FREE EDITION · NOTES + 3 SAMPLE MCQS

CUET · CHEMISTRY · CLASS XII · CODE 306

Alcohols, Phenols and Ethers

CUET unit: Alcohols, Phenols and Ethers

By **UniDrill** · NCERT-grounded study material

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📌 Snapshot

- Introduces three oxygen-bearing classes — alcohols (-OH on sp3 C of aliphatic system), phenols (-OH on sp2 C of aromatic ring) and ethers (R-O-R′/R-O-Ar) — and develops their nomenclature, preparation, physical and chemical behaviour (NCERT §7, p. 193–194).
- Establishes the central acid-strength order **phenol > water > primary > secondary > tertiary alcohol**, explained by stability of phenoxide vs. alkoxide ions (NCERT §7.4.4, p. 205–207).
- Builds reaction logic around two bond-cleavage modes — O-H cleavage (acidity, esterification) and C-O cleavage (HX/Lucas test, PX3, SOCl2, dehydration, oxidation) — which is the single most tested theme in CUET (NCERT §7.4.4, p. 204–210).
- Covers phenol-specific chemistry — Kolbe carboxylation, Reimer-Tiemann formylation, ortho/para electrophilic substitution and bromine-water tribromophenol test (NCERT §7.4.4, p. 211–213).
- Closes with ethers — Williamson synthesis (S_N2, primary halide), acid dehydration of alcohols, and HI cleavage with mechanism-driven product prediction including the anisole and t-alkyl special cases (NCERT §7.6, p. 215–220).

📖 Detailed Notes

2.1 Core concepts

- **Classification of alcohols/phenols** — Mono-, di-, tri- or polyhydric based on number of -OH groups; monohydric alcohols are further sub-classified by hybridisation of the C bearing -OH into Csp3-OH (primary, secondary, tertiary, allylic, benzylic) and Csp2-OH (vinylic, aryl). Phenols are similarly classified as mono-, di-, trihydric (NCERT §7.1.1–7.1.2, p. 194–195).
- **Ethers** are simple/symmetrical if the two R/Ar groups are identical (e.g., diethyl ether) and mixed/unsymmetrical otherwise (e.g., C2H5OC6H5) (NCERT §7.1.3, p. 195).
- **IUPAC nomenclature** — Alcohol = parent alkane with terminal "e" replaced by "ol", chain numbered to give -OH the lowest locant; polyhydric alcohols retain the "e" and add di/tri-ol (ethane-1,2-diol). Phenols use ortho/meta/para nomenclature in

common names but locants in IUPAC (2-methylphenol). Ethers are named with the smaller group as alkoxy substituent on the larger parent (e.g., methoxybenzene = anisole) (NCERT §7.2, p. 195–198; Table 7.1, p. 196; Table 7.2, p. 197).

- **Structures** — In alcohols, C-O-H angle is slightly less than 109°28′ due to lone-pair repulsion on O; in phenols, C-O bond (136 pm) is shorter than in methanol because of partial double-bond character from conjugation of O lone pair with the ring and sp2 carbon; in ethers C-O-C angle is slightly greater than tetrahedral due to bulky R groups (NCERT §7.3, p. 198–199).
- **Preparation of alcohols** — (i) Acid-catalysed hydration of alkenes follows Markovnikov's rule via a carbocation intermediate; (ii) Hydroboration-oxidation with (BH3)2 then H2O2/OH gives anti-Markovnikov alcohol in excellent yield (boron adds to the less substituted carbon); (iii) Catalytic hydrogenation (Pt/Pd/Ni) or NaBH4/LiAlH4 reduction of aldehydes gives 1° and of ketones gives 2° alcohols; LiAlH4 reduces carboxylic acids/esters to 1° alcohols; (iv) Grignard reagents with HCHO give 1° alcohol, with other aldehydes give 2° alcohol, with ketones give 3° alcohol (NCERT §7.4.1, p. 199–201).
- **Preparation of phenols** — (1) Chlorobenzene + fused NaOH at 623 K/320 atm then acidification (Dow process); (2) benzene → benzenesulphonic acid (oleum) → fuse with NaOH → acidify; (3) Aniline → diazonium salt at 273–278 K → warm with water; (4) **Cumene process** — isopropylbenzene + air → cumene hydroperoxide → dilute acid → phenol + acetone (industrial, gives acetone as by-product) (NCERT §7.4.2, p. 201–202).
- **Physical properties** — Boiling points rise with carbon number and fall with branching; alcohols and phenols boil far higher than comparable hydrocarbons, ethers and haloalkanes because of intermolecular **H-bonding** through -OH; ethers lack H-bonding so b.p. ≈ alkanes of similar mass; lower alcohols are miscible with water in all proportions, solubility falls as the hydrophobic alkyl tail grows (NCERT §7.4.3, p. 203–204; §7.6.2, p. 217).
- **Acidity of alcohols and phenols** — Both are Brønsted acids (reaction with Na/K/Al gives alkoxide/phenoxide + H2); **phenols also react with aqueous NaOH** but alcohols do not. Electron-releasing alkyl groups raise electron density on O and weaken acidity, so the order is 1° > 2° > 3° alcohol. Alcohols are weaker acids than water (alkoxides are stronger bases than OH–). Phenol (pKa ≈ 10) is about a million times more acidic than ethanol (pKa ≈ 15.9) because the phenoxide ion stabilises negative charge by delocalisation over the ring (five resonance structures), while alkoxide localises the charge on O. Electron-withdrawing groups (especially -NO2 at ortho/para) further raise phenol's acidity (p-nitrophenol pKa 7.1; 2,4,6-trinitrophenol = picric acid is a strong acid); -CH3 (cresols) lowers acidity (NCERT §7.4.4, p. 204–207; Table 7.3, p. 207).
- **Reactions involving O-H cleavage** — (1) Reaction with metals; (2) **Esterification** with carboxylic acids (H2SO4 catalyst, reversible), with acid anhydrides (H2SO4),

and with acid chlorides (in pyridine to neutralise HCl); acetylation of salicylic acid gives aspirin (NCERT §7.4.4, p. 205–208).

- **Reactions involving C-O cleavage (alcohols only, except phenol + Zn)** — (1) ROH + HX → RX (Lucas test: alcohol + conc. HCl/ZnCl2 — 3° gives immediate turbidity, 2° gives turbidity in 5 min, 1° gives no turbidity at room temperature); (2) PBr3 converts alcohol → alkyl bromide; (3) **Dehydration** with conc. H2SO4 / H3PO4 / Al2O3 — ethanol → ethene at 443 K; ease of dehydration 3° > 2° > 1° (more stable carbocation); mechanism = protonation → carbocation (slow, rate-determining) → loss of proton; (4) **Oxidation** — primary alcohol → aldehyde (with CrO3 anhydrous or PCC) → carboxylic acid (with acidified KMnO4); secondary alcohol → ketone (CrO3); tertiary alcohol resists oxidation but under harsh conditions undergoes C-C cleavage; Cu/573 K dehydrogenates 1°/2° alcohols to aldehydes/ketones while dehydrating 3° alcohols (NCERT §7.4.4, p. 208–210).
- **Reactions of phenols only** — (i) **Nitration** — dilute HNO3 / 298 K gives o- and p-nitrophenols (separable by steam distillation because o-isomer is steam-volatile due to **intramolecular H-bonding** while p-isomer associates by intermolecular H-bonding); conc. HNO3 gives 2,4,6-trinitrophenol (picric acid). (ii) **Halogenation** — Br2 in CHCl3/CS2 at low temperature gives monobromophenols (mainly p-); Br2 in water gives **2,4,6-tribromophenol** as a white precipitate. (iii) **Kolbe's reaction** — phenoxide + CO2 gives ortho-hydroxybenzoic acid (salicylic acid). (iv) **Reimer-Tiemann** — phenol + CHCl3 + aq. NaOH introduces -CHO at the ortho position, giving salicylaldehyde via a benzal-chloride intermediate. (v) Phenol + Zn dust → benzene. (vi) Oxidation with chromic acid → benzoquinone (NCERT §7.4.4, p. 211–213).
- **Commercial alcohols** — Methanol ("wood spirit") made by CO + 2H2 over ZnO-Cr2O3 catalyst at high T, P; b.p. 337 K; toxic (causes blindness/death). Ethanol made by fermentation of sugars (invertase converts sucrose → glucose + fructose; zymase converts these to ethanol + CO2 anaerobically; zymase is inhibited above ~14% ethanol). Now also made by hydration of ethene. Denaturation = adding CuSO4 + pyridine to make it unfit for drinking (NCERT §7.5, p. 214).
- **Preparation of ethers** — (1) **Acid dehydration of alcohols** — ethanol with conc. H2SO4 at 413 K gives ethoxyethane (S_N2 attack of alcohol on protonated alcohol); works only for primary, unhindered alkyl groups at low T; fails for 2°/3° (elimination wins). (2) **Williamson synthesis** — RX + R′O–Na+ → R-O-R′ (S_N2); best with primary RX (with 2°/3° halide elimination dominates — e.g. CH3ONa + (CH3)3CBr gives 2-methylpropene exclusively); phenoxides are also used to give aryl ethers (NCERT §7.6.1, p. 215–217).
- **Reactions of ethers** — (1) **HX cleavage** — dialkyl ether + excess HX (HI > HBr > HCl) gives two alkyl halides; mixed ethers cleave by S_N2 with I– attacking the less substituted C, so the smaller alkyl group becomes the alkyl iodide; if one group is tertiary the reaction switches to S_N1 (stable 3° carbocation) and the 3° group ends up as the halide; **alkyl aryl ethers** (e.g., anisole + HI) cleave at the alkyl-O bond

giving phenol + alkyl halide because aryl-O is stronger (partial double-bond, sp2 C cannot undergo S_N) and phenols do not react further with HI. (2) **Electrophilic substitution in aryl alkyl ethers** — alkoxy group is activating and ortho/para directing: anisole + Br2/CH3COOH gives p-bromoanisole (90%) without FeBr3; Friedel-Crafts alkylation/acylation with AlCl3 gives o-/p- products; nitration with conc. HNO3/H2SO4 gives o-/p-nitroanisole (NCERT §7.6.3, p. 217–220).

2.2 Definitions to memorise

Term	Definition	Page
Alcohol	-OH attached to sp3 C of an aliphatic system (RCH2OH, etc.)	193
Phenol	-OH attached directly to sp2 C of an aromatic ring (C6H5OH)	193
Ether	Compound R-O-R′ or R-O-Ar (H of an alcohol/phenol -OH replaced by alkyl/aryl)	193
Allylic alcohol	-OH on an sp3 C adjacent to a C=C	194
Benzylic alcohol	-OH on an sp3 C next to an aromatic ring	194
Vinylic alcohol	-OH directly on a sp2 C of C=C (CH2=CH-OH)	195
Markovnikov's rule (hydration)	In acid hydration of unsymmetrical alkenes, H goes to the C with more H, OH to the more substituted C (via more stable carbocation)	199
Hydroboration-oxidation	(BH3)2 adds anti-Markovnikov to alkene, then H2O2/aq. NaOH gives the alcohol with B replaced by OH	200
Cumene process	Cumene → cumene hydroperoxide (air, O2) → phenol + acetone (dilute acid) — main industrial route to phenol	202
Lucas test	Conc. HCl + ZnCl2 — 3° alcohol gives immediate turbidity, 2° in ~5 min, 1° no turbidity at RT	208
Esterification	Alcohol/phenol + acid (or acid chloride/anhydride) → ester (acetylation when CH3CO- is introduced; aspirin from salicylic acid)	207–208
Kolbe's reaction	Sodium phenoxide + CO2 → ortho-hydroxybenzoic acid (salicylic acid)	212
Reimer-Tiemann reaction	Phenol + CHCl3 + aq. NaOH → salicylaldehyde (-CHO at ortho)	213
Williamson synthesis	RX + R′O–Na+ → R-O-R′ (S_N2; works best with primary halide)	215
Denatured alcohol	Ethanol made unfit to drink by adding CuSO4 (colour) and pyridine (foul smell)	214
Picric acid	2,4,6-trinitrophenol — a strong acid because three -NO2 groups stabilise the phenoxide	211

2.3 Diagrams / processes to remember

- Fig. 7.1 — Structures of methanol, phenol and methoxymethane showing bond angles and C-O bond lengths (136 pm in phenol, 141 pm in ether) (p. 198).
- Resonance structures (I–V) of phenoxide ion showing delocalisation of negative charge onto ortho and para carbons of the ring — basis of phenol's acidity (p. 206).
- Three-step mechanism of acid-catalysed hydration of alkene — protonation → nucleophilic water attack → deprotonation (p. 199).
- Three-step mechanism of ethanol dehydration — protonation → carbocation (slow, RDS) → loss of H+ to give ethene (p. 209).
- HI cleavage mechanism of an ether — protonation to oxonium, then S_N2 attack of I– on the less substituted C (for primary/secondary), but S_N1 path with retention of the tertiary group as the halide when one alkyl is 3° (p. 218).
- Industrial cumene → cumene hydroperoxide → phenol + acetone scheme (p. 202).
- Intramolecular H-bonding in o-nitrophenol vs. intermolecular in p-nitrophenol — explains steam volatility (p. 211).
- Table 7.3 pKa data: phenol 10.0; o/p-nitrophenol 7.2/7.1; m-nitrophenol 8.3; cresols ≈ 10.2; ethanol 15.9 (p. 207).

2.4 Common confusions / NTA trap points

- **Acidity order** — Students often write tertiary > secondary > primary alcohol; the correct order (per NCERT) is **primary > secondary > tertiary**, because electron-releasing alkyls destabilise the alkoxide. The full chain is phenol > water > 1° > 2° > 3° alcohol.
- **Markovnikov vs anti-Markovnikov** — Acid-catalysed hydration gives Markovnikov product (OH on more substituted C); hydroboration-oxidation gives the anti-Markovnikov product. NTA often pairs these in the same MCQ.
- **Lucas test timings** — 3° = immediate; 2° = within ~5 minutes; 1° = no turbidity at RT. Mixing these up is a frequent trap.
- **Br2 in CS2/CHCl3 vs Br2 in water** — Low-polarity solvent at low T gives monobromophenol (mainly p-); aqueous bromine gives the **white precipitate 2,4,6-tribromophenol** — used as a test for phenol.
- **HI cleavage of anisole** — Always gives **phenol + CH3I** (never methanol + iodobenzene), because the aryl-O bond is stronger and phenols can't undergo nucleophilic substitution at sp2 C.
- **Williamson with tertiary halide** — Gives the alkene (elimination), not the ether; the correct combination for t-butyl methyl ether is t-butoxide + methyl halide, not methoxide + t-butyl halide.
- **Steam-volatile isomer** — o-nitrophenol (intramolecular H-bonding) is steam-volatile; p-nitrophenol (intermolecular H-bonding) is not.

🎯 Practice MCQs

Q1. The acid-catalysed hydration of propene gives propan-2-ol as the major product. Which statement best explains this observation?

A. Water adds anti-Markovnikov because hydration is concerted

B. Protonation gives the more stable secondary carbocation, which is then trapped by water at C-2

C. Boron of the catalyst adds to the less substituted carbon, placing OH on C-2

D. The reaction proceeds via a free-radical chain, with OH adding to the terminal carbon

Q2. Which reagent system converts a primary alcohol cleanly to an **aldehyde without over-oxidation to the carboxylic acid?**

A. Acidified KMnO4

B. Acidified K2Cr2O7 with reflux

C. Pyridinium chlorochromate (PCC)

D. Hot alkaline KMnO4 followed by acidification

Q3. Arrange in the **correct order of increasing acid strength: ethanol, phenol, p-cresol, p-nitrophenol.**

A. ethanol < phenol < p-cresol < p-nitrophenol

B. p-nitrophenol < phenol < p-cresol < ethanol

C. ethanol < p-cresol < phenol < p-nitrophenol

D. ethanol < phenol < p-nitrophenol < p-cresol

📊 PYQ Alignment

This chapter is one of the most heavily tested in CUET (UG) Chemistry, typically yielding 2–4 MCQs per paper since 2022. Recurring question types include identification of

products of Williamson synthesis, HI cleavage of mixed/aryl alkyl ethers, Lucas test outcomes, acidity ordering of substituted phenols/alcohols, choice of oxidising reagent (PCC vs KMnO4) and named reactions of phenol (Kolbe, Reimer-Tiemann, bromine water).

CUET 2025 — Actual PYQs from this chapter

Q.29 (CUET 2025) Which reagents convert benzene → methyl benzoate? (A) $Br_2/FeBr_3$ (B) Mg, dry ether (C) CO_2, H_3O^+ (D) Methanol, conc. H_2SO_4

- A) — B) — C) — D) —

Tests: Ethers — Williamson, HI cleavage Answer: Not in extracted key

Q.40 (CUET 2025) Arrange compounds in increasing order of acidic strength: (A) 3-nitrophenol (B) 3,5-dinitrophenol (C) 2,4,6-trinitrophenol (D) Phenol

- A) — B) — C) — D) —

Tests: Phenols Answer: Not in extracted key

Q.46 (CUET 2025) When ethanol and ethoxyethane react with H_2SO_4 at 443 K and 413 K respectively, the products formed are:

- A) Ethane and ethoxyethane B) Ethylmethyl ether and butene C) Ethylmethyl ether and propene D) Ethene and ethoxyethane

Tests: Alcohol/ether dehydration Answer: Not in extracted key

Q.47 (CUET 2025) The major product in the reaction of anisole with bromine in ethanoic acid is:

- A) o-bromoanisole B) p-bromoanisole C) m-bromoanisole D) o-bromoanisole and p-bromoanisole

Tests: Ethers — Williamson, HI cleavage Answer: Not in extracted key

Q.49 (CUET 2025) Which is the most reactive hydrogen halide for cleavage of ethers?

- A) HF B) HCl C) HBr D) HI

Tests: Ethers — Williamson, HI cleavage Answer: Not in extracted key

Q.50 (CUET 2025) Which type of ether is anisole?

- A) Dialkyl ether B) Diaryl ether C) Phenyl alkyl ether D) Alkoxy alkyl ether

Tests: Ethers — Williamson, HI cleavage Answer: Not in extracted key

Q.33 (CUET 2025) What happens when C_2H_5–O–R is treated with HX?

- A) RX and C_2H_5OH formed B) ROH and C_2H_5X formed C) $C_2H_4X_2$ and ROH formed D) RX and C_2H_5X formed

Tests: Ether cleavage with HX Answer: Not in extracted key

CUET 2024 — Actual PYQs from this chapter

Q.10 (CUET 2024) Correct increasing order of boiling points: Pentan-1-ol, n-Butane, Pentanal, Ethoxyethane

- A) Ethoxyethane < Pentanal < n-Butane < Pentan-1-ol B) Pentanal < n-Butane < Ethoxyethane < Pentan-1-ol C) n-Butane < Pentanal < Ethoxyethane < Pentan-1-ol D) n-Butane < Ethoxyethane < Pentanal < Pentan-1-ol

Tests: Boiling point of alcohols/ethers Answer: Not in extracted key

Q.11 (CUET 2024) Identify product D in the reaction sequence starting from phenol involving: ● Zn dust ● CH_3Cl / $AlCl_3$ ● $K_2Cr_2O_7$ / H_2SO_4 ● H_2SO_4 + HNO_3 Options:

- A) o-Nitrobenzoic acid B) p-Nitrobenzoic acid C) o,p-Dinitrobenzoic acid D) m-Nitrobenzoic acid

Tests: Phenols Answer: Not in extracted key

CUET 2023 — Actual PYQs from this chapter

Q.49 (CUET 2023) Arrange the following in increasing order of boiling point: (A) Pentan-1-ol (B) n-Butane (C) Pentan-1-al (D) Ethoxyethane Options:

- A) B < D < C < A B) B < C < A < D C) D < B < C < A D) D < B < A < C

Tests: Boiling point of alcohols/ethers Answer: Not in extracted key