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CHAPTER NOTES

Alcohols, Phenols and Ethers Class 12 Notes — CBSE Chemistry Chapter 11

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Alcohols, Phenols and Ethers Class 12 Notes — CBSE Chemistry Chapter 11

Chapter 11 — **Alcohols, Phenols and Ethers** — covers three important classes of oxygen-containing organic compounds. This chapter carries **6-8 marks** in Board exams and is rich in reactions and conversions. Master the distinction tests, oxidation reactions, and the acidity comparison between alcohols and phenols.

Key Concepts

Alcohols (R–OH)

Classification and Preparation

1. From Alkenes (Hydration): $CH_2=CH_2 + H_2O \rightarrow (H_2SO_4)\ CH_3CH_2OH$ (Markovnikov)

2. From Grignard Reagent:

HCHO + RMgX → 1° alcohol

RCHO + R'MgX → 2° alcohol

R_2CO + R'MgX → 3° alcohol

3. Reduction of Aldehydes/Ketones: $RCHO + H_2/Ni \rightarrow RCH_2OH$ (or $NaBH_4$, $LiAlH_4$)

4. Hydrolysis of Haloalkanes: RX + aq. KOH → ROH + KX

Reactions of Alcohols

Reaction	Reagent	Product
Dehydration	Conc. H_2SO_4, 443 K	Alkene (Saytzeff's rule)
Oxidation (1° alcohol)	PCC or mild oxidant	Aldehyde
Oxidation (1° alcohol)	$KMnO_4$ or $K_2Cr_2O_7/H^+$	Carboxylic acid
Oxidation (2° alcohol)	$K_2Cr_2O_7/H^+$	Ketone
Oxidation (3° alcohol)	Strong oxidant	Cleaves to smaller molecules
Esterification	R'COOH + H_2SO_4	Ester (R'COOR) + H_2O
With Na metal	Na	Alkoxide (R–ONa) + $H_2\uparrow$
With HBr	HBr	R–Br + H_2O

Lucas Test (distinguishes 1°, 2°, 3° alcohols): Add anhydrous $ZnCl_2$ + conc. HCl.
3° → immediate turbidity | 2° → turbidity in 5 min | 1° → no turbidity at room temperature

Dehydration Order

Ease of dehydration: 3° > 2° > 1° (follows carbocation stability)
Temperature: 1° needs 443 K, 2° needs ~400 K, 3° needs ~350 K

Phenols (ArOH)

Preparation

1. Cumene Process (Industrial):
$C_6H_5CH(CH_3)_2 + O_2 \rightarrow C_6H_5C(CH_3)_2OOH \xrightarrow{(H_2SO_4)} C_6H_5OH + (CH_3)_2CO$
(Phenol + Acetone — both useful products!)

2. From Diazonium Salt: $ArN_2^+Cl^- + H_2O \xrightarrow{(warm)} ArOH + N_2 + HCl$

3. Dow Process: $C_6H_5Cl + NaOH \xrightarrow{(623\ K,\ 300\ atm)} C_6H_5ONa \xrightarrow{(HCl)} C_6H_5OH$

Acidity of Phenols

Phenol is more acidic than alcohol because phenoxide ion ($C_6H_5O^-$) is stabilised by resonance with the benzene ring. The negative charge delocalises over the ring.

Acidity order: Water (pKa 15.7) < Ethanol (15.9) < Phenol (10.0)
Phenol reacts with NaOH but NOT with $NaHCO_3$ (unlike carboxylic acids)

Reactions of Phenols

Kolbe Reaction: $C_6H_5ONa + CO_2 \rightarrow$(125°C, 4-7 atm) sodium salicylate $\rightarrow$(HCl) salicylic acid
Reimer-Tiemann Reaction: $C_6H_5OH + CHCl_3 + NaOH \rightarrow$ salicylaldehyde (ortho-hydroxybenzaldehyde)
Coupling with Diazonium Salt: $C_6H_5OH + C_6H_5N_2^+Cl^- \rightarrow$ p-hydroxyazobenzene (orange dye)

Phenol undergoes **electrophilic substitution** easily (–OH is activating, ortho-para directing):

- **Bromination:** $C_6H_5OH + 3Br_2(aq) \rightarrow$ 2,4,6-tribromophenol↓ (white ppt) — used as a test!
- **Nitration:** With dilute $HNO_3 \rightarrow$ o- and p-nitrophenol

Ethers (R–O–R')

Preparation — Williamson Synthesis

R–ONa + R'–X → R–O–R' + NaX
Best with primary alkyl halides (SN2). Tertiary halides give elimination (alkene) instead!

Reactions of Ethers

Cleavage by HI (excess): $R–O–R' + 2HI \rightarrow R–I + R'–I + H_2O$
(HI is used because I^- is the best nucleophile)

For $ArOCH_3$ (anisole): $ArOCH_3 + HI \rightarrow ArOH + CH_3I$
(C–O bond of aryl group doesn't break — phenol is formed, not aryl halide)

Important Definitions

Term	Definition
Alcohol	Organic compound with –OH group on saturated carbon
Phenol	Organic compound with –OH group directly on benzene ring
Ether	Organic compound with C–O–C linkage
Dehydration	Removal of water from alcohol to form alkene
Williamson Synthesis	Preparation of ether from alkoxide and alkyl halide
Kolbe Reaction	Carboxylation of sodium phenoxide to form salicylic acid

Solved Examples — NCERT Based

Example 1: Grignard Synthesis

Q: How would you prepare propan-1-ol using a Grignard reagent?

Solution:

React ethanal (CH_3CHO) with methylmagnesium bromide (CH_3MgBr):

$CH_3CHO + CH_3MgBr \rightarrow CH_3CH(OMgBr)CH_3 \xrightarrow{(H_3O^+)} CH_3CH(OH)CH_3$

Wait — this gives propan-2-ol (secondary). For propan-1-ol:

Use $HCHO + C_2H_5MgBr \rightarrow C_2H_5CH_2OH$ (propan-1-ol, primary)

Example 2: Acidity Comparison

Q: Arrange in increasing acidity: ethanol, phenol, p-nitrophenol, p-methylphenol

Solution:

Electron-withdrawing groups ($–NO_2$) increase acidity; electron-donating groups ($–CH_3$) decrease it.

Ethanol < p-methylphenol < phenol < p-nitrophenol

(Most acidic is p-nitrophenol — $-NO_2$ stabilises the phenoxide ion by delocalisation)

Example 3: Distinction Test

Q: How will you distinguish between ethanol and phenol?

Solution:

Test 1 — $FeCl_3$ test: Phenol gives **violet/purple colour** with neutral $FeCl_3$. Ethanol does not.

Test 2 — Bromine water: Phenol gives **white precipitate** of 2,4,6-tribromophenol. Ethanol does not react.

Example 4: Williamson Synthesis

Q: Prepare methyl tert-butyl ether (MTBE) using Williamson synthesis. Which alkoxide and which halide should you use?

Solution:

Use sodium methoxide + tert-butyl chloride? NO — 3° halide will give elimination!

Correct method: $\mathbf{(CH_3)_3CONa + CH_3I \rightarrow (CH_3)_3COCH_3}$

Use tert-butoxide (bulky is fine for alkoxide) + methyl iodide (primary halide → SN2)

Important Questions for Board Exams

1 Mark Questions

1. Why is phenol more acidic than ethanol?
2. What is Lucas reagent?
3. Write the product of Kolbe's reaction.
4. What happens when phenol reacts with bromine water?

2 Mark Questions

1. Write the mechanism of acid-catalysed dehydration of ethanol.
2. How will you distinguish between 1°, 2° and 3° alcohols?

3. What is Williamson ether synthesis? Why should tertiary halides not be used?
4. Give the Reimer-Tiemann reaction with equation.

3 Mark Questions

1. Explain the preparation of phenol by cumene process. What is the co-product?
2. How do you convert: (a) ethanol → ethene (b) phenol → salicylic acid (c) phenol → aspirin?
3. Compare the acidity of ethanol, phenol, and p-nitrophenol with reasons.

5 Mark Questions

1. Discuss the preparation and chemical reactions of alcohols. Include oxidation, dehydration, esterification, and reaction with Na.
2. What are phenols? How are they prepared? Discuss their electrophilic substitution reactions and the Kolbe and Reimer-Tiemann reactions.

Quick Revision Points

- Alcohols: 1° → aldehyde → acid; 2° → ketone; 3° → resistant to oxidation
- Dehydration ease: 3° > 2° > 1° (conc. H_2SO_4)
- Lucas test: 3° immediate, 2° in 5 min, 1° no reaction at RT
- Phenol: acidic (resonance-stabilised phenoxide), reacts with NaOH but not $NaHCO_3$
- Cumene process: benzene → cumene → phenol + acetone (industrial)
- Kolbe: PhONa + CO_2 → salicylic acid
- Reimer-Tiemann: PhOH + $CHCl_3$/NaOH → salicylaldehyde
- Williamson: RONa + R'X → ROR' (use 1° halide to avoid elimination)
- Ether cleavage: R–O–R + HI → 2R–I
- Distinction: phenol → violet with $FeCl_3$, white ppt with Br_2 water

← Previous: Haloalkanes and Haloarenes

Next: Aldehydes, Ketones and Carboxylic Acids →