Collegedunia NCERT Formula Sheet

The Ultimate Formula Reference for Class 12 (12th) Chemistry — NCERT 2026-27

Chapter 7: Alcohols, Phenols and Ethers

Classification · Nomenclature · Preparation · Acidity · Reactions of –OH · Williamson · Ether Cleavage · JEE & NEET

Quick Reference — Functional Groups, pK_a & Bond Data

Class	Functional group	Typical pK_a	C–O length	Example
Alcohol	R–OH (sp^3 C–OH)	16–18	142 pm	Methanol (CH_3OH)
Phenol	Ar–OH (sp^2 C–OH)	10.0	136 pm	Phenol (C_6H_5OH)
Water	H–OH	15.7	—	H_2O
Ether	R–O–R′ / Ar–O–R	non-acidic	141 pm	Methoxymethane (CH_3OCH_3)
Carboxylic acid	R–COOH	4–5	—	Acetic acid (for comparison)

1 Classification (NCERT 7.1)

NCERT Section 7.1 groups alcohols and phenols by (a) the number of –OH groups (mono-/di-/tri-/polyhydric) and (b) the hybridisation of the C bonded to –OH. The second classification is the more useful one because it controls reactivity (alcohols vs phenols vs vinyl alcohols).

Alcohols by –OH count

Monohydric: one –OH (e.g., CH_3OH, methanol).
Dihydric (glycol): two –OH (e.g., $HOCH_2CH_2OH$, ethane-1,2-diol).
Trihydric (glycerol): three –OH (CH_2OH–$CHOH$–CH_2OH, propane-1,2,3-triol).
Polyhydric alcohols carry the suffix *-diol, -triol* (the alkane's 'e' is kept). Increasing –OH count $\Rightarrow$ greater water solubility & viscosity.

Monohydric alcohols by C hybridisation

Csp^3–OH (normal alcohols): –OH on sp^3 C. Sub-classified as:
1° (primary): C–OH has 1 alkyl group, e.g., CH_3CH_2OH.
2° (secondary): 2 alkyl groups, e.g., $(CH_3)_2CHOH$.
3° (tertiary): 3 alkyl groups, e.g., $(CH_3)_3COH$.

Allylic alcohol: –OH on sp^3 C *adjacent* to C=C, e.g., $CH_2=CH-CH_2OH$.
Benzylic alcohol: –OH on sp^3 C attached to an aromatic ring, e.g., $C_6H_5CH_2OH$.
Csp^2–OH (vinylic / enol): –OH directly on C=C, e.g., $CH_2=CH-OH$ (unstable; tautomerises to CH_3CHO).
Allylic / benzylic alcohols give very **stable carbocations** on protonation $\Rightarrow$ fast S$_N$1-type reactions with HX.

Phenols & ethers by structure

Phenol classes: mono- (C_6H_5OH), di- (catechol, resorcinol, quinol), tri- (pyrogallol = benzene-1,2,3-triol).
Ether classes:
Symmetrical / simple: same R/Ar both sides, e.g., $C_2H_5OC_2H_5$ (diethyl ether).
Unsymmetrical / mixed: different groups, e.g., $C_2H_5OCH_3$ (ethyl methyl ether), $C_6H_5OCH_3$ (anisole).
Phenols carry –OH on an sp^2 **aromatic C**; that single fact makes them stronger acids than alcohols by $\sim$8 pK_a units (resonance into the ring).

2 IUPAC Nomenclature (NCERT 7.2)

For alcohols, the alkane suffix 'e' is replaced by 'ol' and the –OH locant is the lowest. For phenols, common and IUPAC names usually coincide for mono-substituents. For ethers, common names list alkyl groups alphabetically with the word ether; IUPAC names treat –OR as an alkoxy substituent on the longer chain.

Naming alcohols

(1) Parent chain = longest C chain containing C–OH.
(2) Drop the 'e' of alkane, add 'ol'; number to give –OH the lowest locant.
(3) Polyhydric: keep 'e', add 'diol/triol' with locants (e.g., ethane-1,2-diol).
(4) Cyclic alcohols: –OH on C-1 of the ring (e.g., cyclohexan-1-ol).
Examples:
CH_3OH → methanol $CH_3CH_2CH_2OH$ → propan-1-ol
$(CH_3)_2CHOH$ → propan-2-ol $(CH_3)_3COH$ → 2-methylpropan-2-ol
$HOCH_2CH_2OH$ → ethane-1,2-diol (ethylene glycol)
CH_2OH-CHOH-CH_2OH → propane-1,2,3-triol (glycerol)

Naming phenols & ethers

Phenols: parent is 'phenol'; substituents prefixed with locants. Common names: cresol (methylphenol), catechol (benzene-1,2-diol), resorcinol (benzene-1,3-diol), quinol/hydroquinone (benzene-1,4-diol).
Ethers (common name): alkyl groups alphabetically, then 'ether'. Examples:
CH_3OCH_3 → dimethyl ether $C_2H_5OC_2H_5$ → diethyl ether
$C_6H_5OCH_3$ → methyl phenyl ether (anisole)
Ethers (IUPAC): smaller –OR group becomes *alkoxy* substituent on the larger parent:
CH_3OCH_3 → methoxymethane $C_2H_5OC_2H_5$ → ethoxyethane
$C_6H_5OCH_3$ → methoxybenzene (anisole)
$CH_3OCH_2CH_2CH_3$ → 1-methoxypropane.

3 Structures & C–O Bond Geometry (NCERT 7.3)

The C–O–H / C–O–C geometry and bond lengths control polarity, H-bonding, and reactivity. Phenol has shorter C–O than methanol because the oxygen lone pair partially conjugates into the aromatic ring.

Geometry of –OH and –O– in the three classes

Methanol: C–O–H angle $\approx 108.9°$ (slightly less than 109.5° tetrahedral; lone-pair repulsion compresses the angle).
Phenol: C–O–H angle $\approx 109°$; C–O bond $= 136$ pm (*shorter* than 142 pm in methanol).
Methoxymethane: C–O–C angle $\approx 111.7°$ (slightly greater than tetrahedral due to bulkier –R / –R repulsion); C–O length $= 141$ pm.
Phenol's C–O shortening is due to (i) **partial double-bond character** from resonance and (ii) the sp^2 aromatic C–O bond (sp^2 C is smaller than sp^3 C).

Why phenol's C–O is shorter

A phenolic oxygen donates one of its lone pairs into the aromatic π-system, putting partial C=O character on the C–O bond. The four resonance forms of phenol place negative charge at *ortho* and *para* ring carbons and positive charge on O. The result: shorter C–O bond, longer O–H bond, more acidic O–H, and ortho/para electrophilic substitution.

4 Preparation of Alcohols (NCERT 7.4.1)

Three NCERT-named routes: (1) from **alkenes** by acid hydration (Markovnikov) or hydroboration–oxidation (anti-Markov.); (2) from **carbonyls** by reduction of RCHO/RCOR′ ($NaBH_4$, $LiAlH_4$, H_2/Ni) or of acids/esters ($LiAlH_4$); (3) from **Grignards** adding to C=O.

From alkenes (i): acid-catalysed hydration

$CH_2{=}CH_2 + H_2O \longrightarrow [H_2SO_4]\ CH_3CH_2OH$
Markovnikov regioselectivity on unsymmetrical alkenes:
$CH_3CH{=}CH_2 + H_2O \longrightarrow [H^+]\ (CH_3)_2CHOH$ (propan-2-ol)
Mechanism (3 steps):
(1) H^+ adds to less-substituted C → more-stable carbocation.
(2) H_2O attacks carbocation (nucleophilic addition).
(3) Deprotonation of oxonium → alcohol.
Gives the **Markovnikov alcohol**: –OH ends up on the more-substituted C. May rearrange (hydride / methyl shift) if a more stable C^+ is accessible.

From alkenes (ii): hydroboration–oxidation

Step 1 (mass-balanced addition of diborane to 6 alkenes):
$6\,RCH{=}CH_2 + (BH_3)_2 \longrightarrow 2\,(RCH_2CH_2)_3B$ (trialkylborane)
Step 2 (oxidative work-up):
$2\,(RCH_2CH_2)_3B + 6\,H_2O_2 \longrightarrow [\text{aq. NaOH}]\ 6\,RCH_2CH_2OH + 2\,B(OH)_3$
Net for propene: $CH_3CH{=}CH_2 \rightarrow CH_3CH_2CH_2OH$ (propan-1-ol, **anti-Markovnikov**).
Boron adds to the sp^2 C carrying **more H** (less substituted), so after oxidation –OH lands on the **less substituted** C. **No rearrangement**; excellent yield. (H. C. Brown, Nobel 1979.)

From alkenes (iii): oxymercuration–demercuration

Two steps (one pot):
$R{-}CH{=}CH_2 \longrightarrow [\text{(i) } Hg(OAc)_2/H_2O]\ R{-}CH(OH){-}CH_2HgOAc$
$R{-}CH(OH){-}CH_2HgOAc \longrightarrow [\text{(ii) } NaBH_4/OH^-]\ R{-}CH(OH){-}CH_3 + Hg$
Net result: *Markovnikov* alcohol **without** carbocation rearrangement (cyclic mercurinium intermediate avoids the open C^+).
Complements acid hydration — same regiochemistry, **no** hydride/methyl shifts. Use when the substrate would otherwise rearrange (e.g., 3,3-dimethylbut-1-ene).

From carbonyl compounds: reduction

Aldehydes → 1° alcohol:

$\text{R–CHO} \xrightarrow{} [\text{H}_2/\text{Pt, Pd or Ni}]\ \text{R–CH}_2\text{OH}$

or $NaBH_4$ / $LiAlH_4$ followed by H_2O work-up.

Ketones → 2° alcohol:

$\text{R–CO–R}' \xrightarrow{} [\text{NaBH}_4 \text{ or LiAlH}_4]\ \text{R–CH(OH)–R}'$

Carboxylic acids → 1° alcohol ($LiAlH_4$ required):

$\text{R–COOH} \xrightarrow{} [\text{(i) LiAlH}_4\text{; (ii) H}_2\text{O}]\ \text{R–CH}_2\text{OH}$

Esters → alcohol (commercial route):

$\text{R–COOR}' \xrightarrow{} [\text{H}_2/\text{catalyst}]\ \text{R–CH}_2\text{OH} + \text{R}'\text{OH}$

$NaBH_4$ reduces aldehydes/ketones *only* — it is mild and **chemoselective for C=O over C=C** (so α, β-unsaturated carbonyls give the allyl alcohol, double bond intact). $LiAlH_4$ is stronger and reduces acids, esters, amides too. **Catalytic H_2/Ni** *will* hydrogenate C=C as well as C=O, so use $NaBH_4$ when the alkene must survive.

From Grignard reagents (NCERT 7.4.1, route 3)

General two-step scheme:

(1) Nucleophilic addition of R–MgX to C=O:

$$\text{R–MgX} + \overset{\delta+}{\text{C}} = \overset{\delta-}{\text{O}} \longrightarrow \text{R–C–OMgX} \text{ (alkoxide adduct)}$$

(2) Acidic hydrolysis:

$$\text{R–C–OMgX} \longrightarrow [\text{H}_2\text{O / H}^+]\ \text{R–C–OH} + \text{Mg(OH)X}$$

Aldehyde/ketone selectivity:

HCHO (methanal) + R–MgX → **1°** alcohol $R–CH_2OH$.

R′–CHO + R–MgX → **2°** alcohol R–CHOH–R′.

R′–CO–R″ + R–MgX → **3°** alcohol R–C(OH)(R′)(R″).

Reaction *must* be done in **dry ether** — water destroys the Grignard ($\text{R–MgX} + \text{H}_2\text{O} \rightarrow \text{R–H} + \text{Mg(OH)X}$).

Markovnikov vs anti-Markovnikov from an alkene

H_3O^+ / dilute H_2SO_4 ⇒ Markovnikov alcohol (–OH on more-substituted C). **B_2H_6 then H_2O_2/OH^-** ⇒ anti-Markovnikov alcohol (–OH on less-substituted C). One alkene, two complementary products — a classic JEE/NEET “predict the major product” setup.

5 Preparation of Phenols (NCERT 7.4.2)

Four NCERT-named routes: (1) Dow process on haloarenes; (2) fusion of benzene-sulphonic acid with NaOH; (3) hydrolysis of diazonium salts; (4) cumene hydroperoxide route (industrial, by-product = acetone).

(1) From haloarenes — Dow process

$C_6H_5Cl + NaOH \longrightarrow [623\text{ K},\ 320\text{ atm}]\ C_6H_5ONa$

$C_6H_5ONa \longrightarrow [H^+]\ C_6H_5OH$ (phenol)

Aryl halides are very inert; harsh conditions (high T & P) are needed because S_NAr on an unactivated ring is very slow. EWGs at *o-/p-* lower the conditions dramatically.

(2) From benzenesulphonic acid

$C_6H_6 + H_2SO_4\text{(oleum)} \longrightarrow C_6H_5SO_3H$ (benzenesulphonic acid)

$C_6H_5SO_3H \longrightarrow [\text{molten NaOH}]\ C_6H_5ONa$

$C_6H_5ONa \longrightarrow [H^+]\ C_6H_5OH$

The –SO_3H is replaced by –OH via molten NaOH (alkali fusion). Acidification of the sodium phenoxide releases phenol.

(3) From diazonium salts

Step 1 — Diazotisation (273–278 K):
$C_6H_5NH_2 + NaNO_2 + HCl \longrightarrow C_6H_5N_2^+Cl^- + NaCl + 2H_2O$
Step 2 — Hydrolysis (warm with H_2O or dilute acid):
$C_6H_5N_2^+Cl^- + H_2O \longrightarrow$ [warm] $C_6H_5OH + N_2\uparrow + HCl$
Starts from **aniline**; gives phenol at the *exact position* the amine occupied — useful when ortho/para electrophilic routes would give the wrong isomer.

(4) From cumene (industrial route)

Step 1 — Air oxidation of cumene:
$C_6H_5CH(CH_3)_2 + O_2 \longrightarrow C_6H_5C(CH_3)_2\text{–O–OH}$ (cumene hydroperoxide)
Step 2 — Acid-catalysed rearrangement:
$C_6H_5C(CH_3)_2OOH \longrightarrow$ [dilute H^+] $C_6H_5OH + (CH_3)_2CO$
Most of the world's phenol is made by this route. Acetone is a valuable **by-product**. Cumene itself = isopropylbenzene (from benzene + propene/$AlCl_3$, Friedel–Crafts).

6 Physical Properties & Hydrogen Bonding (NCERT 7.4.3)

Alcohols and phenols have high boiling points relative to comparable hydrocarbons / haloalkanes / ethers because of **intermolecular hydrogen bonding** (O–H$\cdots$O). Solubility in water follows the same H-bonding logic — it falls as the hydrophobic alkyl/aryl tail grows.

Boiling-point trends

Same class, increasing C count: b.p. rises (stronger van der Waals).
e.g., CH_3OH (338 K) $<$ C_2H_5OH (351 K) $<$ C_3H_7OH (370 K) $<$ C_4H_9OH (391 K).
Isomeric alcohols (branching effect): *more branched* $\Rightarrow$ *lower b.p.* (less surface, weaker dispersion).
butan-1-ol (391 K) $>$ butan-2-ol (372 K) $>$ 2-methylpropan-2-ol (355 K).
Same C count, different class: alcohol $\gg$ ether $>$ alkane
ethanol (351 K) $\gg$ methoxymethane (248 K) $\approx$ propane (231 K).
Alcohols have **H-bonding**; ethers and alkanes don't. The 100 K jump from CH_3OCH_3 to C_2H_5OH (same M = 46) is the H-bonding signature.

Hydrogen bonding in alcohols & phenols

Intermolecular O–H$\cdots$O bonds (≈ 20–30 kJ/mol). **Required:** H on small, electronegative atom (O here); lone pair on the neighbouring O.
Ethers have lone pairs but no O–H, so **no** intermolecular H-bonding (they accept H-bonds from water $\Rightarrow$ partial solubility). Phenol H-bonds in both solid & liquid.

Solubility in water

Lower alcohols (C_1–C_3) are **miscible** with water in all proportions; solubility falls sharply for C_4 and above.
Solubility order in water (same C count): alcohol $>$ ether $\gg$ alkane.
Phenol is slightly soluble in water (8.3 g / 100 g at 293 K), miscible in NaOH (forms phenoxide), freely soluble in organic solvents.
Solubility = competition between (i) H-bonding of –OH with H_2O (helps) and (ii) hydrophobic

alkyl/aryl tail disrupting water structure (hurts). Long tail wins above $\sim$C$_5$.

7 Acidity: Alcohols, Phenols, Water (NCERT 7.4.4)

Both alcohols and phenols are Brønsted acids (donate H$^+$ from –OH). Phenols ($K_a \sim 10^{-10}$) are about **a million times more acidic** than alcohols ($K_a \sim 10^{-18}$) because the phenoxide ion is resonance-stabilised, whereas alkoxide isn't.

General acid–base behaviour

$\text{R–OH} \rightleftharpoons \text{R–O}^- + \text{H}^+$ K_a very small
$\text{Ar–OH} \rightleftharpoons \text{Ar–O}^- + \text{H}^+$ $K_a \approx 10^{-10}$
Reaction with active metals (Na, K, Al) — common to all R/Ar–OH:
$2\,\text{R–OH} + 2\,\text{Na} \longrightarrow 2\,\text{R–ONa} + \text{H}_2\uparrow$
$2\,\text{C}_6\text{H}_5\text{OH} + 2\,\text{Na} \longrightarrow 2\,\text{C}_6\text{H}_5\text{ONa} + \text{H}_2\uparrow$
Phenol-only: reacts with aqueous NaOH (alcohols don't):
$\text{C}_6\text{H}_5\text{OH} + \text{NaOH} \longrightarrow \text{C}_6\text{H}_5\text{ONa} + \text{H}_2\text{O}$
The reaction with NaOH distinguishes **phenol from alcohol**: phenol dissolves in aqueous NaOH (forms phenoxide); ethanol does not react.

pK_a values and acidity order

Increasing pK_a ⇔ decreasing acidity:
Picric acid (0.4) $<$ R–COOH (4–5) $<$ 4-nitrophenol (7.1) $<$ Ar–OH (~ 10) $<$ H–OH (15.7) $<$ R–OH (15.9–18)
Phenol p$K_a \approx$ 10.0 *vs* ethanol p$K_a \approx$ 15.9.
NCERT acidity ladder including hydrocarbons:
Ar–OH $>$ H–OH $>$ R–OH $>$ HC≡CH (terminal alkyne, pK_a 25) $>$ NH$_3$$(38)$ $>$ R–H (~ 50)
Among alcohols (electron-releasing groups destabilise –O$^-$, lower acidity):
CH$_3$OH $> 1^\circ > 2^\circ > 3^\circ$
Tertiary alcohols are the least acidic because three alkyl groups push electron density onto O and destabilise the alkoxide. Methanol is the most acidic ordinary alcohol. Terminal alkynes lie *below* alcohols on the ladder — alkoxide can deprotonate HC≡CR.

Why phenol is more acidic than ethanol

Phenoxide ion C$_6$H$_5$O$^-$ is **resonance-stabilised**: the negative charge is delocalised to the *ortho* and *para* ring carbons (3 additional resonance structures):
Ph–O$^-$ $\leftrightarrow$ [cyclohexadienone with O=C and $^-$on o/p ring C]
Ethoxide CH$_3$CH$_2$O$^-$ has **no** resonance; negative charge sits entirely on O.
$\Rightarrow$ phenoxide is a much more stable conjugate base $\Rightarrow$ phenol is much more acidic.
Resonance *into* the ring also explains phenol's reactions: **ortho/para electrophilic substitution** and the strong activating effect of –OH on the ring.

Substituent effects on phenol acidity

Electron-withdrawing groups (–NO$_2$, –CN, –X) at o-/p- *increase* acidity (further stabilise phenoxide).
Electron-donating groups (–CH$_3$, –OCH$_3$, –NH$_2$) *decrease* acidity.
NCERT substituent-phenol acidity order (pK_a in parentheses, Table 7.5):
Picric acid (0.4) $\gg$ o-NO$_2$-phenol (7.2) $\approx$ p-NO$_2$-phenol (7.1) $>$ phenol (10.0) $>$ p-cresol / 4-methylphenol (10.2) $>$ 4-methoxyphenol (10.2)
Compact NCERT order (for the standard CBSE one-liner):

o,p-nitrophenol $>$ phenol $>$ p-cresol (o,p-methylphenol)
Picric acid (2,4,6-trinitrophenol) is so acidic (pK_a 0.4) it rivals carboxylic acids — three –NO_2 groups stabilise the phenoxide by both –I and –M effects. NCERT also notes that –NO_2 at *meta* only operates by –I (no –M), so m-nitrophenol (pK_a 8.4) is *less* acidic than the o-/p- isomers.

Alcohols do *not* react with NaOH/$NaHCO_3$

Sodium hydroxide is too weak a base to deprotonate ethanol (pK_a 16 vs water 15.7) — equilibrium lies on the alcohol side. Use **Na metal** (or NaH) for alkoxide formation. Phenols, being millions of times more acidic, do react with NaOH but *not* with $NaHCO_3$ (carboxylic acids alone do that — standard CBSE discrimination test).

8 Reactions Involving O–H Cleavage in Alcohols

Beyond the acid–base reactions above (Section 7), NCERT 7.4.4(a) lists **esterification** as the other major O–H cleavage reaction of alcohols (and phenols). Acid-catalysed esterification with carboxylic acids is reversible (Fischer); reaction with acid chlorides / anhydrides is irreversible.

Esterification (Fischer)

$\text{R–OH} + \text{R}'\text{COOH} \rightleftharpoons [\text{conc. } H_2SO_4]\ \text{R}'\text{COOR} + H_2O$
Example: $CH_3CH_2OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ (ethyl ethanoate).
Phenols react more slowly but go cleanly with acyl chlorides / anhydrides in the presence of pyridine:
$C_6H_5OH + (CH_3CO)_2O \longrightarrow [\text{pyridine}]\ C_6H_5OCOCH_3 + CH_3COOH$ (phenyl acetate).
Drive the equilibrium: **remove water** (Dean–Stark trap, conc. H_2SO_4 as dehydrating agent), or use a large excess of one reactant.

Acetylation (acyl chloride / anhydride)

Alcohols: $\text{R–OH} + \text{R}'\text{COCl} \longrightarrow [\text{pyridine}]\ \text{R}'\text{COOR} + \text{HCl}$.
Phenols: $\text{ArOH} + \text{R}'\text{COCl} \rightarrow \text{ArOCOR}' + \text{HCl}$.
Acetic anhydride works equally well; pyridine absorbs the HCl/CH_3COOH by-product.
Sometimes called the **Schotten–Baumann reaction** when run in aqueous NaOH. The reaction is irreversible (no water issue) and is the standard route for synthesising esters from sensitive alcohols.

9 Reactions Involving C–O Cleavage in Alcohols

C–O bond breaks when the alcohol is first protonated to –OH_2^+ (which makes water a good leaving group). The three NCERT-named C–O reactions are: substitution by HX (R–X formation), dehydration to alkene, and reaction with PCl_3/PCl_5/$SOCl_2$.

Reaction with HX (R–OH → R–X)

Reactivity of alcohols: $3^\circ > 2^\circ > 1^\circ$ (carbocation stability $\Rightarrow$ S_N1 ease)
Reactivity of HX: HI $>$ HBr $>$ HCl
$\text{R–OH} + \text{HX} \longrightarrow [\text{anhyd. } ZnCl_2]\ \text{R–X} + H_2O$ (Lucas conditions for HCl)
Lucas test (alcohol classification by speed of cloudiness):
3° R–OH: cloudy *immediately* (S_N1, fast)
2° R–OH: cloudy in $\sim$5 min
1° R–OH: no cloudiness at room T
Mechanism: $3^\circ/2^\circ$ via **S_N1** (protonation $\rightarrow C^+ \rightarrow X^-$ attack); 1° & CH_3OH via **S_N2** (X^- backside attack on protonated alcohol).

Reaction with PCl_3, PCl_5, $SOCl_2$

$3\,\text{R–OH} + PCl_3 \longrightarrow 3\,\text{R–Cl} + H_3PO_3$

$\text{R–OH} + PCl_5 \longrightarrow \text{R–Cl} + POCl_3 + HCl$

$\text{R–OH} + SOCl_2 \longrightarrow [\text{pyridine}]\ \text{R–Cl} + SO_2\uparrow + HCl\uparrow$

$SOCl_2$ is preferred — the two by-products (SO_2, HCl) escape as gases, giving *pure* R–Cl. Analogous PBr_3 / PI_3 (generated in situ from red P + Br_2/I_2) give R–Br / R–I.

Dehydration to alkene

$\text{R–CH}_2\text{–CH}_2\text{OH} \longrightarrow [\text{conc. } H_2SO_4,\ \Delta]\ \text{R–CH=CH}_2 + H_2O$

Conditions for ethanol → ethene: 443 K, 85% H_3PO_4, or 95% H_2SO_4 at 443 K.

Ease of dehydration: $3^\circ > 2^\circ > 1^\circ$ (carbocation stability).

Saytzeff rule: more-substituted alkene is the major product.

Mechanism (3 steps):

(1) Protonation: $\text{R–OH} + H^+ \rightarrow \text{R–OH}_2^+$.

(2) Loss of water: $\text{R–OH}_2^+ \rightarrow R^+ + H_2O$ (slow; rate-determining).

(3) Loss of β-H: $R^+ \rightarrow \text{alkene} + H^+$.

Acid is regenerated — **catalytic**. Reverse reaction = acid-catalysed hydration of alkene (Markovnikov). Same intermediate, opposite direction.

E1 vs S_N1 in alcohol + acid

Both proceed via the same R^+ intermediate. At **high T (443 K)** and concentrated acid, E1 (alkene) wins. At **low T** with X^- present, S_N1 (R–X) wins. For ethanol + conc. H_2SO_4: 413 K → diethyl ether (S_N); 443 K → ethene (E1).

10 Oxidation & Dehydrogenation of Alcohols

NCERT 7.4.4(b) ends with oxidation: 1° alcohol → aldehyde → acid; 2° alcohol → ketone; 3° alcohol resists oxidation. Catalytic dehydrogenation (Cu/573 K) is the milder, gas-phase counterpart.

Oxidation by strong oxidants

Primary alcohol → acid (excess oxidant):

$\text{R–CH}_2\text{OH} \longrightarrow [KMnO_4/K_2Cr_2O_7]\ \text{R–COOH}$

Primary alcohol → aldehyde (mild oxidant, stop at RCHO):

$\text{R–CH}_2\text{OH} \longrightarrow [\text{PCC, } CH_2Cl_2]\ \text{R–CHO}$

PCC = pyridinium chlorochromate, the standard **stop-at-aldehyde** reagent.

Secondary alcohol → ketone:

$\text{R–CHOH–R}' \longrightarrow [K_2Cr_2O_7/H^+]\ \text{R–CO–R}'$

Tertiary alcohol: no oxidation under mild conditions (no α-H on C–OH); only strong acidic $KMnO_4$ at high T cleaves the C–C skeleton.

Lucas/Cr classification: a 1°/2° alcohol turns acidic $K_2Cr_2O_7$ from orange to green; a 3° alcohol leaves it orange.

Catalytic dehydrogenation (Cu, 573 K)

1° alcohol: $\text{R–CH}_2\text{OH} \longrightarrow [\text{Cu, 573 K}]\ \text{R–CHO} + H_2$

2° alcohol: $\text{R–CHOH–R}' \longrightarrow [\text{Cu, 573 K}]\ \text{R–CO–R}' + H_2$

3° alcohol: undergoes *dehydration* (not dehydrogenation), giving the corresponding alkene.

Useful gas-phase industrial method: no aqueous workup, no chromium waste. The class of alcohol controls what comes out — a quick lab classification test on its own.

Distinguishing tests (NCERT)

Lucas ($HCl/ZnCl_2$): 3° instant cloudiness; 2° 5 min; 1° none at RT.
Victor Meyer: 1° → red; 2° → blue; 3° → colourless.
Iodoform (I_2/NaOH): positive for $CH_3CH(OH)R$ (yellow CHI_3 ppt.); only ethanol among 1° alcohols.

11 Electrophilic Aromatic Substitution on Phenols (NCERT 7.5.2)

The –OH group is a strong **activator** and **o-/p-director**. Phenol therefore halogenates, nitrates, and sulphonates far more easily than benzene; even Br_2/water gives *tribromo* phenol without a Lewis acid.

Halogenation

In water (no Lewis acid needed):
$C_6H_5OH + 3\,Br_2 \longrightarrow [H_2O]$ 2,4,6-tribromophenol$\downarrow + 3\,HBr$
In non-polar solvent (CS_2 or $CHCl_3$) at low T:
$C_6H_5OH + Br_2 \longrightarrow [CS_2,\ 273\ K]$ o- and p-bromophenol (mono)
Bromine *water* gives the white ppt. of 2,4,6-tribromophenol — a classical **qualitative test** for phenol. Low T plus a non-polar solvent stops at monobromo.

Nitration

Dilute HNO_3 (293 K):
$C_6H_5OH + HNO_3(dil.) \longrightarrow$ o-nitrophenol $+$ p-nitrophenol
The o-isomer is steam-volatile (intramolecular H-bond) and is separated by steam distillation.
Conc. HNO_3 / H_2SO_4: gives **picric acid**:
$C_6H_5OH \longrightarrow [conc.\ HNO_3/H_2SO_4]$ 2,4,6-trinitrophenol (picric acid)
Industrial picric acid is made via the sulphonation–nitration route (sulphonate first to block oxidation of phenol by HNO_3, then nitrate).

Sulphonation

$C_6H_5OH + H_2SO_4 \longrightarrow$ [cold] o-hydroxybenzenesulphonic acid (major)
$C_6H_5OH + H_2SO_4 \longrightarrow$ [hot] p-hydroxybenzenesulphonic acid (major)
Temperature controls regiochemistry: *ortho* dominates at low T (kinetic product); *para* dominates at high T (thermodynamic product, less steric strain).

Friedel–Crafts on phenol

Alkylation: $C_6H_5OH + R–Cl \longrightarrow [anhyd.\ AlCl_3]$ o- $+$ p-alkylphenol
Acylation: $C_6H_5OH + R–COCl \longrightarrow [anhyd.\ AlCl_3]$ o- $+$ p-hydroxyaryl ketone (p-major)
–OH is **strongly activating**, o-/p-directing; F–C proceeds even though $AlCl_3$ partially deactivates the ring via O→Al coordination.

Kolbe's reaction (Kolbe–Schmitt)

$C_6H_5ONa + CO_2 \longrightarrow [400\ K,\ 4–7\ atm]$ sodium salicylate
Sodium salicylate $\longrightarrow [H^+]$ salicylic acid (2-hydroxybenzoic acid)
Phenoxide ion is *much* more reactive than phenol; electrophile CO_2 adds at ortho. Salicylic acid is the precursor to **aspirin** (acetylsalicylic acid) via acetic anhydride.

Reimer–Tiemann reaction

$C_6H_5OH + CHCl_3 + NaOH\ (aq) \longrightarrow [340\ K]$ 2-hydroxybenzaldehyde (salicylaldehyde) $+ NaCl + H_2O$
Reactive intermediate: dichlorocarbene $:CCl_2$ (from $CHCl_3$ + OH^-).
Inserts a **–CHO group at the *ortho*** position of phenol. After workup with HCl, the o-substituted

intermediate hydrolyses to the aldehyde. Useful synthesis of salicylaldehyde.

Oxidation of phenol & reaction with Zn dust

Oxidation ($Na_2Cr_2O_7$):

$C_6H_5OH \longrightarrow [Na_2Cr_2O_7/H^+]$ benzoquinone (1,4-benzoquinone)

Zinc dust distillation:

$C_6H_5OH + Zn \longrightarrow [\Delta]\ C_6H_6 + ZnO$

Zn dust replaces –OH by –H — a quick way to convert a phenol back to the parent benzene. Used in structure-determination workflows.

Phenol is activating *and* o,p-directing — not deactivating

Unlike the halogens (deactivating but o,p-directing), the –OH group is **strongly activating**: phenol halogenates in plain water, nitrates with dilute HNO_3, and undergoes Kolbe / Reimer–Tiemann that benzene can't. The lone pair on O resonance-donates into the ring at *o-/p-* positions.

12 Ethers: Preparation (NCERT 7.6.1)

Two NCERT routes: (1) **dehydration of alcohols** (good for symmetrical 1° ethers only); (2) **Williamson synthesis** (the general route — works for all ethers including mixed and Ar–O–R).

(1) Dehydration of alcohols

Symmetrical ether (Williamson via continuous etherification):

$2\,R\text{–}OH \longrightarrow [\text{conc. } H_2SO_4,\ 413\ K]\ R\text{–}O\text{–}R + H_2O$

Example (ethanol → diethyl ether):

$2\,C_2H_5OH \longrightarrow [\text{conc. } H_2SO_4,\ 413\ K]\ C_2H_5O\text{–}C_2H_5 + H_2O$

Temperature decides product: 413 K → ether (S_N2); 443 K → ethene (E1).

Limitation: works well *only* for primary alcohols. 2° & 3° alcohols dehydrate to alkenes preferentially.

Bimolecular dehydration: protonated $R\text{–}OH_2^+$ attacked by a second R–OH (S_N2) gives R–O–R. Higher T tilts the route to E1 (alkene).

(2) Williamson ether synthesis

Step 1 — Alkoxide formation:

$R\text{–}OH + Na \longrightarrow R\text{–}O^-Na^+ + \frac{1}{2}H_2$

Step 2 — S_N2 displacement:

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

Example (sodium phenoxide + iodomethane → anisole):

$C_6H_5O^-Na^+ + CH_3I \longrightarrow C_6H_5\text{–}O\text{–}CH_3 + NaI$

Use a 1° R′–X (S_N2 ideal). 3° R′–X gives the alkene (E2) only — not the ether. Aryl/vinyl halides do not work (no S_N on sp^2 C). For Ar–O–R, use $Ar\text{–}O^-$ + R–X, not Ar–X + $R\text{–}O^-$.

Williamson: which way for an unsymmetrical ether?

For an unsymmetrical R–O–R′ (one alkyl, one aryl), always pair the **aryl/phenoxide ion ($Ar\text{–}O^-$)** with the **alkyl halide (R–X)**. Reverse pairing ($Ar\text{–}X + R\text{–}O^-Na^+$) fails because aryl halides do not undergo S_N2. Similarly, for two alkyl groups of different class, use the alkoxide from the more hindered alcohol and the 1° alkyl halide as the electrophile.

13 Physical Properties & Reactions of Ethers (NCERT 7.6.2–7.6.3)

Ethers have b.p. similar to comparable alkanes (no H-bonding among themselves) but are partly water-soluble (accept H-bonds from water). Chemically, they are inert towards bases / dilute acids but cleaved by concentrated HX. Aryl ethers also undergo Friedel–Crafts substitution o-/p- to the –OR group.

Physical properties

Boiling point: CH_3OCH_3 (248 K) $\approx$ $CH_3CH_2CH_3$ (231 K) $\ll$ CH_3CH_2OH (351 K).
Solubility in water: comparable to alcohols of similar M (ether O accepts H-bonds from water). Diethyl ether dissolves 8 g/100 g water.
Dipole moment: bent C–O–C ($\sim 112^\circ$); typically $\mu \approx 1.18$ D for Et_2O.
Key idea: ether oxygen has lone pairs $\Rightarrow$ accepts H-bonds (water-soluble) but **has no O–H** $\Rightarrow$ cannot donate $\Rightarrow$ no intermolecular H-bonding $\Rightarrow$ low b.p.

Cleavage by HX

$R\text{–}O\text{–}R' + HX \longrightarrow [\Delta]\ R\text{–}X + R'\text{–}OH$
With excess HX, the alcohol R′–OH further reacts to give R′–X.
Reactivity of HX: HI $>$ HBr $\gg$ HCl (HCl rarely cleaves).
Aryl alkyl ether (e.g., anisole):
$C_6H_5OCH_3 + HI \longrightarrow C_6H_5OH + CH_3I$
Mixed alkyl ether, 1° vs 2° (S_N2 path):
$CH_3O\text{–}CH(CH_3)_2 + HI \longrightarrow CH_3I + (CH_3)_2CHOH$
Mixed alkyl ether, 3° involved — S_N1 exception:
$(CH_3)_3C\text{–}O\text{–}CH_3 + HI \longrightarrow (CH_3)_3C\text{–}I + CH_3OH$
(Stable tert-butyl carbocation forms; I^- traps the 3° C, methanol leaves — **opposite** of the S_N2 rule.)
Rules for the cleavage point: (i) the *aryl* O–C bond is **never** broken (Ar–O–R always gives ArOH + R–I, because Ar–O has partial double-bond character); (ii) for mixed alkyl ethers, I^- attacks the *less hindered* C (S_N2) — so methyl/primary side leaves as R–I; (iii) **exception:** when a 3° alkyl is present, S_N1 via the stable 3° C^+ takes over and the 3° side becomes R–I.

Electrophilic substitution on aryl ethers

The –OR group is strongly **activating** and **o-/p-directing** (lone pair on O resonance-donates). Anisole therefore reacts much like phenol:
Halogenation: $C_6H_5OCH_3 + Br_2/CH_3COOH \rightarrow$ 4-bromoanisole (major) $+$ 2-bromoanisole (minor).
Nitration: $C_6H_5OCH_3 + HNO_3/H_2SO_4 \rightarrow$ 4-nitroanisole (major) $+$ 2-nitroanisole.
Friedel–Crafts acylation: $C_6H_5OCH_3 + CH_3COCl/AlCl_3 \rightarrow$ 4-methoxyacetophenone (major) $+$ 2-methoxyacetophenone.
Friedel–Crafts *alkylation* of anisole also works but tends to be sluggish; acylation is cleaner because the acyl cation is more selective.

JEE/NEET Extension: peroxide hazard of ethers

Open-chain ethers (diethyl ether, THF) slowly autoxidise in air to **explosive peroxides**:
$R\text{–}O\text{–}CHR_2 + O_2 \rightarrow R\text{–}O\text{–}CR_2\text{–}OOH$
Test with $FeSO_4$ / KI before distilling old ether. Always distill the ether *after* removing peroxides (with acidic $FeSO_4$ or basic alumina).

Quick Reference — Acidity & Master Reactions

Compound	pK_a	Reason (acidity decreases down the table)
2,4,6-trinitrophenol	0.4	3 –NO_2 groups stabilise phenoxide by –I and –M
R–COOH	4–5	Carboxylate resonance (2 equivalent O)
4-nitrophenol	7.2	–NO_2 at p- stabilises phenoxide
Phenol (Ar–OH)	10.0	Phenoxide resonance into ring (5 forms)
Water (H–OH)	15.7	Reference
Methanol / Ethanol	15.5 / 15.9	Most acidic ordinary alcohols
2-methylpropan-2-ol	$\sim$18	3 –CH_3 groups destabilise tert-butoxide

Transformation	Reagent / conditions	Product
Alkene → alcohol (Markov.)	H_2O / dil. H_2SO_4	2°/3° alcohol
Alkene → alcohol (anti-M.)	(i) B_2H_6 ; (ii) H_2O_2/OH^-	1° alcohol
Alkene → alcohol (Markov., no rearr.)	(i) $Hg(OAc)_2/H_2O$; (ii) $NaBH_4$	2°/3° alcohol
RCHO / RCOR′ → alcohol	$NaBH_4$ or $LiAlH_4$	1° / 2° alcohol
R–COOH → 1° alcohol	(i) $LiAlH_4$; (ii) H_2O	R–CH_2OH
HCHO / R′CHO / R′COR″ + R-MgX	dry ether, then H_2O	1° / 2° / 3° alcohol
PhCl → phenol (Dow)	NaOH, 623 K, 320 atm; H^+	C_6H_5OH
Cumene → phenol	O_2; dilute H^+	$C_6H_5OH + (CH_3)_2CO$
R–OH → R–Cl	$SOCl_2$ / pyridine	R–Cl (cleanest)
R–OH → R–O–R (sym.)	conc. H_2SO_4, 413 K	R–O–R
R–OH → alkene	conc. H_2SO_4, 443 K	R–CH=CH_2
1° R–OH → R–CHO / R–COOH	PCC *vs* $K_2Cr_2O_7/H^+$	aldehyde *vs* acid
2° R–OH → ketone	$K_2Cr_2O_7/H^+$ or Cu/Δ	R–CO–R′
PhOH + Br_2/H_2O	RT	2,4,6-tribromophenol
PhONa + CO_2 (Kolbe)	400 K, 4–7 atm; H^+	salicylic acid
PhOH + $CHCl_3$/NaOH	340 K, then H^+	salicylaldehyde
Williamson ether	R–O^-Na^+ + R′–X (1°)	R–O–R′
Ar–O–R + HI	Δ	ArOH + R–I (never Ar–I)
$(CH_3)_3C$–O–CH_3 + HI	Δ (S_N1 exception)	$(CH_3)_3C$–I + CH_3OH
PhOH + RCl / RCOCl	anhyd. $AlCl_3$	o-/p-alkyl(acyl)phenol
PhOH + Zn dust	Δ	C_6H_6 + ZnO