Alcohols, Phenols and Ethers

11 Chapter

① PREPARATION OF ALCOHOLS

(i) From alkenes

(a) By acid catalysed hydration :

$CH_3CH=CH_2 + H_2O \xrightleftharpoons{H^+} CH_3-\underset{OH}{CH}-CH_3$ (Major)

(b) By hydroboration - oxidation

$CH_3-CH=CH_2 + (H-BH_2)_2 \rightarrow CH_3-CH_2-CH_2-BH_2$

$\downarrow CH_3CH=CH_2$

$(CH_3CH_2CH_2)_3B \xleftarrow{CH_3CH=CH_2} (CH_3CH_2CH_2)_2BH$

$\downarrow H_2O/3H_2O_2/\bar{O}H$

$3CH_3CH_2CH_2OH + B(OH)_3$

- The alcohol formed looks as if it has been formed by the addition of water to alkene in a way opposite to Markovnikov's rule.

(ii) From carbonyl compounds

(a) By reduction of aldehydes and ketones :

$RCHO + H_2 \xrightarrow{Pd} RCH_2OH$

$RCOR' \xrightarrow{NaBH_4} R-\underset{OH}{CH}-R'$

(b) By reduction of carboxylic acids and esters :

$RCOOH \xrightarrow[(ii)\ H_2O]{(i)\ LiAlH_4} RCH_2OH$

$RCOOH \xrightarrow[H^+]{R'OH} RCOOR' \xrightarrow[Pd]{H_2} RCH_2OH + R'OH$

(iii) From Grignard reagent

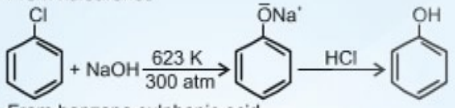
$HCHO + RMgX \rightarrow RCH_2OMgX \xrightarrow{H_2O} RCH_2OH$ (1° alcohol)

$RCHO + R'MgX \rightarrow R-\underset{R'}{CH}-OMgX \xrightarrow{H_2O} R-\underset{R'}{CH}-OH$ (2° alcohol)

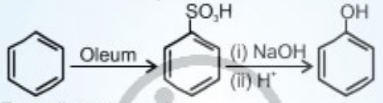
$RCOR + R'MgX \rightarrow R-\underset{R'}{\overset{R}{C}}-OMgX \xrightarrow{H_2O} R-\underset{R'}{\overset{R}{C}}-OH$ (3° alcohol)

② PREPARATION OF PHENOLS

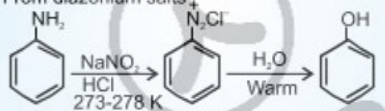
(a) From haloarenes



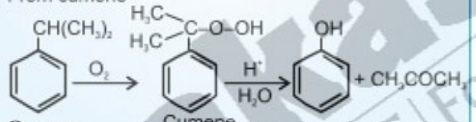
(b) From benzene sulphonic acid



(c) From diazonium salts



(d) From cumene



③ PHYSICAL PROPERTIES

- High boiling points of alcohols are mainly due to the presence of intermolecular hydrogen bonding in them.
- Solubility of alcohols and phenols in water is due to their ability to form hydrogen bonds with water.

④ CHEMICAL REACTIONS :

[A] Reaction of alcohols

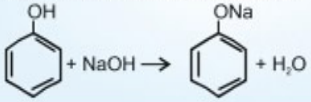
(a) Reactions involving cleavage of O-H bond

(i) Acidity of alcohols and phenols

- Reaction with metals

$2R-O-H + 2Na \rightarrow 2R\bar{O}\overset{+}{Na} + H_2$

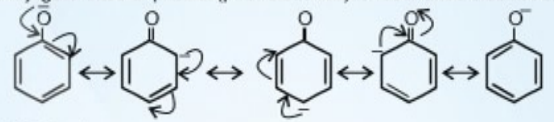
- Phenol reacts with aqueous NaOH



- Acidity of alcohols : Acidic strength order

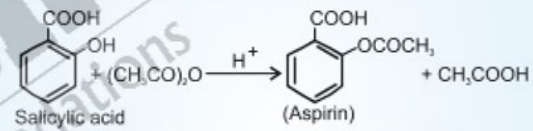
$R-CH_2OH > \underset{R}{\overset{R}{CHOH}} > \underset{R}{\overset{R}{C}}-OH$

Acidity of phenols : Phenols are more acidic than alcohol because conjugate base of phenol (phenoxide ion) is resonance stabilised.



(ii) Esterification :

$Ar/R-O-H + R'COOH \xrightleftharpoons{H^+} \underset{Ester}{Ar/ROCOR'} + H_2O$



(b) Reactions involving cleavage of C-O bond in alcohols

(i) Reaction with hydrogen halides : (Lucas test)

$ROH + HX \rightarrow R-X + H_2O$

- Lucas reagent (Conc. HCl and $ZnCl_2$)
- Tertiary alcohol produce turbidity with Lucas reagent immediately
- Primary alcohols do not produce turbidity at room temperature.

(ii) Reaction with phosphorus trihalides :

$3R-OH + PX_3 \rightarrow 3R-X + H_3PO_3$ (X = Cl, Br)

(iii) Dehydration : $C_2H_5OH \xrightarrow[443\ K]{H_2SO_4} CH_2=CH_2 + H_2O$

Relative ease of dehydration : Tertiary > Secondary > Primary

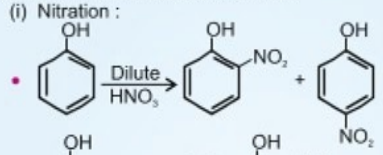
(iv) Oxidation

- $RCH_2OH \xrightarrow{CrO_3} RCHO$
- $CH_3-CH=CH-CH_2OH \xrightarrow{PCC} CH_3-CH=CH-CHO$
- $R-\underset{OH}{CH}-R' \xrightarrow{CrO_3} R-\underset{O}{\overset{\|}{C}}-R'$
- $RCH_2OH \xrightarrow[573\ K]{Cu} RCHO$
- $R-\underset{OH}{CH}-R' \xrightarrow[573\ K]{Cu} R-\underset{O}{\overset{\|}{C}}-R'$
- $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-OH \xrightarrow[573\ K]{Cu} CH_3-C=CH_2$ (CH_3 on C)

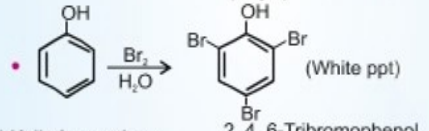
[B] Reaction of phenols :

(a) Electrophilic aromatic substitution

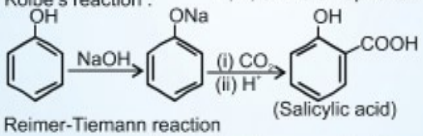
(i) Nitration :



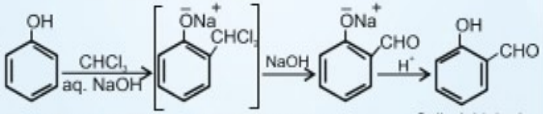
(ii) Halogenation



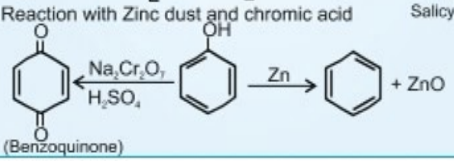
(b) Kolbe's reaction :



(c) Reimer-Tiemann reaction



(d) Reaction with Zinc dust and chromic acid



⑤ PREPARATION OF COMMERCIALLY IMPORTANT ALCOHOLS

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

Ethanol : $C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} \underset{Glucose}{C_6H_{12}O_6} + \underset{Fructose}{C_6H_{12}O_6}$

$C_6H_{12}O_6 \xrightarrow{Zymase} 2C_2H_5OH + 2CO_2$

- Ethanol is made unfit for drinking by mixing in it some copper sulphate and pyridine. It is known as denaturation of alcohol.

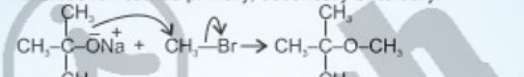
⑥ ETHERS

Preparation of ethers

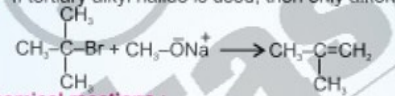
(a) Dehydration of alcohols : $CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} C_2H_5OC_2H_5$

(b) Williamson synthesis : $R\text{–}X + R'\text{–}\overset{+}{\bar{O}}Na \xrightarrow{S_N2} R\text{–}O\text{–}R' + NaX$

- Alkyl halide is primary
- Alkoxide ion can be primary, secondary or tertiary.



- If tertiary alkyl halide is used, then only alkene is formed.



Chemical reactions :

(i) Cleavage of C–O bond in ether : $R\text{–}O\text{–}R + HX \rightarrow RX + R\text{–}OH$

- The order of reactivity of halogen halides HI > HBr > HCl
- Cleavage of ether takes place with concentrated HI or HBr at high temperature.

Example 1 : $CH_3\text{–}O\text{–}C_2H_5 \xrightarrow[HI]{Excess} CH_3\text{–}I + C_2H_5\text{–}I$

Step-1: $CH_3\text{–}\ddot{O}\text{–}CH_2CH_3 + H\text{–}I \rightleftharpoons CH_3\text{–}\overset{H}{\overset{+}{O}}\text{–}CH_2CH_3 + \bar{I}$

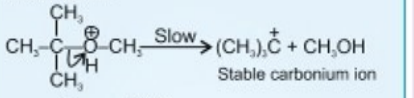
Step-2: $\bar{I} + CH_3\text{–}\overset{H}{\overset{+}{O}}\text{–}CH_2CH_3 \xrightarrow{S_N2} CH_3\text{–}I + CH_3CH_2OH$

Step-3: $CH_3CH_2\text{–}\ddot{O}\text{–}H + H\text{–}I \rightleftharpoons CH_3CH_2\text{–}\overset{\oplus}{O}H_2 + \bar{I}$

Step-4: $\bar{I} + CH_3\text{–}CH_2\text{–}\overset{+}{O}H_2 \xrightarrow{S_N2} CH_3CH_2\text{–}I + H_2O$

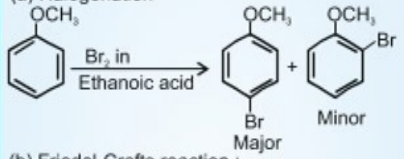
Example 2 : $CH_3\text{–}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}\text{–}O\text{–}CH_3 + HI \xrightarrow{S_N1} CH_3OH + (CH_3)_3C\text{–}I$

Mechanism :



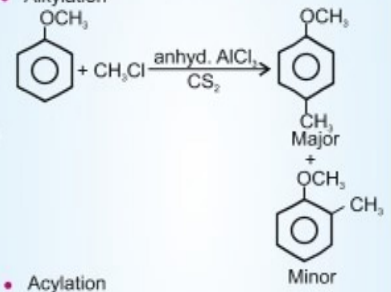
(ii) **Electrophilic substitution**

(a) Halogenation

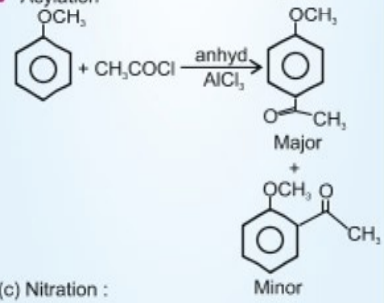


(b) Friedel-Crafts reaction :

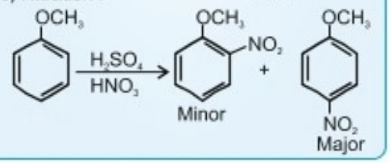
- Alkylation



- Acylation

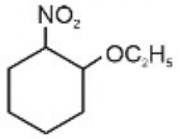


(c) Nitration :



Sharpen Your Understanding

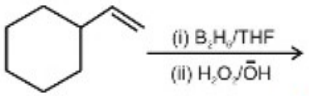
1. IUPAC name of the given compound is



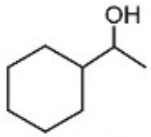
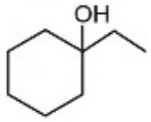
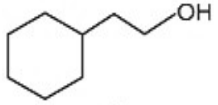
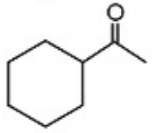
[NCERT Pg. 328]

(1) 2-Ethoxy-1-nitrocyclohexane
(2) 1-Ethoxy-2-nitrocyclohexane
(3) 1-Ethoxy-6-nitrocyclohexane
(4) 6-Ethoxy-1-nitrocyclohexane

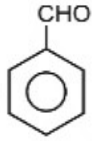
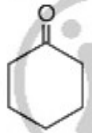
2. Major product of the given reaction is



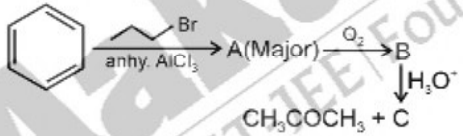
[NCERT Pg. 330]

(1) 
(2) 
(3) 
(4) 

3. Which among the following compounds on reaction with methyl magnesium bromide followed by hydrolysis gives a tertiary alcohol? [NCERT Pg. 331]

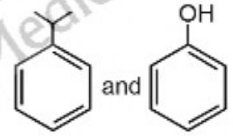
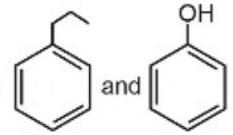
(1) 
(2) HCHO
(3) 
(4) 

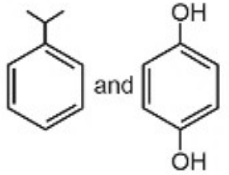
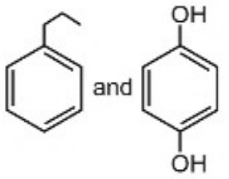
4. Consider the following reaction sequence



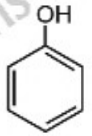
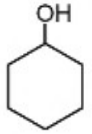
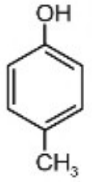
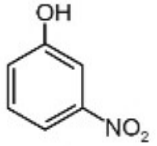
Product A and C respectively are

[NCERT Pg. 332]

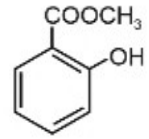
(1) 
(2) 

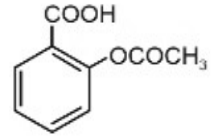
(3) 
(4) 

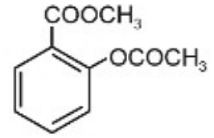
5. Most acidic compound among the following is [NCERT Pg. 337]

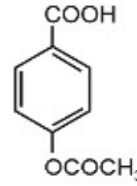
(1) 
(2) 
(3) 
(4) 

6. When salicyclic acid is treated with acetyl chloride in presence of pyridine the product obtained is [NCERT Pg. 338]

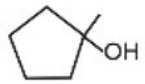
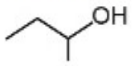
(1) 

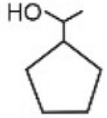
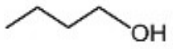
(2) 

(3) 

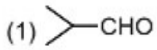
(4) 

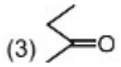
7. The alcohol which will react at slowest rate with conc. HCl and $ZnCl_2$ is [NCERT Pg. 338]

(1)  (2) 

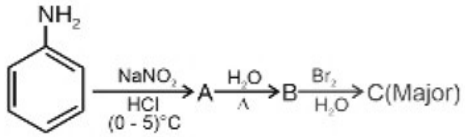
(3)  (4) 

8. When tert butyl alcohol is reacted with Cu at 573 K then the product obtained is [NCERT Pg. 340]

(1)  (2) 

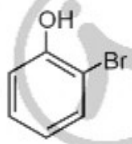
(3)  (4) 

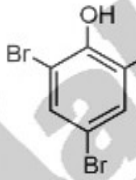
9. Consider the following reaction sequence



[NCERT Pg. 332, 342]

Major product (C) is

(1)  (2) 

(3)  (4) 

10. In Kolbe's reaction electrophile used is [NCERT Pg. 342]

(1) CO_2 (2) $:CCl_2$

(3) $H-\overset{+}{C}=O$ (4) $\overset{+}{C}Cl_3$

11. Consider the following reaction sequence

$$C_2H_5OH \xrightarrow{Na} A \xrightarrow{(CH_3)_3C-Cl} B(Major)$$

Major product B is [NCERT Pg. 335, 346]

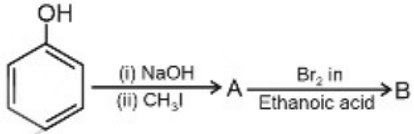
(1) $(CH_3)_3C-OC_2H_5$

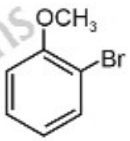
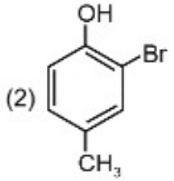
(2) $CH_3-\underset{CH_3}{\underset{|}{C}}=CH_2$

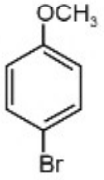
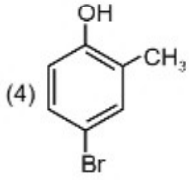
(3) $CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2-O-C_2H_5$

(4) $C_2H_5-C(CH_3)_3$

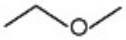
12. In the given reaction sequence major product (B) is [NCERT Pg. 346, 349]



(1)  (2) 

(3)  (4) 

13. The ether which is most difficult to cleave on heating with HBr is [NCERT Pg. 348]

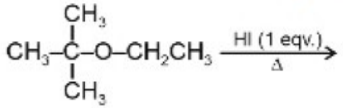
(1) 

(2) $Ph-CH_2-O-CH_2-Ph$

(3) $Ph-O-CH_3$

(4) $Ph-O-Ph$

14. Major products of the given reaction are [NCERT Pg. 348]



(1) $(CH_3)_3C–I$ and C_2H_5OH

(2) $(CH_3)_3C–OH$ and C_2H_5I

(3) $(CH_3)_3C–OH$ and $CH_2=CH_2$

(4) $(CH_3)_3C–I$ and CH_3CH_3

15. Salicylaldehyde is obtained as major product when phenol reacts with [NCERT Pg. 343]

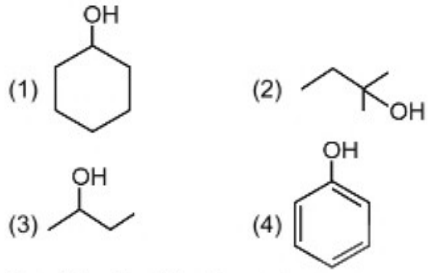
(1) CH_2Cl_2 and aq. NaOH

(2) CCl_4 and aq. NaOH

(3) $CHCl_3$ and aq. NaOH

(4) CH_3Cl and aq. NaOH

16. The compound which will react at fastest rate with sodium hydroxide is [NCERT Pg. 335, 336]



17. Consider the following statements [NCERT Pg. 326, 327, 331]

a. Phenol is also known as carbolic acid.

b. Phenyl ethyl ether is known as anisole.

c. Glycerol is a dihydric alcohol.

The correct statement(s) is/are

(1) a and b only (2) b and c only

(3) a only (4) a, b and c

18. Correct order of boiling points of the given compounds is

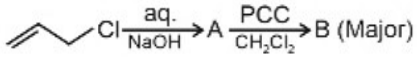
CH_3CH_2OH CH_3OCH_3 $CH_3CH_2CH_3$

(a) (b) (c) [NCERT Pg. 334]

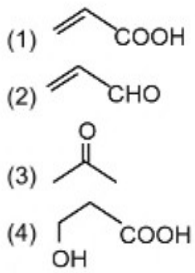
(1) (b) > (a) > (c) (2) (a) > (c) > (b)

(3) (a) > (b) > (c) (4) (c) > (a) > (b)

19. Consider the following reaction sequence



Product B is [NCERT Pg. 340]



20. Incorrect statement among the following is [NCERT Pg. 327, 334, 344, 345]

(1) Methanol is miscible with water in all proportions

(2) Resorcinol is benzene-1,3-diol

(3) Zymase converts glucose into ethanol

(4) Diethyl ether is formed as major product on heating mixture of ethanol and sulphuric acid at 443 K

Thinking in Context

1. In vinylic alcohols, –OH group is bonded to _____ hybridized cabon. [NCERT Pg. 325]

2. Structure of 3-Methylbutoxybenzene is _____. [NCERT Pg. 327]

3. In hydration of alkene in acidic medium, the intermediate formed is a _____ [NCERT Pg. 329]

4. Ethanoic acid is reduced to _____ in excellent yield by $LiAlH_4$ [NCERT Pg. 330]

5. Benzene diazonium chloride is hydrolysed to _____ by warming with water. [NCERT Pg. 332]

6. Cumene is oxidized in the presence of air to_____ [NCERT Pg. 332]

7. Alcohols on reaction with acid anhydrides form _____ [NCERT Pg. 337]

8. Lucas reagent is _____ [NCERT Pg. 338]

9. Secondary alcohols are oxidized to _____ by chromic anhydride [NCERT Pg. 340]

10. When vapours of isobutanol is passed over heated copper at 573 K then the product formed is _____ [NCERT Pg. 340]

11. o-Nitrophenol and p-nitrophenol mixture can be separated by _____ [NCERT Pg. 341]

12. p-Nitrophenol is less volatile than o-Nitrophenol due to _____ which causes the association of molecules. [NCERT Pg. 341]

13. With _____, phenol is converted to 2, 4, 6-trinitrophenol. [NCERT Pg. 341]

14. Phenol on reaction with Br_2 in presence of CS_2 at 273 K forms _____ as major product [NCERT Pg. 342]

15. In Kolbe's reaction of phenol _____ is formed as main reaction product. [NCERT Pg. 342, 343]

16. Phenol is converted to _____ on heating with zinc dust. [NCERT Pg. 343]

17. _____ is known as wood spirit. [NCERT Pg. 344]

18. The commercial alcohol is made unfit for drinking by mixing in it some _____ and _____ [NCERT Pg. 344]

19. In Williamson synthesis of ether the reaction involves _____ attack of an alkoxide ion on primary alkyl halide [NCERT Pg. 345]

20. Cleavage of methyl-tert-butyl ether by HI follows ____ mechanism. [NCERT Pg. 348]

❑ ❑ ❑