-nitrophenol $pK_a = 7.1$
- Phenol $pK_a = 10.0$
- p-Cresol $pK_a = 10.2$
- Ethanol $pK_a = 15.9$
- Methanol $pK_a = 15.5$
- Water $pK_a = 15.7$

Lower $pK_a \Rightarrow$ stronger acid. Phenols beat alcohols by $\sim 10^6$.

Distinguishing tests

- **Phenol vs alcohol:** $FeCl_3$ aqueous solution. Phenol gives a violet/purple colour; alcohols give no colour.
- **Phenol:** Bromine water $\rightarrow$ white precipitate of 2,4,6-tribromophenol.
- **Phenol vs alcohol:** NaOH (aq). Phenol dissolves to give sodium phenoxide; alcohol does not.
- **1° vs 2° vs 3° alcohols:** Lucas reagent (conc. HCl + $ZnCl_2$). 3° turbid instantly, 2° in 5 min, 1° on heating.
- **Oxidation differentiation:** 3° alcohols do not get oxidised by acidified $KMnO_4$; 1° and 2° do.

The chapter in a single sentence

The reactivity of an oxygen-containing organic functional group is governed by **three things**: (i) whether it has an O–H bond (alcohols and phenols do, ethers do not), (ii) whether the carbon attached to oxygen is sp^3 (alcohol) or sp^2 aromatic (phenol), and (iii) the degree of substitution on the carbinol carbon (1°/2°/3°). Every reaction in this chapter falls out of these three structural facts.