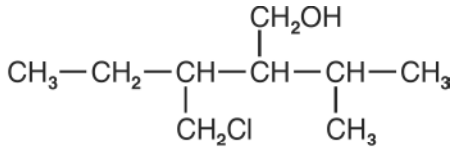
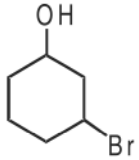
Unit - 11

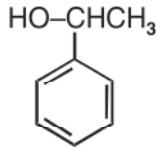
ALCOHOLS, PHENOLS AND ETHERS

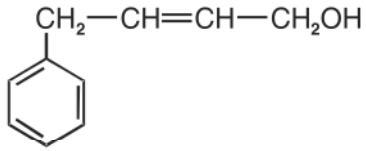
1. Write IUPAC names of the following compounds :

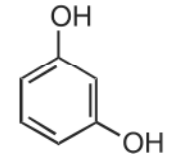
(i) 

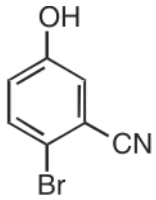
(ii) 

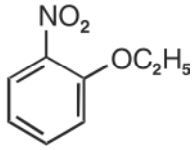
(iii) $CH \equiv C-CH_2OH$

(iv) 

(v) 

(vi) 

(vii) 

(viii) 

(ix) $C_6H_5OC_3H_7$

(x) $CH_3CH_2OCH_2CH_2CH_2Cl$

2. Write the structures of the compounds whose names are given below :

(i) 3, 5-dimethoxyhexane-1, 3, 5-triol

(ii) cyclohexylmethanol

(iii) 2-ethoxy-3-methylpentane

(iv) 3-chloromethylpentan-2-ol

(v) p-nitroanisole

3. Describe the following reactions with example :

(i) Hydroboration oxidation of alkenes

(ii) Acid catalysed dehydration of alcohols at 443K.

(iii) Williamson synthesis

(iv) Reimer-Tiemann reaction.

(v) Kolbe's reaction

(vi) Friedel-Crafts acylation of Anisole.

4. Complete the following reactions :

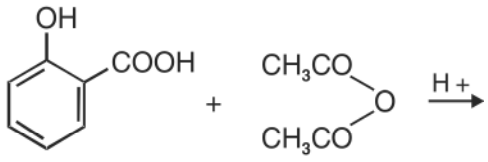
(i) $CH_3CH_2CH_2CHO \xrightarrow{Pd/H_2}$

(ii) $CH_3CHO \xrightarrow[(ii)\ H^+/H_2O]{(i)\ CH_3MgBr}$

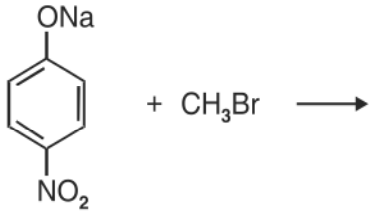
(iii) $CH_3CH_2OH \xrightarrow{Cu/573K}$

(iv) $C_6H_5OH + Br_2 \xrightarrow{H_2O}$

(v)

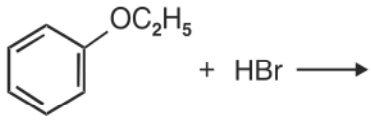


(vi)



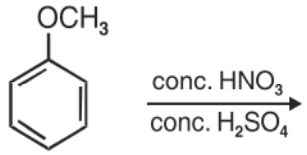
(vii) $CH_3CH_2CH_2O - CH_3 + HBr \longrightarrow$

(viii)

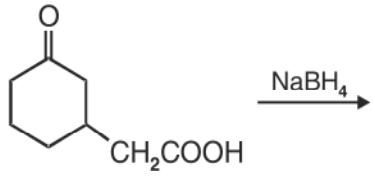


(ix) $(CH_3)_3C - O - C_2H_5 + HI \longrightarrow$

(x)



(xi)



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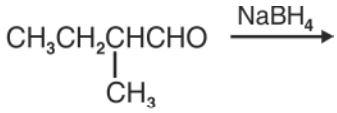
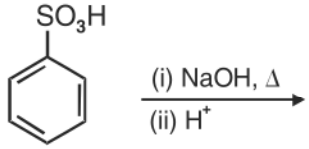
(xiii) 

(xiv) 

5. What happens when :

(i) aluminium reacts with tert-butyl alcohol

(ii) phenol is oxidised with chromic acid

(iii) cumene is oxidised in the presence of air and the product formed is treated with dilute acid.

(iv) phenol is treated with conc. HNO_3.

(v) phenol is treated with chloroform in presence of dilute NaOH.

6. How will you convert

(i) propene to propan-l-ol.

(ii) anisole to phenol

(iii) butan-2-one to butan-2-ol

(iv) ethanal to ethanol

(v) phenol to ethoxybenzene

(vi) 1-phenylethene to 1-phenylethanol

(vii) formaldehyde to cyclohexylmethanol

(viii) butyl bromide to pentan-1-ol.

(ix) toluene to benzyl alcohol

(x) 1-propoxypropane to propyl iodide

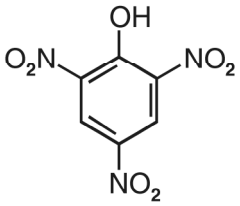
(xi) ethyl bromide to 1-ethoxyethane

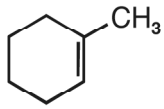
(xii) methyl bromide to 2-methoxy-2-methylpropane

(xiii) ethyl bromide to ethoxybenzene

(xiv) ethanol to benzyl ethyl ether.

7. Identify the missing reactant or product A to D in the following equations:

(i) $(A) + HNO_3 + H_2SO_4 \longrightarrow$ 

(ii)  $+$ dil. $H_2SO_4 \longrightarrow$ (B)

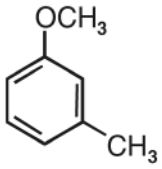
(iii) $(C) + H_2O \xrightarrow{H^+} CH_3(CH_2)_2\,C(CH_3)\,(OH)\,(CH_2)_2CH_3$

(vi) $CH_3OC_6H_5 + HI \longrightarrow$ (D)

8. Identify X, Y and Z in the following sequence of reactions :

(i) Phenol $\xrightarrow{Zn\ dust}$ X $\xrightarrow[Anhyd.\ AlCl_3]{CH_3Cl}$ Y $\xrightarrow[OH^-]{KMnO_4}$ Z

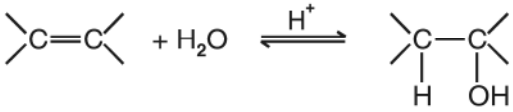
(ii) Ethanol $\xrightarrow{PBr_3}$ X $\xrightarrow{alc.\ KOH}$ Y $\xrightarrow{dil.H_2SO_4}$ Z

(iii)  $\xrightarrow{HI}$ X $+ CH_3I$

X + conc. $HNO_3 \longrightarrow$ Y (a dinitro compound)

X + Br_2(aq) $\longrightarrow$ Z (a tribromo product)

10. Write the mechanism for following reactions :

(i) 

(acid catalysed hydration of alkenes)

(ii) $CH_3 - CH_2 - OH \xrightarrow[443\ K]{H^+} CH_2 = CH_2$
(acid catalysed dehydration of alcohols)

(iii) $2CH_3CH_2OH \xrightarrow[413\ K]{H^+} CH_3CH_2OCH_2CH_3$
(acid catalysed nucleophilic substitution reaction)

(iv) $CH_3OCH_3 + HI \longrightarrow CH_3OH + CH_3I$

(v) $(CH_3)_3C - O - CH_3 + HI \longrightarrow CH_3OH + (CH_3)_3\ CI$

11. Give reason for the following :

(i) The C–O–C bond angle in dimethyl ether is (111.7°)

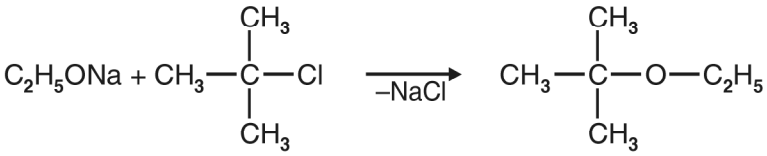
(ii) Alcohols have higher boiling points than ethers of comparable molecular masses.

(iii) Phenols are more acidic than alcohols.

(iv) Nitrophenol is more acidic than o-methoxyphenol.

(v) Phenol is more reactive towards electrophilic substitution reaction than benzene.

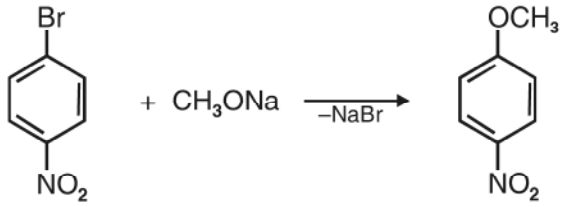
(vii) The following is not an appropriate method for the preparation of t-butyl ethyl ether :



(a) What would be the major product of this reaction?

(b) Write suitable reaction for the preparation of t–butyl ethyl ether.

(viii) The following is not an appropriate method for the preparation of 1-methoxy-4-nitrobenzene;



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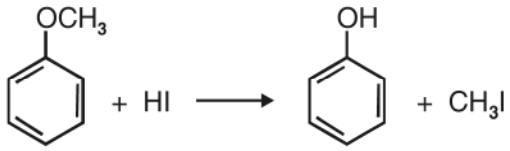
(x) Write the suitable reaction for the preparation of 1–methoxy–4–nitrobenzene

(ix) o-nitrophenol is steam volatile but p-nitrophenol is not.

(x) phenol is less polar than ethanol.

(xi) The phenyl methyl ether reacts with HI fo form phenol and iodomethane and not iodobenzene and methanol.



(xii) methanol is less acidic than water.

(xiii) alcohols can act as weak base as well as weak acids.

(xiv) phenols do not give protonation reaction readily.

(xvi) absolute ethanol can not be obtained by factional distillation of ethanol and water mixture.

12. Arrange the following in the increasing order of property shown :

(i) methanol, ethanol, diethylether, ethyleneglycol. (Boiling points)

(ii) phenol, o-nitrophenol, m-nitrophenol, p-nitrophenol. (Acid strength)

(iii) dimethylether, ethanol, phenol. (Solubility in water)

(iv) n-butanol, 2-methylpropan-1-ol, 2-methylpropan-2-ol. (Acid strength)

13. Give a chemical test to distinguish between the following pair of compounds.

(i) n-propyl alcohol and isopropylalcohol

(ii) methanol and ethanol

(iii) cyclohexanol and phenol.

(iv) propan-2-ol and 2-methylpropan-2-ol.

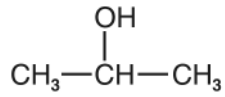
(v) phenol and anisole

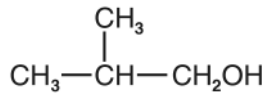
(vi) ethanol and diethyl ether

*14. Which of the following compounds gives fastest reaction with HBr and why?

(i) $(CH_3)_3COH$

(ii) $CH_3CH_2CH_2OH$

(iii) 

(iv) 

*15. What is the function of $ZnCl_2$ (anhyd) in Lucas test for distinction between 1°, 2° and 3° alcohols.

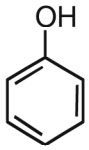
16. An alcohol A ($C_4H_{10}O$) on oxidation with acidified potassium dichromate gives carboxylic acid B ($C_4H_8O_2$). Compound A when dehydrated with conc. H_2SO_4 at 443 K gives compound C. Treatment of C with aqueous H_2SO_4 gives compound D ($C_4H_{10}O$) which is an isomer of A. Compound D is resistant to oxidation but compound A can be easily oxidised. Identify A, B, C and D and write their structures.

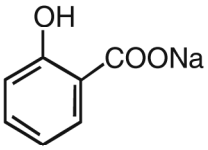
[**Ans. :** [A] : $(CH_3)_2CHCH_2OH$ [B] : $CH_3CH(CH_3)COOH$

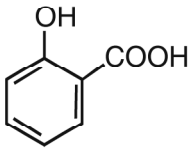
[C] : $(CH_3)_2C = CH_2$ [D] : $(CH_3)_3C - OH$

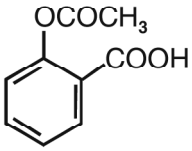
*17. An organic compound A having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$. When A is treated with NaOH and CO_2 at 400 K under pressure, compound B is obtained. Compound B on acidification gives compound C which reacts with acetyl chloride to form D which is a popular pain killer. Deduce the structure of A, B, C and D. What is the common name of Drug D?

[**Ans. :**

(A) 

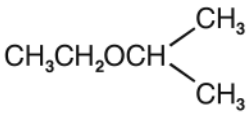
(B) 

(C) 

(D) 

Aspirin

19. An ether A ($C_5H_{12}O$) when heated with excess of hot concentrated HI produced two alkyl halides which on hydrolysis from compounds B and C. Oxidation of B gives an acid D whereas oxidation of C gave a ketone E. Deduce the structures of A, B, C, D and E.

[**Ans. :** (A) 

(B) CH_3CH_2OH

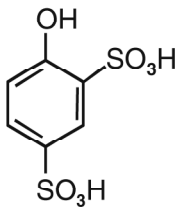
(C) $CH_3CHOHCH_3$

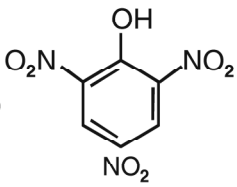
(D) CH_3COOH

(E) CH_3COCH_3

20. Phenol, C_6H_5OH when it first reacts with concentrated sulphuric acid, forms Y.Y is reacted with concentrated nitric acid to form Z. Identify Y and Z and explain why phenol is not converted commercially to Z by reacting it with conc. HNO_3.

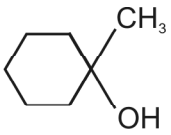
[**Ans. :**

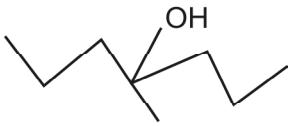
(Y) 

(Z)  (Picric acid)

Phenol is not reacted directly with conc. HNO_3 because the yield of picric acid is very poor]

21. Synthesise the following alcohols from suitable alkenes.

(a) 

(b) 

22. How are the following ethers prepared by williumson synthesis?

(a) Ethoxybenzene (b) 2–methoxy–2–methylpropane