26 Chapter

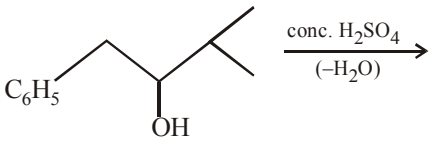
ALCOHOLS, PHENOLS AND ETHERS

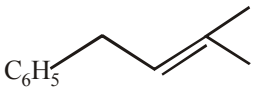
A SINGLE CORRECT CHOICE TYPE

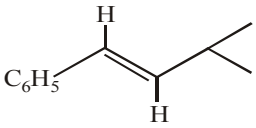
Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

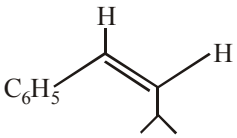
1. Which of the following is most reactive towards aqueous HBr ?
(a) 1-Phenyl - 2- propanol
(b) 1- Phenyl - 1- propanol
(c) 3-Phenyl - 1 - propanol
(d) 2- Phenyl - 1 - propanol

2. The following alcohol is treated with conc. H_2SO_4, the major product obtained is

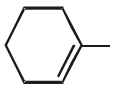


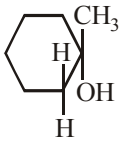
(a) 

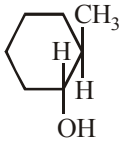
(b) 

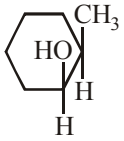
(c) 

(d) All the three will be formed in equal amounts

3.  $\xrightarrow[(ii)\ H_2O_2,\ OH^-]{(i)\ B_2H_6}$ X. The compound X is

(a) 

(b) 

(c) 

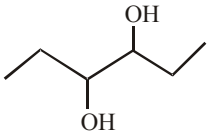
(d) Both (b) and (c)

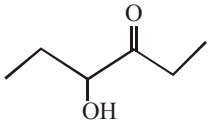
4. Give the nature of A and B in the given reaction.

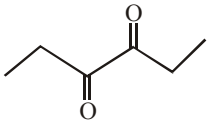
$$B \xleftarrow[H^+]{KMnO_4} (CH_3)_3COH \xrightarrow{KMnO_4/OH^-} A$$

(a) A and B both are $(CH_3)_2 C = CH_2$
(b) A and B, both are $(CH_3)_2CO + CH_2O$
(c) A is $(CH_3)_3COH$, while B is $(CH_3)_2C = CH_2$ or $(CH_3)_2CO$
(d) A and B, both are $(CH_3)_3COH$, i.e. there is no reaction

5. Which of the following is liable to be oxidised by periodic acid ?

(a) 

(b) 

(c) 

(d) All the three

6. 1-Methylcylopentene can be converted into 2-methylcyclopentanol by
(a) acid catalysed hydration
(b) hydroboration
(c) epoxide formation followed by reduction with $LiAlH_4$
(d) oxymercuration-demercuration

7. 2-Methylpropanol – 2 can be obtained by the acid catalysed hydration of
(a) $CH_3CH_2CH = CH_2$ (b) $CH_3CH = CHCH_3$
(c) $(CH_3)_2C=CHCH_3$ (d) either of the three

MARK YOUR RESPONSE					
	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ			

8. Arrange the following alcohols in order of increasing ease of dehydration

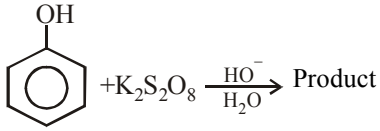
CH_3CH_2OH (I) $\quad C_6H_5CH_2OH$ (II)

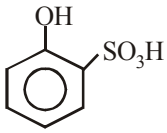
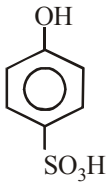
Cl_3CCH_2OH (III) $\quad F_3CCH_2OH$ (IV)

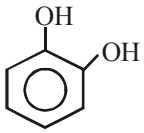
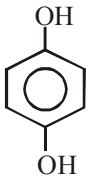
(a) II < I < IV < III (b) IV < III < II < I

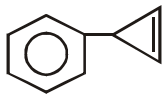
(c) IV < III < I < II (d) II < I < III < IV

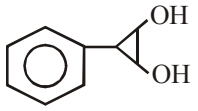
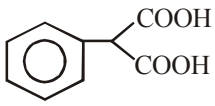
9. Identify the nature of product in the following reaction

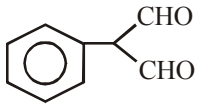
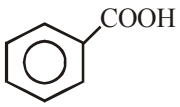


(a)  (b) 

(c)  (d) 

10.  $\xrightarrow[(ii)\ HIO_4]{(i).\ alk.\ KMnO_4}$ P. The compound P should be

(a)  (b) 

(c)  (d) 

11. Anisole is treated with HI under two different conditions.

$$C + D \xleftarrow{HI(g)} C_6H_5OCH_3 \xrightarrow{conc.HI} A + B$$

The nature of A to D will be

(a) A and B are CH_3I and C_6H_5OH, while C and D are CH_3OH and C_6H_5I

(b) A and B are CH_3OH and C_6H_5I, while C and D are CH_3I and C_6H_5OH

(c) Both A and B as well as both C and D are CH_3I and C_6H_5OH

(d) A and B are CH_3I and C_6H_5OH, while there is no reaction in the second case.

12. The ethereal linkage (–C – O – C–) is cleaved by

(a) HBr (b) HNO_3

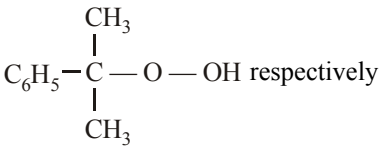
(c) both (d) none

13. Predict the compounds A and B in the following reactions

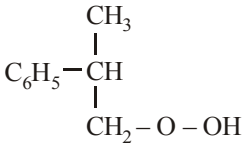
$$CH_3CH_2 - O - CH_2CH_3 + O_2 \xrightarrow{h\nu} A\ ;$$

$$C_6H_5CH(CH_3)_2 \xrightarrow{O_2,\ 95-135^\circ} B$$

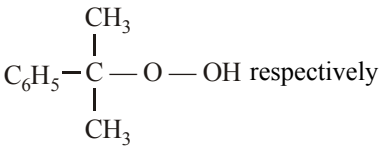
(a) $CH_3CH_2 - O - O - CH_2CH_3$ and

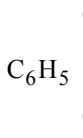
 respectively

(b) $CH_3CH_2 - O - O - CH_2CH_3$ and

 respectively

(c)  and

 respectively

(d) No reaction and  respectively

14. $$Products(P_2) \xleftarrow{anhy.\ HI} (CH_3)_3C - O - CH_3 \xrightarrow{conc.\ HI} Products\ (P_1)$$

The products P_1 and P_2 respectively are

(a) $(CH_3)_3COH + CH_3I$ and $(CH_3)_3CI + CH_3OH$

(b) $(CH_3)_3CI + CH_3OH$ and $(CH_3)_3COH + CH_3I$

(c) $(CH_3)_3CI + CH_3OH$ in both cases

(d) CH_3I and $(CH_3)_3COH$ in both cases

MARK YOUR RESPONSE					
	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ
	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ			

15. Arrange the following in the decreasing order of acidic strength

Phenol, *p* - nitrophenol, *m* - cresol, *p* - cresol
I II III IV

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

16. Which of the following will be most acidic ?

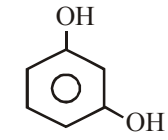
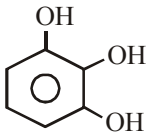
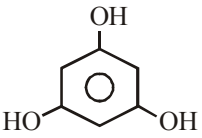
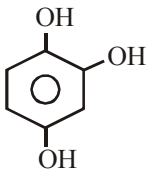
(a) *o*-Aminophenol (b) *p*-Aminophenol
(c) *m*-Aminophenol (d) None

17. Arrange the following in increasing acidic character

Phenol, *m* - nitrophenol, *m* - chlorophenol, *m* - cresol
I II III IV

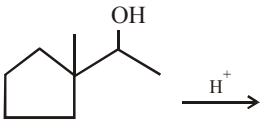
(a) IV < I < III < II (b) IV < I < II < III
(c) I < IV < III < II (d) III < II < IV < I

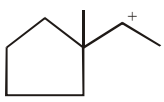
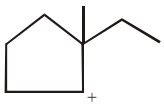
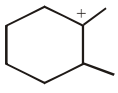
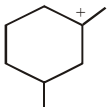
18. Which of the following compound can react with hydroxylamine ?

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

19. 2, 4, 6-Trinitrophenol can be prepared in good yield

(a) by the nitration of 2, 4-dinitrochlorobenzene
(b) by the nitration of 2, 4-dinitrophenol
(c) by both (a) and (b)
(d) neither by (a) nor by (b)

20. Which carbocation is more likely to be formed in the dehydration of 

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

21. Energy of activation is lowest for which reaction ?

(a) $RCH_2\overset{+}{O}H_2 \rightarrow R\overset{+}{C}H_2$

(b) $R_2CH\overset{+}{O}H_2 \rightarrow R_2\overset{+}{C}H$

(c) $R_3C\overset{+}{O}H_2 \rightarrow R_3C^+$

(d) All have same E_{act}

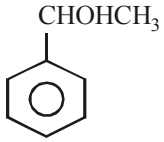
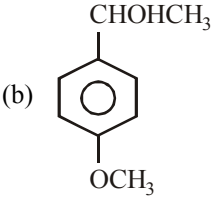
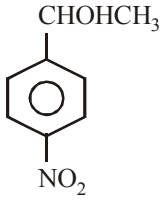
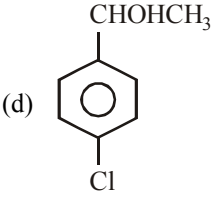
22. Dehydration of an alcohol in presence of sulphuric acid gives alkene

$$CH_3CH_2OH \xrightarrow{H_2SO_4} CH_2 = CH_2 + H_2O$$

Here sulphuric acid acts as

(a) an acid (b) a base
(c) a catalyst (d) all the three

23. Which of the following alcohols is dehydrated most readily with conc. H_2SO_4 ?

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

24. Which of the following is most reactive towards aqueous HBr ?

(a) 1-Phenyl-1-propanol (b) 1-Phenyl-2-propanol
(c) 3-Phenyl-1-propanol (d) None

25. $CH_3CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$

In the above reaction, the leaving group is

(a) OH^- (b) H_2O
(c) $HOZn^-Cl_2$ (d) H_3O^+

MARK YOUR RESPONSE					
	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ
	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ
	25. ⓐⓑⓒⓓ				

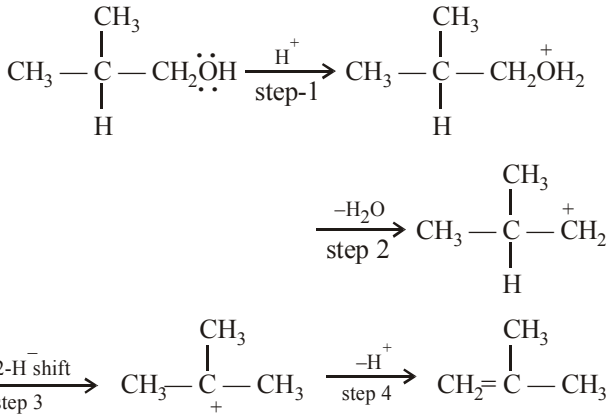
26. Ethanol can be prepared more easily by which reaction ?

(i) $CH_3CH_2Br + H_2O \longrightarrow CH_3CH_2OH$

(ii) $CH_3CH_2Br + Ag_2O\,(\text{in boiling water}) \longrightarrow CH_3CH_2OH$

(a) by (i) reaction
(b) by (ii) reaction
(c) Both reactions proceed at same rate
(d) by none

27. Dehydration of alcohols by conc. H_2SO_4 takes place according to following steps :



The slowest and fastest steps in the above reaction are
(a) step 1 is slowest, while 3 is fastest
(b) step 2 is slowest, while 3 is fastest
(c) step 2 is slowest, while 4 is fastest
(d) all steps proceed at equal rate

28. The major product P in the following reaction is

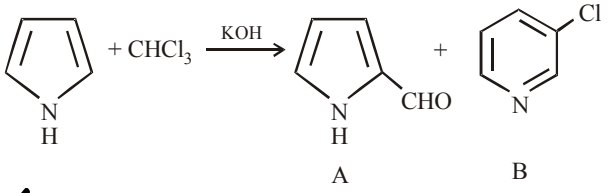
$(CH_3)_3COH + C_2H_5OH \xrightarrow{H^+} P$

(a) $(CH_3)_3COC(CH_3)_3$ (b) $(CH_3)_3COC_2H_5$
(c) $C_2H_5OC_2H_5$ (d) $(CH_3)_2C=CH_2$

29. *tert*-Butyl ethyl ether can't be prepared by which reaction?

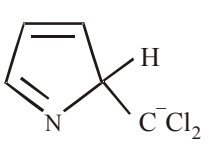
(a) *tert* – Butanol + ethanol $\xrightarrow{H^+}$
(b) *tert*-Butyl bromide + sodium ethoxide $\rightarrow$
(c) Sodium *tert*-butoxide + ethyl bromide $\rightarrow$
(d) Isobutene + ethanol $\xrightarrow{H^+}$

30. Pyrrole is treated with alkaline chloroform to form two products A and B

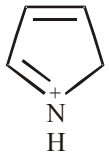


A B

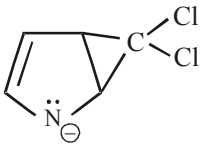
Which of the following intermediate is likely to be formed?



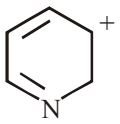
I



II

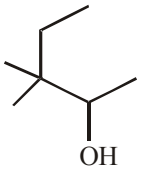


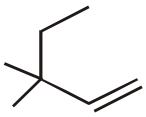
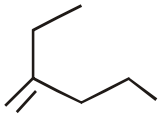
III

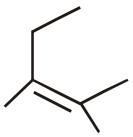
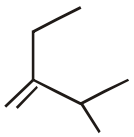


IV

(a) I and IV (b) I and III
(c) III and IV (d) I, III and IV

31.  $\xrightarrow{\text{Conc. } H_2SO_4}$ Major product is

(a)  (b) 

(c)  (d) 

32. $Y \xleftarrow[CH_3ONa]{CH_3OH} H_2C-CHCH_3 \xrightarrow[H^+]{CH_3OH} X$ (O)

Here X and Y respectively are

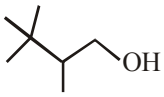
(a) CH_2-CHCH_3 (OCH$_3$, OH) and $HOCH_2-CHCH_3$ (OCH$_3$)

(b) $HOCH_2-CHCH_3$ (OCH$_3$) and CH_2-CHCH_3 (OCH$_3$, OH)

(c) CH_2-CHCH_3 (OCH$_3$, OH) in both cases

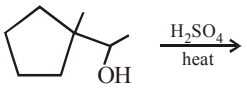
(d) $HOCH_2-CHCH_3$ (OCH$_3$) in both cases

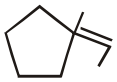
MARK YOUR RESPONSE	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ
	31. ⓐⓑⓒⓓ	32. ⓐⓑⓒⓓ			

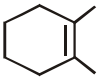
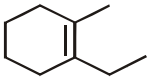
33. Which type of carbocation is/are formed when  is treated with an acid?

(a) 1º (b) 2º
(c) 3º (d) All the three

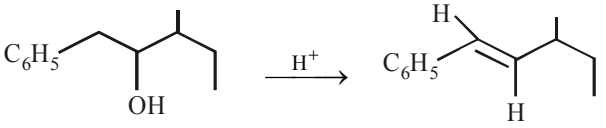
34. The most probable product in the reacion given below is

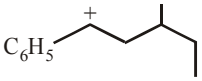
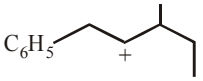


(a)  (b) 

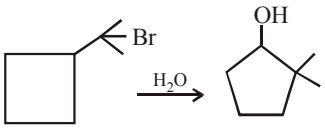
(c)  (d) 

35. The precursor carbocation to the product in the following reaction is



(a)  (b) 

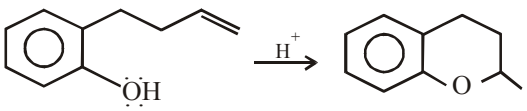
(c) Either of the two (d) None of the two

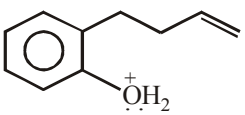
36. 

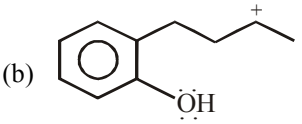
The driving force in the above reaction is

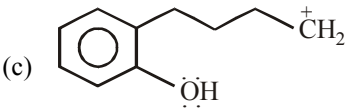
(a) conversion of 1º carbocation to 2º carbocation
(b) conversion of 1º carbocation to 3º carbocation
(c) releif in steric strain due to expansion of ring
(d) both a & c

37. Which of the following ion is formed in the following reaction?



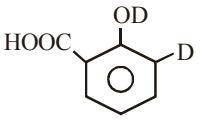
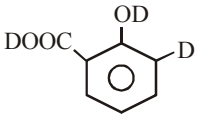
(a) 

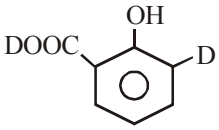
(b) 

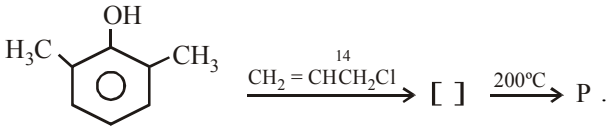
(c) 

(d) All the three

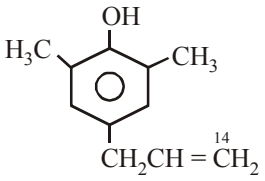
38. 

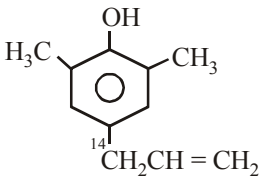
(a)  (b) 

(c)  (d) Reaction not possible

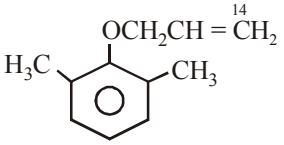
39. 

Here P is

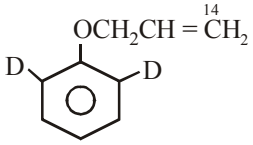
(a) 

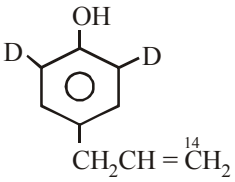
(b) 

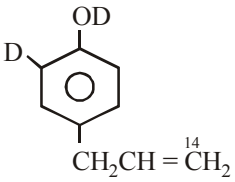
(c) Both

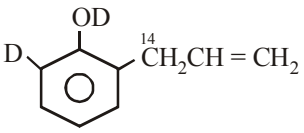
(d) 

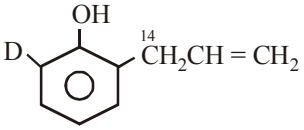
MARK YOUR RESPONSE	33. ⓐⓑⓒⓓ	34. ⓐⓑⓒⓓ	35. ⓐⓑⓒⓓ	36. ⓐⓑⓒⓓ	37. ⓐⓑⓒⓓ
	38. ⓐⓑⓒⓓ	39. ⓐⓑⓒⓓ			

40.  heat → X ; X is

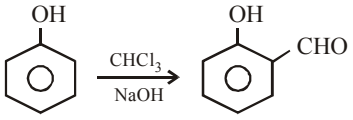
(a) 

(b) 

(c) 

(d) 

41. Which electrphile is likely to be formed as an intermediate in the following electrophilic substitution reaction ?



(a) $\overset{+}{C}HCl_2$ (b) $\overset{+}{C}HO$

(c) $:\overset{+}{C}Cl_2$ (d) $:CCl_2$

42. Phenol is converted into bakelite by heating it with formaldehyde in presence of alkali or acid. Which statement is true regarding this reactions ?

(a) The electrophilie in both cases is $CH_2 = O$

(b) The electrophile in both cases is $CH_2 = \overset{+}{O}H$

(c) The electrophile is $CH_2 = O$ in presence of alkali and $CH_2 = \overset{+}{O}H$ in presence of acid

(d) It is a nucleophilic substitution reaction

43. Which reacts faster with HCl?

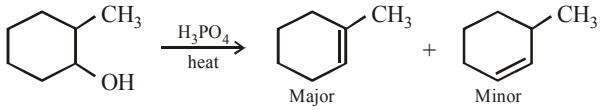
(a) CH_3CH_2OH (b) CH_3OH

(c) Both at the same rate (d) None of these

44. Which reacts rapidly with Lucas reagent?

(a) $CH_2=CHCH_2OH$ (b) $(CH_3)_3COH$

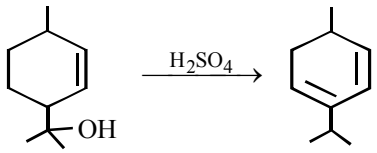
(c) Both (a) and (b) (d) CH_3CH_2OH

45. 

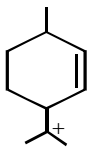
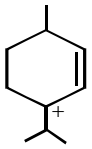
The above reaction is in example of

(a) regiospecific (b) regioselective

(c) stereoselective (d) stereospecific

46. 

Which carbocation is involved in the above reaction ?

(a)  (b) 

(c) Both (d) None

47. Pick up the rearrangement involving migration to electron deficient oxygen?

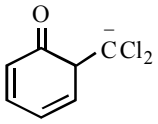
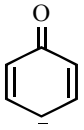
(a) Pinacol - pinacolone rearrangement

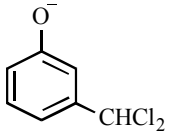
(b) Hafmann rearrangement

(c) Baeyer - Villiger reaction

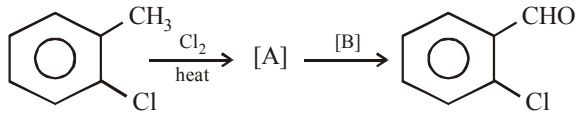
(d) None of these

48. Which of the following is not formed as an intermediate in the Reimer- Tiemann reaction between phenol and alkaline chloroform ?

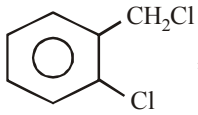
(a)  (b) 

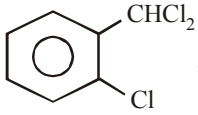
(c)  (d) $:CCl_2^{2-}$

MARK YOUR RESPONSE	40. ⓐⓑⓒⓓ	41. ⓐⓑⓒⓓ	42. ⓐⓑⓒⓓ	43. ⓐⓑⓒⓓ	44. ⓐⓑⓒⓓ
	45. ⓐⓑⓒⓓ	46. ⓐⓑⓒⓓ	47. ⓐⓑⓒⓓ	48. ⓐⓑⓒⓓ	

49. 

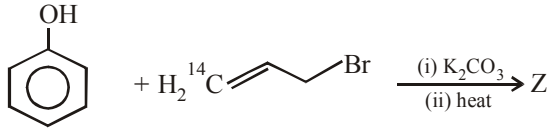
Compound [A] and reagent [B] respectively are

(a)  , aq. $Pb(NO_3)_2/CO_2$

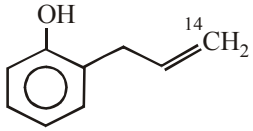
(b)  , H_2O

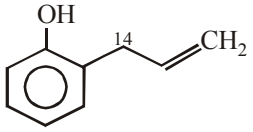
(c) either of the two

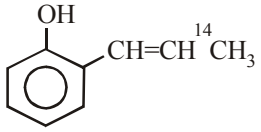
(d) None

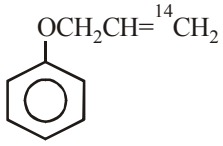
50. 

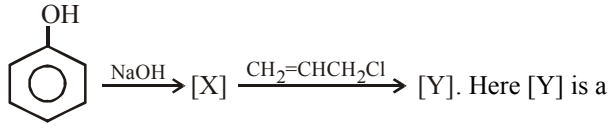
Here Z is

(a) 

(b) 

(c) 

(d) 

51. 

(a) single compound

(b) mixture of two compounds

(c) mixture of three compounds

(d) no reaction is possible

52. Phenol undergoes electrophilic substitution more easily than benzene because

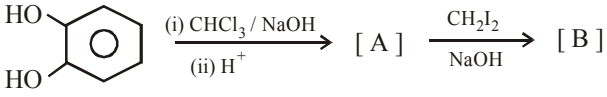
(a) –OH group exhibits +M effect and hence increases the electron density on the *o*- and *p*-positions.

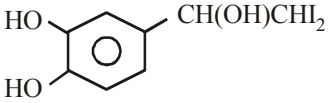
(b) oxocation is more stable than the carbocation

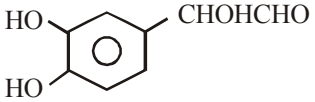
(c) both (a) and (b)

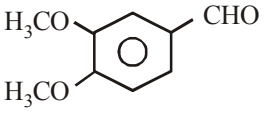
(d) –OH group exhibits acidic character

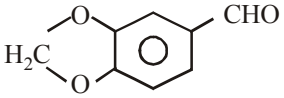
53. Identify the prodcut [B] in the following reaction

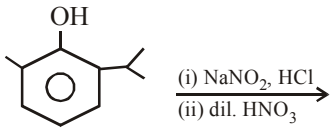


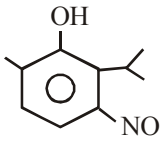
(a) 

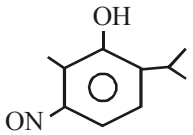
(b) 

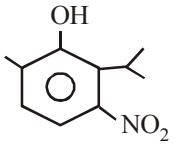
(c) 

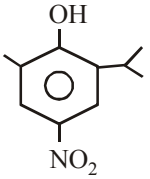
(d) 

54. 

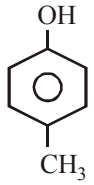
(a) 

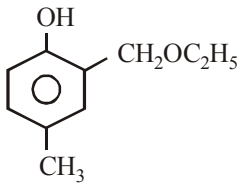
(b) 

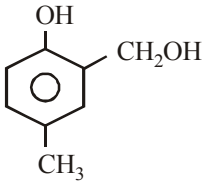
(c) 

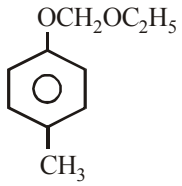
(d) 

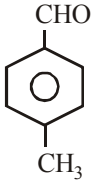
MARK YOUR RESPONSE	49. ⓐⓑⓒⓓ	50. ⓐⓑⓒⓓ	51. ⓐⓑⓒⓓ	52. ⓐⓑⓒⓓ	53. ⓐⓑⓒⓓ
	54. ⓐⓑⓒⓓ				

55.  $+ CH_2(OC_2H_5)_2 \xrightarrow{H^+}$ Z, Z is

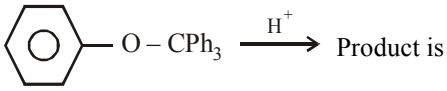
(a) 

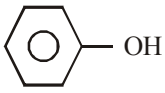
(b) 

(c) 

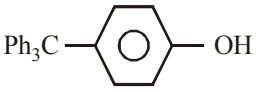
(d) 

56. Predict the product in the following reaction

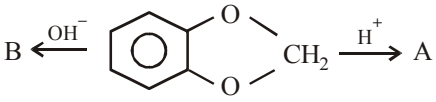


(a) 

(b) Ph_3COH

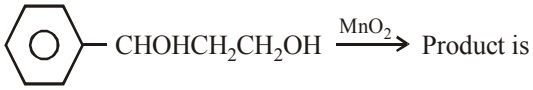
(c) 

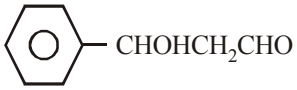
(d) All the three

57. 

A and B are

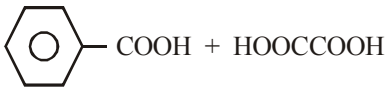
	A	B
(a)	Catechol + Methanal	Catechol + Methanal
(b)	Catechol + Methanal	Sodium salt of catechol + Methanal
(c)	No reaction	Catechol + Methanal
(d)	Catechol + Methanal	No reaction

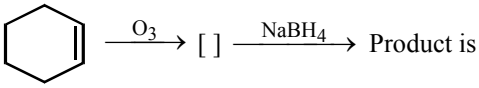
58. 

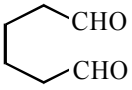
(a) 

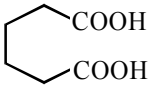
(b) 

(c) 

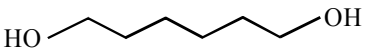
(d) 

59. 

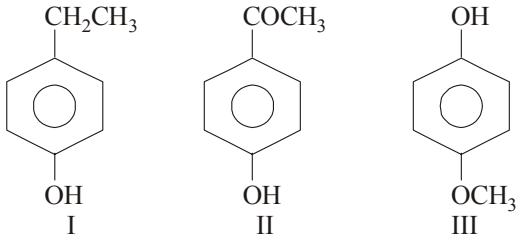
(a) 

(b) 

(c) mixture of (a) and (b)

(d) 

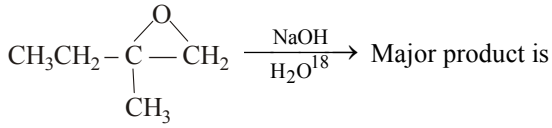
60. Which of the following is the correct order of the acidity of the three compounds ?

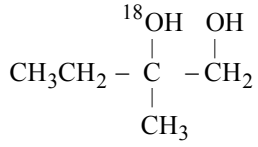


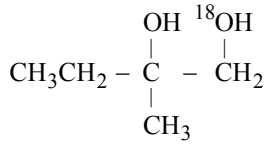
(a) II > III > I (b) III > II > I

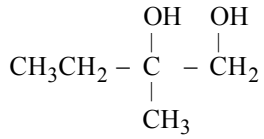
(c) II > I > III (d) III > I > II

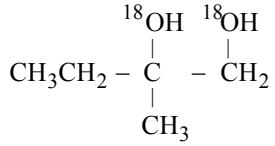
MARK YOUR RESPONSE	55. ⓐⓑⓒⓓ	56. ⓐⓑⓒⓓ	57. ⓐⓑⓒⓓ	58. ⓐⓑⓒⓓ	59. ⓐⓑⓒⓓ
	60. ⓐⓑⓒⓓ				

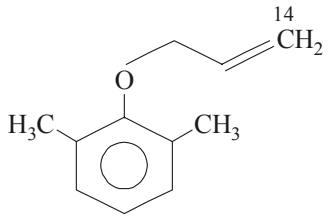
61.  Major product is

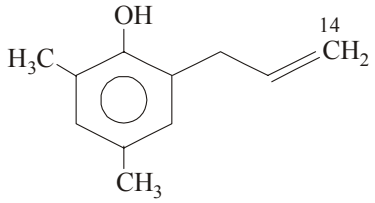
(a) 

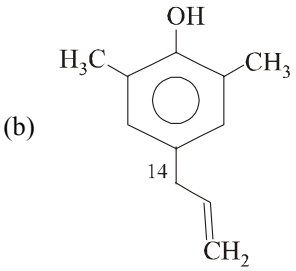
(b) 

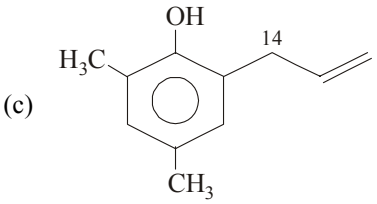
(c) 

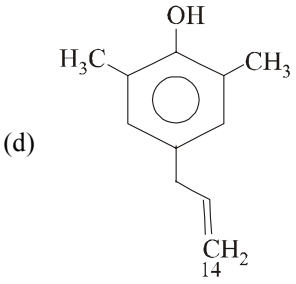
(d) 

62.  *P*. *P* is

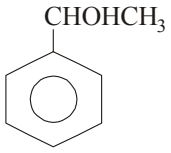
(a) 

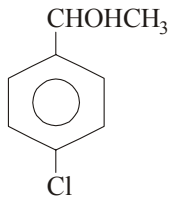
(b) 

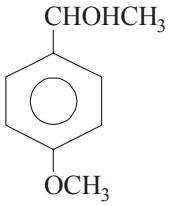
(c) 

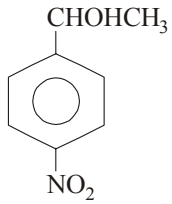
(d) 

63. Which of the following is dehydrated most readily ?

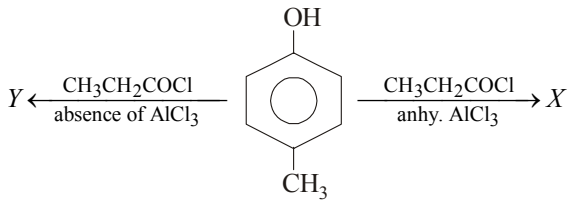
(a) 

(b) 

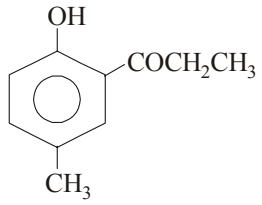
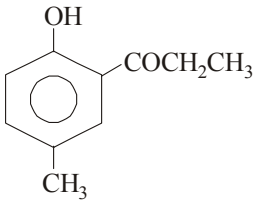
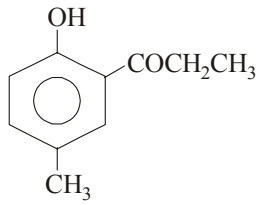
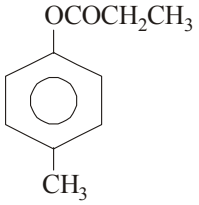
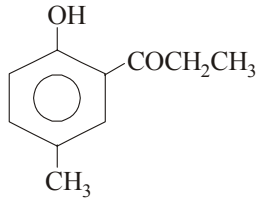
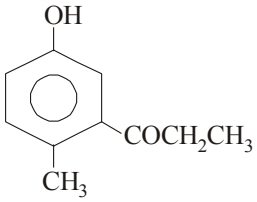
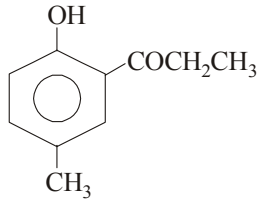
(c) 

(d) 

MARK YOUR RESPONSE	61. ⓐⓑⓒⓓ	62. ⓐⓑⓒⓓ	63. ⓐⓑⓒⓓ		

64. 

X and *Y* respectively are

	X	*Y*
(a)		
(b)		
(c)		
(d)		No reaction

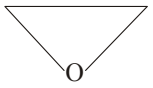
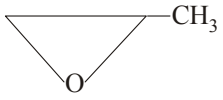
65. Ethyl magnesium bromide when treated with methanol forms an addition product which when hydrolysed with water in presence of acids forms propanol. What would be the major product when the above reaction is carried out in the following sequence ?

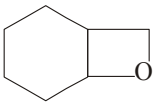
$$CH_3CH_2MgBr \xrightarrow[(ii)\ HCHO]{(i)\ H_3O^+}$$

(a) $CH_3CH_2CH_2OH$ (b) CH_3CH_2CHO

(c) CH_3CH_3 (d) $CH_3\overset{\overset{OH}{|}}{C}HCH_3$

66. Primary alcohols can be obtained from Grignard reagent by reacting with

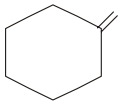
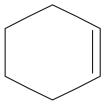
(i)  (ii) 

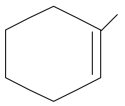
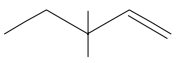
(iii)  (iv) 

(a) (i) (b) (i) and (iii)

(c) (i), (ii) and (iii) (d) All the four

67. Acid catalysed hydration, hydroboration-oxidation, and oxymercuration-demercuration will give different products in

(a)  (b) 

(c)  (d) 

68. Which of the following statements is incorrect for the reactions between HBr and tertiary butanol ?

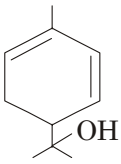
(a) $(CH_3)_3COH + HBr \rightleftharpoons (CH_3)_3CO^+H_2 + Br^-$ first step

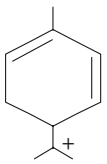
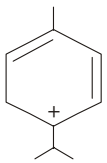
(b) $(CH_3)_3CO^+H_2 \longrightarrow (CH_3)_3C^+ + H_2O$ slow step

(c) $(CH_3)_3C^+ + Br^- \longrightarrow (CH_3)_3C - Br$ S_{N^1} fast

(d) $(CH_3)_3C^+ + Br^- \longrightarrow (CH_3)_3CBr$ S_{N^1} slow

69. Which of the carbocations is more likely to be formed when

 is heated with conc H_2SO_4 ?

(a)  (b) 

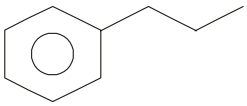
(c) both in equal amounts (d) None

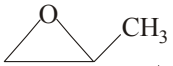
MARK YOUR RESPONSE					
	64. ⓐⓑⓒⓓ	65. ⓐⓑⓒⓓ	66. ⓐⓑⓒⓓ	67. ⓐⓑⓒⓓ	68. ⓐⓑⓒⓓ
	69. ⓐⓑⓒⓓ				

70. Benzene is heated with large excess of 80% H_2SO_4 in D_2O, the product formed will be

(a) $C_6H_5SO_3D$ (b) C_6H_5D

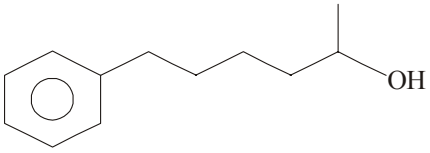
(c) C_6H_5OD (d) C_6D_6

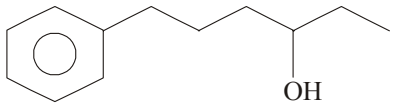
71.  $\xrightarrow[\text{(ii) Mg, ether}]{\text{(i) NBS}}$ [A]

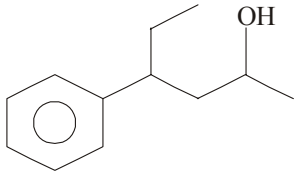
(i)  [B]

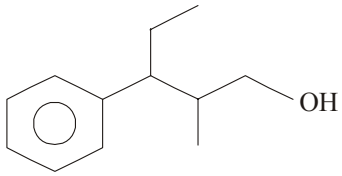
(ii) H^+

Here compound B can be

(a) 

(b) 

(c) 

(d) 

MARK YOUR RESPONSE	70. ⓐⓑⓒⓓ	71. ⓐⓑⓒⓓ			

B COMPREHENSION TYPE

This section contains groups of questions. Each group is followed by some multiple choice questions based on a paragraph. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

PASSAGE-1

Alkyl halides and alcohols easily undergo nucleophilic substitution either through S_N1 or S_N2 mechanism. The relative ease of these two processes depends upon the nature of the substrate (alkyl group as well as leaving group), nature of nucleophile and also upon the nature of solvent.

S_N1 mechanism involves the formation of carbocation as intermediate while S_N2 mechanism involves the formation of a transition pentavlent state. S_N1 is the main mechanism in 3° alkyl halides and alcohols, while S_N2 mechanism is the path adopted by most of the 1° alkyl halides; 2° alkyl halides may follow S_N1 as well as S_N2.

1. Which of the following solvent will give maximum yield for an alkyl halide undergoing S_N1 mechanism?

(a) Water (b) Ethanol

(c) Diethyl ether (d) *n*-Hexane

2. Rearrangement of alkyl groups occur when hydrogen halides react with alcohols except with most primary alcohols. The best explanation is that

(a) The 1° carbocations are unstable and hence not formed

(b) The 1° carbocations are unable to undergo rearrangement

(c) Both are true

(d) Both are false

3. Neopentyl alcohol, Me_3CCH_2OH, reacts with HX according to

(a) S_N1 mechanism

(b) S_N2 mechanism

(c) Both

(d) None

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ		

PASSAGE-2

Although chlorobenene is inert to nucleophilic substitution, it gives quantitative yield of phenol when heated with aq. NaOH at high temperature and under high pressure. Phenol, so formed, is a weaker acid than the carboxylic acid; hence it dissolves only in strong bases like NaOH, but not weak like $NaHCO_3$. It reacts with acid chlorides and acid anhydrides in the absence of $AlCl_3$ to form esters. As far as electrophilic substitution in phenol is concerned, the –OH is an activating group, hence its presence enhances the electrophilic substitution in the *o*- and *p*-positions.

Condensation with formaldehyde is one of the important property of phenol. The condensation may take place in presence of acids or alkalis and leads to the formation of bakelite, an important industrial polymer.

4. Conversion of chlorobenzene into phenol involves
- (a) modified S_N1 mechanism
- (b) modified S_N2 mechanism
- (c) both (a) and (b)
- (d) elimination - addition mechanism

5. The *o*-acylation of phenols with acid anhydrides can be catalyzed by
- (a) sulphuric acid (b) NaOH
- (c) both (d) none

6. Phenol undergoes electrophilic substitution more readily than benzene because
- (a) the intermediate carbocation is a resonance hybrid of more resonanting structures than that from benzene
- (b) the intermediate is more stable as it has positive charge on oxygen, which can be better accommodated than on carbon
- (c) in one of the canonical structures, every atom (except hydrogen) has complete octet
- (d) the –OH group is *o, p*–directing which like all other *o,p*-directing groups is activating

7. Phenol undergoes electrophilic substitution more readily in presence of alkali than the phenol itself because
- (a) of the formation of a more stable carbocation as an intermediate
- (b) of the formation of a more stable carbanion as an intermediate
- (c) of the formation of a more stable neutral intermediate
- (d) in presence of alkali, a stronger electrophile is produced

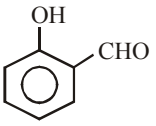
8. Condensation of phenol with formaldehyde is an electrophilic substitution, in which
- (a) $CH_2 = O$ as such is the electrophile in both acidic as well as basic medium
- (b) $CH_2 = O$ is the real electrophile in acidic medium while in basic medium $\overset{+}{C}H_2 - O^-$ is the real electrophile
- (c) $CH_2 = \overset{+}{O}H$ and $CH_2 = O$ are the electrophiles in acidic and basic medium respectively.
- (d) $CH_2 = O$ and $\overset{+}{C}H_2 - O^-$ are the electrophiles in acidic and basic medium respectively

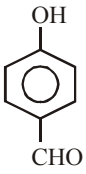
PASSAGE-3

An organic compound X gives positive Libermann reaction. It also reacts with alkaline chloroform to give a product with on hydrolysis produces two isomeric compounds Y an Z, the isomer Y restores Schiff's reagent colour, while the steam-volatile isomer Z does not respond Schiff's reagent.

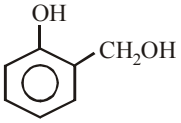
9. Compound X contains a
- (a) primary amino group
- (b) secondary amino group
- (c) phenolic group
- (d) either (b) and (c)

10. Compound Y should be

(a) 

(b) 

(c) Either of the two

(d) 

11. The compound Z does not give colour which Schif's reagent beacuse
- (a) it has no aldehydic group
- (b) the –CHO group in the compound is not free
- (c) the –CHO group is sterically hindered
- (d) None of the three

MARK YOUR RESPONSE					
	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ
	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ		

12. The conversion of X to Y is an example of :

(a) electrophilic substitution

(b) nucleophilic substitution

(c) free radical substitution

(d) benzyne formation

13. Which intermediate is likely to be formed in the conversion of X to Y?

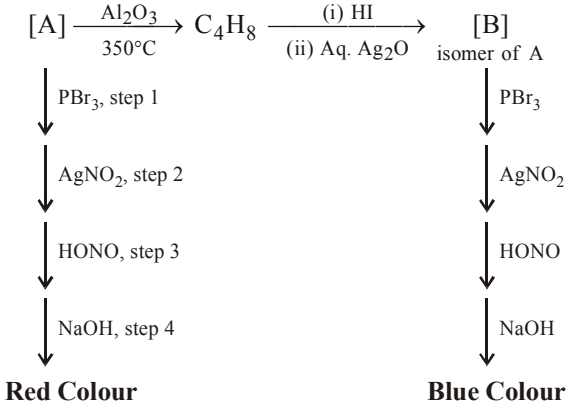
(a) $\overset{+}{C}HO$ (b) $\overset{-}{C}HO$

(c) $:CCl_2$ (d) $:CCl_2^{2-}$

PASSAGE-4

Alcohols are isomeric to ethers and the two differ in their reactivity. Alcohols are very reactive while ethers are comparatively very inert; however ethers react with HI at high temperature to form alkyl halides. Higher alcohols from C-3 onwards can exist 1°, 2° or 3° alcohols which can be distinguished by their oxidation, dehydrogenation and behaviour of their respective nitro derivatives toward nitrous acid.

Observe the following series of reactions carefully and answer the questions listed below the series :



14. In the above series of reactions, A and B respectively are

(a) n-C_4H_9OH and $CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_3$

(b) n-C_4H_9OH and $(CH_3)_3COH$

(b) $CH_3CHOHCH_2CH_3$ and $CH_3CH_2OCH_2CH_3$

(d) n-C_4H_9OH and $CH_3CH_2OCH_2CH_3$

15. Name the isomer of [A] and [B] which reacts with hydriodic acid to form only a single compound

(a) $(CH_3)_3COH$ (b) $CH_3\overset{OH}{\overset{|}{C}}HCH_2CH_3$

(c) $CH_3OCH_2CH_2CH_3$ (d) $CH_3CH_2OCH_2CH_3$

16. At which step, the above series of reactions first differs

(a) step 1 (b) step 2

(c) step 3 (d) step 4

PASSAGE-5

1, 2-Diols, when treated with an aqueous solution of periodic acid give aldehydes or ketones

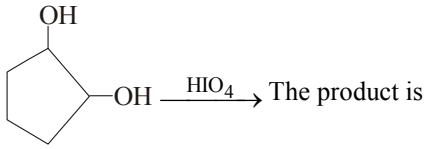
$$\begin{matrix} R-CHOH \\ | \\ R'-CHOH \end{matrix} + HIO_4 \longrightarrow RCHO + R'CHO + HIO_3 + H_2O$$

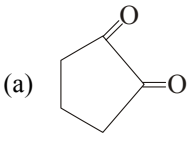
In case of polyhydric alcohols, one mole of periodic acid is consumed between every two adjacent hydroxyl groups. An alcoholic group, attacked on both sides by HIO_4 is converted into carboxylic acid. Periodic acid also oxidises α-hydroxyaldehydes, α-hydroxyketones, in addition to 1, 2-diols.

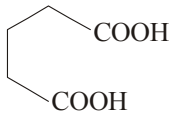
$$CH_2OH-CO-CHOH\ CH_2OH \longrightarrow$$

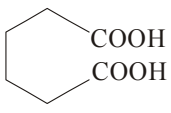
$$CH_2OH\ COOH + H\ COOH + HCHO$$

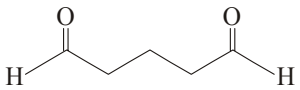
Periodic oxidation has been used for determining the structure of compounds by knowing the number of moles of periodic acid consumed and nature of the product formed.

17.  The product is

(a) 

(b) 

(c) 

(d) 

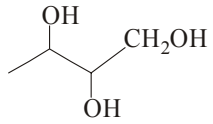
MARK YOUR RESPONSE	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ
	17. ⓐⓑⓒⓓ				

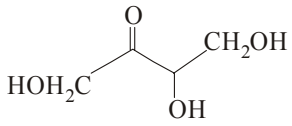
18. When glycerol is oxidised with periodic acid, the products formed are

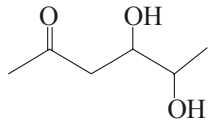
(a) methanal (b) formic acid

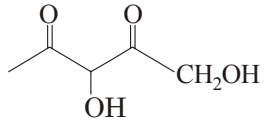
(c) iodic acid (d) all the three

19. 3 An organic compound consumes two moles of periodic acid per mole of compound and form glycollic acid, formic acid and formaldehyde, the compound is

(a) 

(b) 

(c) 

(d) 

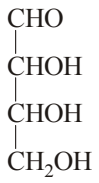
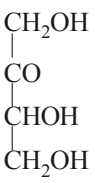
20. Glucose, $CHO(CHOH)_4CH_2OH$ is oxidised with periodic acid, how many moles of formic acid and formaldehyde are obtained respectively by one mole of glucose ?

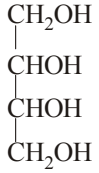
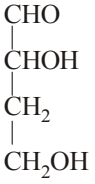
(a) 5, 1 (b) 4, 2

(c) 3, 3 (d) 4, 1

21. Compound (X) $\xrightarrow{3HIO_4}$ 2 HCHO + HCOOH + CO_2 .

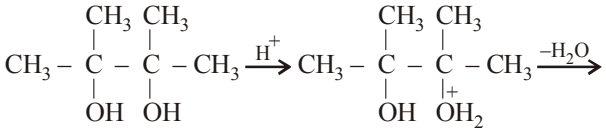
The compound X is

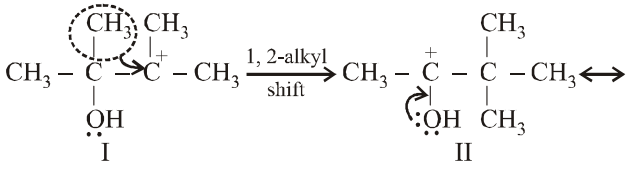
(a)  (b) 

(c)  (d) 

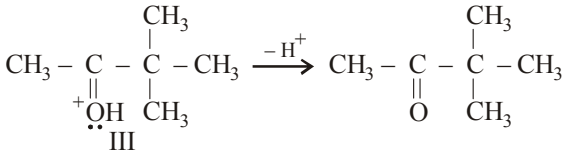
PASSAGE-6

On heating with acids, 1, 2-glycols are converted into aldehydes or ketones. The reaction is known as pinacol-pinacolone rearrangement. The mechanism of the reaction involves following four steps.





I II



III

22. Which of the following steps is rate determining ?

(a) Protonation of the – OH group

(b) Elimination of H_2O

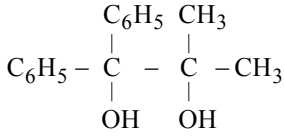
(c) 1, 2-alkyl shift to form 3° carbocation

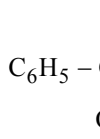
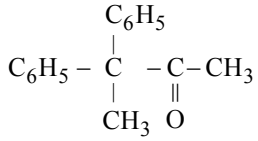
(d) Deprotonation of the protonated carbonyl group

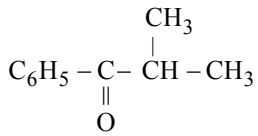
23. Which of the intermediate ions is more stable ?

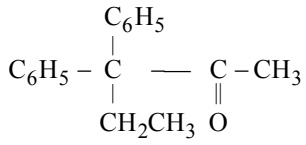
(a) I (b) II

(c) III (d) all equal

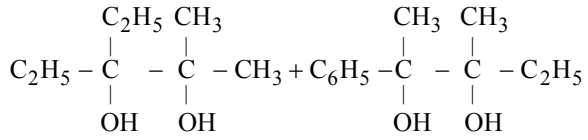
24.  Major product is

(a)  (b) 

(c) 

(d) 

MARK YOUR RESPONSE	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ
	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ			

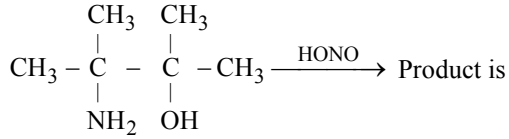
25. 

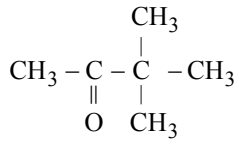
$\xrightarrow[\text{heat}]{H_2SO_4}$

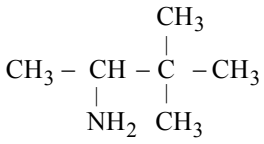
Number of ketones formed in the above reaction is

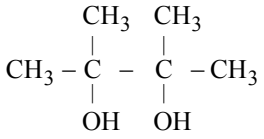
(a) 2 (b) 3

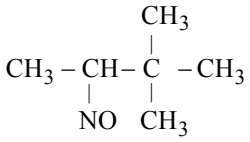
(c) 4 (d) 6

26.  Product is

(a) 

(b) 

(c) 

(d) 

MARK YOUR RESPONSE	25. ⓐⓑⓒⓓ	26. ⓐⓑⓒⓓ			

C REASONING TYPE

In the following questions two Statement-1 (Assertion) and Statement-2 (Reason) are provided. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct. Mark your responses from the following options:

(a) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(b) Both Statement-1 and Statement-2 are true and Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is true but Statement-2 is false.
(d) Statement-1 is false but Statement-2 is true.

1. **Statement-1** : Ethers behave as bases in the presence of mineral acids.

Statement-2 : Due to the presence of lone pairs of electrons on oxygen.

2. **Statement-1** : In Lucas test, 3° alcohols react immediately.

Statement-2 : An equimolar mixture of anhyd. $ZnCl_2$ and conc. HCl is called Lucas reagent.

3. **Statement-1** : Reimer-Tiemann reaction of phenol with CCl_4 in NaOH at 340 K gives salicyclic acid as the major product.

Statement-2 : The reaction occurs through intermediate formation of dichlorocarbene.

4. **Statement-1** : Phenol is more reactive than benzene towards electrophilic substitution reaction.

Statement-2 : In the case of phenol, the intermediate carbocation is more resonance stabilized.

5. **Statement-1** : Phenol on oxidation with $KMnO_4$ gives *meso*-tartaric acid.

Statement-2 : Pure phenol is colourless but turn pink due to oxidation to phenoquinone.

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ

6. **Statement-1** : High boiling point of glycerol is due to hydrogen bonding.

Statement-2 : Glycerol decomposes much below its boiling point and evaporation is carried in vacuum.

7. **Statement-1** : *ter* - Butyl methyl ether is not prepared by the reaction of *ter*-butyl bromide with sodium methoxide.

Statement-2 : Sodium methoxide is a strong nucleophile

8. **Statement-1** : With HI, anisole gives iodobenzene and methyl alcohol.

Statement-2 : Iodide ion combines with smaller group to avoid steric hindrance.

9. **Statement-1** : With HI at 373 K, *ter*-butyl methyl ether gives *ter*-butyl iodide and methanol.

Statement-2 : The reaction occurs by S_{N^2} mechanism.

MARK YOUR RESPONSE	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	

D MULTIPLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE OR MORE is/are correct.

1. 2-Phenylbutanol-2 can be prepared by which of the following combinations ?

(*a*) $C_6H_5COCH_3 + C_2H_5MgBr$

(*b*) $C_2H_5COCH_3 + C_6H_5MgBr$

(*c*) $C_6H_5COC_2H_5 + CH_3MgBr$

(*d*) $C_6H_5COC_6H_5 + C_2H_5MgBr$

2. Which of the following combination can't be used for preparing an ether ?

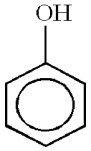
(a) $C_6H_5OH + (CH_3)_2\ SO_4$

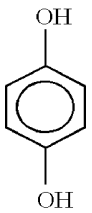
(b) $C_6H_5Br + CH_3CH_2OH$

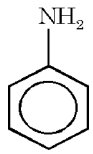
(c) $p\text{-}NO_2C_6H_4Br + CH_3CH_2OH$

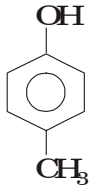
(d) $C_6H_5OH + (CH_3)_3CBr$

3. Which of the following gives *p*-benzoquinone on oxidation ?

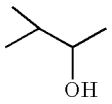
(*a*) 

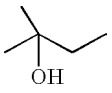
(*b*) 

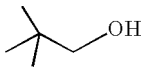
(*c*) 

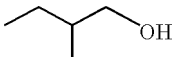
(*d*) 

4. Which of the following alcohol will mainly give the rearranged chloride, when treated with HCl?

(a) 

(b) 

(c) 

(d) 

5. Which of the following can't be prepared by the typical Williamson reaction ?

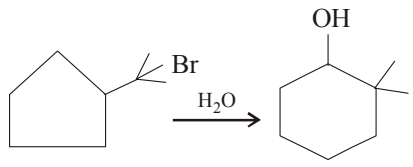
(a) R_3COCR_3

(b) ArOAr

(c) RCH = CHOCH = CHR′

(d) $C_6H_5CH_2OC_2H_5$

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ

6. 

The above reaction involves

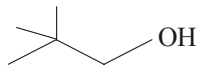
(a) Conversion of 2° to 3° carbocation

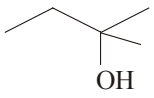
(b) Conversion of 3° to 2° carbocation

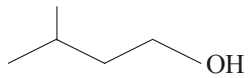
(c) Expansion of ring

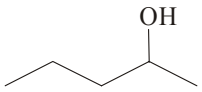
(d) Conversion of 3° to the more stable benzylic carbocation

7. Which compound on dehydration with conc. phosphoric acid undergoes rearrangement to 3° carbocation?

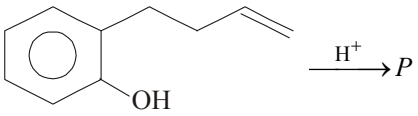
(a) 

(b) 

(c) 

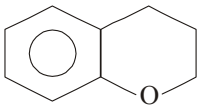
(d) 

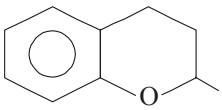
8. Pick up the correct statements in the following reaction

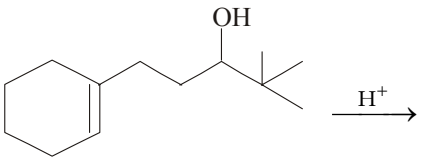


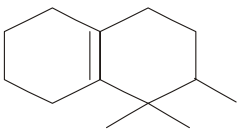
(a) protonation occurs at –OH

(b) protonation occurs at C = C linkage

(c) *P* is 

(d) *P* is 

9. 



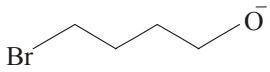
The above transformation involves

(a) protonation at the C = C linkage

(b) protonation at –OH group

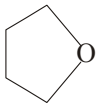
(c) formation of 2° carbocation

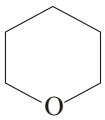
(d) formation of 3° carbocation

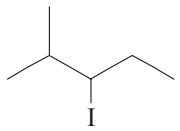
10. 

undergoes intramolecular nucleophilic substitution of the type..... giving.....

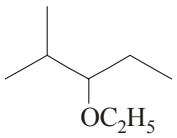
(a) $S_{N}1$ (b) $S_{N}2$

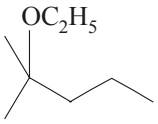
(c) 

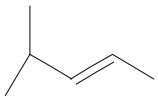
(d) 

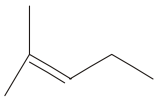
11. 

Possible products are

(a) 

(b) 

(c) 

(d) 

12. 2, 4, 6 -Tribromophenol can be prepared by the bromination of

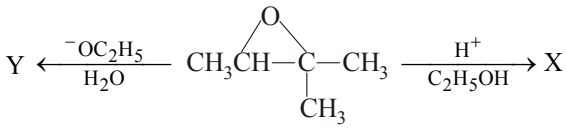
(a) phenol

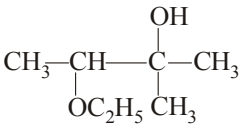
(b) salicylic acid

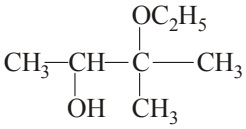
(c) *p*-hydroxybenzenesulphonic acid

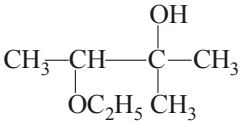
(d) *p*-bromophenol

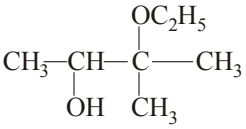
MARK YOUR RESPONSE					
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ
	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ			

13. 

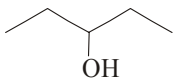
(a) X is 

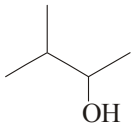
(b) X is 

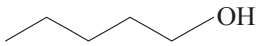
(c) Y is 

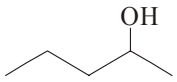
(d) Y is 

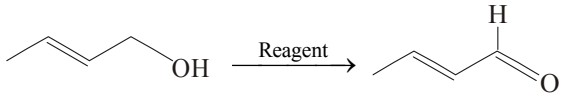
14. An organic compound *X* on dehydration gives an alkene capable of showing geometrical isomerism, the compound *X* is

(a) 

(b) 

(c) 

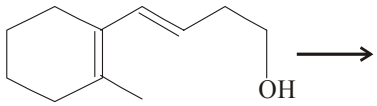
(d) 

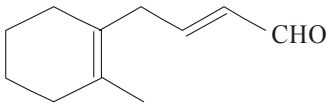
15. 

Reagent in the above reaction may be

(a) Collines reagent (b) Tollen′s reagent

(c) PCC (d) PDC

16. 



The above reaction can be achieved by the use of

(a) PCC (b) Jones reagent

(c) 9 - BBN (d) Adkines catalyst

17. In which of the following reactions, ether is formed as a major product ?

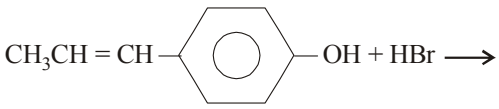
(a) $CH_3CH_2Cl + Ag_2O$ (dry)

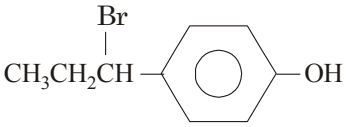
(b) $CH_3CH_2Cl + C_6H_5ONa \rightarrow$

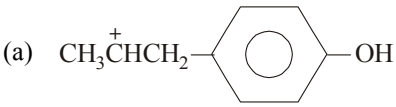
(c) $(CH_3)_3CONa + CH_3Cl$

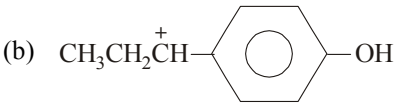
(d) $CH_3CH_2ONa + ClC(CH_3)_3$

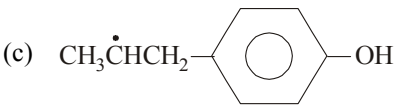
18. Which of the following intermediate is formed in the reaction

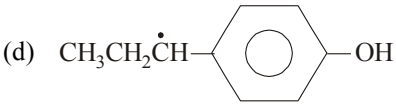




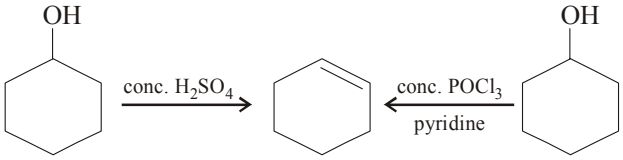
(a) 

(b) 

(c) 

(d) 

MARK YOUR RESPONSE	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ
	18. ⓐⓑⓒⓓ				

19. 

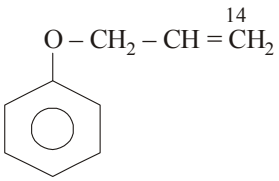
Which of the following statement is true regarding above reaction ?

(a) Dehydration by conc. H_2SO_4 is slower than with $POCl_3$

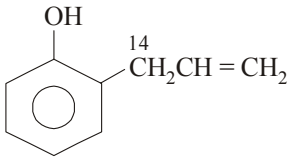
(b) Both involve carbocation as intermediate

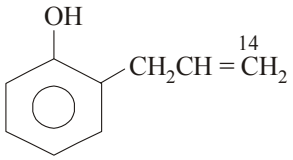
(c) Dehydration by $POCl_3$ involves elimination of – $OPOCl_2$ which is a better leaving group.

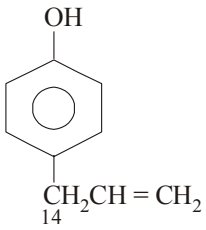
(d) Elimination of – $OPOCl_2$ and abstraction of proton by pyridine take place simultaneously.

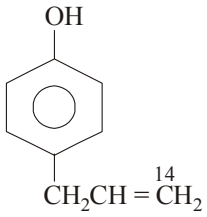
20. 

$\xrightarrow{200°}$ P. Product (P) may be

(a) 

(b) 

(c) 

(d) 

MARK YOUR RESPONSE	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ			

E MATRIX-MATCH TYPE

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labeled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column -I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:
If the correct matches are A–p, s and t; B–q and r; C–p and q; and D–s then the correct darkening of bubbles will look like the given.

	p	q	r	s	t
A	●			●	●
B		●	●		
C	●	●			
D				●	

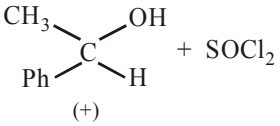
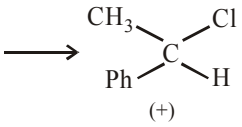
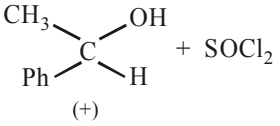
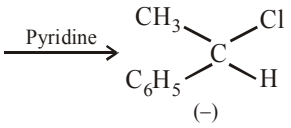
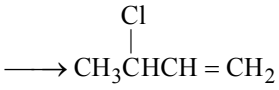
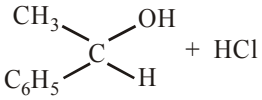
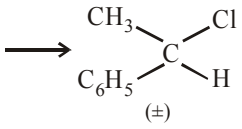
1.

Column-I	Column-II
(A) Hemiacetal	p. Hydrolysed by acids
(B) Acetal	q. Hydrolysed by bases
(C) Glycosides	r. Carbohydrates
(D) Ether	s. Ziesel method

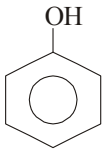
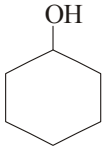
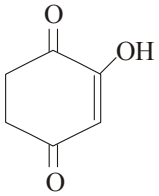
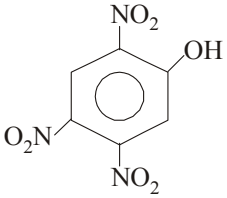
MARK YOUR RESPONSE	1.

	p	q	r	s
A	●			
B		●	●	
C	●	●		
D				●

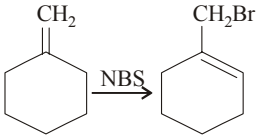
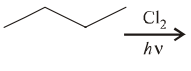
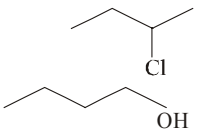
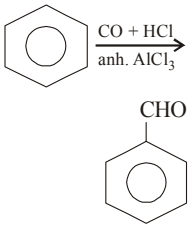
2.

Column-I		Column-II	
(A)		p.	S_Ni
			
(B)		q.	S_N2
			
(C)	$CH_3CH=CHCH_2OH+SOCl_2$	r	S_Ni
			
(D)		s.	S_Ni'
			

3.

Column I		Column II
(A)		p. Reacts with sodium acetylide, $HC\equiv\bar{C}\,Na^+$
(B)		q. Reacts with sodium hydroxide, NaOH
(C)		r. Reacts with sodamide, $NaNH_2$
(D)		s. Reacts with sodium bicarbonate, $NaHCO_3$

4.

Column I		Column II
(A)		p. Electrophilic substitution
(B)		q. Free radical rearrangement
(C)		r. Carbocation intermediate with rearrangement
(D)		s. Paramagnetic intermediate

MARK YOUR RESPONSE

2.

	p	q	r	s
A	Ⓟ	Ⓠ	Ⓡ	Ⓢ
B	Ⓟ	Ⓠ	Ⓡ	Ⓢ
C	Ⓟ	Ⓠ	Ⓡ	Ⓢ
D	Ⓟ	Ⓠ	Ⓡ	Ⓢ

3.

	p	q	r	s
A	Ⓟ	Ⓠ	Ⓡ	Ⓢ
B	Ⓟ	Ⓠ	Ⓡ	Ⓢ
C	Ⓟ	Ⓠ	Ⓡ	Ⓢ
D	Ⓟ	Ⓠ	Ⓡ	Ⓢ

4.

	p	q	r	s
A	Ⓟ	Ⓠ	Ⓡ	Ⓢ
B	Ⓟ	Ⓠ	Ⓡ	Ⓢ
C	Ⓟ	Ⓠ	Ⓡ	Ⓢ
D	Ⓟ	Ⓠ	Ⓡ	Ⓢ

Answerkey

A Single Correct Choice Type

1	(b)	**2**	(b)	**3**	(b)	**4**	(c)	**5**	(d)	**6**	(b)	**7**	(c)	**8**	(c)	**9**	(d)	**10**	(c)
11	(c)	**12**	(a)	**13**	(c)	**14**	(b)	**15**	(c)	**16**	(c)	**17**	(a)	**18**	(c)	**19**	(b)	**20**	(c)
21	(c)	**22**	(d)	**23**	(b)	**24**	(a)	**25**	(c)	**26**	(b)	**27**	(c)	**28**	(b)	**29**	(b)	**30**	(b)
31	(c)	**32**	(b)	**33**	(d)	**34**	(c)	**35**	(a)	**36**	(c)	**37**	(b)	**38**	(c)	**39**	(b)	**40**	(c)
41	(d)	**42**	(c)	**43**	(b)	**44**	(c)	**45**	(b)	**46**	(c)	**47**	(c)	**48**	(d)	**49**	(c)	**50**	(b)
51	(c)	**52**	(c)	**53**	(d)	**54**	(d)	**55**	(b)	**56**	(d)	**57**	(d)	**58**	(c)	**59**	(d)	**60**	(c)
61	(b)	**62**	(d)	**63**	(c)	**64**	(b)	**65**	(c)	**66**	(b)	**67**	(d)	**68**	(d)	**69**	(b)	**70**	(d)
71	(c)																		

B Comprehension Type

1	(a)	**6**	(c)	**11**	(b)	**16**	(c)	**21**	(b)	**26**	(a)
2	(d)	**7**	(c)	**12**	(a)	**17**	(d)	**22**	(b)		
3	(a)	**8**	(c)	**13**	(c)	**18**	(d)	**23**	(b)		
4	(d)	**9**	(c)	**14**	(a)	**19**	(b)	**24**	(b)		
5	(c)	**10**	(b)	**15**	(d)	**20**	(a)	**25**	(a)		

C Reasoning Type

1	(a)	**3**	(c)	**5**	(b)	**7**	(b)	**9**	(c)
2	(b)	**4**	(a)	**6**	(b)	**8**	(d)		

D Multiple Correct Choice Type

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

E Matrix-Match Type

1. A-q; B-p; C-p, r; D-p, s

2. A-r; B-q; C-s; D-p

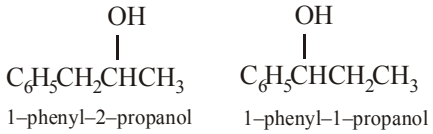
3. A-p, q, r; B-p, q, r; C-p, q, r, s; D-p, q, r, s

4. A-q, s; B-s; C-r; D-p;

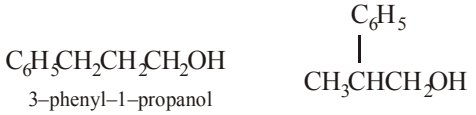
Solutions

A Single Correct Choice Type

1. (b) It is a nucleophilic substitution reaction, 1-phenyl -1-propanol will be most reactive because of formation of more stable benzyl type of carbocation.

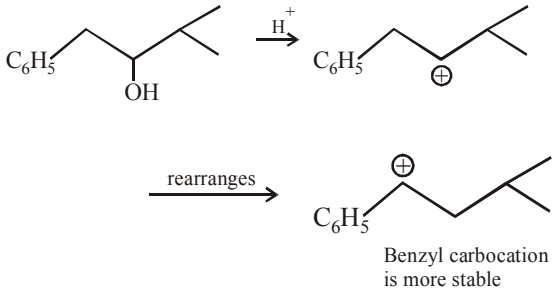


1–phenyl–2–propanol 1–phenyl–1–propanol

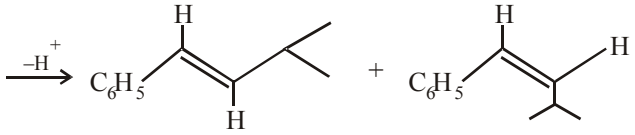


3–phenyl–1–propanol 2–phenyl–1–propanol

2. (b)



Benzyl carbocation is more stable



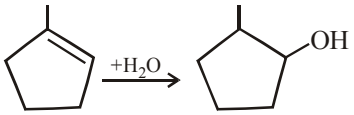
trans–(more stable due to steric relief) *cis*– (less stable due to bulky gps. lying on same side)

3. **(b)** Hydroboration – oxidation reaction of alkenes leads to anti-Markovnikov's hydration. Further addition of water adds in *syn*-manner, i.e., H and OH are added to the same face of the double bond leading *trans*-product. In short, hydroboration-oxidation of alkenes is regioselective as well as stereoselective.

4. **(c)** *tert*-Alcohols are not oxidised under alkaline conditions because they do not have any H on C having OH group. However, *tert*-alcohols when heated with strong acidic reagents, they undergo dehydration to form alkenes which then undergo oxidation to form ketones.

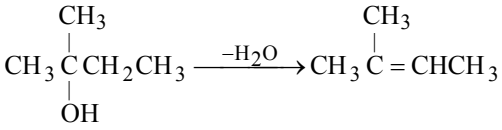
5. **(d)** Compounds containing two or more OH or > C = O groups, or –OH and > C =O on adjacent carbon atoms are oxidisable. Positive oxidation by periodic acid can be confirmed by carrying out oxidation in presence of $AgNO_3$ when white precipitate of $AgIO_3$ is formed.

6. **(b)**

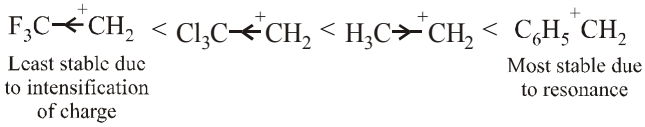


The reaction involves *anti*-Markovnikov's hydration which is possible only in hydroboration (acid catalysed hydration and oxymercuration demercuration leads to Markovnikov's hydration). Epoxide formation followed by $LiAlH_4$ leads to diol.

7. **(c)** Proceed backward i.e., remove a molecule of water to get the alkene.



8. **(c)** Higher the stability of the carbocation, more easily it is formed and more will be the ease of its dehydration. Stability of the carbocations of the corresponding alcohols is

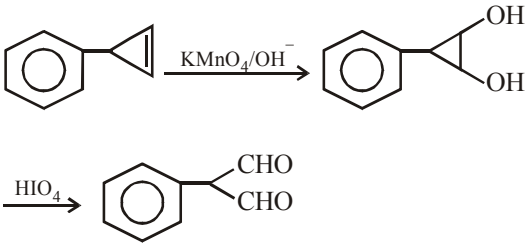


Least stable due to intensification of charge Most stable due to resonance

$$F_3CCH_2OH < Cl_3CCH_2OH < H_3CCH_2OH < C_6H_5CH_2OH$$ (Ease of dehydration)

9. **(d)** Oxidation of phenol by $K_2S_2O_8$ is an example of Elbs persulphate oxidation.

10. **(c)**



11. **(c)** Although in both cases products are CH_3I and C_6H_5OH; the two reactions follow different mechanism.

$$C_6H_5-O-CH_3 \xrightarrow[S_N2]{HI(g)} CH_3I + C_6H_5OH$$

$$C_6H_5-O-CH_3 \xrightarrow[S_N1]{conc.HI} CH_3I + C_6H_5OH$$

Remember that during S_{N1} reaction, CH_3^+ is formed because it is more stable than $C_6H_5^+$.

12. **(a)** Cleavage of ethers by acid is a nucleophilic substitution reaction which is possible only in case of HI and HBr, but not in HNO_3 and H_2SO_4. The reason being the fact that I^- and Br^- are less sterically hindered in attacking the substrate in comparison to NO_3^- and SO_4^{2-}.

13. **(c)** Ethers, when exposed to air in presence of light, form ether peroxides. Cumene (isopropylbenzene), when heated in presence of oxygen also forms peroxide, here oxidation occurs at benzylic carbon.

14. **(b)** When one of the alkyl groups is 3º and another is 1º, nature of reagent determines the type of mechanism (S_N1 or S_N2). A polar solvent or reagent capable of forming ions (viz. conc. HI) will cause S_N1 reaction, while a non-polar solvent or a reagent not capable of forming ions will cause S_N2 reaction.

15. **(c)** Recall that $-NO_2$ group increases, while $-CH_3$ decreases acidity of the phenol. Further, in case of $-CH_3$ group acid-weakening effect is due to +I effect, *m*-methyl will exert powerful +I effect than the *p*-methyl. Hence the acidic order will be

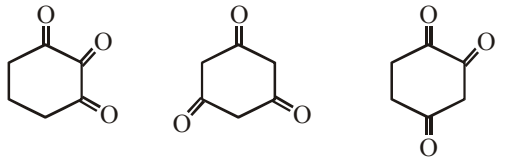
$$\underset{\text{II}}{p-\text{nitrophenol}} > \underset{\text{I}}{\text{phenol}} > \underset{\text{IV}}{p-\text{cresol}} > \underset{\text{III}}{m-\text{cresol}}$$

16. **(c)** $-NH_2$ group shows +M effect (an acid-weakening factor) in case of *o*– and *p*–aminophenols, but not in *m*-aminophenol which thus should be more acidic among the three isomers.

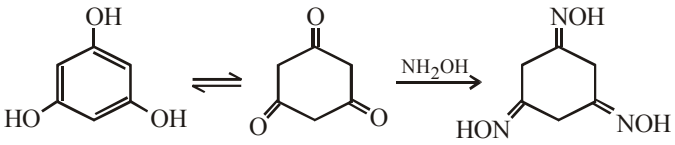
17. **(a)** Here the substituents are present in *m*-position, so they will not show any mesomeric effect; only inductive effect operates, $-NO_2$ group has + charge on N, so it has more a electron-withdrawing inductive effect than Cl ; *m*-nitrophenol will be more acidic than *m*-chlorophenol. Methyl group is acid-weakening group. Hence the relative acidic strength is

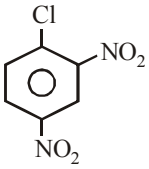
$$\underset{\text{IV}}{m-\text{cresol}} < \underset{\text{I}}{\text{phenol}} < \underset{\text{III}}{m-\text{chlorophenol}} < \underset{\text{II}}{m-\text{nitrophenol}}$$

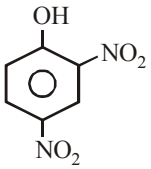
18. **(c)** We know that phenols show keto-enol tautomerism and the stability of the keto form depends upon the number of keto group (more the number of keto groups, higher will be stability of the keto tautomer). Thus trihydric phenols should exist in keto form in considerable amount but only when the two keto groups are not on adjacent carbon atoms which decreases stability due to positive charge on adjacent carbon atoms.



Unstable Stable Unstable



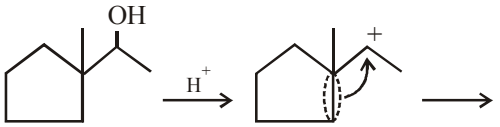
19. **(b)**  ; All the three goups deactivate the benzene ring toward electrophilic substitution(nitration).



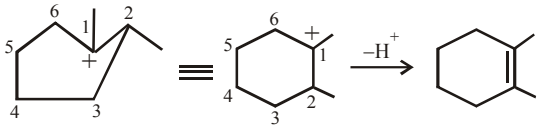
(i) –OH group activates the ortho position

(ii) The two $-NO_2$ (deactivating) groups prevent the oxidation of benzene ring

(iii) All the three groups cooperate for the new coming group for the same position.

20. **(c)** 

2º cabocation



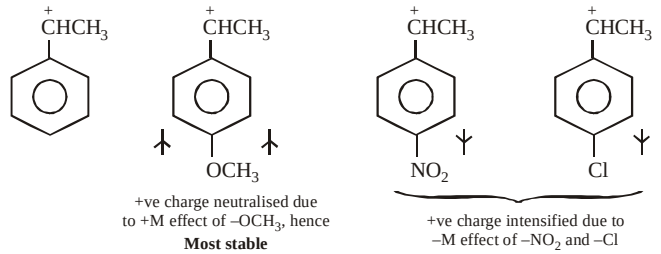
21. **(c)** Higher is the stability of a species, more likely it is formed, hence lower will be the E_{act} for its precursor.

22. **(d)** $$CH_3CH_2OH \xrightarrow[(\text{from } H_2SO_4)]{H^+} CH_3CH_2\overset{+}{O}H_2 \rightarrow CH_3\overset{+}{C}H_2$$

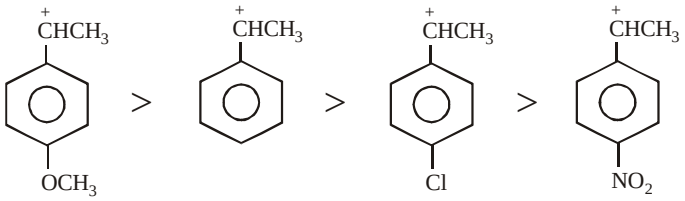
$$\xrightarrow[(\text{from } H_2SO_4)]{HSO_4^-} CH_2 = CH_2 + H_2SO_4$$

Thus note that H_2SO_4 is acting as an acid in step (i), as a base in step (iii). Since it is regenerated back as such it also acts as a catalyst.

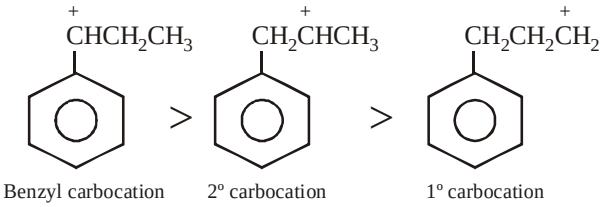
23. **(b)** The reaction involves the formation of carbocation as intermediate. Hence more the stability of the carbocation, more will be the rate of reaction. Let us draw the structure of the corresponding carbocation and observe the relative stability of the four benzyl carbocations.



The relative stability of the four carbocations is



24. **(a)** Here also, carbocation is formed as an intermediate, hence the species capable of forming most stable carbocation will be most reactive.



25. **(c)** Zinc chloride is a Lewis acid and coordinates with the alcoholic group.

$$R\text{–}\ddot{\underset{\cdot\cdot}{O}}H + ZnCl_2 \longrightarrow R - \overset{+}{O}(H) - \overset{\ominus}{Z}nCl_2$$

$$\longrightarrow R^+ + HO - \overset{\ominus}{Z}nCl_2$$

$$R \quad Cl^- (\text{from HCl}) \rightarrow RCl \quad H$$

$$H \quad HO^- - ZnCl_2 \rightarrow H_2O \quad ZnCl_2$$

26. **(b)** Heavy metal ions, particularly Ag^+, catalyse S_{N^1} reaction because of presence of empty orbital.

$$CH_3CH_2Br + Ag^+ \rightleftharpoons [CH_3CH_2 .... X .... Ag]^+$$

$$\xrightarrow[(-AgX)]{\text{slow}} CH_3CH_2^+ \xrightarrow[\text{from } H_2O]{OH^-} CH_3CH_2OH$$

27. **(c)** Step 2 involves the formation of carbonium ion by the loss of weakly basic H_2O molecule. It is slowest step. Step 4 involves the conversion of an unstable (or intermediate) into a quite stable product, hence it is fastest step.

28. **(b)** *tert* - Butyl alcohol is preferentially protonated because its corresponding carbocation is highly stable than that of C_2H_5OH

$$(CH_3)_3COH \xrightarrow{H} (CH_3)_3C\overset{+}{O}H_2 \xrightarrow{-H_2O}$$

$$(CH_3)_3C^+ \xrightarrow{CH_3CH_2\ddot{O}H}$$

Stable

$$(CH_3)_3C\overset{H}{\overset{+}{O}}CH_2CH_3 \xrightarrow{-H} (CH_3)_3COCH_2CH_3$$

The *tert*-butyl cation is preferentially attacked by CH_3CH_2OH rather than bulky $(CH_3)_3COH$

29. **(b)** $(CH_3)_3CBr$ $NaOC_2H_5$ can't be applied for synthesising the ether because sod. ethoxide, being a strong base, will preferentially cause elimination reaction.

$$(CH_3)_3CBr \xrightarrow{^-OC_2H_5} (CH_3)_2C \quad CH_2 \quad HBr$$

In isobutene + ethanol, isobutene will form *tert*-butyl cation which reacts with ethanol, a nucleophile to form ether.

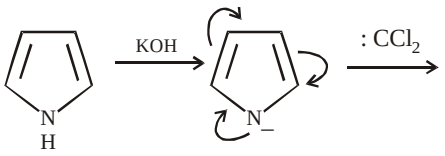
$$(CH_3)_2C = CH_2 \xrightarrow{H} (CH_3)_2\overset{+}{C}CH_3$$

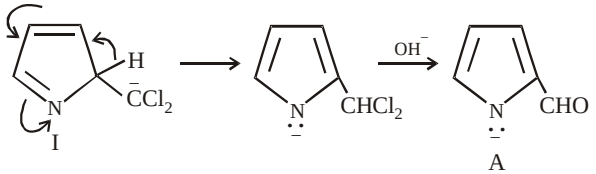
$$\xrightarrow[(ii)\ -H]{(i)\ CH_3CH_2OH} (CH_3)_3COCH_2CH_3$$

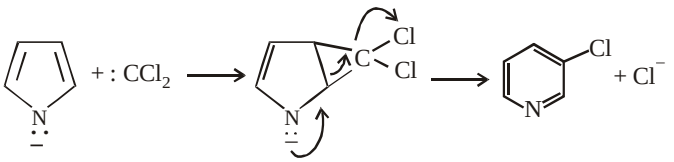
30. **(b)** It is an example of Reimer-Tiemann reaction

$$CHCl_3 \xrightarrow{OH^-} :\bar{C}Cl_3 \xrightarrow{-Cl^-} :CCl_2$$

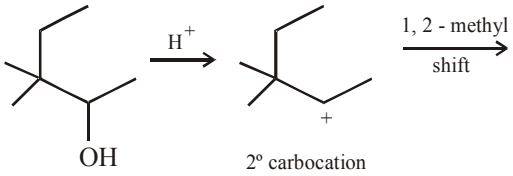
Dichlorocarbene

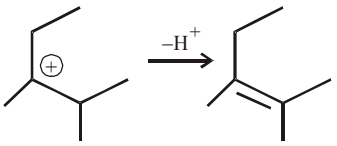




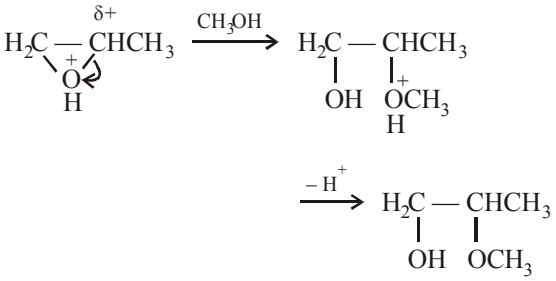


31. **(c)** It is an example of dehydration of alcohol. The 2º carbocation formed at first stage rearranges to the more stable 3º.

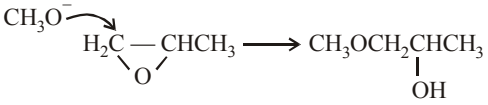




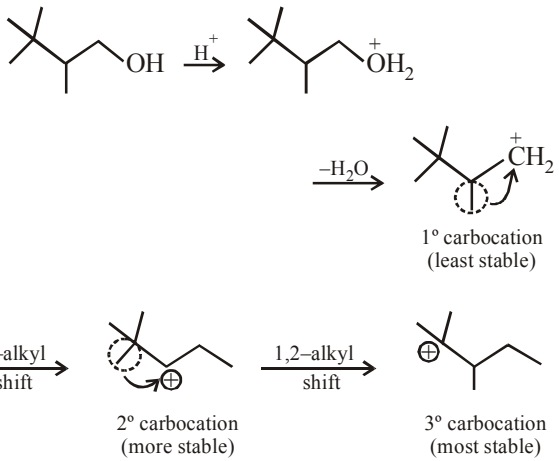
32. **(b)** In the acid-catalysed ring opening of an unsymmetrical ethoxide, the nucleophile attacks primarily at the more substituted carbon atom because such atom of the protonated epoxide acquires a considerable positive charge. This resembles like a more stable 2º or 3º carbocation and hence the reaction is $S_{N}1$ like.



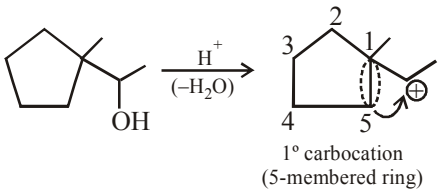
In case of CH_3ONa, $^{-}OCH_3$, being a strong nucleophile, opens the strained epoxide ring in a direct $S_{N}2$ reaction, i.e. by attacking at the least hindered carbon atom.

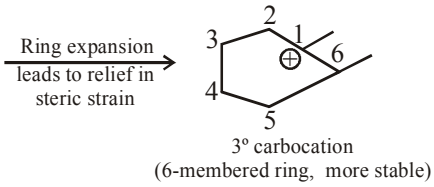


33. **(d)**

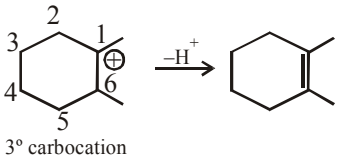


34. **(c)**

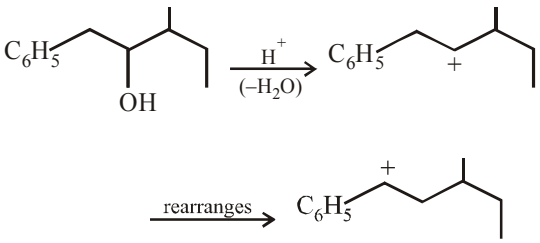


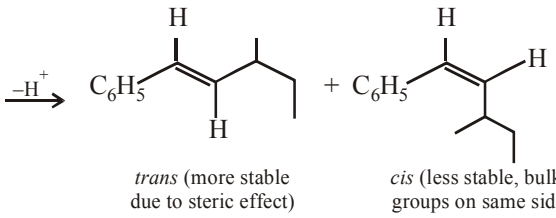


or

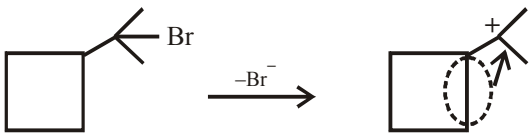


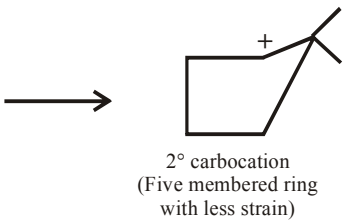
35. **(a)**



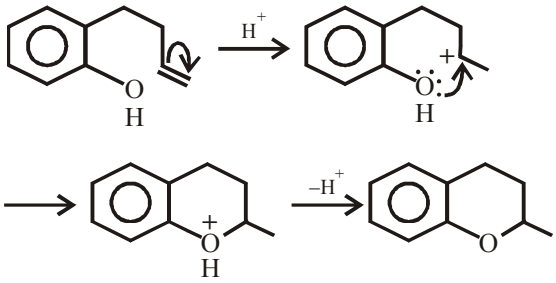


36. **(c)**

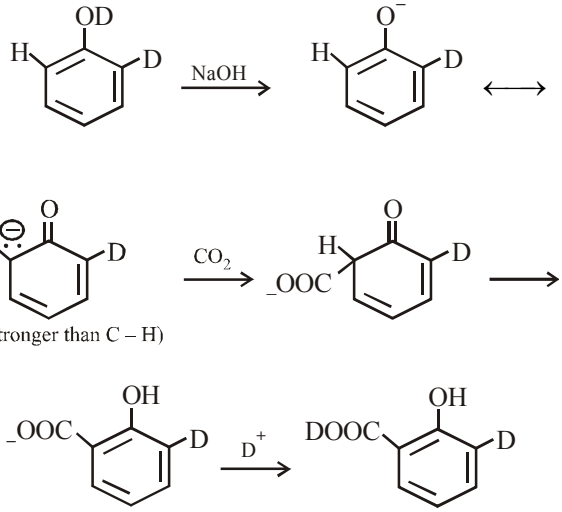




37. **(b)**



38. **(c)**



(C-D is stronger than C – H)

39. **(b)** The reaction is an example of Claisen rearangement in which allyl phenyl ethers, on heating, is forming *p*-allylphenol because *o*-positions are not free. Further, in the formation of *p*-product allyl group migrates twice, the labelled C^{14} comes to its original position.

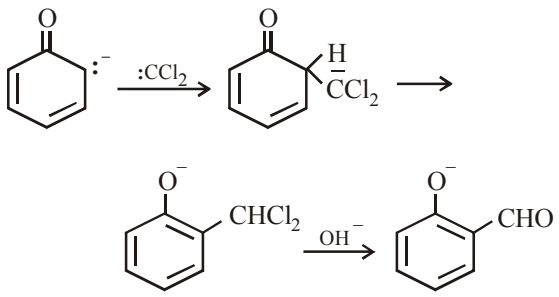
40. **(c)** Remember that in migration to ortho position, allyl group rearranges only once, hence position of C^{14} is changed.

41. **(d)**

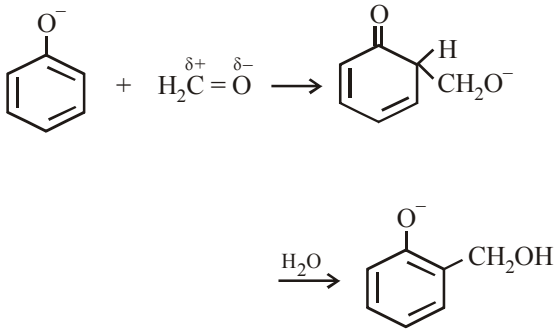
$$HCCl_3 + NaOH \rightarrow NaCl + H_2O + :\overset{\bullet}{C}Cl_3$$

$$\rightarrow \quad :CCl_2 + Cl^-$$

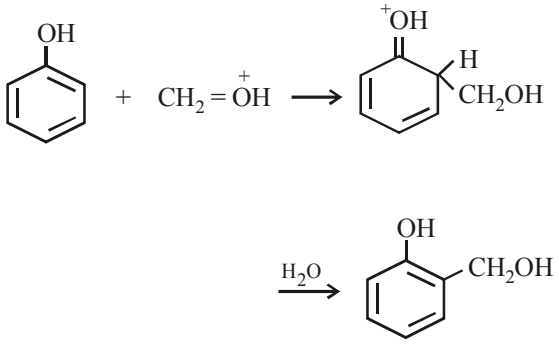
Dichlorocarbene
(a neutral electrophile)



42. **(c)** Condensation of phenol with formaldehyde is an electrophilic substitution reaction. Base converts phenol into phenoxide ion which, being more reactive, reacts easily with $CH_2 = O$ (a weak electrophile).



In presence of acid, $CH_2 = O$ (a weak electrophile) is protonated to $CH_2 = \overset{+}{O}H$ (a strong electrophile) which easily reacts with phenol (a weak nucleophile).

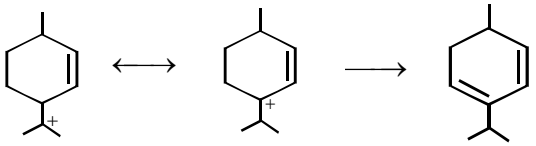


43. **(b)** Most of primary alcohols and CH_3OH react by S_N2 mechanism which is more easier in CH_3OH than in other primary alcohols because transition state of CH_3OH is more stable due to smaller size of the CH_3 group.

44. **(c)** $CH_2 = CH\overset{+}{C}H_2$ and $(CH_3)_3\overset{+}{C}$ are quite stable.

45. **(b)** Reactions where one of the products is major are known as regioselective.

46. **(c)**

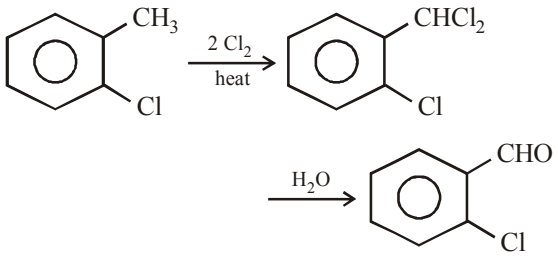


3° 3° allylic (more stable)

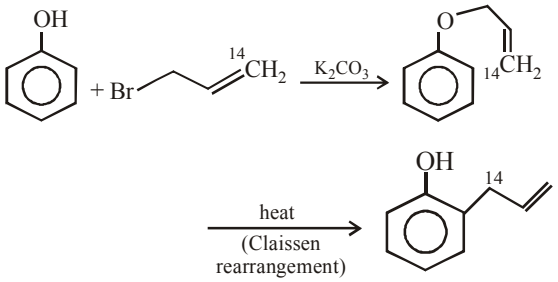
47. **(c)** In pinacol rearrangement, the group or atom migrates to electron – deficient carbon, while in Hofmann rearrangement migration to electron -deficient nitrogen takes place.

48. **(d)** Dichlorocarbene is a neutral species, not ionic.

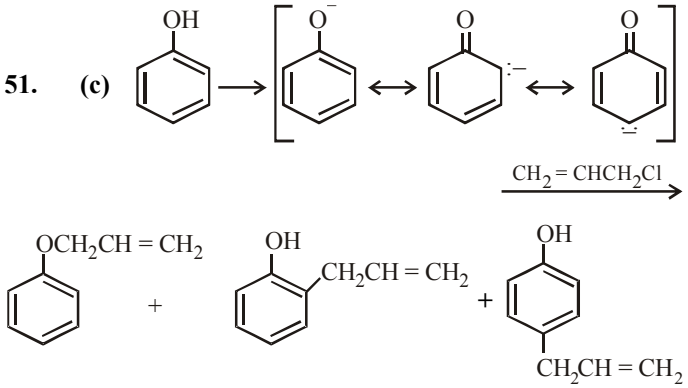
49. **(c)**



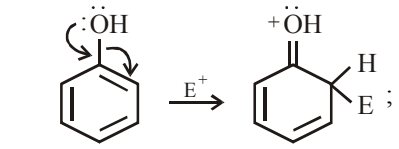
50. **(b)**



51. **(c)**

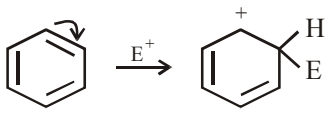


52. **(c)**



+ M effect in phenol activates benzene ring

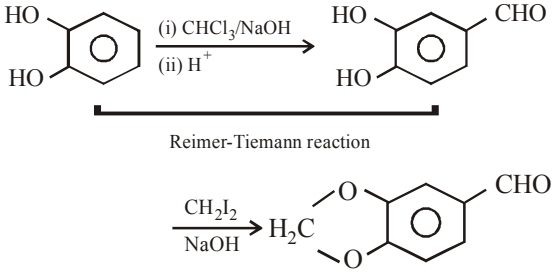
Oxonium ion (more stable)



Carbonium ion (less stable)

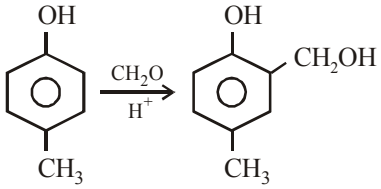
High stability of oxonium ion (oxocation) is because here every atom (except H) has a complete octet of electrons, while in carbocations, carbon bearing positive charge is having six electrons.

53. **(d)**

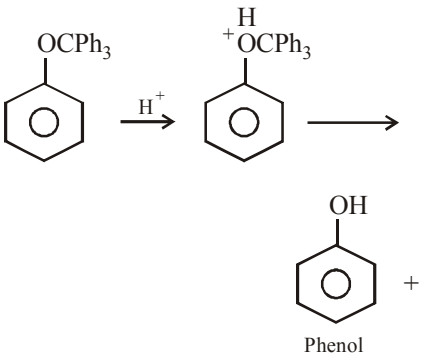


54. **(d)** Nitrosonium ion will go to *p*-position with respect to –OH group. Further dil. HNO_3 oxidises –NO group to $-NO_2$ group.

55. **(b)** $CH_2(OC_2H_5)_2$ is an acetal of formaldehyde with ethanol ; in presence of acid it decomposes to CH_2O and C_2H_5OH



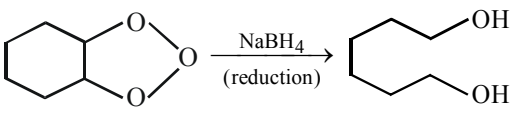
56. **(d)**



57. **(d)** The compound is a cyclic acetal ; hence it is stable to alkalies and hydrolysed by acids.

58. **(c)** MnO_2 selectively oxidises the alcoholic groups of allylic and benzylic alcohols (1º or 2º) to carbonyl compounds.

59. **(d)**



Ozonide

61. **(b)** Base catalysed epoxide opening is a typical S_N2 reaction in which attack of the nucleophile takes place at the less hindered expoxide.

62. **(d)** It is an example of Claisen rearrangement.

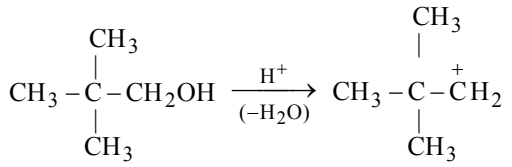
63. **(c)** The corresponding benzyl cation is most stable.

B COMPREHENSION TYPE

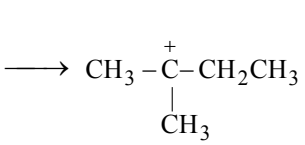
1. **(a)** Water (a polar solvent) has highest dielectric constant, so it will enhance ionisation of the alkyl halide to form carbocation.

2. **(d)** Primary alcohols, can form carbocations which may also undergo rearrangement, if structure permits (see next question). However, primary alcohols usually undergo S_N2 mechanism because of easy approach of the nucleophile on the less sterically hindered alkyl group and also because of relatively less stability of the 1° carbocation.

3. **(a)** Neopentyl alcohol is, although, a 1° alcohol, it undergoes S_N1 mechanism because of steric hindrance due to bulky alkyl group.

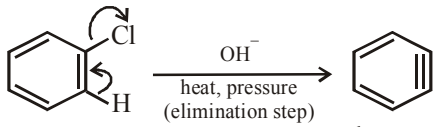


1° carbocation

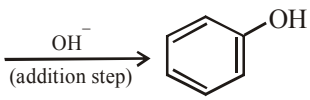


3° carbocation

4. **(d)**

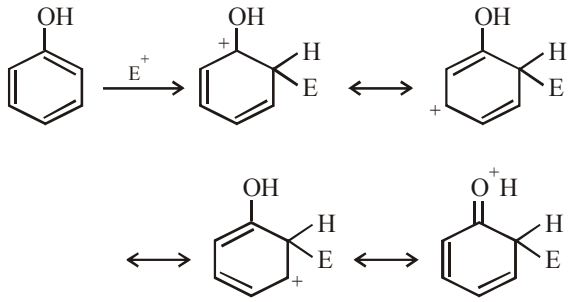


benzyne



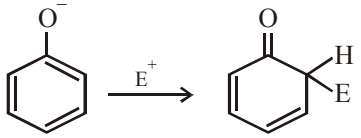
5. **(c)** Acid (H_2SO_4) converts acid anhydride to the more powerful electrophile, $CH_3\overset{+}{C}=O$ group. On the other hand, base (NaOH) converts phenol to the more powerful nucleophile, phenoxide ion.

6. **(c)**



Oxonium cation
(every atom has octet)

7. **(c)**



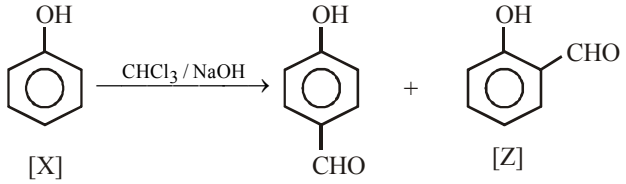
Fairly stable neutral
conjugated ketone

8. **(c)** In presence of acids, $CH_2 = O$ is protonated to form $CH_2=\overset{+}{O}H$ in which carbon is more electron deficient than that in $CH_2 = O$. In presence of OH^-, phenol is converted into phenoxide, $C_6H_5O^-$ which being a stronger nucleophile is easily attacked by weaker nucleophile, the unprotonated $CH_2 = O$.

9. **(c)** Libermann reaction is given by phenols as well as secondary amines, but the subsequent reactions indicate it to be a phenol.

10–11.(b–b)

Phenols react with $CHCl_3$/NaOH to form *o*-and *p*-hydroxybenzaldehydes (Reimer-Tiemann reaction).



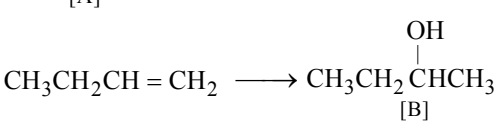
[X] [Y] [Z]

intramolecular H-bond
possible, –CHO not free

12–13.(a–c)

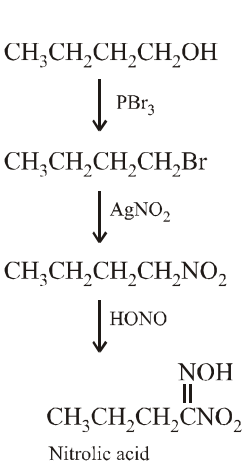
It is an example of electrophilic substitution, the electrophile is dichlorocarbene (an electron-deficient species) which is neutral in nature.

14. **(a)**

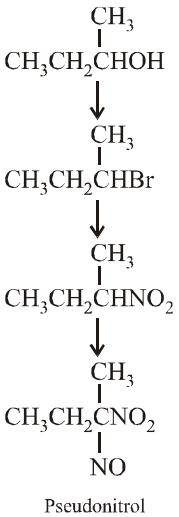


15. **(d)** $CH_3CH_2OCH_2CH_3 \xrightarrow{HI} 2CH_3CH_2I$

16. **(c)**



Nitrolic acid



Pseudonitrol

C Reasoning Type

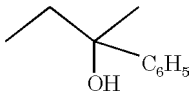
1. **(a)** **R** is the correct explanation of **A**.

2. **(b)** The correct explanation is : In Lucas test, tertiary alcohols react immediately because of the formation of the more stable tertiary carbocations.

3. **(c)** The correct reason is : Nucleophilic attack of phenolate ion through the *ortho*-carbon atom occurs on CCl_4 (a neutral electrophile) to form an intermediate which on hydrolysis gives salicylic acid (ArSE reaction).

4. **(a)** **R** is the correct explanation of **A**. Due to +M effect of $-\ddot{O}H$, its intermediate carbocation is more stable than the one in benzene.

D Multiple Correct Choice Type

1. **(a,b,c)**  is a 3° alcohol ; the first three combinations can be applied for its preparation.

2. **(b,d)** The combination $C_6H_5Br + CH_3CH_2OH$ has non-reactive C_6H_5Br, while in the combination $C_6H_5OH + Me_3CBr$, Me_3CBr being *tert*-halide will undergo elimination reaction rather substitution. Hence, only combinations (*a*) and (*c*) can be used for preparing ether.

$C_6H_5OH + (CH_3)_2SO_4 \xrightarrow{S_N} C_6H_5OCH_3$;

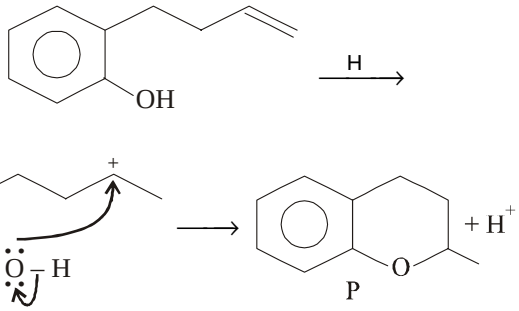
p-$NO_2C_6H_4Br + CH_3CH_2OH \xrightarrow{Ar\,S_N}$

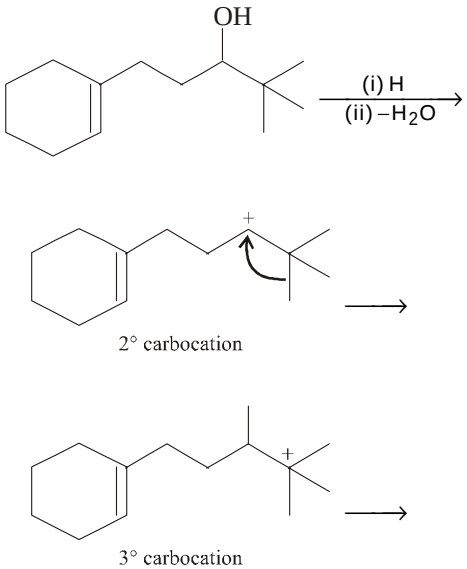
p-$NO_2C_6H_4OCH_2CH_3$

3. **(a,b,c)** Aniline as well as phenol are highly activated compounds towards electrophilic reactions (oxidation), hence all the three will be easily oxidised to *p*-benzoquinone, but not (d).

4. **(a,c,d)** Option (*b*) will form the most stable (3°) carbocations, hence it does not rearrange.

5. **(a,b,c)** *tert*- and *sec*-carbocations are liable to undergo elimination reaction in presence of strong alkoxide bases. Aryl and vinyl halides do not undergo nucleophilic substitution.

8. **(b,d)** 

9. **(b,c,d)** 

E MATRIX-MATCH TYPE

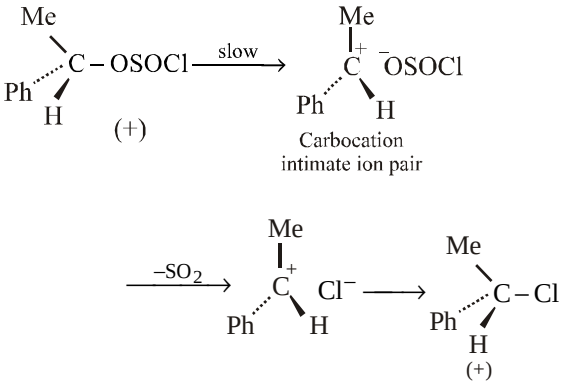
1. A-q; B-p; C-p, r; D-p, s

Hemiacetals are resistant to acids but can be hydrolysed by alkalis. On the other hand, acetals and ethers are hydrolysed by acids but not by alkalis. Glycosides are hemiacetals or acetals having carbohydrate moiety as one of the constituent. Ethers when heated with HI gives CH_3I which on treatment with $AgNO_3$ gives AgI (Ziesel method).

2. A-r; B-q; C-s; D-p

(A) We know that S_{N^1} reactions involve racemization as well as inversion, while S_{N^2} reactions involve inversion of configuration. However, here configuration is completely retained. This is because of the formation of a true intermediate in which carbocation and the anion ^-OSOCl (ion pair) is present in a solvent cage and hence attack by Cl^- ion is likely to occur only on the same side of the R^+ from which OSOCl is departed. Such reactions in which entering and leaving groups are present in the same side of the molecule are known as intramolecular or internal nucleophilic substitution, S_{N^i}.

$$R-OH \quad ClSOCl \longrightarrow R-OSOCl \quad HCl$$



(B) When reaction between ROH and $SOCl_2$ is carried out in presence of a basic solvent like pyridine, the product RCl is found to have inverted configuration. This is so because the HCl formed in the first step is taken up by pyridine to form $C_5H_5NH^+Cl^-$ and now Cl^- being an effective nucleophile attacks the alkyl chlorosulphite 'from the back' as in a normal S_{N^2} reaction.

(C) This is an example of intramolecular nucleophilic substitution (S_N^i) involving allylic system which has also undergone allylic rearrangement. Such reaction is designated as $S_N^{i'}$ (intramolecular nucleophilic substitution with allylic inversion).

(D) This is an example of usual S_{N^1} reaction.