FREE NOTES · NCERT + JEE/NEET LEVEL

Alcohols, Phenols & Ethers

Classification and naming, preparation of alcohols and phenols, physical properties, acidity, reactions of the O–H bond, C–O bond and ring, distinguishing tests, and ethers: preparation and reactions.

01 Classification & naming
02 Preparing alcohols
03 Preparing phenols
04 Physical properties
05 Acidity
06 Reactions of alcohols
07 Reactions of phenol (ring)
08 Ethers
09 Named reactions & distinguishing tests
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01 Classification & naming

- **Alcohols:** –OH on sp^3 carbon. Mono-, di- (glycol), tri-hydric (glycerol). 1°, 2°, 3° by the carbon holding –OH. Allylic and benzylic alcohols too.
- **Phenols:** –OH directly on a benzene ring (sp^2 C).
- **Ethers:** R–O–R′. Symmetrical (CH_3OCH_3) or unsymmetrical ($CH_3OC_2H_5$).

Formula	Common	IUPAC
$CH_3CH(OH)CH_3$	Isopropyl alcohol	Propan-2-ol
$(CH_3)_3COH$	tert-Butyl alcohol	2-Methylpropan-2-ol
$HOCH_2CH_2OH$	Ethylene glycol	Ethane-1,2-diol
$C_6H_4(OH)_2$ (1,2 / 1,3 / 1,4)	Catechol / Resorcinol / Hydroquinone	Benzene-1,2-diol etc.
$C_6H_5OCH_3$	Anisole	Methoxybenzene

Shape: C–O–H in methanol ~108.9°; C–O–C in dimethyl ether ~111.7° (bigger due to bulky groups).

02 Preparing alcohols

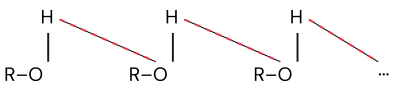
From	Reagent	Product
Alkene	H_2O / H^+ (acid hydration)	Markovnikov alcohol
Alkene	**B_2H_6 then H_2O_2/OH^-** (hydroboration-oxidation)	Anti-Markovnikov alcohol (looks like it)
Aldehyde / ketone	H_2/Pd, $NaBH_4$, $LiAlH_4$	1° / 2° alcohol
Acid / ester	$LiAlH_4$ (or ester + H_2/catalyst)	1° alcohol
HCHO + RMgX	then H_3O^+	1° alcohol
RCHO (other) + RMgX	then H_3O^+	2° alcohol
Ketone + RMgX	then H_3O^+	3° alcohol

03 Preparing phenols

- **From haloarene:** chlorobenzene + NaOH at 623 K, 300 atm, then acid.
- **From benzenesulphonic acid:** fuse with NaOH, then acid.
- **From diazonium salt:** warm with water: $C_6H_5N_2^+Cl^- + H_2O \rightarrow C_6H_5OH + N_2 + HCl$.
- **From cumene** (industrial): cumene + O_2 → cumene hydroperoxide → H^+/H_2O → **phenol + acetone**.

04 Physical properties

- Alcohols and phenols have **high boiling points** due to intermolecular H-bonding (ethanol 351 K vs propane 231 K vs methoxymethane 248 K).
- Boiling point rises with chain length, falls with branching.
- Lower alcohols are **water-soluble** (H-bond with water); solubility falls as the alkyl chain grows.
- Ethers: low b.p. (no O–H, no H-bonds between them), but slightly water-soluble (O accepts H-bond from water).



dashed = hydrogen bonds ⇒ high boiling point

Hydrogen bonding between alcohol molecules

05 Acidity

- Alcohols are very weak acids: 2ROH + 2Na → 2RONa + H_2. Order: **1° > 2° > 3°** (alkyl +I pushes electrons onto O). Water is a stronger acid than alcohols.
- **Phenol is more acidic** than alcohol: phenoxide ion is stabilised by resonance (negative charge spread over the ring). Phenol reacts with NaOH, not with $NaHCO_3$.
- **Electron-withdrawing** groups (–NO_2) at o/p increase acidity; **electron-releasing** groups (–CH_3) decrease it.

ACIDITY ORDER TO REMEMBER

picric acid (2,4,6-trinitrophenol) > p-nitrophenol > o-nitrophenol > m-nitrophenol > phenol > p-cresol > water > ethanol

06 Reactions of alcohols

Reaction	Reagent	Result
Esterification	RCOOH / H^+ (or RCOCl, $(RCO)_2O$)	Ester (reversible; remove water)
With HX	HCl + anhydrous $ZnCl_2$ (Lucas)	3°: instant turbidity; 2°: ~5 min; 1°: none at room temp
With PX_3, $SOCl_2$		Alkyl halide
Dehydration	conc. H_2SO_4, 443 K (1°)	Alkene; ease 3° > 2° > 1° (carbocation)
Oxidation 1°	PCC → aldehyde; $KMnO_4/K_2Cr_2O_7$ → acid	
Oxidation 2°	CrO_3	Ketone
3°	Not oxidised easily; Cu/573 K gives alkene	
Dehydrogenation	Cu, 573 K	1° → aldehyde, 2° → ketone

07 Reactions of phenol (ring)

–OH strongly **activates** the ring and directs to **ortho and para**.

- **Nitration:** dilute HNO_3 (298 K) → o- and p-nitrophenol (separated by steam distillation: o- is steam volatile due to **intramolecular** H-bond). Conc. HNO_3 → **picric acid**.
- **Bromination:** Br_2 in CS_2 (low temp) → mono-bromophenols; **bromine water** → white ppt of **2,4,6-tribromophenol**.
- **Kolbe's reaction:** sodium phenoxide + CO_2 (4–7 atm, 400 K), then H^+ → **salicylic acid** (o-hydroxybenzoic acid) → aspirin.
- **Reimer-Tiemann:** phenol + $CHCl_3$ + aq. NaOH, then H^+ → **salicylaldehyde**.
- **With Zn dust:** phenol → benzene.
- **Oxidation:** $Na_2Cr_2O_7/H_2SO_4$ → benzoquinone.

08 Ethers

- **By dehydration:** $2C_2H_5OH$, conc. H_2SO_4, **413 K** → $C_2H_5OC_2H_5$ (at 443 K you get ethene). Works for 1° alcohols only.
- **Williamson synthesis:** R–X + $R'O^-Na^+$ → R–O–R'. Use a **1° halide** with any alkoxide; with a 3° halide you get elimination (alkene). For tert-butyl methyl ether: $(CH_3)_3CO^-Na^+ + CH_3Br$, not $(CH_3)_3CBr + CH_3ONa$.
- **Cleavage by HI:** R–O–R' + HI → ROH + R'I. With mixed alkyl groups, I^- goes to the **smaller** group (SN2); with a 3° group it goes to the 3° side (SN1). Anisole + HI → **phenol + CH_3I** (never iodobenzene).
- Anisole: $-OCH_3$ activates the ring, o/p directing (halogenation, Friedel-Crafts, nitration).

09 Named reactions & distinguishing tests

Test	Gives
Lucas test	Distinguishes 1°/2°/3° alcohols (turbidity time)
Neutral $FeCl_3$	Phenol: violet colour; alcohol: none
Bromine water	Phenol: white ppt
Iodoform (I_2 + NaOH)	Yellow CHI_3 for $CH_3CH(OH)–$ alcohols (ethanol, propan-2-ol), not methanol
Na metal	Alcohol/phenol give H_2; ether doesn't

10 JEE Extra + Tricks

JEE LEVEL

- Lucas test ($ZnCl_2$ + HCl): 3° alcohol turbidity immediately, 2° in ~5 min, 1° no turbidity at room temperature.
- Acidity: phenol (pK_a ~10) > water > alcohols; o/p-nitrophenol more acidic, cresols less acidic than phenol.
- Reimer–Tiemann ($CHCl_3$/NaOH ⇒ salicylaldehyde); Kolbe (CO_2/NaOH ⇒ salicylic acid); phenol + Br_2 water ⇒ 2,4,6-tribromophenol (white ppt).
- Williamson ether synthesis: use 1° alkyl halide + alkoxide (3° halide gives elimination).
- Ethers with HI: smaller alkyl forms iodide (S_N2); with 3° alkyl, 3° alkyl iodide forms (S_N1). Anisole + HI ⇒ phenol + CH_3I.
- Dehydration: 3° alcohols easiest; conc. H_2SO_4 at 443 K ⇒ alkene, at 413 K ⇒ ether.

11 Solved questions, mistakes & practice

Q1. Why is o-nitrophenol more volatile than p-nitrophenol?

o- has intramolecular H-bond (no association); p- has intermolecular H-bonds, so a higher b.p.

Q2. Prepare propan-2-ol from a Grignard reagent.

$CH_3CHO + CH_3MgBr \rightarrow (CH_3)_2CHOMgBr \rightarrow H_3O^+ \rightarrow (CH_3)_2CHOH$.

Q3. Products of $CH_3OC_2H_5 + HI$?

$CH_3I + C_2H_5OH$ (I^- attacks the smaller methyl).

- Writing iodobenzene from anisole + HI.
- Saying phenol reacts with $NaHCO_3$ (it's too weak an acid).
- Using a 3° halide in Williamson synthesis.
- Mixing 413 K (ether) and 443 K (alkene) in dehydration.

1. Which gives the Lucas test instantly?
2. Product of Reimer-Tiemann reaction?
3. Which is more acidic: phenol or ethanol?
4. Industrial source of phenol that also gives acetone?

ANSWERS

1) 3° alcohol · 2) Salicylaldehyde · 3) Phenol · 4) Cumene process

12 Quick revision: 5 minutes before the exam

PREPARATION

- HCHO/RCHO/R_2CO + RMgX ⇒ 1°/2°/3°.
- Hydroboration ⇒ anti-Markovnikov.
- Cumene ⇒ phenol + acetone.

ACIDITY

- Phenol > water > alcohol.
- $-NO_2$ ↑ acidity, $-CH_3$ ↓.
- 1° > 2° > 3° alcohol.

PHENOL REACTIONS

- Br_2 water ⇒ 2,4,6-tribromophenol.
- Kolbe ⇒ salicylic acid.
- Reimer-Tiemann ⇒ salicylaldehyde.

ETHERS

- Williamson: 1° halide + alkoxide.
- Anisole + HI ⇒ phenol + CH_3I.
- H_2SO_4 413 K ⇒ ether.

Have a doubt? Ask the AI Doubt Solver at padhaiadda.netlify.app, or take the mock test on this chapter.