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Introduction

Alcohols and Phenols

- Alcohols: Hydroxyl (—OH) group replaces hydrogen in aliphatic hydrocarbons.
- Phenols: Hydroxyl (—OH) group directly attached to aromatic benzene ring (C_6H_5OH).
- Simple phenol (C_6H_5OH) is also called carbolic acid.

Ethers

- Ethers: Alkoxy (R–O) or aryloxy (Ar–O) group replaces hydrogen in hydrocarbons.
- General formula: $C_nH_{2n+2}O$, where $n > 1$.

Solved Examples

- **Ex 1:** Identify the compound type: C_2H_5OH.
  Answer: Alcohol (ethyl alcohol) with one —OH group attached to aliphatic carbon.
- **Ex 2:** Identify C_6H_5OH.
  Answer: Phenol, —OH attached to benzene ring.
- **Ex 3:** Identify $C_2H_5OCH_3$.
  Answer: Ether (unsymmetrical), alkoxy group between two different alkyl groups.

Practice Set

- Q1: Which compound is a phenol?
  A. C_2H_5OH
  B. C_6H_5OH
  C. $C_2H_5OCH_3$
  D. CH_3OH
- Q2: General formula of ethers is:
  A. $C_nH_{2n+1}OH$
  B. $C_nH_{2n}O$

Prepzy

C. $C_nH_{2n+2}O$

D. $C_nH_{2n+1}O$

- Q3: Which compound is an ether?

A. C_6H_5OH

B. C_2H_5OH

C. $C_2H_5OCH_3$

D. CH_3OH

Answer Key

- Q1: B - Phenol has —OH attached to benzene ring.
- Q2: C - Ethers have formula $C_nH_{2n+2}O$.
- Q3: C - $C_2H_5OCH_3$ is an ether with two different alkyl groups.

Memory Aids

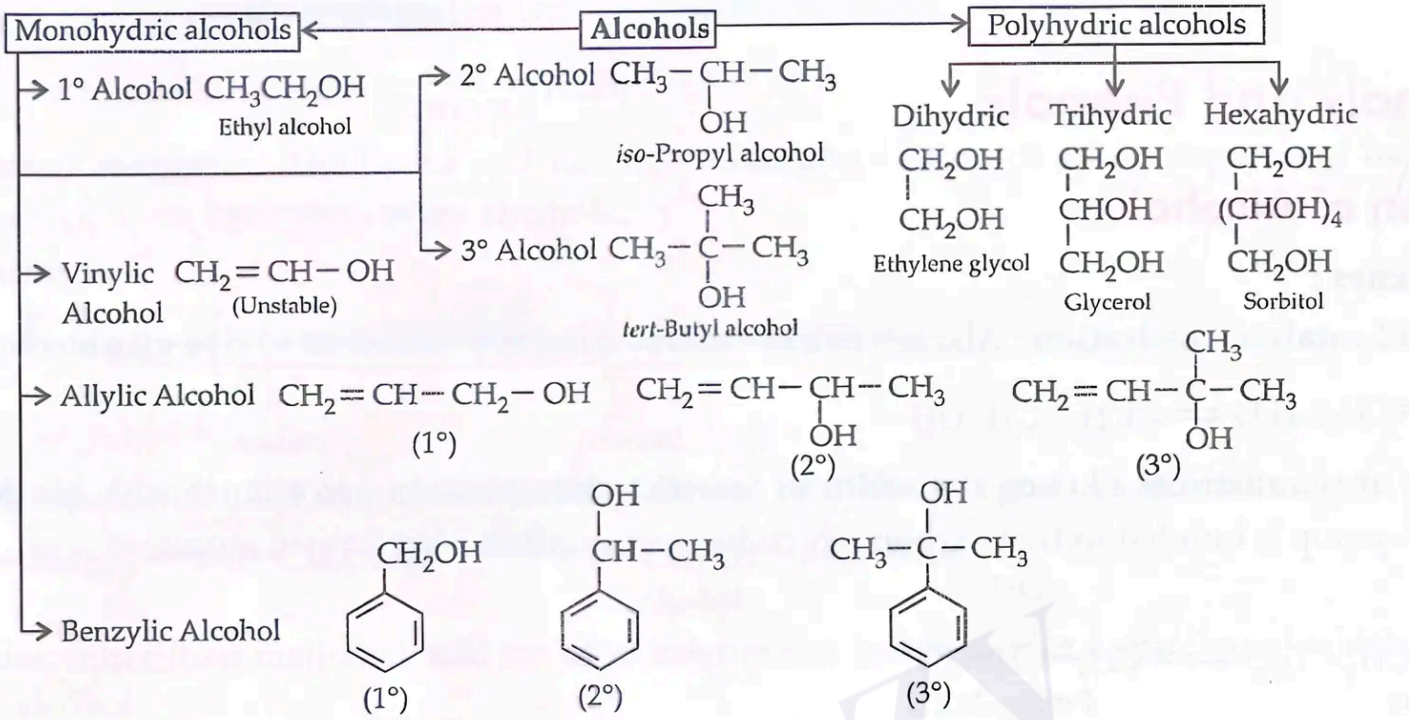
- Alcohol = Hydroxyl (—OH) on aliphatic carbon.
- Phenol = Hydroxyl (—OH) on benzene ring.
- Ethers = Oxygen linking two alkyl/aryl groups.

Classification of Alcohols, Phenols and Ethers

Alcohols

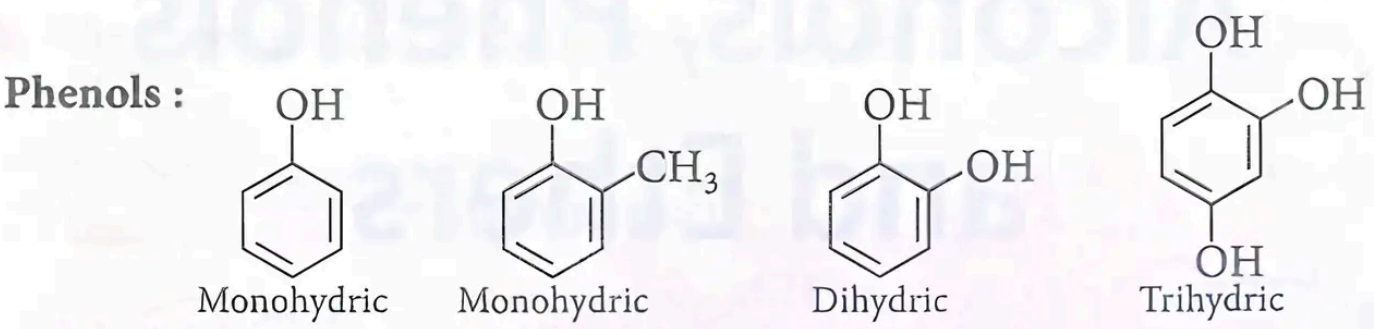
- Classified by number of —OH groups: Monohydric (1 —OH), Polyhydric (multiple —OH).
- Monohydric alcohols classified by carbon attachment:
  - Primary (1°): —OH on carbon attached to 1 other carbon (e.g., ethyl alcohol).
  - Secondary (2°): —OH on carbon attached to 2 other carbons (e.g., isopropyl alcohol).
  - Tertiary (3°): —OH on carbon attached to 3 other carbons (e.g., tert-butyl alcohol).
- Special monohydric types:
  - Vinylic alcohol (unstable)
  - Allylic alcohol (—OH near double bond)
  - Benzylic alcohol (—OH attached to benzene ring carbon)
- Polyhydric alcohols:

- Dihydric (2 —OH), e.g., ethylene glycol
- Trihydric (3 —OH), e.g., glycerol
- Hexahydric (6 —OH), e.g., sorbitol



Phenols

- Phenols have —OH directly attached to benzene ring.
- Classified by number of —OH groups:
  - Monohydric phenols: 1 —OH (e.g., phenol, cresol)
  - Dihydric phenols: 2 —OH groups
  - Trihydric phenols: 3 —OH groups



Ethers

- Classified by alkyl/aryl groups attached to oxygen:
- Simple/Symmetrical: Both groups same (e.g., diethyl ether $C_2H_5OC_2H_5$).
- Mixed/Unsymmetrical: Different groups (e.g., $C_2H_5OCH_3$).

Solved Examples

- **Ex 1:** Classify CH_3CH_2OH.
  Answer: Monohydric primary alcohol.
- **Ex 2:** Classify $C_6H_4(OH)_2$.
  Answer: Dihydric phenol.
- **Ex 3:** Classify $C_2H_5OC_6H_5$.
  Answer: Unsymmetrical ether.

Practice Set

- Q1: Which is a tertiary alcohol?
  A. CH_3CH_2OH
  B. $(CH_3)_3COH$
  C. $CH_3CHOHCH_3$
  D. C_6H_5OH
- Q2: Which phenol has two —OH groups?
  A. Phenol
  B. Catechol
  C. Cresol
  D. Resorcinol
- Q3: Which ether is symmetrical?
  A. $C_2H_5OC_6H_5$
  B. CH_3OCH_3
  C. $C_2H_5OCH_3$
  D. $C_6H_5OCH_3$

Answer Key

- Q1: B - Tertiary alcohol has —OH on carbon attached to 3 carbons.
- Q2: B - Catechol is a dihydric phenol with 2 —OH groups.
- Q3: B - CH_3OCH_3 has identical alkyl groups, symmetrical ether.

Memory Aids

- Primary alcohol: —OH on carbon with 1 carbon neighbor.
- Phenols: Number of —OH groups changes reactivity.
- Ethers: Symmetry depends on alkyl/aryl groups.

Nomenclature

Alcohols

- Common system: Named as alkyl alcohol (e.g., methyl alcohol).
- IUPAC system: Named as alkanols by replacing ‘e’ of alkane with ‘-ol’ (e.g., methanol from methane).
- Cyclic alcohols: Use prefix ‘cyclo’ and number —OH group as attached to C-1 (e.g., cyclohexanol).

Solved Examples

- **Ex 1:** Name CH_3CH_2OH.
  - Step 1: Identify alkane: Ethane.
  - Step 2: Replace ‘e’ with ‘ol’: Ethanol.

Practice Set

- Q1: What is the IUPAC name of CH_3CH_2OH?
  - A. Ethanol
  - B. Ethyl alcohol

    - C. Methanol
    - D. Methyl alcohol
- Q2: How are cyclic alcohols named?
    - A. Using prefix ‘cyclo’ and numbering —OH at C-1
    - B. As alkyl alcohols
    - C. Using ‘diol’ suffix
    - D. Using ‘phenol’
- Q3: Which of the following is a correct IUPAC name?
    - A. Propyl alcohol
    - B. Propanol
    - C. Propanediol
    - D. Cyclopropanol

Answer Key

- Q1: A. Ethanol - IUPAC replaces ‘e’ of ethane with ‘-ol’.
- Q2: A. Using prefix ‘cyclo’ and numbering —OH at C-1 - standard for cyclic alcohols.
- Q3: B. Propanol - correct IUPAC name for 3-carbon alcohol.

Memory Aids

- Alcohols: Alkane ‘e’ → ‘ol’
- Cyclic alcohols: ‘cyclo’ + —OH at C-1

Phenols

Phenols

- Phenol: Hydroxy derivative of benzene, common and IUPAC name.
- Substituted phenols use ortho (1,2-), meta (1,3-), para (1,4-) for positions.
- Dihydroxy benzenes named as 1,2-, 1,3-, 1,4-benzenediol.

Solved Examples

- **Ex 1:** Name 1,4-dihydroxybenzene.
  - Step 1: Identify benzene ring with two —OH groups at 1 and 4.
  - Step 2: Name as 1,4-benzenediol.

Practice Set

- Q1: What is the common name of hydroxybenzene?
  - A. Phenol
  - B. Benzene diol
  - C. Cyclohexanol
  - D. Benzenol
- Q2: What does ‘ortho’ indicate in substituted phenols?
  - A. 1,2-disubstituted positions
  - B. 1,3-disubstituted positions
  - C. 1,4-disubstituted positions
  - D. No substitution
- Q3: How are dihydroxy derivatives of benzene named?
  - A. Benzenediol with position numbers
  - B. Alkyl alcohols
  - C. Cycloalkanes
  - D. Phenols without numbers

Answer Key

- Q1: A. Phenol - simplest hydroxybenzene name.
- Q2: A. 1,2-disubstituted positions - ortho means adjacent positions.
- Q3: A. Benzenediol with position numbers - indicates dihydroxy substitution.

Memory Aids

- Phenol = hydroxybenzene
- Ortho = adjacent (1,2-), Meta = 1,3-, Para = 1,4-
- Dihydroxy benzene = benzenediol

Ethers

Ethers

- Common names: Alkyl/aryl groups in alphabetical order + ‘ether’ (e.g., ethyl methyl ether).
- If alkyl groups same, prefix ‘di’ added (e.g., diethyl ether).
- IUPAC: Hydrocarbon derivative with H replaced by —OR or —OAr.
- Parent hydrocarbon chosen as larger R group.

Solved Examples

- **Ex 1:** Name $CH_3OCH_2CH_3$.
  - Step 1: Identify alkyl groups: CH_3 (methyl), CH_2CH_3 (ethyl).
  - Step 2: Alphabetical order: ethyl methyl ether.

Practice Set

- Q1: What is the common name of CH_3OCH_3?
  - A. Methyl ether
  - B. Dimethyl ether
  - C. Ethyl methyl ether
  - D. Diethyl ether
- Q2: According to IUPAC, ethers are derivatives where H is replaced by?
  - A. —OH
  - B. —OR or —OAr
  - C. —COOH
  - D. —NH_2
- Q3: How is the parent hydrocarbon chosen in IUPAC naming of ethers?
  - A. Smaller R group
  - B. Larger R group
  - C. Alphabetically first group
  - D. Based on molecular weight

Answer Key

- Q1: B. Dimethyl ether - both alkyl groups same, prefix ‘di’ used.
- Q2: B. —OR or —OAr - ethers have H replaced by these groups.
- Q3: B. Larger R group - chosen as parent hydrocarbon.

Memory Aids

- Ethers: Alphabetical alkyl/aryl + ‘ether’
- Same alkyl groups: prefix ‘di’
- IUPAC: H replaced by —OR or —OAr

Structures of Functional Groups

Alcohols

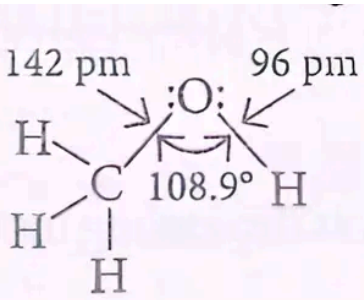
- O atom in hydroxyl (–OH) group attached to C-atom by sigma (σ) bond.
- Bond formed by overlap of sp^3 hybridised orbital of C with sp^3 hybridised orbital of O.

Phenols

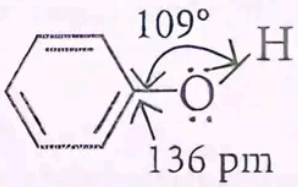
- –OH group attached to sp^2 hybridised C-atom of aromatic ring.

Ethers

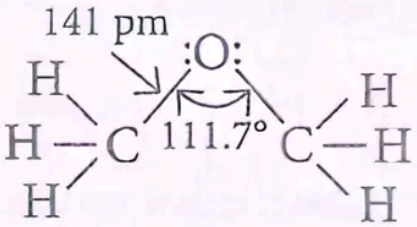
- O atom has four electron pairs: two bond pairs and two lone pairs.
- Electron pairs arranged approximately tetrahedrally around O atom.



Methanol



Phenol



Methoxymethane

Solved Examples

- **Ex 1:** Identify hybridisation of O in methanol.
  Solution: O in methanol is sp^3 hybridised due to tetrahedral electron pair arrangement.
- **Ex 2:** Compare bond angles in phenol and methoxymethane.
  Solution: Phenol O–C bond angle ~109°, methoxymethane O–C–C bond angle ~111.7° due to different hybridisation and bonding.

Practice Set

- **Q1:** What is the hybridisation of oxygen in alcohols?
  A. sp^2
  B. sp^3
  C. sp
  D. dsp^2
- **Q2:** In phenol, the –OH group is attached to which type of carbon?
  A. sp^3 carbon
  B. sp^2 carbon
  C. sp carbon
  D. None of these
- **Q3:** Which arrangement best describes electron pairs around oxygen in ethers?
  A. Linear
  B. Trigonal planar
  C. Tetrahedral
  D. Octahedral

Answer Key

- **Q1:** B. sp^3 – Oxygen in alcohols is sp^3 hybridised due to tetrahedral electron pair geometry.
- **Q2:** B. sp^2 – Phenol's –OH is attached to sp^2 hybridised carbon of aromatic ring.
- **Q3:** C. Tetrahedral – Oxygen in ethers has two bond pairs and two lone pairs arranged tetrahedrally.

Memory Aids

- Alcohol O: sp^3 hybridised, sigma bond with C.
- Phenol O: attached to sp^2 aromatic C.
- Ethers: O electron pairs tetrahedral (2 bond + 2 lone pairs).

Alcohols and Phenols

Introduction

- Alcohols contain one or more hydroxyl (-OH) groups attached to saturated carbon atoms.
- Phenols have hydroxyl groups attached directly to an aromatic benzene ring.
- Both classes show distinct physical and chemical properties due to their structure.

Solved Examples

- Ex 1: Identify the functional group in ethanol and phenol.
  Answer: Ethanol - hydroxyl group on alkane; Phenol - hydroxyl group on benzene ring.

Practice Set

- Q1: Which group is present in phenol?
  A. Alkyl group
  B. Hydroxyl attached to benzene

C. Carbonyl group
D. Carboxyl group

- Q2: Alcohols differ from phenols in that alcohols have -OH attached to?
  A. Aromatic ring
  B. Saturated carbon
  C. Unsaturated carbon
  D. Nitrogen atom
- Q3: Which compound is a phenol?
  A. CH3CH2OH
  B. C6H5OH
  C. CH3COOH
  D. C6H5CH3

Answer Key

- Q1: B - Phenol has hydroxyl group attached to benzene ring.
- Q2: B - Alcohols have -OH on saturated carbon atoms.
- Q3: B - C6H5OH is phenol.

Memory Aids

- Phenol = benzene + OH
- Alcohol = alkane + OH

Preparation of Alcohols

From Alkenes

- **Acid catalysed hydration:** Alkene + H_2O (acid catalyst) → Alcohol
- Markovnikov's rule: -OH attaches to carbon with fewer H atoms in unsymmetrical alkenes.
- **Hydroboration-oxidation:** Alkene + B_2H_6 → trialkylborane → oxidation with H_2O_2/OH^- → alcohol (anti-Markovnikov product)

From Carbonyl Compounds

- **Reduction of aldehydes and ketones:** Aldehydes → primary alcohols; Ketones → secondary alcohols using H_2/metal or $NaBH_4$/$LiAlH_4$.
- **Reduction of carboxylic acids and esters:** $LiAlH_4$ reduces acids/esters to primary alcohols.
- **From Grignard reagents:** Aldehydes/ketones + R-MgX → adduct → hydrolysis → alcohols (1°, 2°, 3° depending on substrate).

Solved Examples

- Ex 1: Acid catalysed hydration of propene gives propan-2-ol (Markovnikov addition).
- Ex 2: Hydroboration-oxidation of propene gives propan-1-ol (anti-Markovnikov addition).
- Ex 3: Reduction of acetaldehyde with $NaBH_4$ gives ethanol (primary alcohol).

Practice Set

- Q1: Acid catalysed hydration of ethene produces?
  A. Ethanol
  B. Ethane
  C. Ethanal
  D. Ethyne
- Q2: Hydroboration-oxidation of propene yields?
  A. Propan-2-ol
  B. Propan-1-ol
  C. Propene oxide
  D. Propanal
- Q3: Grignard reagent reaction with formaldehyde followed by hydrolysis gives?
  A. Primary alcohol
  B. Secondary alcohol
  C. Tertiary alcohol
  D. Ketone

Answer Key

- Q1: A - Ethene + H_2O (acid) → Ethanol.
- Q2: B - Hydroboration-oxidation adds -OH anti-Markovnikov.
- Q3: A - Formaldehyde + R-MgX → primary alcohol after hydrolysis.

Memory Aids

- Markovnikov: -OH to carbon with fewer H.
- Hydroboration: anti-Markovnikov addition.
- Grignard + formaldehyde → 1° alcohol.

Preparation of Phenol

From Haloarenes (Dow's Process)

- Chlorobenzene + NaOH (623 K, 300 atm) → sodium phenoxide → acidification → phenol.

From Benzenesulphonic Acid

- Benzenesulphonic acid + molten NaOH → sodium phenoxide → acidification → phenol.
- Benzene + oleum → benzenesulphonic acid.

From Diazonium Salts

- Benzene diazonium chloride + warm water/dilute acid → phenol + N_2 + HCl.
- Preparation: Benzene → nitration → nitrobenzene → reduction → aniline → diazotisation → diazonium salt.

From Cumene (Industrial Method)

- Cumene + O_2 → cumene hydroperoxide → acid treatment → phenol + acetone.
- Cumene prepared by Friedel-Crafts alkylation of benzene with propyl chloride or propene.

Solved Examples

- Ex 1: Dow's process converts chlorobenzene to phenol using NaOH at high T and P.
- Ex 2: Diazonium salt hydrolysis produces phenol and nitrogen gas.

Practice Set

- Q1: Dow's process uses which reagent?
  A. NaCl
  B. NaOH
  C. HCl
  D. H_2SO_4
- Q2: Benzene diazonium chloride on hydrolysis gives?
  A. Aniline
  B. Phenol
  C. Nitrobenzene
  D. Benzene
- Q3: Industrial phenol production uses?
  A. Benzene sulfonation
  B. Cumene oxidation
  C. Diazotisation
  D. Friedel-Crafts alkylation

Answer Key

- Q1: B - NaOH used in Dow's process.
- Q2: B - Hydrolysis of diazonium salt yields phenol.
- Q3: B - Cumene oxidation is industrial method.

Memory Aids

- Dow's: Haloarene + NaOH → phenol.
- Diazonium salt → phenol + N_2.
- Cumene → phenol + acetone industrially.

Physical Properties

Alcohols

- Lower alcohols: colourless liquids with characteristic smell.
- Higher alcohols: colourless, odourless waxy solids.
- Solubility: Decreases with alkyl size; increases with branching due to hydrogen bonding.
- Boiling points: Increase with carbon number; decrease with branching (van der Waals forces).

Phenols

- Physical state: Colourless crystalline solids or liquids with phenolic odour.
- Boiling points: Higher than aromatic hydrocarbons due to intermolecular hydrogen bonding.
- Solubility: Less soluble than alcohols due to large hydrophobic benzene ring.

Solved Examples

- Ex 1: Explain why phenol has higher boiling point than benzene.
  Answer: Due to intermolecular hydrogen bonding.

Practice Set

- Q1: Lower alcohols are usually?
  A. Solids
  B. Liquids

C. Gases
D. Waxy solids

- Q2: Phenols have higher boiling points than?
  A. Alcohols
  B. Aromatic hydrocarbons
  C. Alkanes
  D. Ethers
- Q3: Solubility of alcohols in water decreases with?
  A. Branching
  B. Increase in alkyl size
  C. Decrease in alkyl size
  D. None

Answer Key

- Q1: B - Lower alcohols are liquids.
- Q2: B - Phenols have higher boiling points than aromatic hydrocarbons.
- Q3: B - Solubility decreases with larger alkyl groups.

Memory Aids

- Hydrogen bonding raises boiling points.
- Branching increases solubility.

Chemical Properties of Alcohols

General

- Alcohols act as nucleophiles (O-H bond cleavage) and electrophiles (C-O bond cleavage).
- Acidity order: 1° > 2° > 3° alcohols.
- Electron releasing groups decrease acidity.
- Reactivity order for C-O bond cleavage: 3° > 2° > 1°.
- 3° alcohols resist oxidation in neutral/alkaline but oxidize in acidic medium forming carboxylic acids.
- Dehydration follows Saytzeff rule: more substituted alkene is major product.

- Ease of dehydration: 3° > 2° > 1° (carbocation stability).

Tests to Distinguish Alcohols

- Victor Meyer test: Color changes identify 1°, 2°, 3° alcohols.
- Lucas test: Cloudiness time indicates alcohol type (3° immediate, 2° in 5-10 min, 1° no cloudiness).

Solved Examples

- Ex 1: Lucas test cloudiness order: 3° > 2° > 1° alcohol.
- Ex 2: Victor Meyer test color for 1° alcohol is blood red.

Practice Set

- Q1: Order of acidity in alcohols?
  A. 3° > 2° > 1°
  B. 1° > 2° > 3°
  C. 2° > 1° > 3°
  D. Equal
- Q2: Lucas test shows immediate cloudiness for?
  A. 1° alcohol
  B. 2° alcohol
  C. 3° alcohol
  D. Phenol
- Q3: Dehydration of alcohols follows?
  A. Markovnikov rule
  B. Saytzeff rule
  C. Anti-Markovnikov rule
  D. None

Answer Key

- Q1: B - Acidity decreases from 1° to 3° due to electron releasing groups.

- Q2: C - 3° alcohols react fastest in Lucas test.
- Q3: B - Dehydration follows Saytzeff rule.

Memory Aids

- Saytzeff: More substituted alkene formed.
- Lucas: Cloudiness time indicates alcohol type.
- Victor Meyer: Color test for alcohol types.

Chemical Properties of Phenols

Acidic Nature

- Phenols are more acidic than alcohols due to:
- (i) -OH attached to electronegative sp^2 carbon of benzene, increasing O-H bond polarity.
- (ii) Phenoxide ion stabilized by resonance, unlike phenol.
- Electron withdrawing groups increase acidity; electron releasing groups decrease acidity.

Chemical Reactions

- Bromination: Phenol + Br_2 → 2,4,6-tribromophenol (white precipitate).
- Nitration: Phenol + HNO_3 → nitrophenols, picric acid.
- Sulfonation: Phenol + H_2SO_4 → phenol sulfonic acid.
- Neutralization: Phenol + Na/NaOH → sodium phenoxide.
- Oxidation: Phenol + $Na_2Cr_2O_7/H_2SO_4$ → p-benzoquinone.
- Kolbe’s reaction: Sodium phenoxide + CO_2 → salicylic acid.
- Hydrogenation: Phenol + H_2/Ni → cyclohexanol.
- Reimer-Tiemann: Sodium phenoxide + $CHCl_3$/NaOH → salicylaldehyde.
- Alkylation: Phenol + $CH_3Cl/AlCl_3$ → cresols.

Identification Tests

- Ferric chloride test: Phenol + $FeCl_3$ → violet color.

- Bromine water test: Phenol + Br_2 water → white precipitate (2,4,6-tribromophenol).

Solved Examples

- Ex 1: Phenol + Br_2 → 2,4,6-tribromophenol (white precipitate).
- Ex 2: Ferric chloride test gives violet color with phenol.

Practice Set

- Q1: Phenol is more acidic than alcohol because?
  A. sp^3 carbon
  B. Resonance stabilization
  C. Less electronegative carbon
  D. No resonance
- Q2: Bromine water test with phenol produces?
  A. Yellow solution
  B. White precipitate
  C. No reaction
  D. Red color
- Q3: Kolbe’s reaction produces?
  A. Salicylic acid
  B. Benzoic acid
  C. Phenol
  D. Benzene

Answer Key

- Q1: B - Phenoxide ion resonance stabilizes phenol's acidity.
- Q2: B - 2,4,6-tribromophenol precipitates as white solid.
- Q3: A - Kolbe’s reaction forms salicylic acid.

Memory Aids

- Phenol acidity due to resonance and sp^2 carbon.

- Bromination gives white precipitate.
- Kolbe's reaction forms salicylic acid.

Some Commercially Important Alcohols

Methanol Production

- Methanol (CH_3OH) is produced by catalytic hydrogenation of carbon monoxide (CO) using hydrogen gas (H_2).
- Catalyst: Zinc oxide-chromium oxide ($ZnO\text{-}Cr_2O_3$).
- Conditions: High temperature (573-673 K) and high pressure (200-300 atm).
- Reaction: $CO + 2H_2 \rightarrow CH_3OH$ (methanol).

$$CO + 2H_2 \xrightarrow[200\text{-}300\ atm,\ 573\text{-}673\ K]{ZnO-Cr_2O_3} CH_3OH$$

Methanol Properties and Uses

- Colourless liquid, highly poisonous.
- Small ingestion causes blindness; large ingestion causes death.
- Used as solvent in paints, varnishes, and for making formaldehyde.

Ethanol Production

- Produced by fermentation of sugars in molasses, sugarcane, or fruits (e.g., grapes).
- Enzymes involved: Invertase breaks sucrose into glucose and fructose; zymase converts glucose into ethanol and CO_2.
- Reaction: $C_{12}H_{22}O_{11} + H_2O \rightarrow$ glucose + fructose $\rightarrow$ ethanol + CO_2.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}\ ;\ \underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2\underset{\text{Ethanol}}{C_2H_5OH} + 2CO_2$$

Ethanol Properties and Uses

- Colourless liquid used as solvent in paint industry and preparation of carbon compounds.
- Commercial alcohol is denatured by adding copper sulphate and pyridine to make it unfit for drinking.

Ethylene Glycol Uses

- Used as antifreeze in car radiators.
- 50% aqueous solution freezes at -34°C.
- Used as de-icing fluid for airplane wings.

Different types of alcohols :

Types	Composition
Absolute alcohol	100% ethanol
Rectified spirit	95% alcohol + 5% water
Denatured spirit	95% ethanol + 5% methanol
Methylated spirit	90% ethanol + 9% methanol + 1% other poisonous substances
Power alcohol	80% petrol + 20% ethanol

Types of Alcohol

- Absolute alcohol: 100% ethanol.
- Rectified spirit: 95% alcohol + 5% water.
- Denatured spirit: 95% ethanol + 5% methanol.
- Methylated spirit: 90% ethanol + 9% methanol + 1% poisonous substances.
- Power alcohol: 80% petrol + 20% ethanol.
- Different types have different uses and purity levels.

Solved Examples

- **Ex 1:** Write the reaction for methanol production from CO and H_2.
  Answer: $CO + 2H_2 \rightarrow CH_3OH$ (ZnO-Cr_2O_3, 573-673 K, 200-300 atm)
- **Ex 2:** Write the fermentation reaction of glucose to ethanol.
  Answer: $C_6H_{12}O_6 \xrightarrow{\text{zymase}} 2C_2H_5OH + 2CO_2$

Practice Set

- **Q1:** Which catalyst is used in methanol production?
  A. Cu-Cr_2O_3
  B. ZnO-Cr_2O_3
  C. Fe_2O_3
  D. Al_2O_3
- **Q2:** What is the main enzyme that converts glucose to ethanol in fermentation?
  A. Invertase
  B. Zymase
  C. Amylase
  D. Catalase
- **Q3:** Which type of alcohol is made unfit for drinking by adding copper sulphate and pyridine?
  A. Absolute alcohol
  B. Rectified spirit
  C. Denatured alcohol
  D. Methylated spirit

Answer Key

- **Q1:** B - ZnO-Cr_2O_3 is the catalyst used for methanol production.
- **Q2:** B - Zymase converts glucose into ethanol and CO_2 during fermentation.
- **Q3:** C - Denatured alcohol is made unfit for drinking by adding copper sulphate and pyridine.

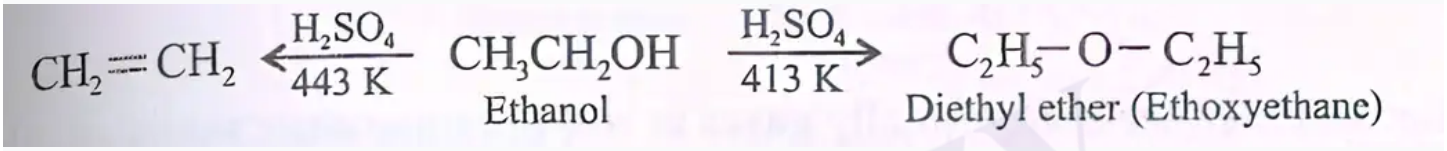
Memory Aids

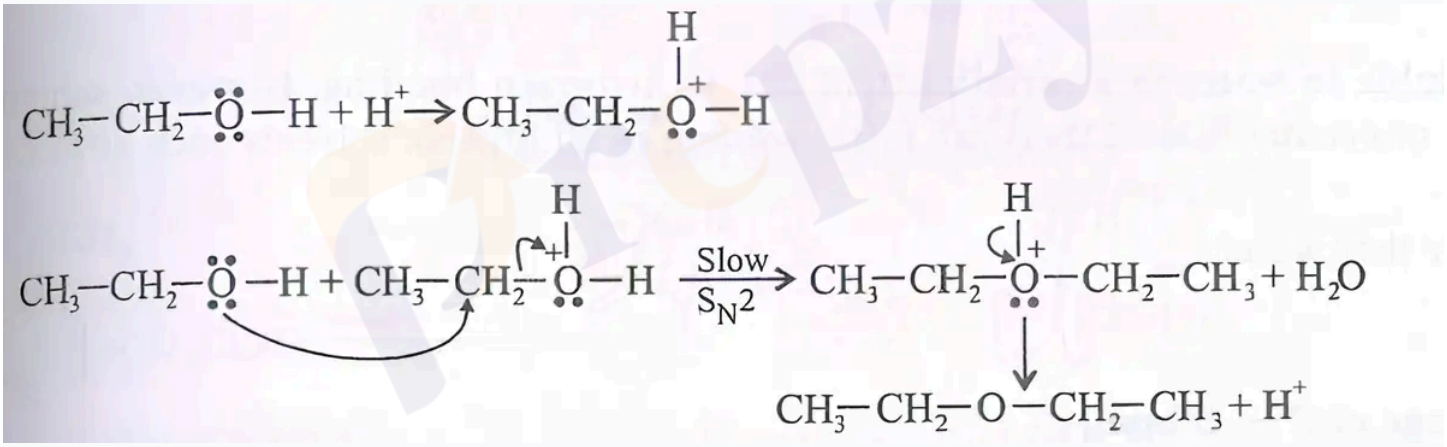
- Methanol production catalyst: ZnO-Cr_2O_3 (Zinc-Chrome combo).
- Fermentation enzymes: Invertase breaks sucrose; Zymase forms ethanol.
- Denatured alcohol = ethanol + copper sulphate + pyridine (unfit for drinking).

Preparation from Alcohols (by Dehydration)

Explanation

- Primary alcohols heated with protic acid (H_2SO_4) at 413 K undergo dehydration to form ethers.
- At higher temperature (443 K), the same reaction forms alkenes or alcohols instead.
- Suitable only for simple ethers with primary, unhindered alkyl groups at low temperature.
- Mechanism: Acid-catalyzed nucleophilic bimolecular substitution (S_N2).
- At low temperature, substitution (ether formation) dominates; at high temperature, elimination (alkene formation) dominates.
- Secondary and tertiary alcohols mainly undergo elimination to form alkenes, not ethers.





Solved Examples

- **Ex 1:** Ethanol + H_2SO_4 at 413 K → Diethyl ether + H_2O
- **Ex 2:** Ethanol + H_2SO_4 at 443 K → Ethene + H_2O

Practice Set

- Q1: Which alcohol gives ether on dehydration at low temperature?
  A. Primary
  B. Secondary

C. Tertiary
D. All

- Q2: What is the major product when ethanol is heated with H_2SO_4 at 443 K?
  A. Diethyl ether
  B. Ethanol
  C. Ethene
  D. Water
- Q3: The mechanism of ether formation from alcohol dehydration is:
  A. S_N1
  B. S_N2
  C. E1
  D. E2

Answer Key

- Q1: A - Primary alcohols form ethers at low temperature by substitution.
- Q2: C - Ethene is formed at higher temperature by elimination.
- Q3: B - Ether formation follows S_N2 mechanism.

Memory Aids

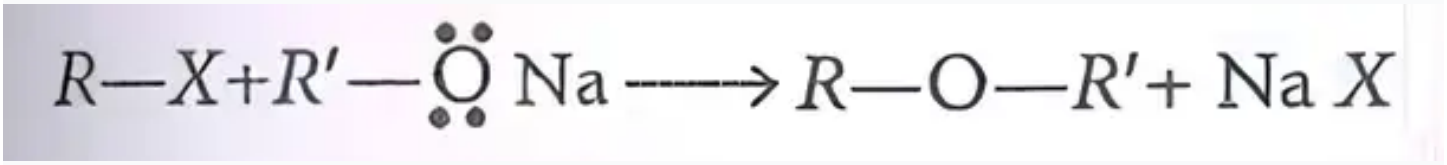
- Primary alcohol + H_2SO_4 at low temp → ether (S_N2)
- At high temp → alkene (elimination)
- Secondary/tertiary alcohols → alkene only

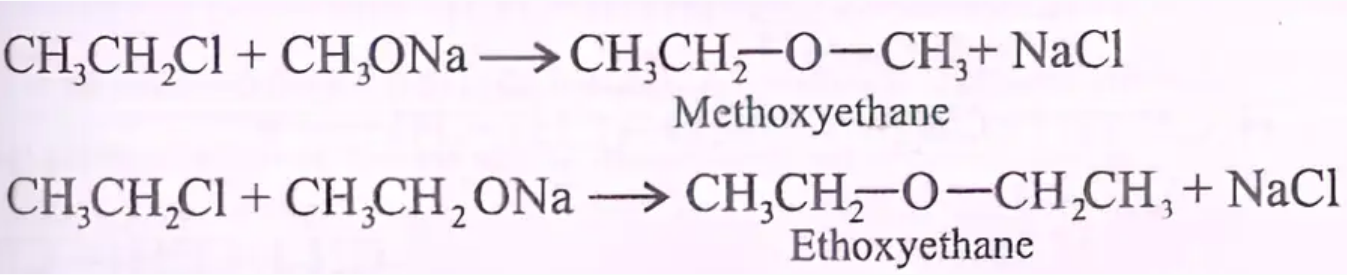
Preparation from Alkyl Halides (Williamson Synthesis)

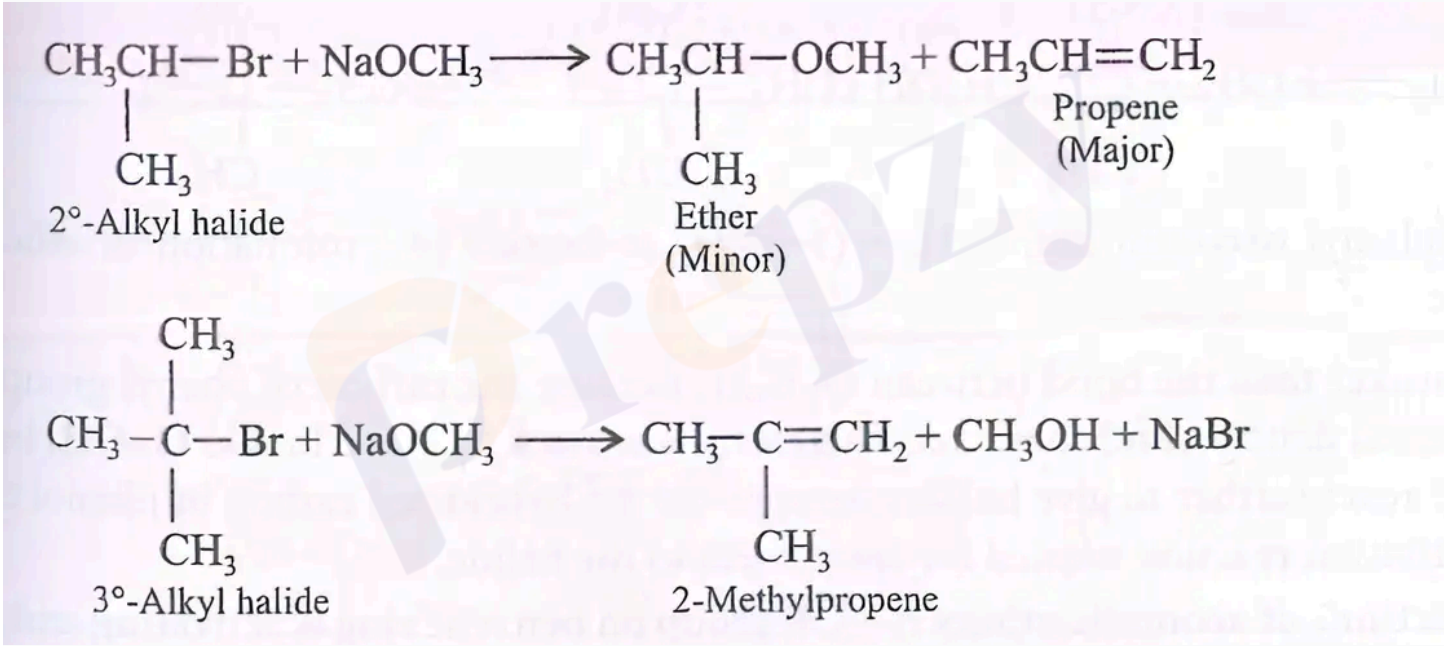
Explanation

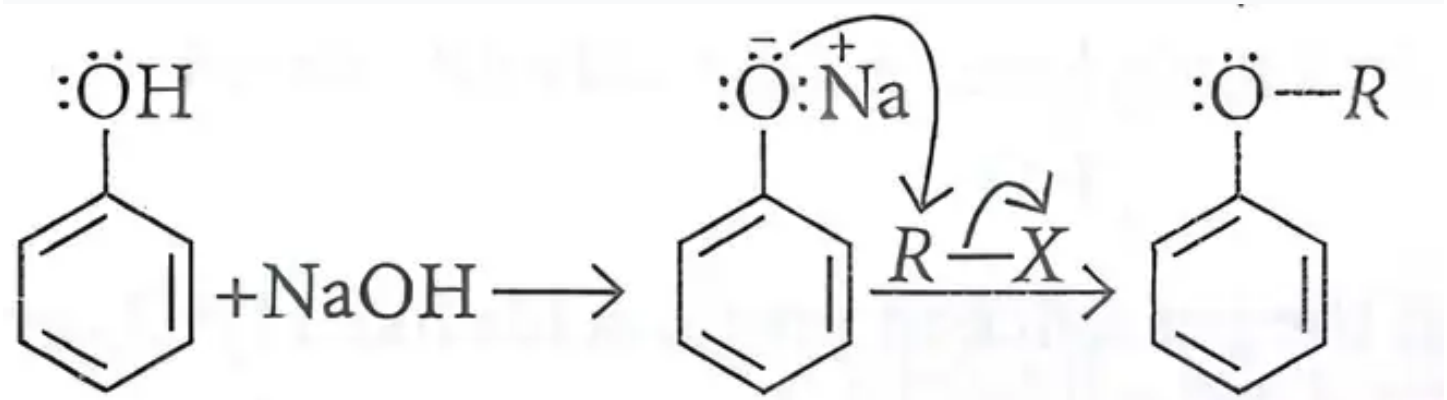
- Primary alkyl halide reacts with sodium alkoxide to form ether via S_N2 mechanism.
- R and R' groups can be same or different, allowing preparation of simple or mixed ethers.
- Secondary and tertiary alkyl halides are unsuitable due to elimination competing with substitution.

- Alkoxide ion is a stronger base than nucleophile, causing elimination in secondary/tertiary halides.
- Phenols react with NaOH to form phenoxide ion, which then reacts with alkyl halides to form aryl ethers.









Solved Examples

- **Ex 1:** $CH_3CH_2Cl + CH_3ONa \rightarrow CH_3CH_2OCH_3 + NaCl$
- **Ex 2:** $C_6H_5OH + NaOH \rightarrow C_6H_5O^-Na^+$; then $C_6H_5O^-Na^+ + R\text{-}X \rightarrow C_6H_5\text{-}O\text{-}R + NaX$

Practice Set

- Q1: Williamson synthesis is suitable for:
  A. Primary alkyl halides only
  B. Secondary alkyl halides only
  C. Tertiary alkyl halides only
  D. Primary and secondary alkyl halides
- Q2: Phenol reacts with NaOH to form:
  A. Phenol sodium salt
  B. Sodium phenoxide
  C. Sodium hydroxide
  D. Phenyl halide
- Q3: In Williamson synthesis, elimination occurs mainly with:
  A. Primary alkyl halides
  B. Secondary alkyl halides
  C. Tertiary alkyl halides
  D. Aryl halides

Answer Key

- Q1: A - Only primary alkyl halides give ethers via S_N2.
- Q2: B - Phenol + NaOH forms sodium phenoxide.
- Q3: C - Tertiary alkyl halides favor elimination, no ether formed.

Memory Aids

- Williamson synthesis: Primary alkyl halide + sodium alkoxide → ether (S_N2)
- Secondary/tertiary alkyl halides → elimination (alkene)
- Phenol + NaOH → sodium phenoxide → reacts with alkyl halide to form aryl ether

Physical Properties

Explanation

- Dimethyl and diethyl ethers are gases at room temperature; others are colorless liquids with ethereal smell.
- Ethers have bent structure, giving them polarity (net dipole moment).
- Boiling points are lower than alcohols due to absence of hydrogen bonding.
- Soluble in water to some extent due to hydrogen bonding; solubility decreases with molecular mass.
- Soluble in organic solvents like alcohol, chloroform, benzene.
- Density less than water (lighter than water).

Solved Examples

- **Ex 1:** Diethyl ether is liquid at room temperature with characteristic smell.
- **Ex 2:** Boiling point of ether < alcohol of similar molecular weight.

Practice Set

- Q1: Which ether is gaseous at room temperature?
  A. Diethyl ether
  B. Dimethyl ether
  C. Dipropyl ether
  D. Di-n-butyl ether
- Q2: Ethers are polar because:
  A. They have hydrogen bonding
  B. They have bent structure
  C. They are ionic
  D. They have linear structure
- Q3: Ethers have lower boiling points than alcohols because:
  A. They have weaker intermolecular forces
  B. They have hydrogen bonding
  C. They are ionic
  D. They have higher molecular weight

Answer Key

- Q1: B - Dimethyl ether is gaseous at room temperature.
- Q2: B - Bent structure causes net dipole moment.
- Q3: A - Absence of hydrogen bonding lowers boiling point.

Memory Aids

- Small ethers (dimethyl, diethyl) are gases; others liquids.
- Bent structure → polarity.
- No hydrogen bonding → lower boiling points than alcohols.

Chemical Reactions

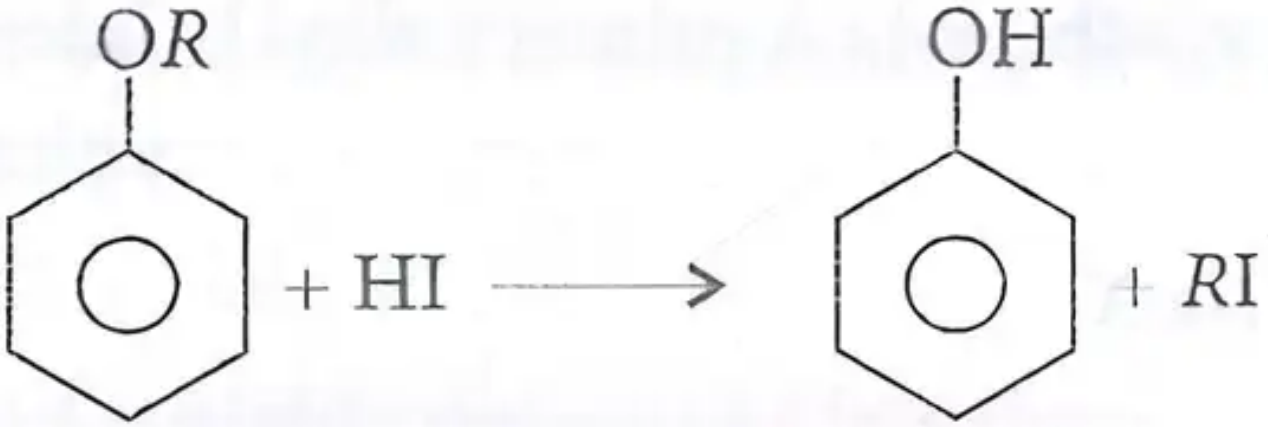
Explanation

- Ethers react with hydrogen halides (HX) to cleave C–O bond, forming alcohol and alkyl halide.
- Reaction follows S_N2 mechanism for primary and secondary alkyl groups.
- Reactivity order of HX: HCl < HBr < HI (strongest acid).
- Alkyl aryl ethers cleave at R–O bond; Ar–O bond is more stable due to partial double bond character.
- In mixed ethers, smaller alkyl group forms alkyl halide if 1° or 2°; tertiary alkyl halide forms via S_N1 mechanism.
- Anisole forms methylphenyl oxonium ion on protonation; O–CH_3 bond breaks preferentially.
- Phenols do not form halides due to sp^2 hybridized carbon preventing nucleophilic substitution.
- Electrophilic substitution on aromatic ethers: OR group activates ring, directs ortho/para; para product major.

Reactions involving cleavage of C — O bond :

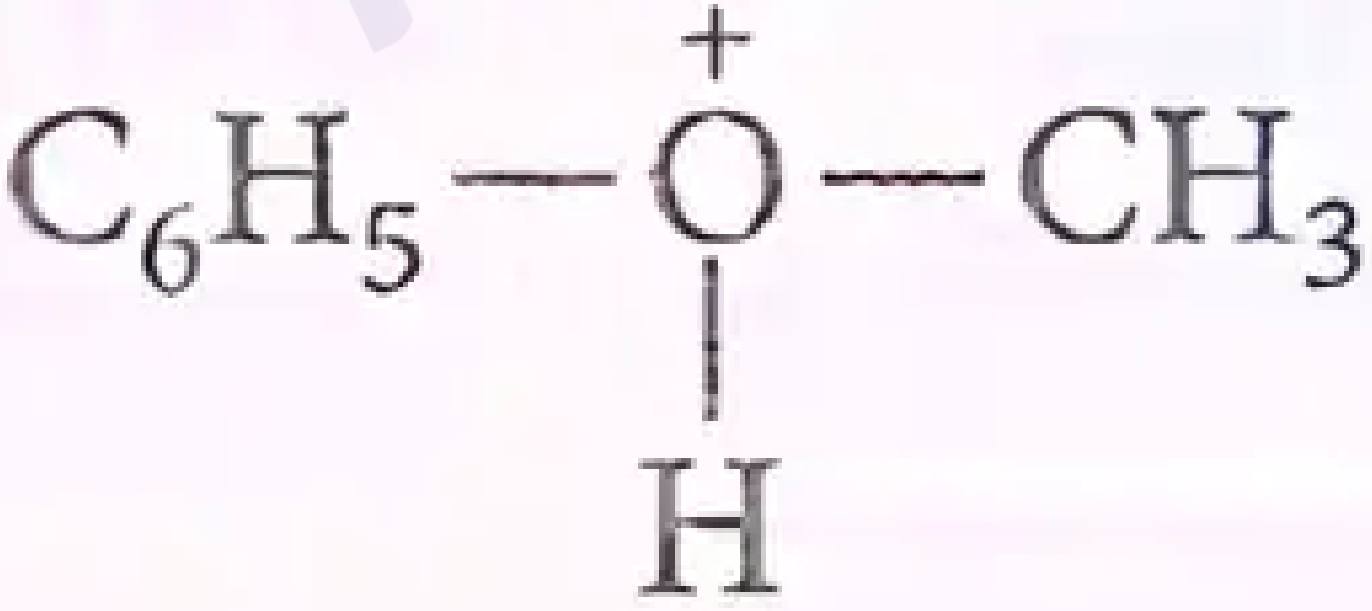
$$R-O-R + HX \xrightarrow{S_N2} ROH + RX$$

Simple ether

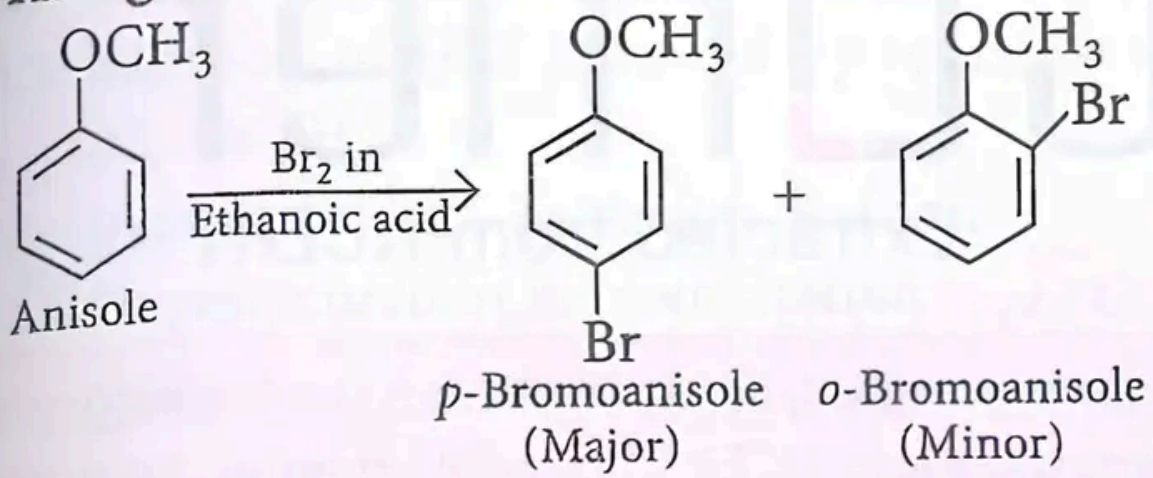


$$CH_3OCH_2CH_3 + HI \longrightarrow CH_3I + CH_3CH_2OH \; ; \; CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}H-O-CH_3 + HI \longrightarrow CH_3I + CH_3-\underset{\displaystyle CH_3}{\overset{|}{C}}H-OH$$

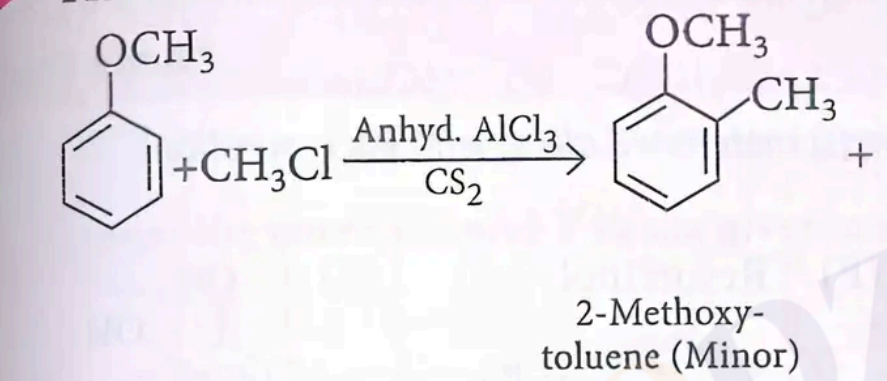
$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{+}{O}(H)-CH_3 \xrightarrow{slow} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C^+}}} + CH_3OH \; ; \; CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{C^+}}} + I^- \xrightarrow{fast} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-I$$

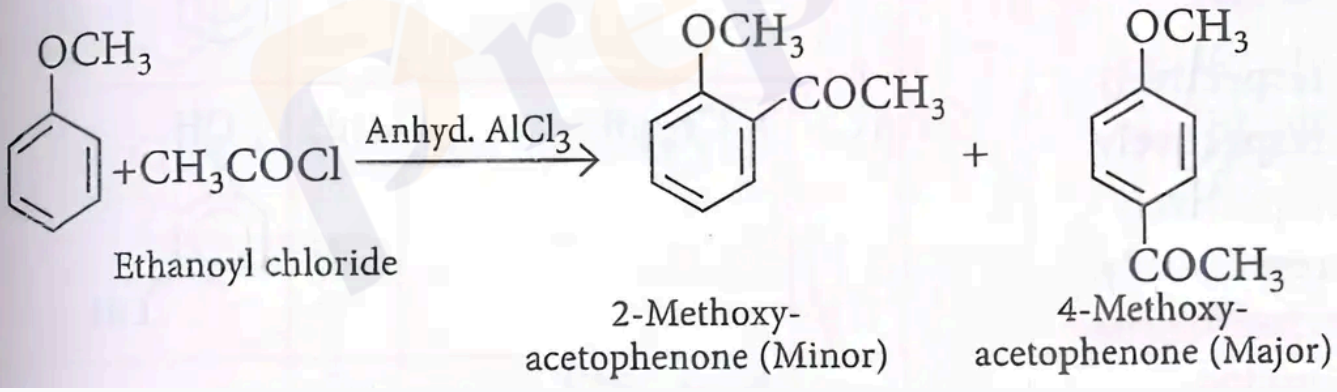


Halogenation :

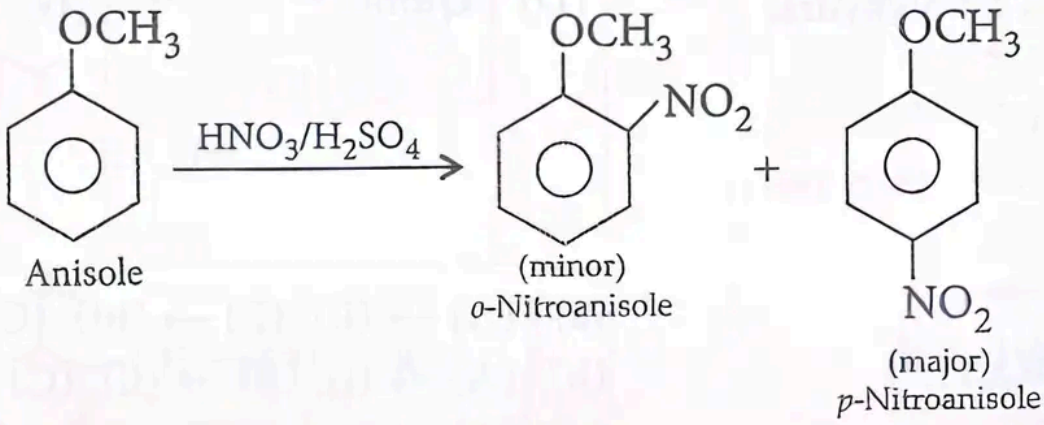


Friedel-Crafts reaction :





Nitration :



Solved Examples

- **Ex 1:** C_2H_5-O-C_2H_5 + HI → C_2H_5I + C_2H_5OH
- **Ex 2:** Mixed ether cleavage: smaller alkyl group forms alkyl halide.
- **Ex 3:** Tertiary alkyl halide formed via S_N1 mechanism in ether cleavage.

Practice Set

- Q1: Order of reactivity of hydrogen halides in ether cleavage is:
  A. HI < HBr < HCl
  B. HCl < HBr < HI
  C. HBr < HI < HCl
  D. HCl < HI < HBr
- Q2: In ether cleavage, which bond breaks in alkyl aryl ethers?
  A. Ar–O
  B. R–O
  C. C–C
  D. C–H
- Q3: In mixed ethers, which alkyl halide forms when one group is tertiary?
  A. Primary alkyl halide
  B. Secondary alkyl halide
  C. Tertiary alkyl halide
  D. No alkyl halide

Answer Key

- Q1: B - Reactivity increases from HCl to HI.
- Q2: B - R–O bond breaks; Ar–O bond is stable.
- Q3: C - Tertiary alkyl halide forms via S_N1.

Memory Aids

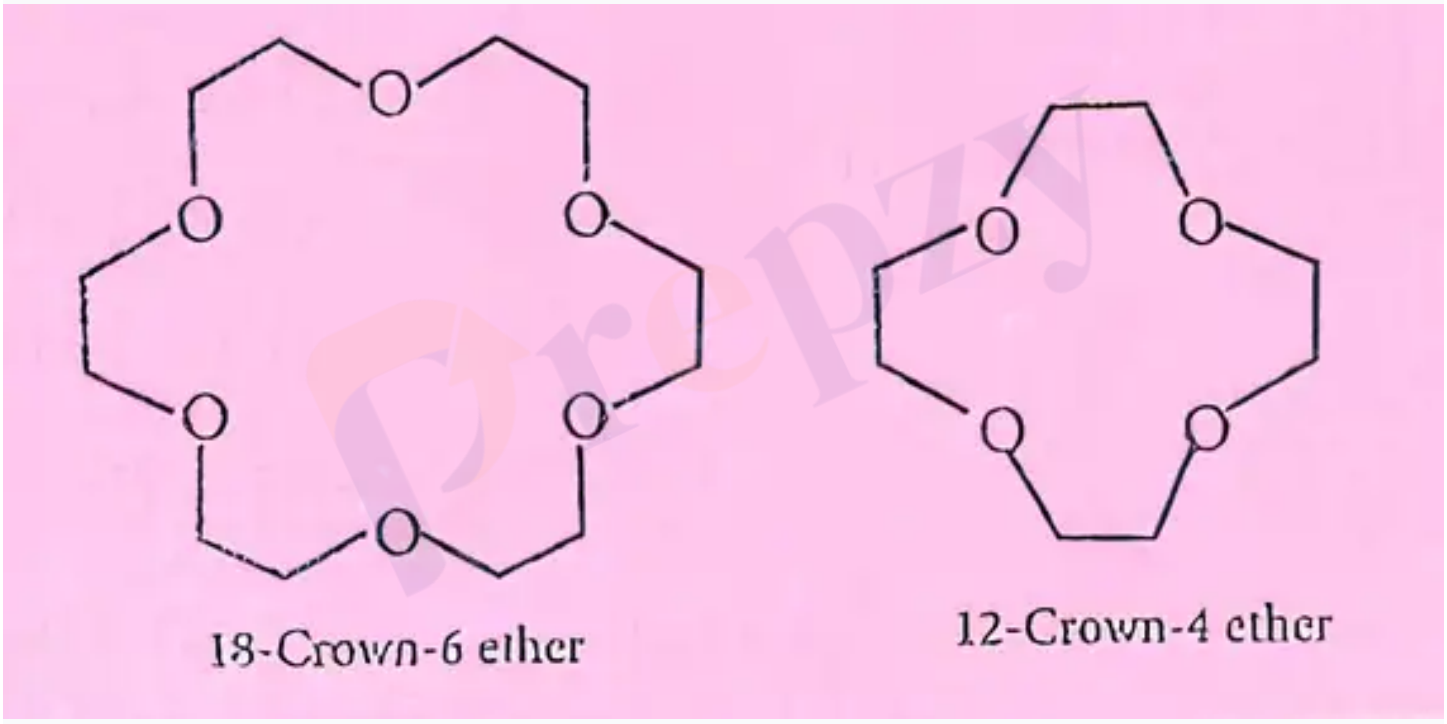
- HX reactivity: HCl < HBr < HI
- Alkyl aryl ethers break R–O bond, not Ar–O
- Mixed ethers: smaller alkyl halide forms unless tertiary group present

- Tertiary alkyl halide forms via S_N1

Crown Ethers

Explanation

- Cyclic polyethers with at least four -OCH_2CH_2- units.
- Named crown ethers due to crown-like ring shape.
- Example: 18-Crown-6 (18 atoms in ring, 6 oxygen atoms).
- Can complex metal ions inside the ring, useful in ion transport and phase transfer catalysis.



Solved Examples

- **Ex 1:** 18-Crown-6 binds K^+ ion selectively.
- **Ex 2:** 12-Crown-4 binds smaller ions like Na^+.

Practice Set

- Q1: Crown ethers are named based on:
  A. Number of carbon atoms
  B. Number of oxygen atoms
  C. Ring size and number of oxygen atoms
  D. Number of hydrogen atoms
- Q2: 18-Crown-6 has:
  A. 18 oxygen atoms
  B. 6 carbon atoms
  C. 18 atoms in ring and 6 oxygen atoms
  D. 6 atoms in ring and 18 oxygen atoms
- Q3: Crown ethers are useful because they:
  A. React with metals
  B. Bind metal ions inside ring
  C. Are acidic
  D. Are gases

Answer Key

- Q1: C - Named by ring size and oxygen count.
- Q2: C - 18 atoms total, 6 oxygen atoms.
- Q3: B - Bind metal ions inside ring.

Memory Aids

- Crown ethers = cyclic polyethers with repeating -OCH_2CH_2- units
- 18-Crown-6 = 18 atoms ring, 6 oxygen atoms
- Bind metal ions selectively