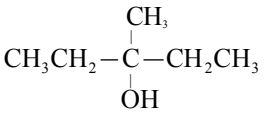
CHAPTER 25

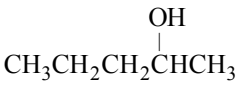
Alcohols, Phenols and Ethers

1. During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 the initiation step is **[2003]**

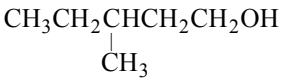
(a) formation of carbocation
(b) elimination of water
(c) formation of an ester
(d) protonation of alcohol molecule

2. Among the following compounds which can be dehydrated very easily is **[2004]**

(a) 

(b) 

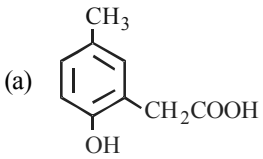
(c) $CH_3CH_2CH_2CH_2CH_2OH$

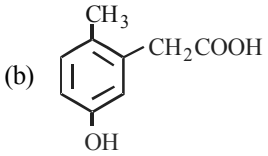
(d) 

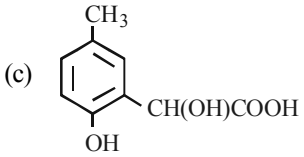
3. The best reagent to convert pent-3-en-2-ol into pent-3-en-2-one is **[2005]**

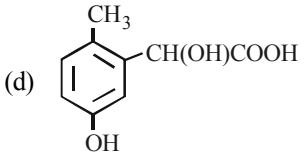
(a) Pyridinium chloro-chromate
(b) Chromic anhydride in glacial acetic acid
(c) acidic dichromate
(d) Acidic permanganate

4. *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 carboxylic acid. The structure of the carboxylic acid is **[2005]**

(a) 

(b) 

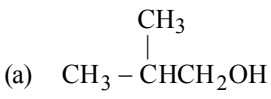
(c) 

(d) 

5. HBr reacts with $CH_2 = CH - OCH_3$ under anhydrous conditions at room temperature to give **[2006]**

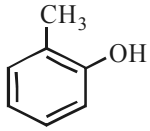
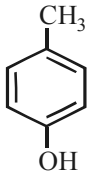
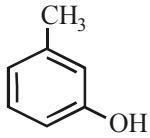
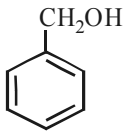
(a) $BrCH_2 - CH_2 - OCH_3$
(b) $H_3C - CHBr - OCH_3$
(c) CH_3CHO and CH_3Br
(d) $BrCH_2CHO$ and CH_3OH

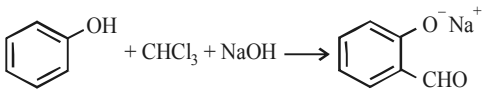
6. Among the following the one that gives positive iodoform test upon reaction with I_2 and NaOH is **[2006]**

(a) 

(b) $PhCHOHCH_3$
(c) $CH_3CH_2CH(OH)CH_2CH_3$
(d) $C_6H_5CH_2CH_2OH$

7. The structure of the compound that gives a tribromo derivative on treatment with bromine water is **[2006]**

(a) 
(b) 
(c) 
(d) 

8. 

The electrophile involved in the above reaction is **[2006]**

(a) trichloromethyl anion $(\overset{\ominus}{C}Cl_3)$
(b) formyl cation $(\overset{\oplus}{C}HO)$
(c) dichloromethyl cation $(\overset{\oplus}{C}HCl_2)$
(d) dichlorocarbene $(:CCl_2)$

9. In the following sequence of reactions,

$$CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow[ether]{Mg} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$$

the compound D is **[2007]**

(a) propanal (b) butanal
(c) *n*-butyl alcohol (d) *n*-propyl alcohol

10. Phenol, when it first reacts with concentrated sulphuric acid and then with concentrated nitric acid, gives **[2008]**

(a) 2, 4, 6-trinitrobenzene
(b) *o*-nitrophenol
(c) *p*-nitrophenol
(d) nitrobenzene

11. The major product obtained on interaction of phenol with sodium hydroxide and carbon dioxide is **[2009]**

(a) salicylaldehyde (b) salicylic acid
(c) phthalic acid (d) benzoic acid

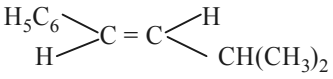
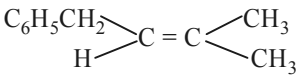
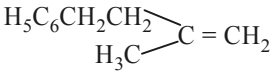
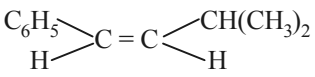
12. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is **[2010]**

(a) 2-Butanol
(b) 2- Methylpropan-2-ol
(c) 2-Methylpropanol
(d) 1- Butanol

13. The main product of the following reaction is

$$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{conc.H_2SO_4} ?$$

[2010]

(a) 
(b) 
(c) 
(d) 

14. Consider thiol anion $(RS^{\ominus})$ and alkoxy anion $(RO^{\ominus})$. Which of the following statements is correct ? **[2011RS]**

(a) $RS^{\ominus}$ is less basic but more nucleophilic than $RO^{\ominus}$
(b) $RS^{\ominus}$ is more basic and more nucleophilic than $RO^{\ominus}$
(c) $RS^{\ominus}$ is more basic but less nucleophilic than $RO^{\ominus}$
(d) $RS^{\ominus}$ is less basic and less nucleophilic than $RO^{\ominus}$

15. The correct order of acid strength of the following compounds : **[2011RS]**

(A) Phenol (B) *p*–Cresol
(C) *m*–Nitrophenol (D) *p*–Nitrophenol
(a) D > C > A > B (b) B > D > A > C
(c) A > B > D > C (d) C > B > A > D

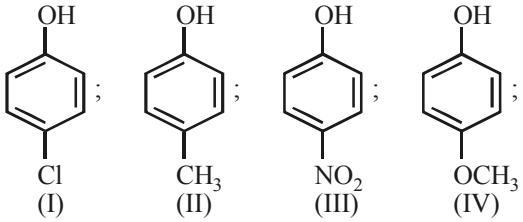
16. Consider the following reaction :

$C_2H_5OH + H_2SO_4 \longrightarrow$ Product

Among the following, which one cannot be formed as a product under any conditions ? **[2011RS]**

(a) Ethylene (b) Acetylene
(c) Diethyl ether (d) Ethyl-hydrogen sulphate

17. Arrange the following compounds in order of decreasing acidity : **[2013]**



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

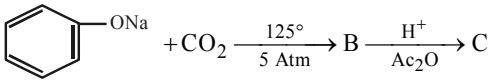
18. An unknown alochol is treated with the "Lucas reagent" to determine whether the alcohol is primary, secondary or tertiary. Which alcohol reacts fastest and by what mechanism : **[2013]**

(a) secondary alcohol by S_N1
(b) tertiary alcohol by S_N1
(c) secondary alcohol by S_N2
(d) tertiary alcohol by S_N2

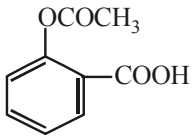
19. The most suitable reagent for the conversion of $R-CH_2-OH \rightarrow R-CHO$ is: **[2014]**

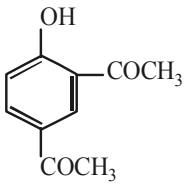
(a) $KMnO_4$
(b) $K_2Cr_2O_7$
(c) CrO_3
(d) PCC (Pyridinium Chlorochromate)

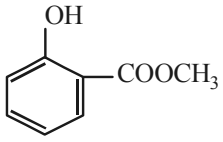
20. Sodium phenoxide when heated with CO_2 under pressure at 125°C yields a product which on acetylation produces C **[2014]**

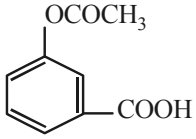


The major product C would be

(a) 

(b) 

(c) 

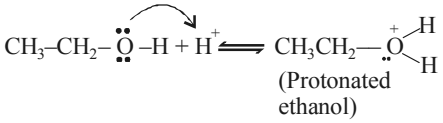
(d) 

Answer Key														
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
(d)	(a)	(a)	(c)	(b)	(b)	(c)	(d)	(d)	(b)	(b)	(b)	(a)	(a)	(a)
16	17	18	19	20										
(b)	(c)	(b)	(d)	(a)										

SOLUTIONS

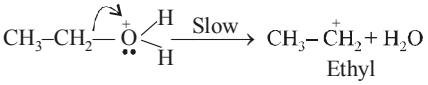
1. (d) The dehydration of alcohol to form alkene occurs in following three step. Step (1) is initiation step.

Step (1) Formation of protonated alcohol.



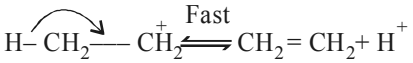
(Protonated ethanol)

Step (2) Formation of carbocation



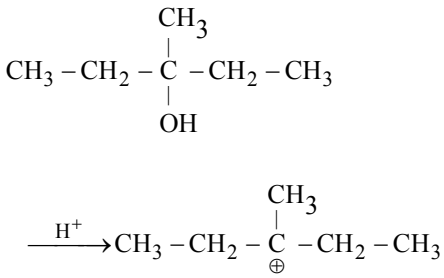
Ethyl carbocation

Step (3) Elimination of a proton to form ethene

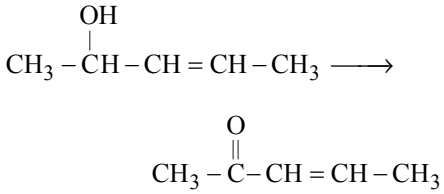


ethene

2. (a) 3-methyl pentan-3-ol will be dehydrated most readily since it produces tertiary carbonium ion as intermediate.

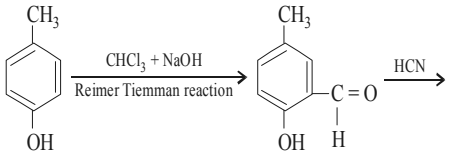


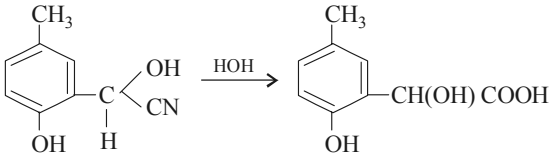
3. (a)



Pyridiminum chloro-chromate (PCC) is specific for the conversion.

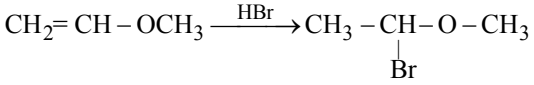
4. (c)





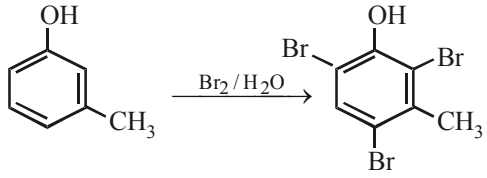
Cyanohydrin

5. (b) Methyl vinyl ether under anhydrous condition at room temperature undergoes addition reaction.

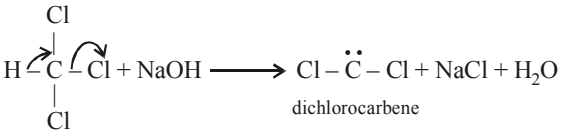


6. (b) Only those alcohols which contain $-CHOHCH_3$ group undergo haloform reaction. Among the given options only (b) contain this group, hence undergo haloform reaction.

7. (c) NOTE OH group activates the benzene nucleus and



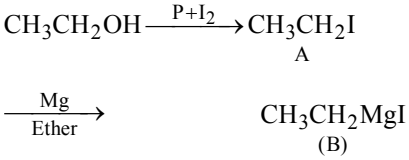
8. (d) NOTE This is Riemer-Tiemann reaction and the electrophile is dichlorocarbene.

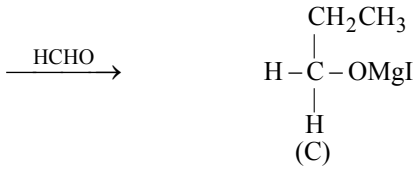


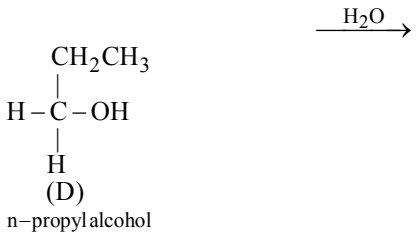
dichlorocarbene

α-elimination

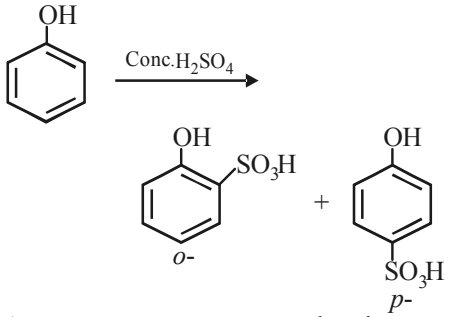
9. (d)



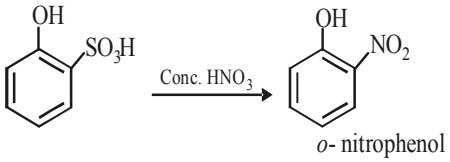




10. (b) Phenol on reaction with conc. H_2SO_4 gives a mixture of *o*- and *p*- products (i.e., $-SO_3H$ group, occupies *o*-, *p*- position). At room temperature *o*-product is more stable, which on treatment with conc. HNO_3 will yield *o*-nitrophenol.

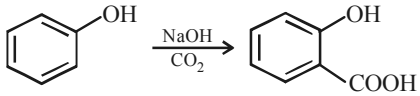


At room temperature *o*- product is more stable



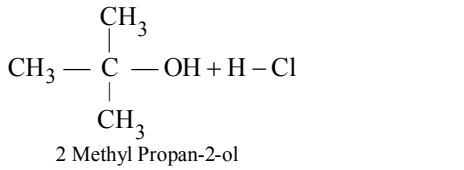
Hence (b) is the correct answer.

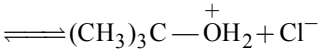
11. (b)

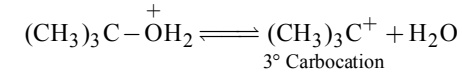


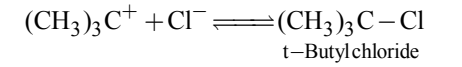
12. (b) Tertiary alcohols react fastest with conc. HCl and anhydrous $ZnCl_2$ (lucas reagent) as its mechanism proceeds through the formation of stable tertiary carbocation.

Mechanism





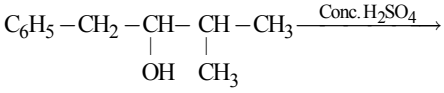


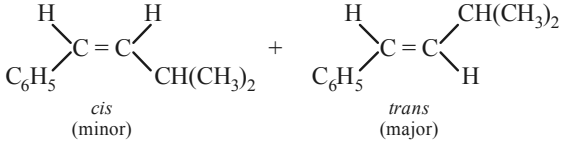


13. (a) Whenever dehydration can produce two different alkenes, major product is formed according to **Saytzeff rule** *i.e.* more substituted alkene (alkene having lesser number of hydrogen atoms on the two doubly bonded carbon atoms) is the major product.

Such reactions which can produce two or more structural isomers but one of them in greater amounts than the other are called **regioselective** *;* in case a reaction is 100% regioselective, it is termed as **regiospecific.**

In addition to being regioselective, alcohol dehydrations are **stereoselective** (*a reaction in which a single starting material can yield two or more stereoisomeric products, but gives one of them in greater amount than any other).*

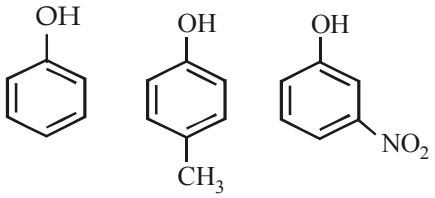


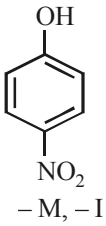


14. (a) On moving down a group, the basicity & nucleophilicity are inversely related, i.e. nucleophilicity increases while basicity decreases. i.e $RS^{\ominus}$ is more nucleophilic but less basic than $RO^{\ominus}$. This opposite

behaviour is because of the fact that basicity and nucleophilicity depends upon different factors. Basicity is directly related to the strength of the H–element bond, while nucleophilicity is indirectly related to the electronegativity of the atom to which proton is attached.

15. (a)

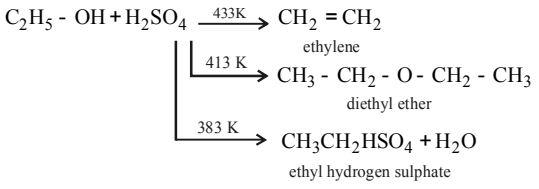




Electron withdrawing substituents increases the acidity of phenols; while electron releasing substituents decreases acidity. Since the + I effect is maximum in ortho position, followed by meta and least in para, thus the correct order of acidity will

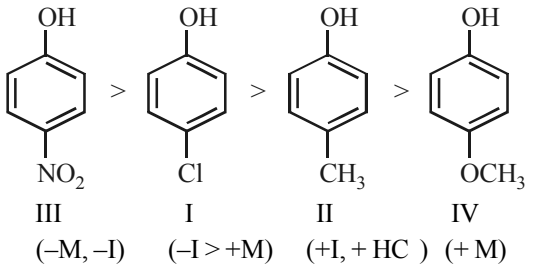
D > C > A > B

16. (b)



Acetylene is not formed under any conditions.

17. (c) Electron withdrawing substituents like $–NO_2$, –Cl increase the acidity of phenol while electron releasing substituents like $– CH_3$, $– OCH_3$ decreases acidity. hence the correct order of acidity will be



18. (b) Reaction of alcohols with Lucas reagent proceeds through carbocation formation, S_N1 mechanism.

Further 3° carbocations (from tertiary alcohols) are highly stable thus reaction proceeds through S_N1 mechanism.

19. (d) An excellent reagent for oxidation of 1° alcohols to aldehydes is PCC.

$$R - CH_2 - OH \xrightarrow{PCC} R - CHO$$

20. (a)