

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 ₃ OH)
Phenol	Ar-OH (sp^2 C-OH)	10.0	136 pm	Phenol (C ₆ H ₅ OH)
Water	H-OH	15.7	—	H ₂ O
Ether	R-O-R' / Ar-O-R	non-acidic	141 pm	Methoxymethane (CH ₃ OCH 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., CH₃OH, methanol).

Dihydric (glycol): two -OH (e.g., HOCH₂CH₂OH, ethane-1,2-diol).

Trihydric (glycerol): three -OH (CH₂OH-CHOH-CH₂OH, propane-1,2,3-triol).

Polyhydric alcohols carry the suffix *-diol*, *-triol* (the alkane's 'e' is kept). Increasing -OH count ⇒ 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., CH₃CH₂OH.

2° (secondary): 2 alkyl groups, e.g., (CH₃)₂CHOH.

3° (tertiary): 3 alkyl groups, e.g., (CH₃)₃COH.

Allylic alcohol: -OH on sp^3 C adjacent to $\text{C}=\text{C}$, e.g., $\text{CH}_2=\text{CH}-\text{CH}_2\text{OH}$.

Benzylic alcohol: -OH on sp^3 C attached to an aromatic ring, e.g., $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$.

$Csp^2\text{-OH}$ (vinylic / enol): -OH directly on $\text{C}=\text{C}$, e.g., $\text{CH}_2=\text{CH}-\text{OH}$ (unstable; tautomerises to CH_3CHO).

Allylic / benzylic alcohols give very **stable carbocations** on protonation \Rightarrow fast S_N1 -type reactions with HX .

Phenols & ethers by structure

Phenol classes: mono- ($\text{C}_6\text{H}_5\text{OH}$), di- (catechol, resorcinol, quinol), tri- (pyrogallol = benzene-1,2,3-triol).

Ether classes:

Symmetrical / simple: same R/Ar both sides, e.g., $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$ (diethyl ether).

Unsymmetrical / mixed: different groups, e.g., $\text{C}_2\text{H}_5\text{OCH}_3$ (ethyl methyl ether), $\text{C}_6\text{H}_5\text{OCH}_3$ (anisole).

Phenols carry -OH on an sp^2 **aromatic C**; that single fact makes them stronger acids than alcohols by ~ 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:

$\text{CH}_3\text{OH} \rightarrow$ methanol $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \rightarrow$ propan-1-ol

$(\text{CH}_3)_2\text{CHOH} \rightarrow$ propan-2-ol $(\text{CH}_3)_3\text{COH} \rightarrow$ 2-methylpropan-2-ol

$\text{HOCH}_2\text{CH}_2\text{OH} \rightarrow$ ethane-1,2-diol (ethylene glycol)

$\text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{OH} \rightarrow$ 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:

$\text{CH}_3\text{OCH}_3 \rightarrow$ dimethyl ether $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow$ diethyl ether

$\text{C}_6\text{H}_5\text{OCH}_3 \rightarrow$ methyl phenyl ether (anisole)

Ethers (IUPAC): smaller -OR group becomes *alkoxy* substituent on the larger parent:

$\text{CH}_3\text{OCH}_3 \rightarrow$ methoxymethane $\text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightarrow$ ethoxyethane

$\text{C}_6\text{H}_5\text{OCH}_3 \rightarrow$ methoxybenzene (anisole)

$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_3 \rightarrow$ 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 $\approx 108.9^\circ$ (slightly less than 109.5° tetrahedral; lone-pair repulsion compresses the angle).

Phenol: C-O-H angle $\approx 109^\circ$; C-O bond = 136 pm (*shorter* than 142 pm in methanol).

Methoxymethane: C-O-C angle $\approx 111.7^\circ$ (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

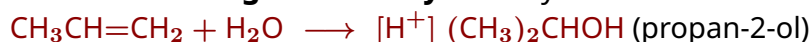
A phenolic oxygen donates one of its lone pairs into the aromatic π -system, putting partial C=O character on the C-O bond. The four resonance forms of phenol place negative charge at *ortho* and *para* ring carbons and positive charge on O. The result: shorter C-O bond, longer O-H bond, more acidic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

Markovnikov regioselectivity on unsymmetrical alkenes:



Mechanism (3 steps):

(1) H^+ adds to less-substituted C \rightarrow more-stable carbocation.

(2) H_2O attacks carbocation (nucleophilic addition).

(3) Deprotonation of oxonium \rightarrow 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):



Step 2 (oxidative work-up):

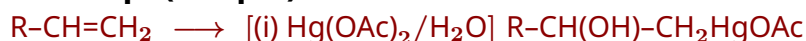


Net for propene: $\text{CH}_3\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (propan-1-ol, **anti-Markovnikov**).

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):



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:

$R-CHO \xrightarrow{[H_2/Pt, Pd \text{ or } Ni]} R-CH_2OH$
 or $NaBH_4 / LiAlH_4$ followed by H_2O work-up.

Ketones → 2° alcohol:

$R-CO-R' \xrightarrow{[NaBH_4 \text{ or } LiAlH_4]} R-CH(OH)-R'$

Carboxylic acids → 1° alcohol (**LiAlH₄** required):

$R-COOH \xrightarrow{[(i) LiAlH_4; (ii) H_2O]} R-CH_2OH$

Esters → alcohol (commercial route):

$R-COOR' \xrightarrow{[H_2/catalyst]} R-CH_2OH + R'OH$

$NaBH_4$ 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 H₂/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 $C=O$:



(2) Acidic hydrolysis:

**Aldehyde/ketone selectivity:**

$HCHO$ (methanal) + $R-MgX \rightarrow 1^\circ$ alcohol $R-CH_2OH$.

$R'-CHO + R-MgX \rightarrow 2^\circ$ alcohol $R-CHOH-R'$.

$R'-CO-R'' + R-MgX \rightarrow 3^\circ$ alcohol $R-C(OH)(R')(R'')$.

Reaction *must* be done in **dry ether** — water destroys the Grignard ($R-MgX + H_2O \rightarrow R-H + Mg(OH)X$).

Markovnikov vs anti-Markovnikov from an alkene

$H_3O^+ / \text{dilute } H_2SO_4 \Rightarrow$ Markovnikov alcohol ($-OH$ on more-substituted C). **B_2H_6 then H_2O_2/OH^-** \Rightarrow 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

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

$C_6H_5ONa \xrightarrow{[H^+]} C_6H_5OH$ (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

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

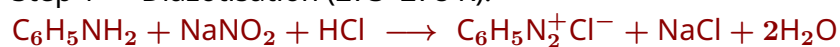
$C_6H_5SO_3H \longrightarrow [molten NaOH] C_6H_5ONa$

$C_6H_5ONa \longrightarrow [H^+] C_6H_5OH$

The $-\text{SO}_3\text{H}$ is replaced by $-\text{OH}$ via molten NaOH (alkali fusion). Acidification of the sodium phenoxide releases phenol.

(3) From diazonium salts

Step 1 — Diazotisation (273–278 K):



Step 2 — Hydrolysis (warm with H_2O or dilute acid):



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:



Step 2 — Acid-catalysed rearrangement:



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** ($\text{O-H} \cdots \text{O}$). 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) < $\text{C}_2\text{H}_5\text{OH}$ (351 K) < $\text{C}_3\text{H}_7\text{OH}$ (370 K) < $\text{C}_4\text{H}_9\text{OH}$ (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 $\text{C}_2\text{H}_5\text{OH}$ (same $M = 46$) is the H-bonding signature.

Hydrogen bonding in alcohols & phenols

Intermolecular $\text{O-H} \cdots \text{O}$ bonds ($\approx 20\text{--}30$ 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 ($\text{C}_1\text{--}\text{C}_3$) 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 $-\text{OH}$ 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



Reaction with active metals (Na, K, Al) — common to all R/Ar-OH:



Phenol-only: reacts with aqueous NaOH (alcohols don't):



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 $pK_a \Leftrightarrow$ decreasing acidity:



Phenol $pK_a \approx 10.0$ vs ethanol $pK_a \approx 15.9$.

NCERT acidity ladder including hydrocarbons:



Among alcohols (electron-releasing groups destabilise $-O^-$, lower acidity):



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 $HC \equiv CR$.

Why phenol is more acidic than ethanol

Phenoxide ion $C_6H_5O^-$ is **resonance-stabilised**: the negative charge is delocalised to the *ortho* and *para* ring carbons (3 additional resonance structures):



Ethoxide $CH_3CH_2O^-$ has **no** resonance; negative charge sits entirely on O.

\Rightarrow phenoxide is a much more stable conjugate base \Rightarrow phenol is much more acidic.

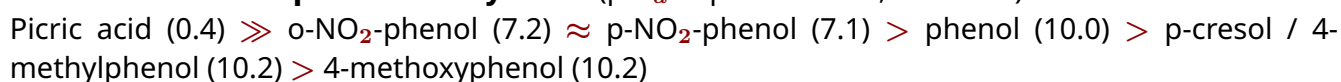
Resonance *into* the ring also explains phenol's reactions: **ortho/para electrophilic substitution** and the strong activating effect of $-OH$ on the ring.

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):



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/NaHCO₃

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 NaHCO₃ (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)



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:



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: $R-OH + R'COCl \longrightarrow [\text{pyridine}] R'COOR + HCl$.

Phenols: $ArOH + R'COCl \rightarrow ArOCOR' + HCl$.

Acetic anhydride works equally well; pyridine absorbs the HCl/CH₃COOH 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.

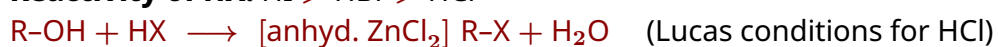
9 Reactions Involving C–O Cleavage in Alcohols

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 \rightarrow R–X)

Reactivity of alcohols: $3^\circ > 2^\circ > 1^\circ$ (carbocation stability $\Rightarrow S_N1$ ease)

Reactivity of HX: $HI > HBr > HCl$



Lucas test (alcohol classification by speed of cloudiness):

3° R–OH: cloudy *immediately* (S_N1 , fast)

2° R–OH: cloudy in ~ 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 

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 .

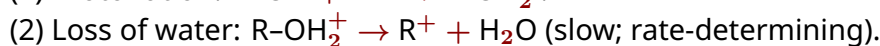
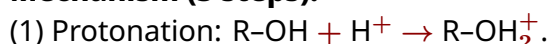
Dehydration to alkene

Conditions for ethanol \rightarrow 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):



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

E1 vs $\text{S}_{\text{N}}1$ 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, $\text{S}_{\text{N}}1$ (R-X) wins. For ethanol + conc. H_2SO_4 : 413 K \rightarrow diethyl ether (S_{N}); 443 K \rightarrow ethene (E1).

10 Oxidation & Dehydrogenation of Alcohols

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

Oxidation by strong oxidants

Primary alcohol \rightarrow acid (excess oxidant):



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



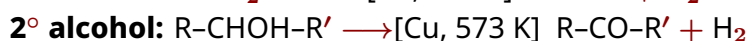
PCC = pyridinium chlorochromate, the standard **stop-at-aldehyde** reagent.

Secondary alcohol \rightarrow ketone:



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 $1^\circ/2^\circ$ alcohol turns acidic $\text{K}_2\text{Cr}_2\text{O}_7$ from orange to green; a 3° alcohol leaves it orange.

Catalytic dehydrogenation (Cu, 573 K)

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/ZnCl₂): 3° instant cloudiness; 2° 5 min; 1° none at RT.

Victor Meyer: 1° → red; 2° → blue; 3° → colourless.

Iodoform (I₂/NaOH): positive for CH₃CH(OH)R (yellow CHI₃ 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 Br₂/water gives *tribromo* phenol without a Lewis acid.

Halogenation

In water (no Lewis acid needed):



In non-polar solvent (CS₂ or CHCl₃) at low T:



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 HNO₃ (293 K):



The *o*-isomer is steam-volatile (intramolecular H-bond) and is separated by steam distillation.

Conc. HNO₃ / H₂SO₄: gives **picric acid**:



Industrial picric acid is made via the sulphonation-nitration route (sulphonate first to block oxidation of phenol by HNO₃, then nitrate).

Sulphonation

Temperature controls regiochemistry: *ortho* dominates at low T (kinetic product); *para* dominates at high T (thermodynamic product, less steric strain).

Friedel-Crafts on phenol

-OH is **strongly activating**, *o-/p*-directing; F-C proceeds even though AlCl₃ partially deactivates the ring via O→Al coordination.

Kolbe's reaction (Kolbe-Schmitt)

Phenoxide ion is *much* more reactive than phenol; electrophile CO₂ adds at *ortho*. Salicylic acid is the precursor to **aspirin** (acetylsalicylic acid) via acetic anhydride.

Reimer-Tiemann reaction

Reactive intermediate: dichlorocarbene :CCl₂ (from CHCl₃ + 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 ($\text{Na}_2\text{Cr}_2\text{O}_7$):



Zinc dust distillation:



Zn dust replaces $-\text{OH}$ by $-\text{H}$ — 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 $-\text{OH}$ 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)

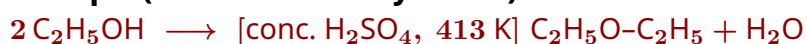
Two NCERT routes: (1) **dehydration of alcohols** (good for symmetrical 1° ethers only); (2) **Williamson synthesis** (the general route — works for all ethers including mixed and Ar-O-R).

(1) Dehydration of alcohols

Symmetrical ether (Williamson via continuous etherification):



Example (ethanol \rightarrow diethyl ether):



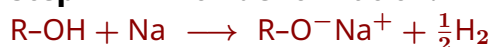
Temperature decides product: 413 K \rightarrow ether ($\text{S}_{\text{N}}2$); 443 K \rightarrow ethene (E1).

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

Bimolecular dehydration: protonated R-OH_2^+ attacked by a second R-OH ($\text{S}_{\text{N}}2$) gives R-O-R . Higher T tilts the route to E1 (alkene).

(2) Williamson ether synthesis

Step 1 — Alkoxide formation:



Step 2 — $\text{S}_{\text{N}}2$ displacement:



Example (sodium phenoxide + iodomethane \rightarrow anisole):



Use a 1° $\text{R}'\text{-X}$ ($\text{S}_{\text{N}}2$ ideal). 3° $\text{R}'\text{-X}$ 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 $\text{Ar-O}^- + \text{R-X}$, not $\text{Ar-X} + \text{R-O}^-$.

Williamson: which way for an unsymmetrical ether?

For an unsymmetrical $\text{R-O-R}'$ (one alkyl, one aryl), always pair the **aryl/phenoxide ion (Ar-O^-)** with the **alkyl halide (R-X)**. Reverse pairing ($\text{Ar-X} + \text{R-O}^-\text{Na}^+$) fails because aryl halides do not undergo $\text{S}_{\text{N}}2$. 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 $\text{CH}_3\text{CH}_2\text{CH}_3$ (231 K) \ll $\text{CH}_3\text{CH}_2\text{OH}$ (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



With excess HX, the alcohol $\text{R}'\text{–OH}$ further reacts to give $\text{R}'\text{–X}$.

Reactivity of HX: $\text{HI} > \text{HBr} \gg \text{HCl}$ (HCl rarely cleaves).

Aryl alkyl ether (e.g., anisole):



Mixed alkyl ether, 1° vs 2° ($\text{S}_{\text{N}}2$ path):



Mixed alkyl ether, 3° involved — $\text{S}_{\text{N}}1$ exception:



(Stable tert-butyl carbocation forms; I^- traps the 3° C, methanol leaves — **opposite** of the $\text{S}_{\text{N}}2$ rule.)

Rules for the cleavage point: (i) the *aryl* O–C bond is **never** broken (Ar–O–R always gives $\text{ArOH} + \text{R–I}$, because Ar–O has partial double-bond character); (ii) for mixed alkyl ethers, I^- attacks the *less hindered* C ($\text{S}_{\text{N}}2$) — so methyl/primary side leaves as R–I ; (iii) **exception:** when a 3° alkyl is present, $\text{S}_{\text{N}}1$ 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: $\text{C}_6\text{H}_5\text{OCH}_3 + \text{Br}_2/\text{CH}_3\text{COOH} \rightarrow$ 4-bromoanisole (major) + 2-bromoanisole (minor).

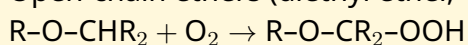
Nitration: $\text{C}_6\text{H}_5\text{OCH}_3 + \text{HNO}_3/\text{H}_2\text{SO}_4 \rightarrow$ 4-nitroanisole (major) + 2-nitroanisole.

Friedel–Crafts acylation: $\text{C}_6\text{H}_5\text{OCH}_3 + \text{CH}_3\text{COCl}/\text{AlCl}_3 \rightarrow$ 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**:



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 $-\text{NO}_2$ groups stabilise phenoxide by $-I$ and $-M$
R-COOH	4-5	Carboxylate resonance (2 equivalent O)
4-nitrophenol	7.2	$-\text{NO}_2$ 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	~ 18	3 $-\text{CH}_3$ groups destabilise tert-butoxide

Transformation	Reagent / conditions	Product
Alkene \rightarrow alcohol (Markov.)	$\text{H}_2\text{O} / \text{dil. H}_2\text{SO}_4$	$2^\circ/3^\circ$ alcohol
Alkene \rightarrow alcohol (anti-M.)	(i) B_2H_6 ; (ii) $\text{H}_2\text{O}_2/\text{OH}^-$	1° alcohol
Alkene \rightarrow alcohol (Markov., no rearr.)	(i) $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$; (ii) NaBH_4	$2^\circ/3^\circ$ alcohol
RCHO / RCOR' \rightarrow alcohol	NaBH_4 or LiAlH_4	$1^\circ / 2^\circ$ alcohol
R-COOH \rightarrow 1° alcohol	(i) LiAlH_4 ; (ii) H_2O	R- CH_2OH
HCHO / R'CHO / R'COR'' + R-MgX	dry ether, then H_2O	$1^\circ / 2^\circ / 3^\circ$ alcohol
PhCl \rightarrow phenol (Dow)	NaOH , 623 K, 320 atm; H^+	$\text{C}_6\text{H}_5\text{OH}$
Cumene \rightarrow phenol	O_2 ; dilute H^+	$\text{C}_6\text{H}_5\text{OH} + (\text{CH}_3)_2\text{CO}$
R-OH \rightarrow R-Cl	$\text{SOCl}_2 / \text{pyridine}$	R-Cl (cleanest)
R-OH \rightarrow R-O-R (sym.)	conc. H_2SO_4 , 413 K	R-O-R
R-OH \rightarrow alkene	conc. H_2SO_4 , 443 K	R- $\text{CH}=\text{CH}_2$
1° R-OH \rightarrow R-CHO / R-COOH	PCC vs $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$	aldehyde vs acid
2° R-OH \rightarrow ketone	$\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$ or Cu/Δ	R-CO-R'
PhOH + $\text{Br}_2/\text{H}_2\text{O}$	RT	2,4,6-tribromophenol
PhONa + CO_2 (Kolbe)	400 K, 4-7 atm; H^+	salicylic acid
PhOH + $\text{CHCl}_3/\text{NaOH}$	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)
$(\text{CH}_3)_3\text{C-O-CH}_3$ + HI	Δ ($\text{S}_\text{N}1$ exception)	$(\text{CH}_3)_3\text{C-I} + \text{CH}_3\text{OH}$
PhOH + RCl / RCOCl	anhyd. AlCl_3	o -/ p -alkyl(acyl)phenol
PhOH + Zn dust	Δ	$\text{C}_6\text{H}_6 + \text{ZnO}$