CHAPTER

11

Alcohols, Phenols and Ethers

11.1 Classification

1. The general molecular formula, which represents the homologous series of alkanols is

(a) $C_nH_{2n+2}O$ (b) $C_nH_{2n}O_2$

(c) $C_nH_{2n}O$ (d) $C_nH_{2n+1}O$ *(2006)*

11.4 Alcohols and Phenols

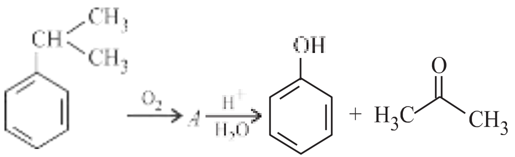
2. Reaction between acetone and methyl magnesium chloride followed by hydrolysis will give

(a) *iso*-propyl alcohol (b) *sec*-butyl alcohol

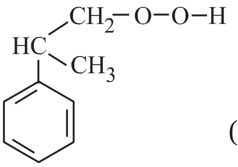
(c) *tert*-butyl alcohol (d) *iso*-butyl alcohol.

(NEET 2020)

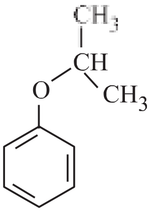
3. The structure of intermediate *A* in the following reaction is



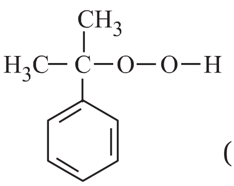
(a)



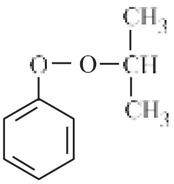
(b)



(c)



(d)



(NEET 2019)

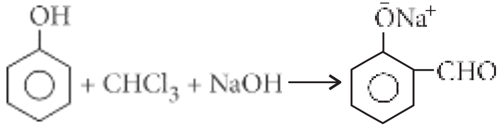
4. When vapours of a secondary alcohol is passed over heated copper at 573 K, the product formed is

(a) a carboxylic acid (b) an aldehyde

(c) a ketone (d) an alkene.

(Odisha NEET 2019)

5. In the reaction,



the electrophile involved is

(a) dichloromethyl cation $(\overset{+}{C}HCl_2)$

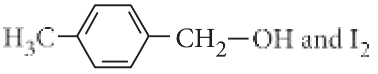
(b) formyl cation $(\overset{+}{C}HO)$

(c) dichloromethyl anion $(\overset{-}{C}HCl_2)$

(d) dichlorocarbene $(:CCl_2)$ *(NEET 2018)*

6. Compound *A*, $C_8H_{10}O$, is found to react with NaOI (produced by reacting *Y* with NaOH) and yields a yellow precipitate with characteristic smell. *A* and *Y* are respectively

(a)



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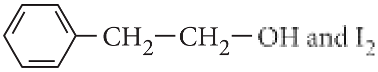
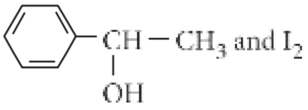
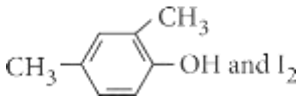


(c)

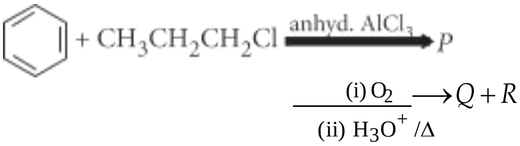


(d)

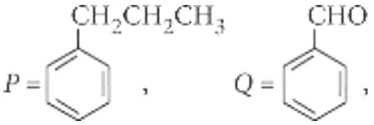


(NEET 2018)

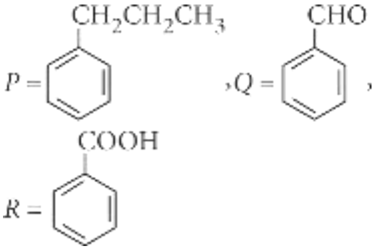
7. Identify the major products *P*, *Q* and *R* in the following sequence of reactions :

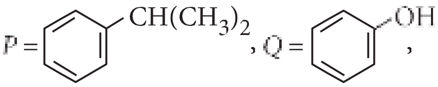


(a)

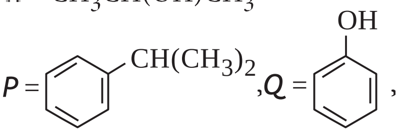


$R = CH_3CH_2-OH$

(b) 

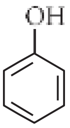
(c) 

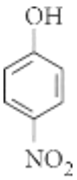
$R = CH_3CH(OH)CH_3$

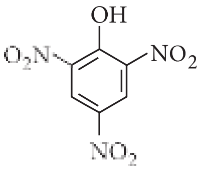
(d) 

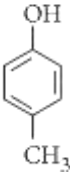
$R = CH_3-CO-CH_3$ *(NEET 2018)*

8. Which one is the most acidic compound?

(a) 

(b) 

(c) 

(d) 

(NEET 2017)

9. Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional group?

(a) –COOH (b) $-CHCl_2$

(c) –CHO (d) $-CH_2Cl$ *(2015)*

10. Which of the following reaction(s) can be used for the preparation of alkyl halides?

(I) $CH_3CH_2OH + HCl \xrightarrow{\text{Anh.}ZnCl_2}$

(II) $CH_3CH_2OH + HCl \longrightarrow$

(III) $(CH_3)_3COH + HCl \longrightarrow$

(IV) $(CH_3)_2CHOH + HCl \xrightarrow{\text{Anh.}ZnCl_2}$

(a) (I) and (II) only (b) (IV) only

(c) (III) and (IV) only

(d) (I), (III) and (IV) only *(2015)*

11. Which of the following will not be soluble in sodium hydrogen carbonate?

(a) 2,4,6-Trinitrophenol

(b) Benzoic acid

(c) *o*-Nitrophenol

(d) Benzenesulphonic acid *(2014)*

12. Number of isomeric alcohols of molecular formula $C_6H_{14}O$ which give positive iodoform test is

(a) three (b) four (c) five (d) two.

(Karnataka NEET 2013)

13. In the following sequence of reactions,

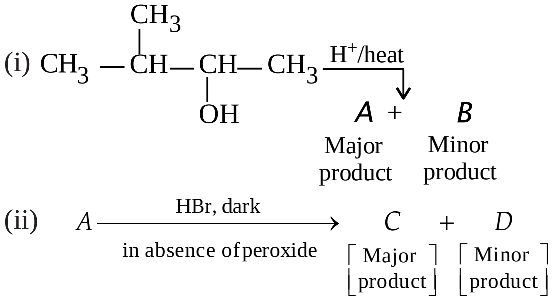
$$CH_3-Br \xrightarrow{KCN} A \xrightarrow{H_3O^+} B \xrightarrow[\text{ether}]{LiAlH_4} C$$

the end product (*C*) is

(a) acetone (b) methane

(c) acetaldehyde (d) ethyl alcohol. *(2012)*

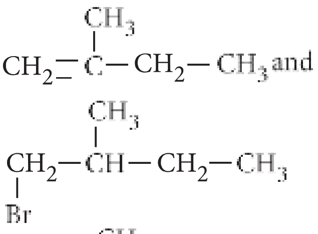
14. In the following reactions,



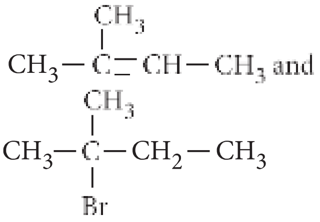
$$\text{(i)}\ CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{OH}{\underset{|}{C}H}-CH_3 \xrightarrow{H^+/\text{heat}} \underset{\text{Major product}}{A} + \underset{\text{Minor product}}{B}$$

$$\text{(ii)}\ A \xrightarrow[\text{in absence of peroxide}]{\text{HBr, dark}} \underset{\text{[Major product]}}{C} + \underset{\text{[Minor product]}}{D}$$

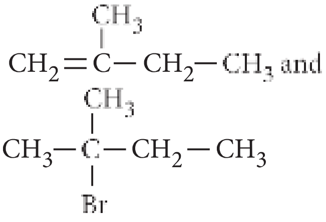
the major products (*A*) and (*C*) are respectively

(a) 

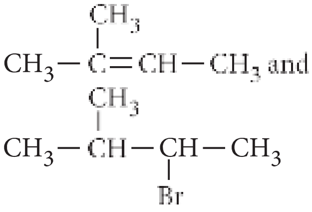
$$CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2-CH_3 \text{ and } \underset{Br}{\underset{|}{CH_2}}-\overset{CH_3}{\overset{|}{C}H}-CH_2-CH_3$$

(b) 

$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 \text{ and } CH_3-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_2-CH_3$$

(c) 

$$CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2-CH_3 \text{ and } CH_3-\overset{CH_3}{\overset{|}{\underset{Br}{\underset{|}{C}}}}-CH_2-CH_3$$

(d) 

$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_3 \text{ and } CH_3-\overset{CH_3}{\overset{|}{C}H}-\underset{Br}{\underset{|}{C}H}-CH_3$$

(2011)

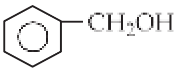
15. Given are cyclohexanol (I), acetic acid (II), 2,4,6-trinitrophenol (III) and phenol (IV). In these the order of decreasing acidic character will be

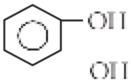
(a) III > II > IV > I (b) II > III > I > IV

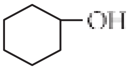
(c) II > III > IV > I (d) III > IV > II > I

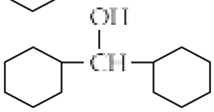
(2010)

16. Which of the following compounds has the most acidic nature?

(a) 

(b) 

(c) 

(d) 

(2010)

17. Among the following four compounds

(i) Phenol (ii) Methyl phenol

(iii) *Meta*-nitrophenol (iv) *Para*-nitrophenol

The acidity order is

(a) (iv) > (iii) > (i) > (ii) (b) (iii) > (iv) > (i) > (ii)

(c) (i) > (iv) > (iii) > (ii) (d) (ii) > (i) > (iii) > (iv)

(2010)

18. When glycerol is treated with excess of HI, it produces

(a) 2-iodopropane (b) allyl iodide

(c) propene (d) glycerol triiodide.

(Mains 2010)

19. Consider the following reaction :

$$\text{Ethanol} \xrightarrow{PBr_3} X \xrightarrow{\text{alc.KOH}} Y \xrightarrow[\text{(ii) } H_2O\text{, heat}]{\text{(i) } H_2SO_4\text{, room temperature}} Z$$

the product Z is

(a) $CH_3CH_2-O-CH_2-CH_3$

(b) $CH_3-CH_2-O-SO_3H$

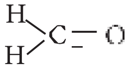
(c) CH_3CH_2OH

(d) $CH_2=CH_2$ *(2009)*

20. $HOCH_2CH_2OH$ on heating with periodic acid gives

(a) 2HCOOH

(b) 
$CHO-CHO$

(c) 2 
$H_2C=O$

(d) $2CO_2$ *(2009)*

21. Consider the following reaction :

$$\text{Phenol} \xrightarrow{\text{Zn dust}} X \xrightarrow[\text{Anhyd. } AlCl_3]{CH_3Cl} Y \xrightarrow{\text{Alkaline } KMnO_4} Z$$

the product Z is

(a) benzaldehyde (b) benzoic acid

(c) benzene (d) toluene. *(2009)*

22. Ethylene oxide when treated with Grignard reagent yields

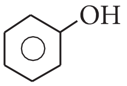
(a) primary alcohol (b) secondary alcohol

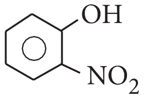
(c) tertiary alcohol (d) cyclopropyl alcohol.

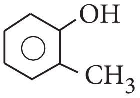
(2006)

23. Which one of the following compounds is most acidic?

(a) $Cl-CH_2-CH_2-OH$

(b) 

(c) 

(d) 

(2005)

24. Which one of the following will not form a yellow precipitate on heating with an alkaline solution of iodine?

(a) $CH_3CH(OH)CH_3$ (b) $CH_3CH_2CH(OH)CH_3$

(c) CH_3OH (d) CH_3CH_2OH *(2004)*

25. *n*-Propyl alcohol and isopropyl alcohol can be chemically distinguished by which reagent?

(a) PCl_5 (b) Reduction

(c) Oxidation with potassium dichromate

(d) Ozonolysis *(2002)*

26. When phenol is treated with $CHCl_3$ and NaOH, the product formed is

(a) benzaldehyde (b) salicylaldehyde

(c) salicylic acid (d) benzoic acid. *(2002)*

27. Which of the following is correct?

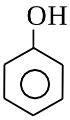
(a) On reduction, any aldehyde gives secondary alcohol.

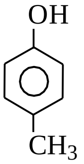
(b) Reaction of vegetable oil with H_2SO_4 gives glycerine.

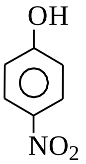
(c) Alcoholic iodine with NaOH gives iodoform.

(d) Sucrose on reaction with NaCl gives invert sugar. *(2001)*

28. The correct acidic order of the following is

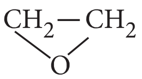
I. 

II. 

III. 

(a) I > II > III (b) III > I > II

(c) II > III > I (d) I > III > II *(2001)*

29. Reaction of  with $RMgX$ leads to the formation of

(a) RCH_2CH_2OH (b) $RCHOHCH_3$

(c) $RCHOHR$

(d) 
R_2CHCH_2OH

(1998)

30. When 3,3-dimethyl-2-butanol is heated with H_2SO_4, the major product obtained is

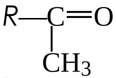
(a) 2,3-dimethyl-2-butene

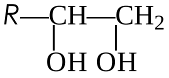
(b) *cis* and *trans* isomers of 2,3-dimethyl-2-butene

(c) 2,3-dimethyl-1-butene

(d) 3,3-dimethyl-1-butene. *(1995)*

31. The alkene $R - CH{=}CH_2$ reacts readily with B_2H_6 and the product on oxidation with alkaline hydrogen peroxides produces

(a) 
$R-\underset{CH_3}{\underset{|}{C}}=O$

(b) 
$R-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

(c) $R - CH_2 - CHO$

(d) $R - CH_2 - CH_2{-}OH$ *(1995)*

32. On heating glycerol with conc. H_2SO_4, a compound is obtained which has bad odour. The compound is
(a) acrolein (b) formic acid
(c) allyl alcohol (d) glycerol sulphate. *(1994)*

33. Ethanol and dimethyl ether form a pair of functional isomers. The boiling point of ethanol is higher than that of dimethyl ether, due to the presence of
(a) H-bonding in ethanol
(b) H-bonding in dimethyl ether
(c) CH_3 group in ethanol
(d) CH_3 group in dimethyl ether. *(1993)*

34. Increasing order of acid strength among *p*-methoxyphenol, *p*-methylphenol and *p*-nitrophenol is
(a) *p*-nitrophenol, *p*-methoxyphenol, *p*-methylphenol
(b) *p*-methylphenol, *p*-methoxyphenol, *p*-nitrophenol
(c) *p*-nitrophenol, *p*-methylphenol, *p*-methoxyphenol
(d) *p*-methoxyphenol, *p*-methylphenol, *p*-nitrophenol. *(1993)*

35. Which one of the following on oxidation gives a ketone?
(a) Primary alcohol (b) Secondary alcohol
(c) Tertiary alcohol (d) All of these *(1993)*

36. What is formed when a primary alcohol undergoes catalytic dehydrogenation?
(a) Aldehyde (b) Ketone
(c) Alkene (d) Acid *(1993)*

37. How many isomers of $C_5H_{11}OH$ will be primary alcohols?
(a) 5 (b) 4 (c) 2 (d) 3 *(1992)*

38. HBr reacts fastest with
(a) 2-methylpropan-1-ol
(b) methylpropan-2-ol
(c) propan-2-ol
(d) propan-1-ol. *(1992)*

39. When phenol is treated with excess bromine water. It gives
(a) *m*-bromophenol
(b) *o*- and *p*-bromophenols
(c) 2,4-dibromophenol
(d) 2,4,6-tribromophenol. *(1992)*

40. The compound which reacts fastest with Lucas reagent at room temperature is
(a) butan-1-ol (b) butan-2-ol
(c) 2-methylpropan-1-ol
(d) 2-methylpropan-2-ol. *(1989)*

41. Which one of the following compounds will be most readily attacked by an electrophile?
(a) Chlorobenzene (b) Benzene
(c) Phenol (d) Toluene *(1989)*

42. Propene, $CH_3CH{=}CH_2$ can be converted into 1-propanol by oxidation. Indicate which set of reagents amongst the following is ideal for the above conversion?
(a) $KMnO_4$ (alkaline)
(b) Osmium tetroxide (OsO_4/CH_2Cl_2)
(c) B_2H_6 and alk. H_2O_2 (d) O_3/Zn *(1989)*

43. Phenol is heated with $CHCl_3$ and aqueous KOH when salicylaldehyde is produced. This reaction is known as
(a) Rosenmund's reaction
(b) Reimer-Tiemann reaction
(c) Friedel-Crafts reaction
(d) Sommelet reaction. *(1989,1988)*

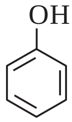
44. Lucas reagent is
(a) conc. HCl and anhydrous $ZnCl_2$
(b) conc. HNO_3 and hydrous $ZnCl_2$
(c) conc. HCl and hydrous $ZnCl_2$
(d) conc. HNO_3 and anhydrous $ZnCl_2$. *(1988)*

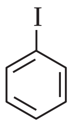
11.5 Some Commercially Important Alcohols

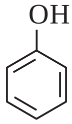
45. Methanol is industrially prepared by
(a) oxidation of CH_4 by steam at 900°C
(b) reduction of HCHO using $LiAlH_4$
(c) reaction of HCHO with a solution of NaOH
(d) reduction of CO using H_2 and $ZnO{-}Cr_2O_3$. *(1992)*

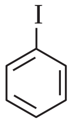
11.6 Ethers

46. Anisole on cleavage with HI gives

(a) 
+ CH_3I

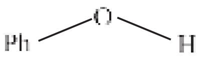
(b) 
+ CH_3OH

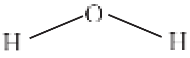
(c) 
+ C_2H_5I

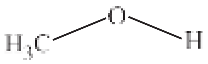
(d) 
+ C_2H_5OH

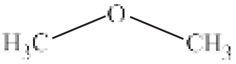
(NEET 2020)

47. The compound that is most difficult to protonate is

(a) 

(b) 

(c) 

(d) 

(NEET 2019)

48. The major products *C* and *D* formed in the following reactions respectively are

$H_3C-CH_2-CH_2-O-C(CH_3)_3 \xrightarrow{\text{excess HI}} C + D$

(a) $H_3C-CH_2-CH_2-I$ and $I-C(CH_3)_3$

(b) $H_3C-CH_2-CH_2-OH$ and $I-C(CH_3)_3$

(c) $H_3C-CH_2-CH_2-I$ and $HO-C(CH_3)_3$

(d) $H_3C-CH_2-CH_2-OH$ and $HO-C(CH_3)_3$

(Odisha NEET 2019)

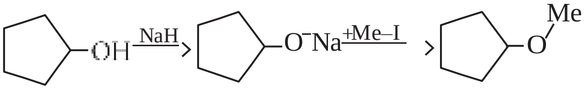
49. The heating of phenyl methyl ether with HI produces

(a) iodobenzene (b) phenol

(c) benzene (d) ethyl chloride.

(NEET 2017)

50. The reaction



can be classified as

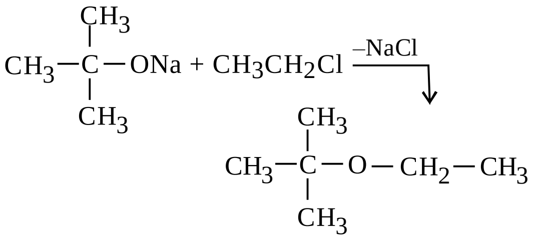
(a) dehydration reaction

(b) Williamson alcohol synthesis reaction

(c) Williamson ether synthesis reaction

(d) alcohol formation reaction. *(NEET-I 2016)*

51. The reaction,



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-ONa + CH_3CH_2Cl \xrightarrow{-NaCl} CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-CH_2-CH_3$$

is called

(a) Etard reaction

(b) Gattermann-Koch reaction

(c) Williamson synthesis

(d) Williamson continuous etherification process.

(2015, Cancelled)

52. Among the following sets of reactants which one produces anisole?

(a) CH_3CHO ; *RMgX*

(b) C_6H_5OH ; NaOH ; CH_3I

(c) C_6H_5OH ; neutral $FeCl_3$

(d) $C_6H_5CH_3$; CH_3COCl ; $AlCl_3$ *(2014)*

53. Identify *Z* in the sequence of reactions :

$$CH_3CH_2CH=CH_2 \xrightarrow{HBr/H_2O_2} Y \xrightarrow{C_2H_5ONa} Z$$

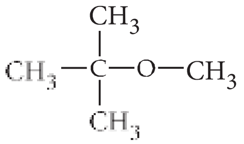
(a) $CH_3-(CH_2)_3-O-CH_2CH_3$

(b) $(CH_3)_2CH-O-CH_2CH_3$

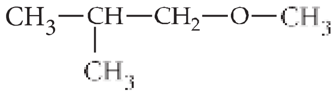
(c) $CH_3(CH_2)_4-O-CH_3$

(d) $CH_3CH_2-CH(CH_3)-O-CH_2CH_3$ *(2014)*

54. Among the following ethers, which one will produce methyl alcohol on treatment with hot concentrated HI?

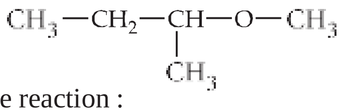
(a) 

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-O-CH_3$

(b) 

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-O-CH_3$

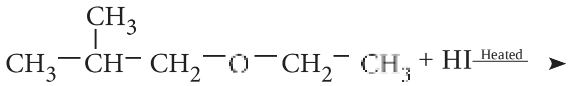
(c) $CH_3-CH_2-CH_2-O-CH_3$

(d) 

$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-O-CH_3$

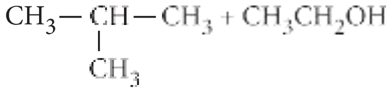
(NEET 2013)

55. In the reaction :

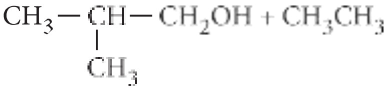


$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-O-CH_2-CH_3 + HI \xrightarrow{\text{Heated}}$

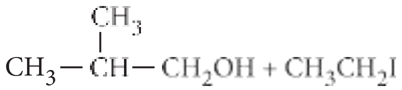
which of the following compounds will be formed?

(a) 

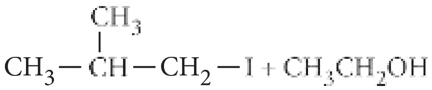
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3 + CH_3CH_2OH$

(b) 

$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2OH + CH_3CH_3$

(c) 

$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2OH + CH_3CH_2I$

(d) 

$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-I + CH_3CH_2OH$ *(2007)*

56. The major organic product in the reaction is

$CH_3-O-CH(CH_3)_2 + HI \longrightarrow$ products

(a) $CH_3I + (CH_3)_2CHOH$

(b) $CH_3OH + (CH_3)_2CHI$

(c) $ICH_2OCH(CH_3)_2$

(d) 

$\underset{\underset{I}{|}}{C}H_2OC(CH_3)_2$ *(2006)*

57. Ethyl chloride is converted into diethyl ether by

(a) Perkins reaction (b) Grignard reaction

(c) Wurtz synthesis

(d) Williamson's synthesis. *(1999)*

58. Which one of the following compounds is resistant to nucleophilic attack by hydroxyl ions?

(a) Diethyl ether (b) Acetonitrile

(c) Acetamide (d) Methyl acetate *(1998)*

59. The compound which does not react with sodium is
(a) CH_3COOH (b) $CH_3CHOHCH_3$
(c) C_2H_5OH (d) CH_3OCH_3
(1994)

60. Which one is formed when sodium phenoxide is heated with ethyl iodide?
(a) Phenetole (b) Ethyl phenyl alcohol
(c) Phenol (d) None of these *(1988)*

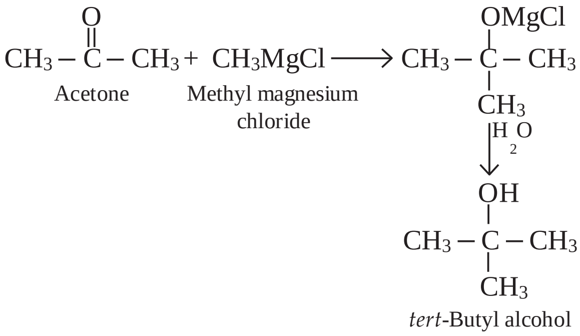
ANSWER KEY

1.	(a)	**2.**	(c)	**3.**	(c)	**4.**	(c)	**5.**	(d)	**6.**	(c)	**7.**	(d)	**8.**	(c)	**9.**	(c)	**10.**	(d)
11.	(c)	**12.**	(b)	**13.**	(d)	**14.**	(b)	**15.**	(a)	**16.**	(b)	**17.**	(a)	**18.**	(a)	**19.**	(c)	**20.**	(c)
21.	(b)	**22.**	(a)	**23.**	(c)	**24.**	(c)	**25.**	(c)	**26.**	(b)	**27.**	(c)	**28.**	(b)	**29.**	(a)	**30.**	(a)
31.	(d)	**32.**	(a)	**33.**	(a)	**34.**	(d)	**35.**	(b)	**36.**	(a)	**37.**	(b)	**38.**	(b)	**39.**	(d)	**40.**	(d)
41.	(c)	**42.**	(c)	**43.**	(b)	**44.**	(a)	**45.**	(d)	**46.**	(a)	**47.**	(a)	**48.**	(a)	**49.**	(b)	**50.**	(c)
51.	(c)	**52.**	(b)	**53.**	(a)	**54.**	(a)	**55.**	(c)	**56.**	(a)	**57.**	(d)	**58.**	(a)	**59.**	(d)	**60.**	(a)

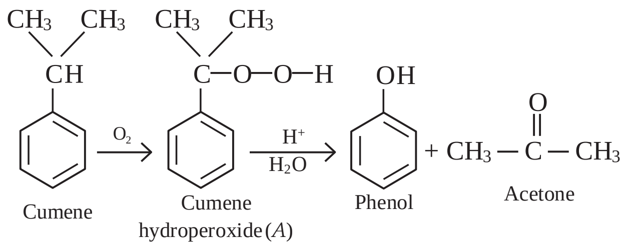
Hints & Explanations

1. (a) : All alcohols follow the general formula $C_nH_{2n+2}O$.
$CH_3OH\ [CH_{2+2}O]$; $C_2H_5OH[C_2H_{(2\times2)+2}O]$
$n = 1$, $n = 2$

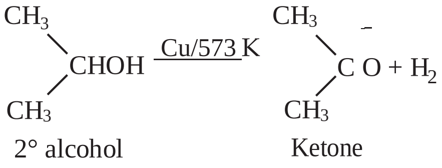
2. (c) :



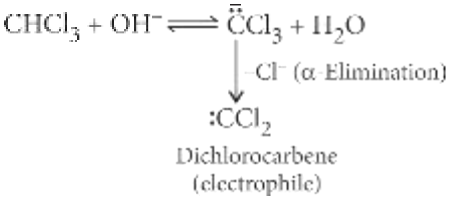
3. (c) :



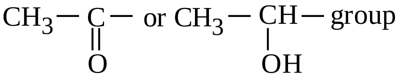
4. (c) :



5. (d) : It is Reimer–Tiemann reaction. The electrophile formed is dichlorocarbene (:CCl_2) which is formed according to the following mechanism :

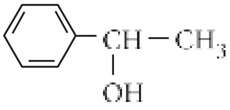


6. (c) : As the compound is giving yellow precipitate with NaOI that shows it is undergoing haloform reaction. Haloform reaction is shown by the compounds having

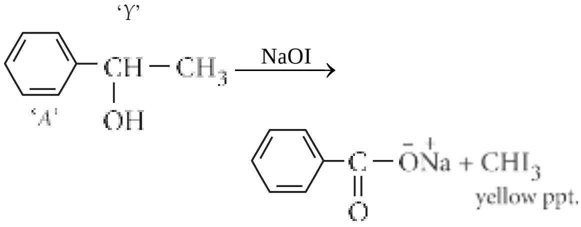


$CH_3-\underset{\underset{O}{\|}}{C}-$ or $CH_3-\underset{\underset{OH}{|}}{CH}-$ group

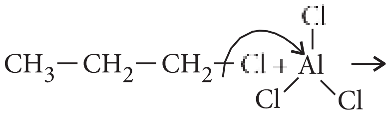
Hence, the compound *A* is

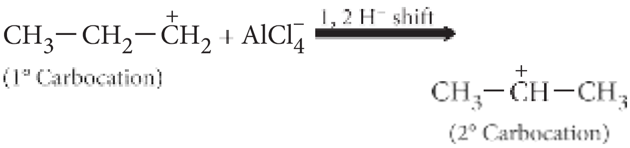


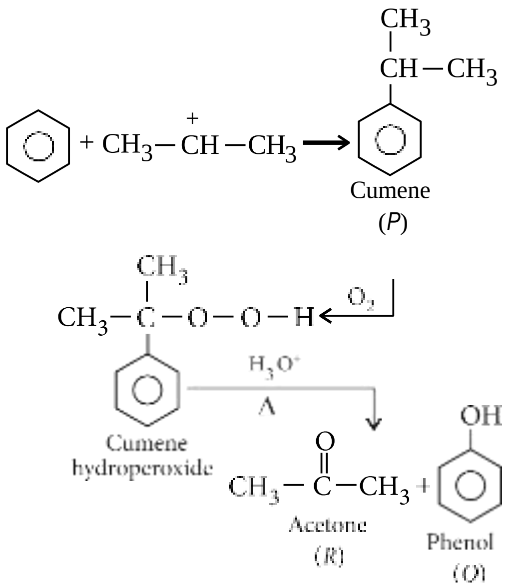
$2NaOH + I_2 \longrightarrow NaOI + NaI + H_2$



7. (d) :

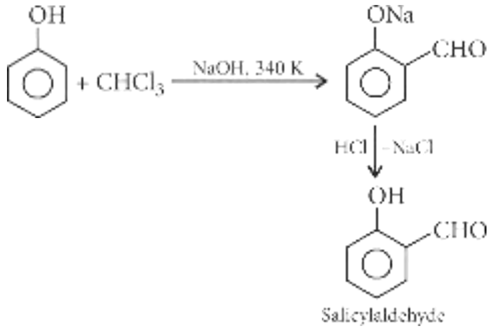






8. (c) : Electron withdrawing groups increase the acidity while electron donating groups decrease the acidity of phenol.

9. (c) : This is Reimer–Tiemann reaction.



10. (d) : 1° and 2° alcohols react with HCl in presence of anhydrous $ZnCl_2$ as catalyst while in case of 3° alcohols $ZnCl_2$ is not required.

11. (c) : The reaction is as follows :

Acid + $NaHCO_3 \rightarrow$ Sodium salt of acid + H_2CO_3
(soluble)

Among all the given compounds, *o*-nitrophenol is weaker acid than HCO_3^-. Hence, it does not react with $NaHCO_3$.

12. (b) : The iodoform test is positive for alcohols with formula $R - CHOH - CH_3$. Among $C_6H_{14}O$ isomers, the ones with positive iodoform test are:

I. $CH_3 - CH_2 - CH_2 - CH_2 - CHOH - CH_3$
2-Hexanol

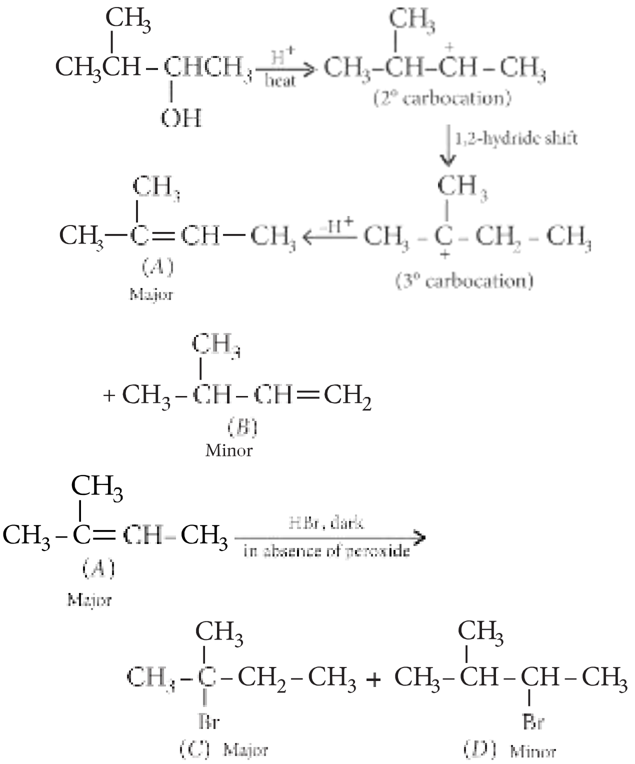
II. $CH_3 - CH_2 - CH(CH_3) - CHOH - CH_3$
3- Methyl-2-pentanol

III. $(CH_3)_2CH - CH_2 - CHOH - CH_3$
4- Methyl-2-pentanol

IV. $(CH_3)_3C - CHOH - CH_3$
3, 3- Dimethyl-2-butanol

13. (d) : $CH_3Br \xrightarrow{KCN} \underset{(A)}{CH_3CN} \xrightarrow{H_3O^+} \underset{(B)}{CH_3COOH} \xrightarrow[ether]{LiAlH_4} \underset{(C)}{CH_3CH_2OH}$

14. (b) :



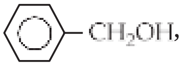
15. (a) : Since, phenols and carboxylic acids are more acidic than aliphatic alcohols, we find that cyclohexanol (I) is least acidic. Out of the two given phenols, III is more acidic than IV. This is because of the presence of three highly electron withdrawing $-NO_2$ groups on the benzene ring which makes the O—H bond extremely polarized. This facilitates the release of H as H^+. Thus, III > IV.

In acetic acid, the electron withdrawing $-\overset{\overset{O}{\|}}{C}-$ in the $-COOH$ group polarises the O—H bond and increases the acidic strength. Acetic acid is therefore more acidic than phenol or cyclohexanol.

∴ The order of acidic character is III > II > IV > I.

16. (b) : Phenol is most acidic of all the given compounds.

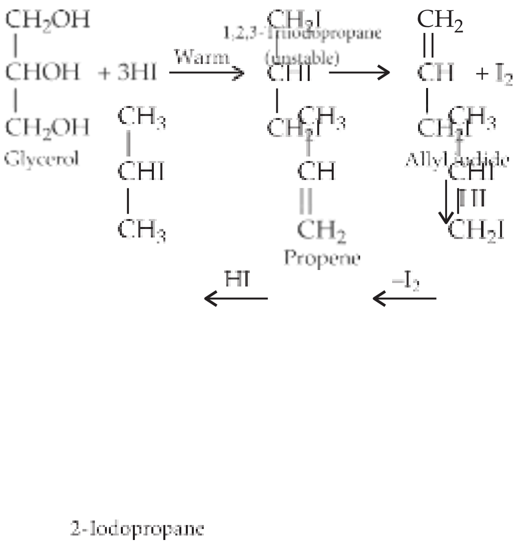
In phenol, the electron withdrawing phenyl ring polarizes the O—H bond, thereby facilitating the release of H as H^+ and hence, phenol is most acidic.

In  the electron withdrawing effect of phenyl ring is somewhat diminished by the $-CH_2$ group and it is therefore, less acidic than phenol. In (c) and (d), $-OH$ group is attached to alkyl groups which, due to their +*I* effect reduce the polarity of $-OH$ bond and so, the acidic strength is low.

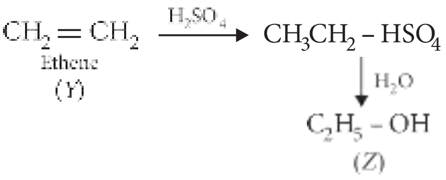
17. (a) : In phenols, the presence of electron releasing groups decrease the acidity, whereas presence of electron withdrawing groups increase the acidity, compared to phenol. Among the *meta* and *para*-nitrophenols, the later is more acidic as the presence of $-NO_2$ group at *para* position stabilises the phenoxide ion to a greater extent than when it is present at *meta* position. Thus, correct order of acidity is :

para-nitrophenol > *meta*-nitrophenol > phenol
(iv) (iii) (i)
> methyl phenol
(ii)

18. (a) :

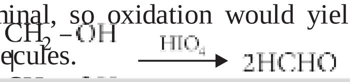


19. (c) : $\underset{\text{Ethanol}}{C_2H_5OH} \xrightarrow{PBr_3} \underset{(X)}{C_2H_5Br} \xrightarrow[\text{halogenation}]{\text{alc.KOH dehydro-}}$



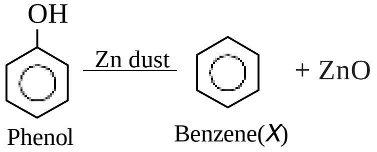
$$\underset{\substack{\text{Ethene}\\(Y)}}{CH_2=CH_2} \xrightarrow{H_2SO_4} CH_3CH_2-HSO_4 \xrightarrow{H_2O} \underset{(Z)}{C_2H_5-OH}$$

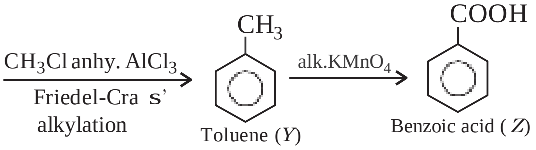
20. (c) : When 1,2-diol like ethylene glycol is treated with HIO_4, each alcoholic group is oxidised to a carbonyl group by HIO_4. Since in glycol, both the –OH groups are terminal, so oxidation would yield two formaldehyde molecules.



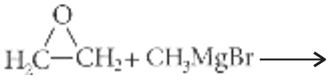
$$CH_2-OH \xrightarrow{HIO_4} 2HCHO$$

21. (b) :



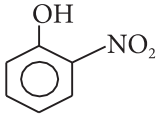


22. (a) :

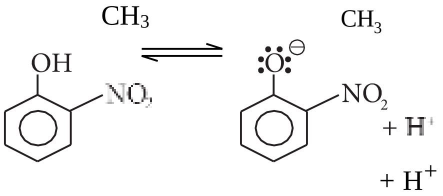


$$CH_3CH_2CH_2OMgBr \xrightarrow{H^+} \underset{\text{primary alcohol}}{CH_3CH_2CH_2OH}$$

23. (c) : Phenols are much more acidic than alcohols, due to the stabilisation of phenoxide ion by resonance.



$-NO_2$ is the electron withdrawing group and helps in stabilizing the negative charge on the oxygen hence equilibrium shifts in ~~forward~~ direction and more H^+ ions remove easily. Hence, it is most acidic.



$-CH_3$ is the electron donating group. Hence, electron density increases on the oxygen and destabilizes the product. Thus, equilibrium shifts in backward direction.

24. (c) : Formation of a yellow precipitate on heating a compound with an alkaline solution of iodine is known as iodoform reaction. Methyl alcohol does not respond to this test. Iodoform test is exhibited by ethyl alcohol, acetaldehyde, acetone, methyl ketones and those alcohols which possess $CH_3CH(OH)-$ group.

25. (c) : *n*-Propyl alcohol on oxidation with potassium dichromate gives an aldehyde which on further oxidation gives an acid. Both aldehyde and acid contain the same number of C atoms as the original alcohol.

i.e.,

$CH_3CH_2CH_2OH$

25°C

2 2 7 2 4

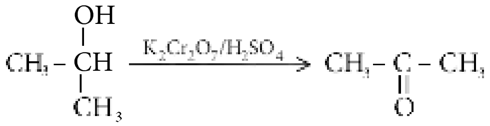
CH CH CHO

$\xrightarrow[\text{K Cr O /H SO}]{}$

3 2

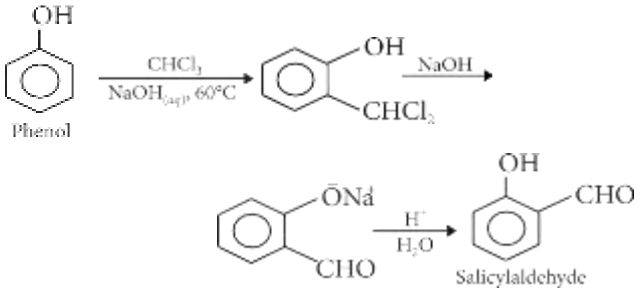
$\xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3CH_2COOH$

Isopropyl alcohol on oxidation gives a ketone with the same number of C atoms as the original alcohol.



$$CH_3-\underset{CH_3}{\overset{OH}{CH}} \xrightarrow{K_2Cr_2O_7/H_2SO_4} CH_3-\underset{O}{\underset{\|}{C}}-CH_3$$

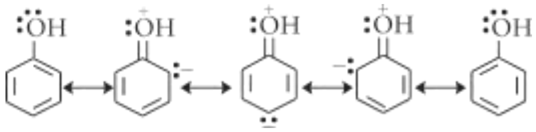
26. (b) : This reaction is called Reimer—Tiemann reaction.



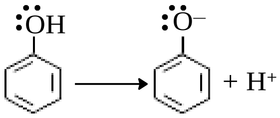
27. (c) : $C_2H_5OH + 4I_2 + NaOH \longrightarrow CHI_3 + NaI + HCOONa + H_2O$

Iodoform is a pale yellow solid which crystallises in hexagonal plates.

28. (b) : Phenol exists as a resonance hybrid of the following structures.

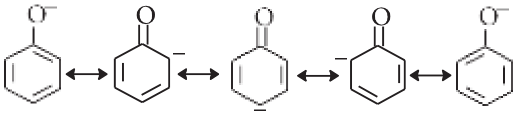


Thus, due to resonance the oxygen atom of the —OH group acquires a positive charge and hence attracts electron pair of the O – H bond leading to the release of hydrogen atom as proton.



Phenoxide ion

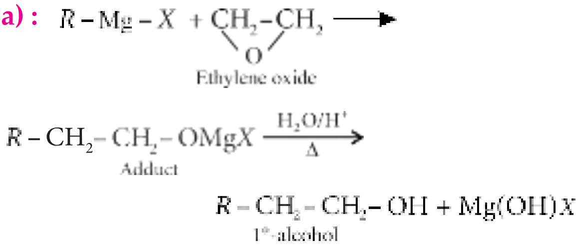
Once the phenoxide ion is formed it stabilises itself by resonance which is more stable than the parent phenol as there is no charge separation.



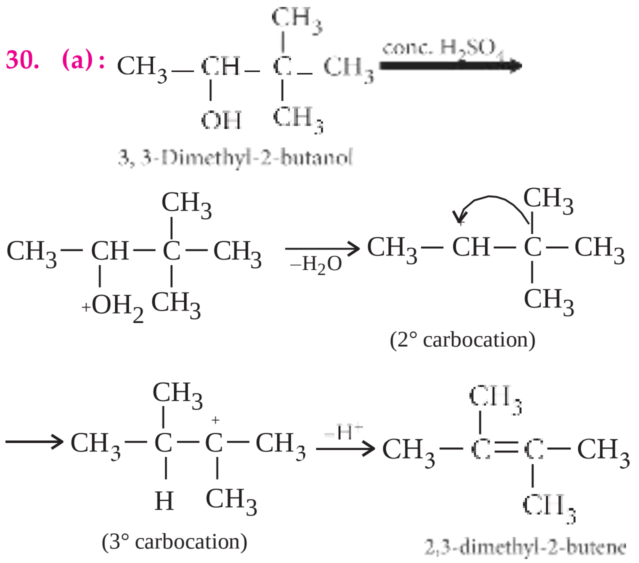
Effect of substituent : Presence of electron withdrawing groups (— NO_2, — X, — CN) increase the acidity of phenols while the presence of electron releasing groups (— NH_2, — CH_3)decrease the acidity of phenols. This explains the following order of acidity:

p-nitrophenol > phenol > *p*-cresol.

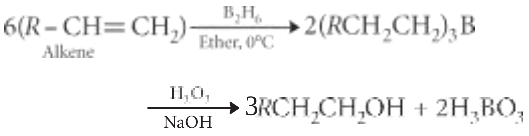
29. (a) :



30. (a) :



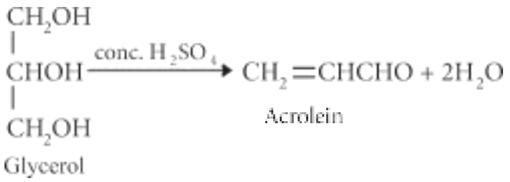
31. (d) :



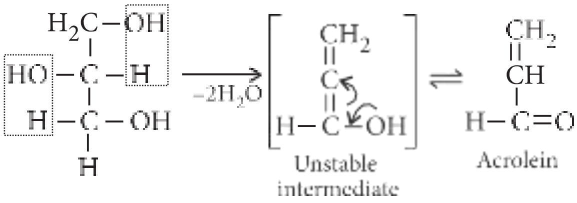
$$6(R-CH=CH_2) \xrightarrow[\text{Ether, 0°C}]{B_2H_6} 2(RCH_2CH_2)_3B \xrightarrow[NaOH]{H_2O_2} 3RCH_2CH_2OH + 2H_3BO_3$$

Alkene

32. (a) :



Mechanism:



33. (a)

34. (d) : — OCH_3, — CH_3 are electron donating groups and decrease the acidic character of phenols. — NO_2, is electron withdrawing group and tends to increase the acidic character. Electron donating effect of — OCH_3 group (+*R* effect) is more than that of — CH_3 group (+*I* effect). Thus, the order is

p-methoxyphenol < *p*-methylphenol < *p*-nitrophenol.

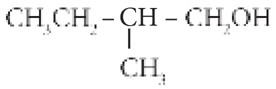
35. (b) : 2° alcohols on oxidation give ketones, 1° alcohols form aldehydes.

36. (a) : Primary alcohol undergoes catalytic dehydrogenation to give aldehyde.

37. (b) : 4-isomers are possible for $C_5H_{11}OH$.

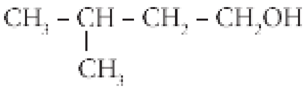
(i) $CH_3CH_2CH_2CH_2CH_2OH$

(ii)



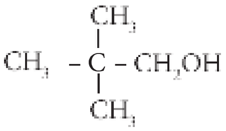
$CH_3CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2OH$

(iii)



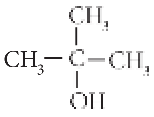
$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2OH$

(iv)



$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2OH$

38. (b) :



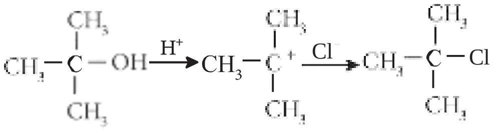
$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$

(methylpropan-2-ol)

, generates 3° carbocation which is very stable intermediate, thus it will react more rapidly with HBr.

39. (d) : Phenol on reaction with excess bromine water gives 2,4,6-tribromophenol.

40. (d) : 2-Methylpropan-2-ol reacts rapidly with Lucas reagent at room temperature.



2-Methyl-2-propanol

41. (c) : –OH group being electron donor increases the electron density in phenol. Thus, the electron density in phenol is higher than that of toluene, benzene and chlorobenzene.

42. (c) :

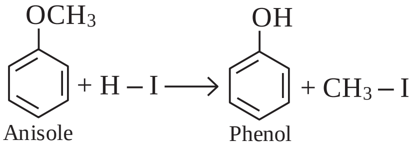
$$CH_3-CH=CH_2 \xrightarrow[\text{Hydroboration}]{BH_3,\ THF} \underset{\text{Tripropylborane}}{(CH_3CH_2CH_2)_3B} \xrightarrow[OH^-]{H_2O_2} \underset{\text{Propan-1-ol}}{3CH_3CH_2CH_2OH}$$

43. (b) : Treatment of phenol with $CHCl_3$ and aqueous hydroxide introduces — CHO group, onto the aromatic ring generally *ortho* to the — OH group. This reaction is known as Reimer—Tiemann reaction.

44. (a)

45. (d) : $CO + 2H_2 \xrightarrow{ZnO\text{-}Cr_2O_3} CH_3OH$

46. (a) :



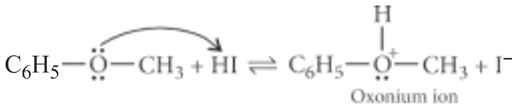
47. (a) : In $Ph-\ddot{O}-H$, the lone pair of oxygen is in conjugation with phenyl group so, it is least basic among the given compounds and is most difficult to protonate.

48. (a) : Ethers are readily attacked by HI to give an alkyl halide and alcohol. But when heated with excess of HI, the product alcohol first formed reacts further with HI to form the corresponding alkyl iodide.

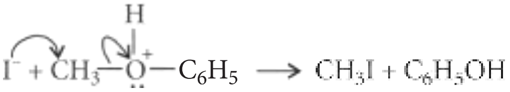
$$R\text{–}O\text{–}R' + \underset{\text{(excess)}}{2HI} \xrightarrow{\text{Heat}} RI + R'I + H_2O$$

49. (b) : In case of phenyl methyl ether, methyl phenyl oxonium ion $\left(C_6H_5-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_3\right)$ is formed by protonation of ether. The $O-CH_3$ bond is weaker than $O-C_6H_5$ bond as $O-C_6H_5$ has partial double bond character. Therefore, the attack by I^- ion breaks $O-CH_3$ bond to form CH_3I.

Step I :



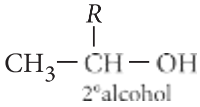
Step II :



50. (c) : Williamson's ether synthesis reaction involves the treatment of sodium alkoxide with a suitable alkyl halide to form an ether.

51. (c) : Williamson synthesis is the best method for the preparation of ethers.

52. (b) : (a) $CH_3CHO + RMgX \xrightarrow{\text{ether}}$



$CH_3-\overset{\overset{R}{|}}{CH}-OH$

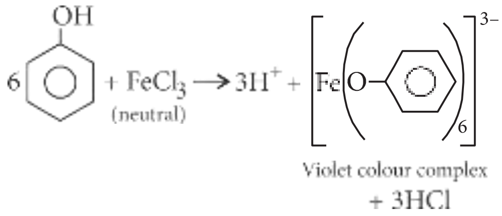
2°alcohol

(b) $C_6H_5OH + NaOH \xrightarrow[-H_2O]{} \underset{\text{Sodium phenoxide}}{C_6H_5ONa}$

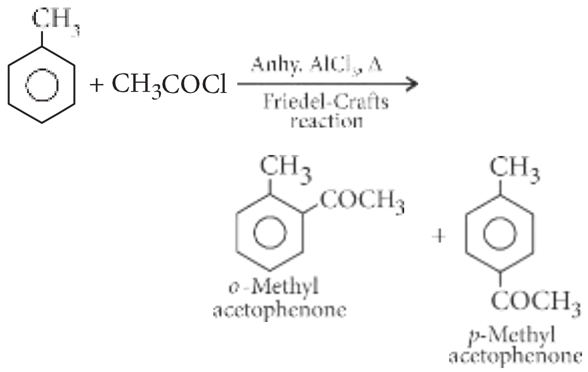
$\underset{\text{Methyl phenyl ether (Anisole)}}{C_6H_5OCH_3} + NaI \xleftarrow[\Delta]{CH_3I}$

(Williamson's synthesis)

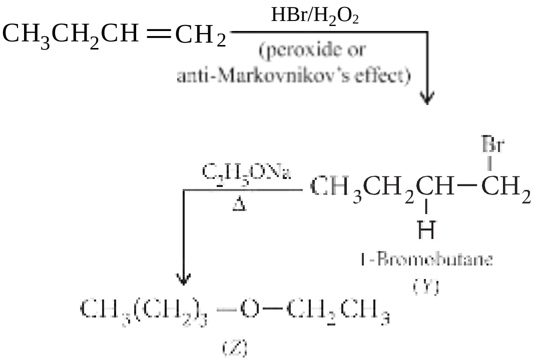
(c)



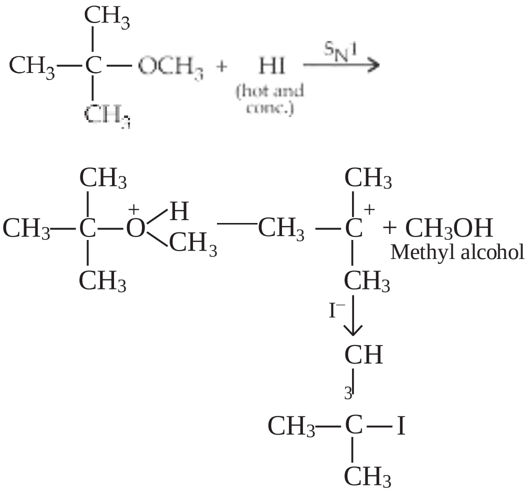
(d)



53. (a) :



54. (a) :



55. (c) : The alkyl iodide produced depends on the nature of the alkyl groups. If one group is Me and the other a primary or secondary alkyl group, it is methyl iodide which is produced. This can be explained on the assumption that the mechanism is S_N2, and because of the steric effect of the larger group, I^- attacks the smaller methyl group.

When the substrate is a methyl *t*-alkyl ether, the products are *t*-*R*I and MeOH. This can be explained by S_N1 mechanism, the carbonium ion produced being the *t*-alkyl since tertiary carbonium ion is more stable than a primary or secondary carbonium ion.

56. (a) : With cold HI, a mixture of alkyl iodide and alcohol is formed. In the case of mixed ethers, the halogen atom attaches to a smaller and less complex alkyl group.

$CH_3OCH(CH_3)_2 + HI \rightarrow CH_3I + (CH_3)_2CHOH$

57. (d) : $C_2H_5-Cl + Na-O-C_2H_5 \longrightarrow C_2H_5-O-C_2H_5 + NaCl$

The above reaction is called as Williamson's synthesis.

58. (a) : Diethyl ether is a saturated compound, so it is resistant to nucleophilic attack by a hydroxyl ion (OH^-). Other compounds have unsaturation and the unsaturated 'C' atom bears partial +ve charge, therefore they undergo easy nucleophilic attack by OH^- ion.

59. (d) : Ethers are very inert. The chemical inertness of ethers is due to absence of active group in their molecules. Since CH_3-O-CH_3 is inert and it does not contain active group, therefore it does not react with sodium.

60. (a) : Phenetole is formed when sodium phenoxide is heated with ethyl iodide.

$$C_6H_5ONa + C_2H_5I \xrightarrow{\Delta} \underset{\text{Phenetole}}{C_6H_5OC_2H_5}$$