

## Alcohols, Phenols and Ethers

1. Phenol on treatment with  $CO_2$  in the presence of NaOH followed by acidification produces compound X as the major product. X on treatment with  $(CH_3CO)_2O$  in the presence of catalytic amount of  $H_2SO_4$  produces



2. Phenol reacts with methyl chloroformate in the presence of NaOH to form product A. A reacts with  $Br_2$  to form product B. A and B are respectively



3. The major product formed in the following reaction is



(2018)

4. The major product of the following reaction is



5. On treatment of the following compound with a strong acid, the most susceptible site for bond cleavage is



**6.** The total number of optically active compounds formed in the following reaction is



(Online 2018)

(Online 2018)



8. In the following reaction sequence :  $I \xrightarrow{\text{KOH}(\text{aq.})} II \xrightarrow{\text{(i) CH}_3\text{MgBr}} III$   $\xrightarrow{\text{(C}_3\text{H}_6\text{Cl}_2)} III \xrightarrow{\text{(i) CH}_3\text{MgBr}} III$   $\xrightarrow{\text{Anhy. ZnCl}_2 + \text{Conc. HCl}} \text{gives turbidity immediately}$ 

The compound I is

C1

9. The major product of the following reaction is OH



10. The product of the reaction given below is



- 11. The most suitable reagent for the conversion of *R*—CH<sub>2</sub>—OH → *R*—CHO is

  (a) PCC (Pyridinium chlorochromate)
  (b) KMnO<sub>4</sub>
  (c) K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>
  (d) CrO<sub>3</sub>
- 12. Arrange the following compounds in order of decreasing acidity.



- 13. Ortho-nitrophenol is less soluble in water than p- and m-nitrophenols because
  - (a) o-nitrophenol shows intramolecular H-bonding
  - (b) o-nitrophenol shows intermolecular H-bonding
  - (c) melting point of *o*-nitrophenol is lower than those of *m* and *p*-isomers
  - (d) *o*-nitrophenol is more volatile in steam than those of *m* and *p*-isomers. (2012)
- 14. Sodium ethoxide has reacted with ethanoyl chloride. The compound that is produced in this reaction is
  - (a) diethyl ether (b) 2-butanone
  - (c) ethyl chloride (d) ethyl ethanoate. (2011)
- **15.** Phenol is heated with a solution of mixture of KBr and KBrO<sub>3</sub>. The major product obtained in the above reaction is
  - (a) 2-bromophenol (b) 3-bromophenol
  - (c) 4-bromophenol (d) 2, 4, 6-tribromophenol.

(2011)

16. The main product of the following reaction is  $C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{Conc.H_2SO_4}$ 



17. From amongst the following alcohols the one that would react fastest with conc.HCl and anhydrous ZnCl<sub>2</sub>, is

- (a) 1-Butanol (b) 2-Butanol (c) 2-Methylpropan-2-ol (d) 2-Methylpropanol , CH₂COOH (2010)18. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is (a) benzoic acid (b) salicylaldehyde (c) salicylic acid (d) phthalic acid. (2009)pent-3-en-2-one is 19. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives (a) nitrobenzene (b) 2, 4, 6-trinitrobenzene (d) pyridinium chlorochromate. (c) o-nitrophenol (d) *p*-nitrophenol. (2008)20. In the following sequence of reactions, very easily?  $CH_{3}CH_{2}OH \xrightarrow{P+I_{2}} A \xrightarrow{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_{2}O} D$ (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH the compound D is (a) propanal (b) butanal (c) *n*-butyl alcohol (d) *n*-propyl alcohol. (2007)(d) CH<sub>3</sub>CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>OH 21. HBr reacts with  $CH_2 = CH - OCH_2$  under anhydrous conditions at room temperature to give (a) CH<sub>3</sub>CHO and CH<sub>3</sub>Br (b) BrCH<sub>2</sub>CHO and CH<sub>3</sub>OH **27.** The IUPAC name of the compound HC (c)  $BrCH_2 - CH_2 - OCH_3$ (2006)(d)  $H_3C - CHBr - OCH_3$ .  $\bigcirc OH \\ + CHCl_3 + NaOH \longrightarrow \bigcirc ONa^+ \\ CHO$ (c) 3,3-dimethyl-1-cyclohexanol (d) 1,1-dimethyl-3-cyclohexanol. 22. The electrophile involved in the above reaction is (a) dichloromethyl cation  $(CHCl_2)$ (a) Heat of vaporisation (b) dichlorocarbene (: CCl<sub>2</sub>) (c) Boiling points (c) trichloromethyl anion  $(\breve{C}Cl_3)$ (d) formyl cation  $(\stackrel{\oplus}{CHO})$ (2006)23. Phenyl magnesium bromide reacts with methanol to give (a) a mixture of anisole and Mg(OH)Br (a) protonation of alcohol molecule (b) a mixture of benzene and Mg(OMe)Br (b) formation of carbocation (c) a mixture of toluene and Mg(OH)Br (c) elimination of water (2006)(d) a mixture of phenol and Mg(Me)Br. (d) formation of an ester. 24. *p*-cresol reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form the compound B. The latter on acidic hydrolysis gives chiral (a) dipolar character of ethers carboxylic acid. The structure of the carboxylic acid is (b) CH(OH)COOH
  - H,COOH (2005)
  - 25. The best reagent to convert pent-3-en-2-ol into
    - (a) acidic permanganate (b) acidic dichromate
    - (c) chromic anhydride in glacial acetic acid
    - (2005)
  - 26. Among the following compounds which can be dehydrated

(b) 
$$CH_3CH_2CH_2CHCH_3$$
 (c)  $CH_3CH_2CH_2CH_2CH_3$   
OH

- (2004)
- - (a) 3,3-dimethyl-1-hydroxy cyclohexane
  - (b) 1,1-dimethyl-3-hydroxy cyclohexane

  - (2004)
- 28. For which of the following parameters the structural isomers C<sub>2</sub>H<sub>5</sub>OH and CH<sub>2</sub>OCH<sub>2</sub> would be expected to have the same values? (Assume ideal behaviour)
  - (b) Vapour pressure at the same temperature
  - (d) Gaseous densities at the same temperature and pressure (2004)
- 29. During dehydration of alcohols to alkenes by heating with concentrated H<sub>2</sub>SO<sub>4</sub> the initiation step is
  - - (2003)
- 30. An ether is more volatile than an alcohol having the same molecular formula. This is due to
  - (b) alcohols having resonance structures
  - (c) inter-molecular hydrogen bonding in ethers
  - (d) inter-molecular hydrogen bonding in alcohols.

(2003)

ANSWER KEY											
1.	(a)	<b>2.</b> (c)	<b>3.</b> (d)	<b>4.</b> (c)	<b>5.</b> (b)	<b>6.</b> (b)	7. (d) 8. (b)	<b>9.</b> (a)	10. (b)	<b>11.</b> (a)	<b>12.</b> (d)
13.	(a)	14. (d)	15. (d)	<b>16.</b> (b)	17. (c)	18. (c)	<b>19.</b> (None)	<b>20.</b> (d)	<b>21.</b> (d)	<b>22.</b> (b)	<b>23.</b> (b)
24.	(b)	<b>25.</b> (d)	<b>26.</b> (c)	<b>27.</b> (c)	<b>28.</b> (d)	<b>29.</b> (a)	<b>30.</b> (d)				







ĊΗ,

or

MeO





There is one chiral carbon in the product. Thus, no. of optically active compounds =  $(2)^1 = 2$ 









5. (b)

MeO



**11.** (a) : PCC is highly effective in oxidizing  $1^{\circ}$  alcohols to aldehydes.

12. (d): Electron donating groups (—CH<sub>3</sub> and —OCH<sub>3</sub>) decrease while electron withdrawing groups (—NO<sub>2</sub> and —Cl) increase the acidity. Since —OCH<sub>3</sub> is a stronger electron donating group than —CH<sub>3</sub> and —NO<sub>2</sub> is stronger electron withdrawing group than —Cl, therefore order of decreasing acidity is III > I > II > IV.

**13.** (a) : *o*-Nitrophenol is stable due to intramolecular hydrogen bonding.



It is difficult to break the H-bonding when dissolved in water thus less soluble.



15. (d) :  $\text{KBr}_{(aq)} + \text{KBrO}_{3(aq)} \longrightarrow \text{Br}_{2(aq)}$ This bromine reacts with phenol gives 2,4,6-tribromophenol.





The preferential formation of this compound is due to conjugation in the compound.

**17.** (c) : The reagent, conc.HCl and anhydrous  $ZnCl_2$  is Lucas reagent, which is used to distinguish between 1°, 2° and 3° alcohols. 3° alcohol + Lucas reagent  $\sim$  Immediate turbidity

3° alcohol + Lucas reagent —> Immediate turbidity. 2° alcohol + Lucas reagent —> Turbidity after 5 mins. 1° alcohol + Lucas reagent —> No reaction.

Thus, the required alcohol is 2-methylpropan-2-ol, i.e.,



18. (c) : The reaction of phenol with NaOH and  $CO_2$  is known as Kolbe-Schmidt or Kolbe's reaction. The product formed is salicylic acid.



**19.** : (None of the option is correct.)



**20.** (d) : CH<sub>3</sub>CH<sub>2</sub>OH 
$$\xrightarrow{P}$$
 CH<sub>3</sub>CH<sub>2</sub>I  $\xrightarrow{Mg}$  CH<sub>3</sub>CH<sub>2</sub>MgI  
(A) (B) HCHO  
H H CHO  
H - C - OH  $\xleftarrow{H_2O}$  H - C - OMgI  
CH<sub>2</sub>CH<sub>3</sub> CH<sub>2</sub>CH<sub>3</sub>  
*n*-propyl (C)  
alcohol  
(D)

**21.** (d) : Methyl vinyl ether is a very reactive gas. It is hydrolysed rapidly by dilute acids at room temperature to give methanol and aldehyde.

However, under anhydrous conditions at room temperature, it undergoes many addition reactions at the double bond.

$$H_{2}C = CH - OCH_{3} \xrightarrow{H^{+}} H_{2}C - \overset{\oplus}{CH} - OCH_{3}$$

$$H \xrightarrow{Br^{-}} H_{3}C - \overset{H}{CH} - OCH_{3}$$

22. (b):



The electrophile is dichlorocarbene, :  $CCl_2$  generated from chloroform by the action of a base. OH<sup>-</sup> + CHCl<sub>3</sub>  $\rightleftharpoons$  HOH + :  $CCl_3^- \rightarrow Cl^-$  + :  $CCl_2$ 

**23.** (b) : CH<sub>3</sub>OH + C<sub>6</sub>H<sub>5</sub>MgBr  $\rightarrow$  C<sub>6</sub>H<sub>6</sub> + Mg(OCH<sub>3</sub>)Br



**25.** (d) : Pyridinium chlorochromate oxidises an alcoholic group selectively in the presence of carbon-carbon double bond.

**26. (c) :** The ease of dehydration of alcohols is tertiary > secondary > primary according to the order of stability of the carbocations.

$$CH_{3} - CH_{2} - CH_{3} - CH_{2} - CH_{3} \xrightarrow{H^{+}} CH_{3} - CH_{2} - CH_{2} - CH_{2} - CH_{3}$$

The more stable carbocation is generated thus more easily it will be dehydrated.

27. (c): 
$$HO$$
  $\rightarrow$  3,3-dimethyl-1-cyclohexanol Malaeular unight

**28.** (d) : Vapour density  $=\frac{\text{Molecular weight}}{2}$ 

As both the compounds have same molecular weights, both will have the same vapour density. Hence, gaseous density of both ethanol and dimethyl ether would be same under identical conditions of temperature and pressure. The rest of these three properties; vapour pressure, boiling point and heat of vaporization will differ as ethanol has hydrogen bonding whereas ether does not.

**29.** (a) : Dehydration of alcohol to alkene in presence of concentrated  $H_2SO_4$  involves following steps :

Thus, the initiation step is protonation of alcohol. **30.** (d): The reason for the lesser volatility of alcohols than ethers is the intermolecular association of a large number of molecules due to hydrogen bonding as - OH group is highly polarised.

No such hydrogen bonding is present in ethers.

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