EXERCISE-01 CHECK YOUR GRASP

SELECT THE CORRECT ALTERNATIVE (ONLY ONE CORRECT ANSWER)

1. Consider the following reaction sequence

$$CH_2 = CH_2 \xrightarrow[\text{cold}]{\text{dil.KMnO}_4} A \xrightarrow[\text{excess}]{PCl_5} B$$

The products (A) and (B) are, respectively :

(A) CH_3CH_2OH and CH_3CH_2Cl (B) CH_3CHO and CH_3CHCl_2

(C) CH_2OH CH_2OH and CH_2ClCH_2Cl (D) CH_2OHCH_2OH and CH_2OHCH_2Cl

2. Consider the following reaction sequence,

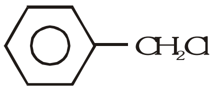
$$CH_3C \equiv CH \xrightarrow[\text{2 mole}]{HCl} A \xrightarrow[\text{Heat}]{\text{aq.KOH}} B$$

The products (A) and (B) are, respectively,

(A) $CH_3CH_2CHCl_2$ and CH_3CH_2CHO (B) $CH_3CCl_2CH_3$ and CH_3COCH_3

(C) $CH_3CCl_2CH_3$ and $CH_3C \equiv CH$ (D) $CH_3CHClCH_2Cl$ and $CH_3CHOHCH_2OH$

3. Consider the following chlorides :



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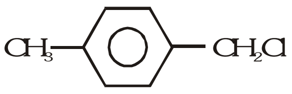
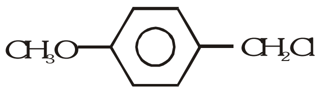
(A)



(B)



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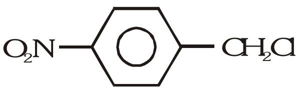
(C)



(D)

The order of reactivity of A, B, C and D towards hydrolysis by S_N1 mechanism is :

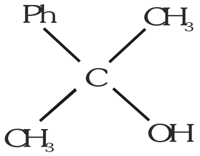
(A) A < B < C < D (B) D < C < B < A (C) D < A < B < C (D) C < B < A < D

4. In the following reaction sequence

$$Ph - C \equiv CH \xrightarrow[Hg^{2+}]{\text{aq.}H_2SO_4} A \xrightarrow[\text{2.}H_2O]{\text{1.}CH_3MgI} B$$

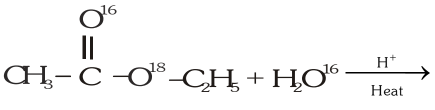
the product (B) is :

(A) $PhCOCH_3$ (B) $PhCH_2CHOHCH_3$ (C)



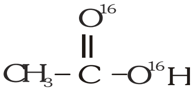
(D) $PhCH_2COCH_3$

5. Consider the following reaction.

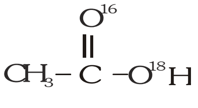


$$CH_3-\overset{\overset{O^{16}}{\|}}{C}-O^{18}-C_2H_5 + H_2O^{16} \xrightarrow[\text{Heat}]{H^+}$$

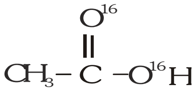
The products formed in the reaction are

(A) 

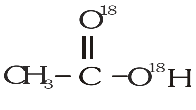
$CH_3-\overset{\overset{O^{16}}{\|}}{C}-O^{16}H$ and $C_2H_5O^{18}H$

(B) 

$CH_3-\overset{\overset{O^{16}}{\|}}{C}-O^{18}H$ and $C_2H_5O^{16}H$

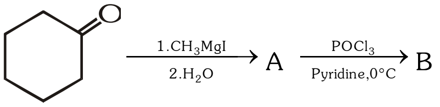
(C) 

$CH_3-\overset{\overset{O^{16}}{\|}}{C}-O^{16}H$ and $C_2H_5O^{16}H$

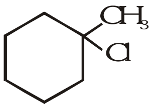
(D) 

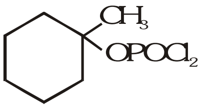
$CH_3-\overset{\overset{O^{18}}{\|}}{C}-O^{18}H$ and $C_2H_5O^{18}H$

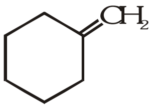
6. Consider the following reaction sequence,

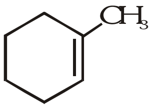


The product (B) is-

(A) 

(B) 

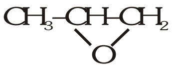
(C) 

(D) 

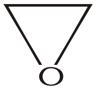
7. Propene is allowed to react with m-chloroperoxobenzoic acid. The product (A) is then reduced with $LiAlH_4$ in dry ether to give (B).

$$CH_3CH = CH_2 \xrightarrow{MCPBA} A \xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4} B$$

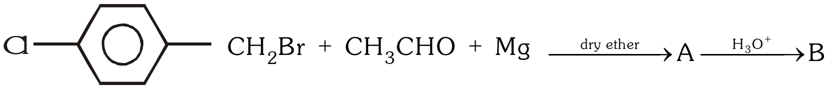
The structure of the product (B) is:

(A) $CH_3CHOHCH_2OH$ (B) $CH_3CH_2CH_2OH$ (C) $CH_3CHOHCH_3$ (D) 

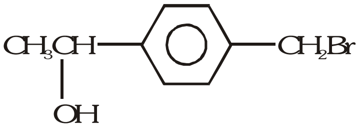
8. 2-Phenylethanol may be prepared by the reaction of phenylmagnesium bromide with :

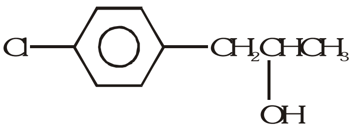
(A) HCHO (B) CH_3CHO (C) CH_3COCH_3 (D) 

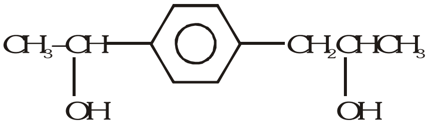
9. In the reaction

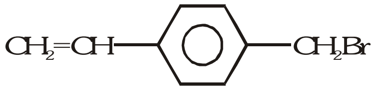


the product (B) is :

(A) 

(B) 

(C) 

(D) 

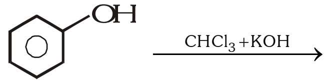
10. The final product in the reaction is :

$$Ph–OH + CCl_4 \xrightarrow{KOH} \text{product}$$

(A) Salicyl aldehyde (B) Salicylic acid (C) Methyl salicylate (D) Benzyl chloride

11. In the reaction of phenol with $CHCl_3$ and aqueous NaOH at 70 C, the eletrophile attacking the ring is :

(A) $CHCl_3$ (B) $\dot{C}HCl_2$ (C) $\ddot{C}Cl_2$ (D) $COCl_2$

12.  Product :

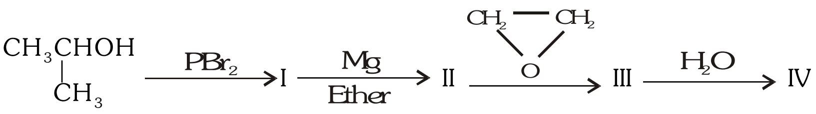
about above reaction the incorrect statement is

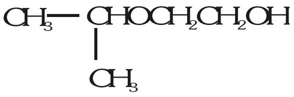
(A) The name of reaction is Riemer teimann's reaction

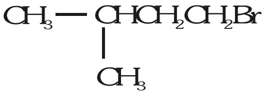
(B) The intermediate in the reaction is dichloro carbene

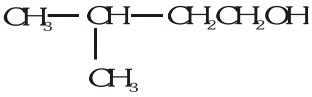
(C) The final product is o-hydroxy benzaldehyde (D) the final product is benzyl chloride

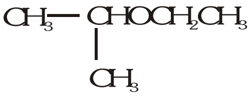
13. The final product (IV) in the sequence of reactions is :



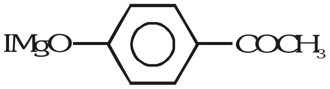
(A) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HOCH_2CH_2OH$

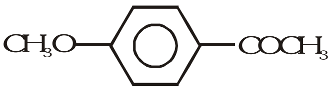
(B) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_2CH_2Br$

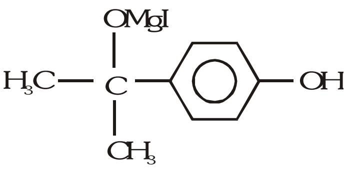
(C) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CH_2OH$

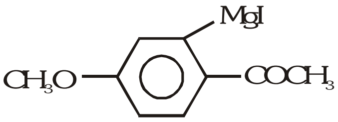
(D) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}HOCH_2CH_3$

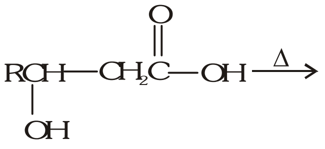
14. The reaction of 1 mol each of p-hydroxyacetophenone and methyl magnesium iodide will give :

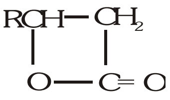
(A) CH$_4$ + 

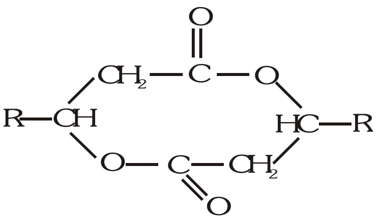
(B) 

(C) 

(D) 

15. The product obtained in the reaction  $R\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2\overset{\overset{\displaystyle O}{\|}}{C}-OH\xrightarrow{\Delta}$? is :

(A) 

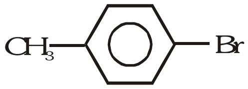
(B) 

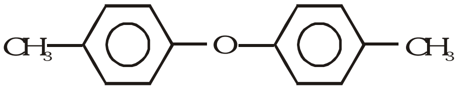
(C) RCH = CHCOOH

(D) None of these

16. The final product obtained in the reaction is :

(A) 

(B) 

(C) 

(D) None of these

17. The acidity of the compounds RCOOH, H_2CO_3, C_6H_5OH, ROH decreases in the order :

(A) RCOOH > H_2CO_3 > C_6H_5OH > ROH
(B) C_6H_5OH > RCOOH > H_2CO_3 > ROH
(C) ROH > C_6H_5OH > RCOOH > H_2CO_3
(D) H_2CO_3 > RCOOH > C_6H_5OH > ROH

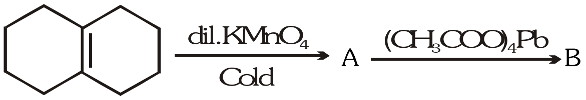
18. Arrange the following in order of decreasing acidic strength. p- nitrophenol (I), p-cresol (II), m-cresol (III), phenol (IV) :

(A) I > II > III > IV
(B) IV > III > II > I
(C) I > III > II > IV
(D) III > II > I > IV

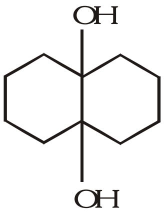
19. For the cleavage of ethers by halogen acids, the order of reactivity of halogen acids is :

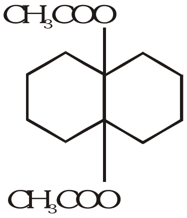
(A) HI > HBr > HCl
(B) HBr > HI > HCl
(C) HCl > HBr > HI
(D) Ethers do not undergo cleavage

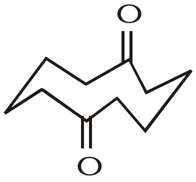
20. Consider the following reactions :

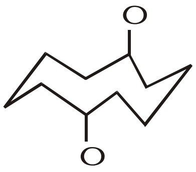


The product (B) is

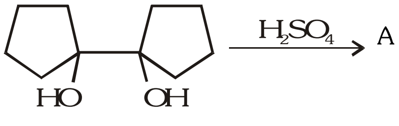
(A) 

(B) 

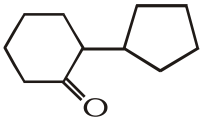
(C) 

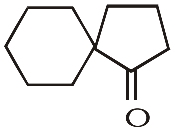
(D) 

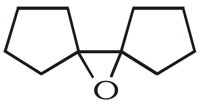
21. The major product (A) formed in the reaction

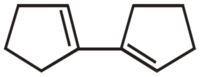


is :

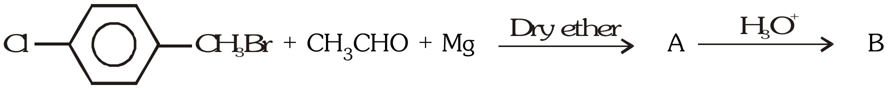
(A) 

(B) 

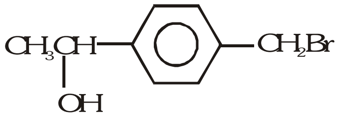
(C) 

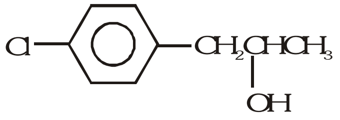
(D) 

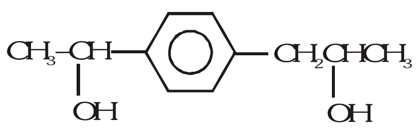
22. In the reaction

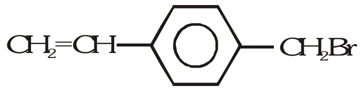


the product (B) is :

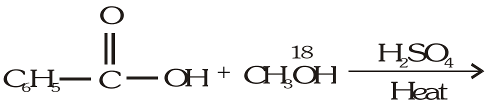
(A) 

(B) 

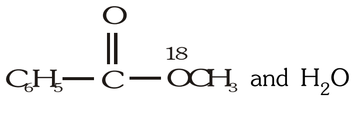
(C) 

(D) 

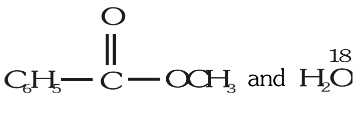
23. The products formed in the reaction are :



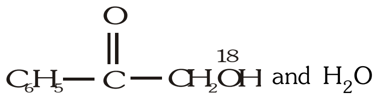
$$C_6H_5-\overset{\overset{O}{\|}}{C}-OH + CH_3\overset{18}{O}H \xrightarrow[\text{Heat}]{H_2SO_4}$$

(A) 

$C_6H_5-\overset{\overset{O}{\|}}{C}-\overset{18}{O}CH_3$ and H_2O

(B) 

$C_6H_5-\overset{\overset{O}{\|}}{C}-OCH_3$ and $H_2\overset{18}{O}$

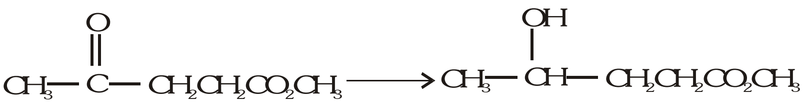
(C) 

$C_6H_5-\overset{\overset{O}{\|}}{C}-CH_2\overset{18}{O}H$ and H_2O

(D) 

$C_6H_5\overset{18}{O}CH_3$, CO and H_2O

24. The conversion



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_2CO_2CH_3 \longrightarrow CH_3-\overset{\overset{OH}{|}}{CH}-CH_2CH_2CO_2CH_3$$

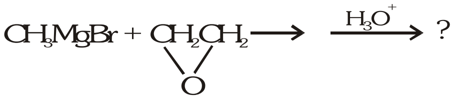
(A) $LiAlH_4$ and then H^+

(B) $NaBH_4$ and then H^+

(C) H_2/ Carbon

(D) None of these

25. Identify the final product of the reaction :



$$CH_3MgBr + \underset{O}{CH_2-CH_2} \longrightarrow \xrightarrow{H_3O^+} ?$$

(A) CH_3OH

(B) CH_3CH_2OH

(C) 

(D) $CH_3CH_2CH_2OH$

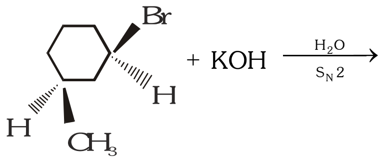
CHECK YOUR GRASP **ANSWER KEY** EXERCISE -1

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	C	B	C	C	A	C	C	D	B	B	C	D	C	A	C	A	A	A	A	C
Que.	21	22	23	24	25															
Ans.	A	B	A	B	D															

EXERCISE–02 BRAIN TEASERS

SELECT THE CORRECT ALTERNATIVES (ONE OR MORE THEN ONE CORRECT ANSWERS)

1. Consider the following reaction.

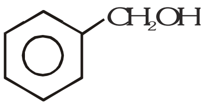


(1R, 3S)-cis-1 -Bromo -3-methylcyclohexane

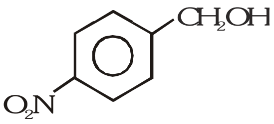
The product formed in the reaction is

(A) (1R, 3S)-cis-3- methylcyclohexanol
(B) (1S,3R)-cis-3-methylcyclohexanol
(C) (1S, 3S)-trans-3-methylcyclohexanol
(D) (1R,3R)-trans-3-methylcyclohexanol

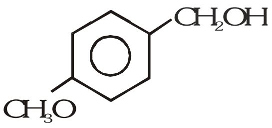
2. Consider the following alcohols



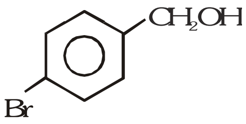
(I)



(II)



(III)



(IV)

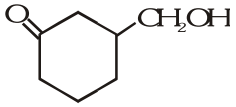
The order of decreasing reactivities of these alcohols towards nucleophilic substitution with HBr is

(A) III > I > IV > II
(B) III > I > II > IV
(C) I > III > IV > II
(D) I > III > II > IV

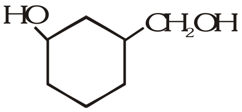
3. The product formed in the following reaction

is

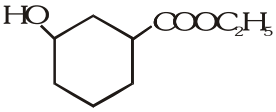
(A)



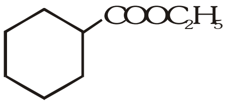
(B)



(C)



(D)



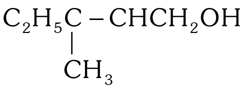
4. Consider the following sequence of reactions.

$C_2H_5C \equiv CH \xrightarrow{CH_3MgBr} A \xrightarrow[2.H_3O^+]{1.HCHO} B$

The product (B) is

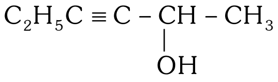
(A) CH_3CH_2OH

(B)



$C_2H_5\underset{\displaystyle CH_3}{\underset{|}{C}}-CHCH_2OH$

(C)



$C_2H_5C \equiv C-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$

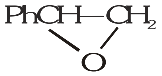
(D) $C_2H_5C \equiv C - CH_2OH$

5. In the transformations

$PhCH = CH_2 \xrightarrow[CH_2Cl_2]{ArCO_3H} A \xrightarrow[2.H_2O]{1.LiAlH_4,Et_2O} B$

the end product (B) is

(A)



(B) $PhCHOH\ CH_3$
(C) $PhCH_2CH_2COAr$
(D) $PhCH_2CH_2OH$

6. The reactivities of methanol (1), 1- propanol (II), 2- butanol (III) and 2- methyl-2- propanol (IV) towards sodium metal follow the order

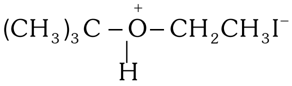
(A) I > II > III > IV (B) IV > III > II > I (C) I > IV > II > III (D) IV > II > III > I

7. In the reaction

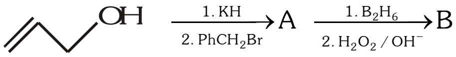
$$(CH_3)_3\ C–O–CH_2CH_3 + \underset{(1\ mole)}{HI} \xrightarrow{heat}$$

the product(s) formed is (are)

(A) $(CH_3)_3$ C–OH and CH_3CH_2I (B) $(CH_3)_3C–I$ and CH_3CH_2OH

(C) $(CH_3)_3C–I$ and CH_3CH_2I (D) 
$(CH_3)_3C-\overset{+}{\underset{H}{O}}-CH_2CH_3I^-$

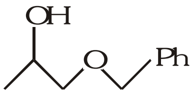
8. Consider the following sequence of reactions.



The end product (B) is

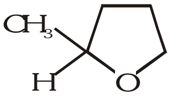
(A) 

(B) 

(C) 

(D) 

9. In the reaction



+ HCl →

the major product formed is

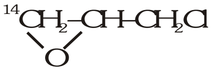
(A) 

(B) 

(B) 

(D) 

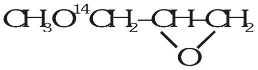
10. Consider the following reaction.

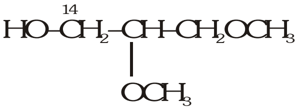


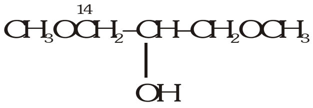
$+CH_3\bar{O} \longrightarrow A$

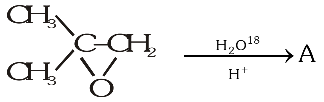
The product (A) is

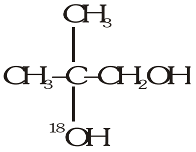
(A) 

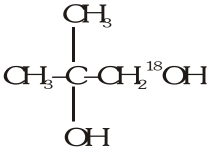
(B) 

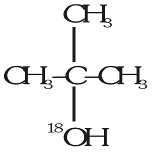
(C) 
$HO-\overset{14}{C}H_2-\underset{OCH_3}{CH}-CH_2OCH_3$

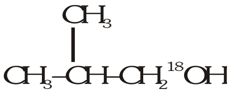
(D) 
$CH_3O\overset{14}{C}H_2-\underset{OH}{CH}-CH_2OCH_3$

11. In the reaction  , the product (A) has the structure :

(A) 
$CH_3-\overset{CH_3}{\underset{^{18}OH}{C}}-CH_2OH$

(B) 
$CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_2{}^{18}OH$

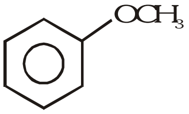
(C) 
$CH_3-\overset{CH_3}{\underset{^{18}OH}{C}}-CH_3$

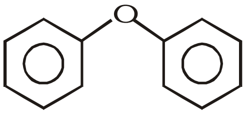
(D) 
$CH_3-\overset{CH_3}{CH}-CH_2{}^{18}OH$

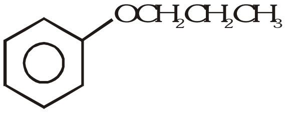
12. The compound which does not react with sodium is

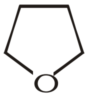
(A) $CH_3CHOHCH_3$ (B) CH_3OCH_3 (C) CH_3COOH (D) CH_3CH_2OH

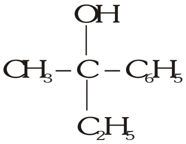
13. Which of the following ethers is not cleaved by concentrated HI even at 525 K ?

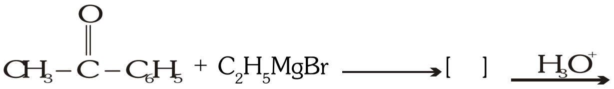
(A) 

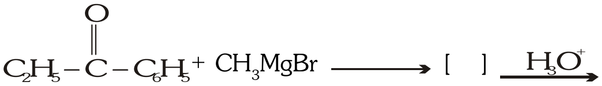
(B) 

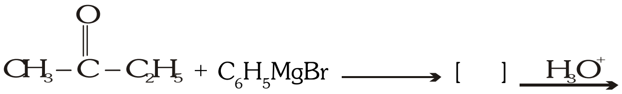
(C) 

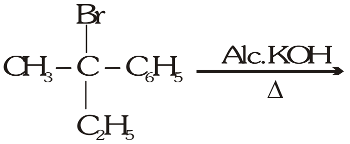
(D) 

14. Which of the following reactions can be used to prepare 
$CH_3-\overset{OH}{\underset{C_2H_5}{C}}-C_6H_5$

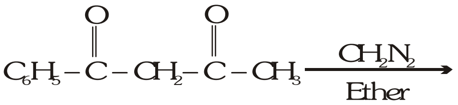
(A) 
$CH_3-\overset{O}{\overset{\|}{C}}-C_6H_5 + C_2H_5MgBr \longrightarrow [\quad] \xrightarrow{H_3O^+}$

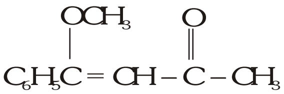
(B) 
$C_2H_5-\overset{O}{\overset{\|}{C}}-C_6H_5 + CH_3MgBr \longrightarrow [\quad] \xrightarrow{H_3O^+}$

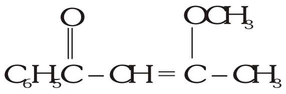
(C) 
$CH_3-\overset{O}{\overset{\|}{C}}-C_2H_5 + C_6H_5MgBr \longrightarrow [\quad] \xrightarrow{H_3O^+}$

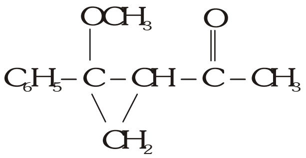
(D) 
$CH_3-\overset{Br}{\underset{C_2H_5}{C}}-C_6H_5 \xrightarrow[\Delta]{Alc.KOH}$

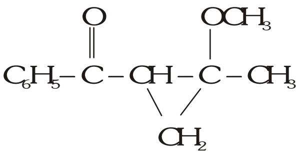
15. What are the products expected in the following reactions ?


$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[Ether]{CH_2N_2}$

(A) 
$C_6H_5\overset{OCH_3}{C}=CH-\overset{O}{\overset{\|}{C}}-CH_3$

(B) 
$C_6H_5\overset{O}{\overset{\|}{C}}-CH=\overset{OCH_3}{C}-CH_3$

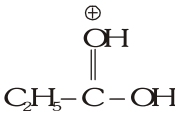
(C) 

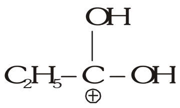
(D) 

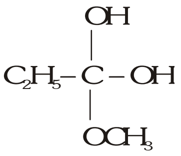
16. Which of the following groups will increase the acidity of phenol?

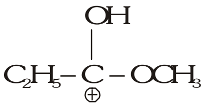
(A) – NO_2 (B) –CN (C) –X (halogen) (D) None of these

17. In the esterification of propanoic acid with methanol in the presence of a mineral acid, which of the following are intermediate species?

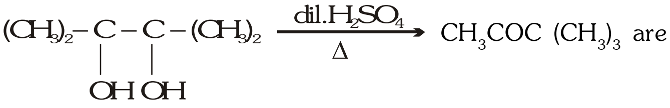
(A) 
$C_2H_5-\overset{\overset{\overset{\oplus}{OH}}{\|}}{C}-OH$

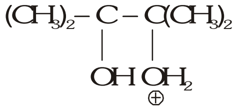
(B) 
$C_2H_5-\underset{\oplus}{\overset{\overset{OH}{|}}{C}}-OH$

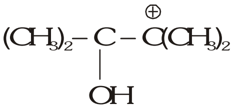
(C) 
$C_2H_5-\underset{\underset{OCH_3}{|}}{\overset{\overset{OH}{|}}{C}}-OH$

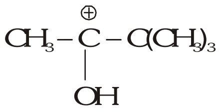
(D) 
$C_2H_5-\underset{\oplus}{\overset{\overset{OH}{|}}{C}}-OCH_3$

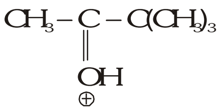
18. The intermediate stages in the conversion


$(CH_3)_2-\underset{\underset{OH}{|}}{C}-\underset{\underset{OH}{|}}{C}-(CH_3)_2 \xrightarrow[\Delta]{dil.H_2SO_4} CH_3COC\ (CH_3)_3$ are

(A) 
$(CH_3)_2-\underset{\underset{OH}{|}}{C}-\underset{\underset{\underset{\oplus}{OH_2}}{|}}{C}(CH_3)_2$

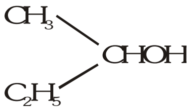
(B) 
$(CH_3)_2-\underset{\underset{OH}{|}}{C}-\overset{\oplus}{C}(CH_3)_2$

(C) 
$CH_3-\underset{\underset{OH}{|}}{\overset{\oplus}{C}}-C(CH_3)_3$

(D) 
$CH_3-\underset{\underset{\underset{\oplus}{OH}}{\|}}{C}-C(CH_3)_3$

19. An alcohol, on treatment with P + I_2 followed by the reaction of the formed product first with $AgNO_2$ and then with HNO_2 and final basicification, gives a blue colour. Which of the following alcohols can it be?

(A) CH_3CH_2OH (B) $(CH_3)_2CHOH$

(C) $(CH_3)_3C - OH$ (D) 

20. Which of the following will result in the formation of an ether?

(A) $(CH_3)_3C\overset{-}{O}\overset{+}{Na} + CH_3CH_2Br \longrightarrow$ (B) $(CH_3)_3CBr + C_2H_5\overset{-}{O}\overset{+}{Na} \longrightarrow$

(C) $C_6H_5ONa + CH_3Br \longrightarrow$ (D) $C_6H_5Br + CH_3\overset{-}{O}\overset{+}{Na} \longrightarrow$

BRAIN TEASERS **ANSWER KEY** EXERCISE -2

Que.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Ans.	C	A	C	D	B	A	B	B	B	B	A	B	B	A,B,C	A,B
Que.	16	17	18	19	20										
Ans.	A,B,C	A,B,C,D	A,B,C,D	B,D	A,C										

EXERCISE–03

MISCELLANEOUS TYPE QUESTIONS

TRUE OR FALSE :

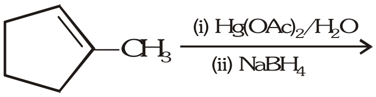
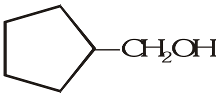
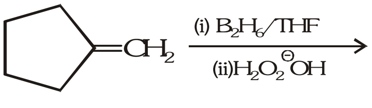
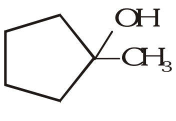
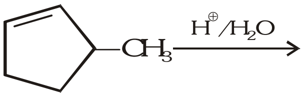
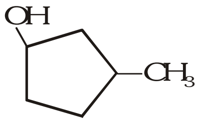
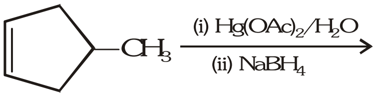
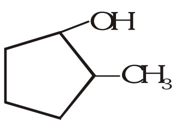
1. Lower alcohols are more soluble in water than higher alcohols.
2. Tertiary alcohols are more reactive towards halogen acids than secondary alcohols.
3. Glycerine is more viscous than ethylene glycol.
4. Tertiary alcohols are more acidic than phenol.
5. Phenol on heating with CCl_4 in presence of NaOH at 340 K followed by acetylation gives aspirin.
6. Phenol does not decompose $NaHCO_3$ to evolve CO_2 but picric acid does.
7. m-Methoxyphenol is a weaker acid than phenol.
8. Sodium ethoxide is prepared by the reaction of ethanol with aqueous sodium hydroxide.

FILL IN THE BLANKS :

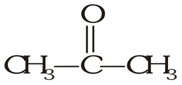
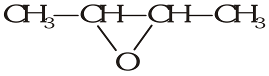
1. Lower alcohols are highly soluble in water due to ……………………
2. The reaction of phenol with a diazonium salt in weak alkaline medium is called……………………
3. Absolute alcohol can be prepared from rectified spirit by …………………… distillation.
4. A mixture of phenol and phthalic anhydride when heated with conc. H_2SO_4 forms ……………………which is used as an ……………………in acid-base titrations.
5. Tertiary alcohols when passed over heated copper undergo ……………………to form……………………
6. One mole of glycerol when heated with two moles of HIO_4 gives two moles of ……………………and one mole of ……………………
7. The acidity of phenol is due to the ……………………of its anion.
8. A…………………… diol has two hydroxyl groups on……………………
9. Phenol is acidic because of resonance stabilization of its conjugate base, namely……………………
10. Amongst the three isomers of nitrophenols, the one that is least soluble in water is……………………

MATCH THE COLUMN

1. Match the column I with column II.

Column-I (Reaction)		Column-II (Possible products)	
(A)		(p)	
(B)		(q)	
(C)		(r)	
(D)		(s)	

2. Match the column I with column II.

	Column-I (substrate + RMgX)		Column-II (Product)
(A)	HCHO	(p)	Tertiary alcohol
(B)	 $CH_3-\overset{O}{\overset{\Vert}{C}}-CH_3$	(q)	First ketone then 3 alcohol
(C)		(r)	Secondary alcohol
(D)	Ester	(s)	Primary alcohol

ASSERTION & REASON QUESTION :

These questions contains, Statement-I (assertion) and Statement-II (reason).

(A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I

(B) Statement-I is True, Statement-II is True ; Statement-II is NOT a correct explanation for Statement-I

(C) Statement-I is True, Statement-II is False.

(D) Statement-I is False, Statement-II is True.

1. **Statement-I** : Solubility on n-alcohols in water decreases with increase in molecular weight.

Because

Statement-II : The relative proportion of the hydrocarbon part in alcohols increases with increasing molecular weight which permits enhanced hydrogen bond with water.

2. **Statement-I** : p- Nitrophenol is a stronger acid than o-nitrophenol.

Because

Statement-II : Intramolecular H-bond makes o-isomer weaker than p-isomer.

3. **Statement-I** : Phenol is more reactive than benzene towards

Because

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

4. **Statement-I** : Tert-Butoxide is a stronger base than OH^- or $C_2H_5O^-$ ion but is a much poorer nucleophile.

Because

Statement-II : A negatively charged ions is always more powerful nucleophile than its conjugate acid.

5. **Statement-I** With Br_2–H_2O, phenol gives 2,4,6- tribromophenol but with Br-CS_2, it gives 4-bromophenol as the major product.

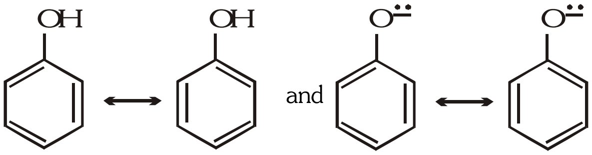
Because

Statement-II : In water ionization of phenol is enhanced but in CS_2, it is greatly suppressed.

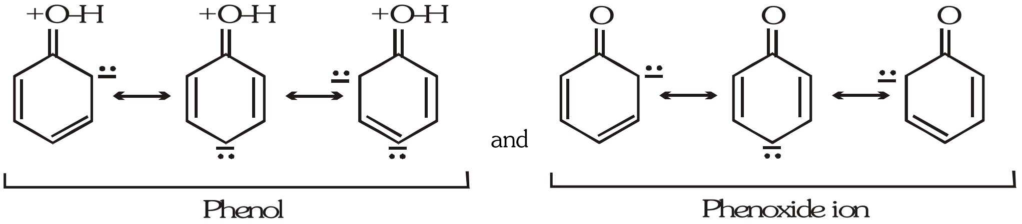
COMPREHENSION BASED QUESTIONS :

Comprehension # 1

Phenols are converted into their salts by aqueous NaOH but not by aqueous bicarbonates. The salts are converted into the free phenols by aqueous mineral acids, carboxylic acid or carbonic acids. Most phenols have K_a value of about 10^{-10}, and are tremondously more acidic than alcohols. The difference in acidity are due to difference in stabilities of reactants and products. Phenol and phenoxide ions contain benzene ring and therefore must be hybrid of Kekuley structures

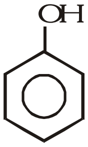


Being basic, oxygen can share more than a pair of electron with the ring.

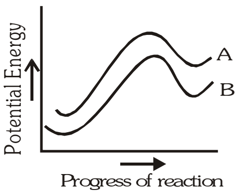


Since energy must be supplied to separate opposite charge, the structure of phenols should contain more energy. The net effect of resonance is therefore to stabilise the phenoxide ion to a greater extent than the phenol and thus to shift the equilibrium towards ionization and make K_a larger than for an alcohol.

1. Which of the following is strongest acid ?

(A) H_2CO_3 (B)  (C) $CH_3–OH$ (D) $CH_3–CH_2–OH$

2. Consider the following curves :



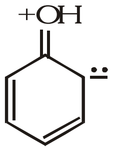
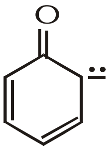
(A) Curve A represents the ionisation of alcohol

(B) Curve B represent the ionisation of Phenols

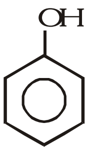
(C) Curve A represents the ionisation of phenol

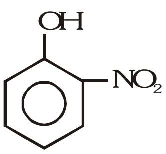
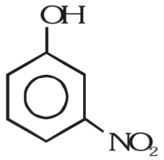
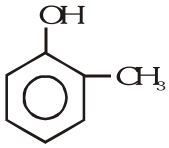
(D) None

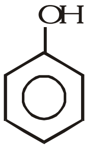
3. Which of the following is more stable:

(A)  (B)  (C) Both (D) Unpredictable

4. Correct order of acidity is

(A) H_2CO_3 > CH_3–OH > 

(B)  >  > 

(C) H_2CO_3 >  > CH_3 – OH

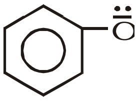
(D) Both B and C

5 Choose the correct statement:

(A) Phenol gives effervescence with $NaHCO_3$

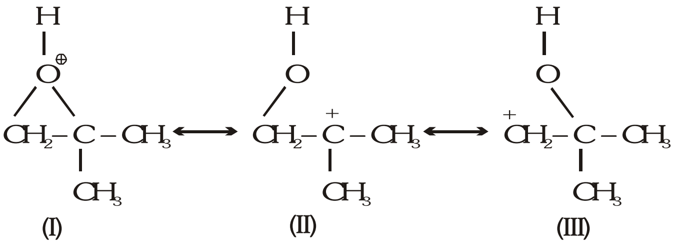
(B) Picric acid is weaker acid than carbonic acid

(C) Picric acid gives effervescence with $NaHCO_3$

(D) $R-\ddot{O}^{-}$ is more stable than 

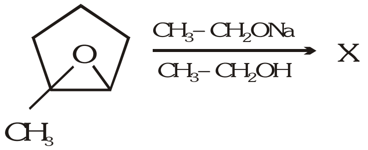
Comprehension # 2

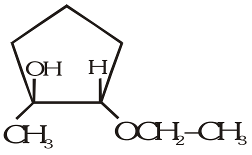
Symmetrically substituted epoxides give the same products in both the acid catalysed and base catalyzed ring opening. An unsymmetrical epoxide gives different products under acid catalysed and base catalysed conditions. Under basic conditions, the alkoxide ion simply attacks the less hindered carbon atom in an SN^2 displacement. Under acidic conditions, the alcohol, attacks the protonated epoxide.

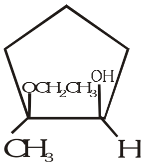


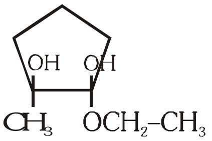
Structure II and III show that the oxirane carbon share part of positive charge. The tertiary carbon bear a larger part of positive charge and it is more strongly electrophilic. The bond between tertiary carbon and oxygen is weaker implying a lower transition state energy for attack at the tertiary carbon. Attack by the weak nucleophilic is sensitive to the strength of electrophilic is sensitive to the strength of electrophile. Centre attack takes place at more electrophilic carbon which is usually the more substituted carbon because it can better support the positive charge.

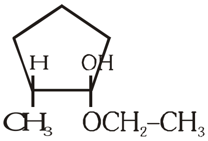
1. What will be the products in following reactions

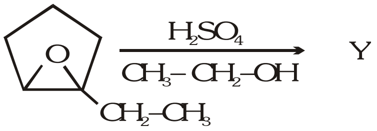


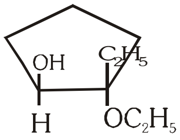
(A) 

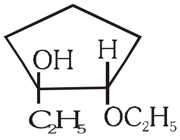
(B) 

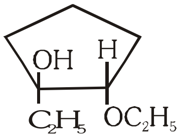
(C) 

(D) 

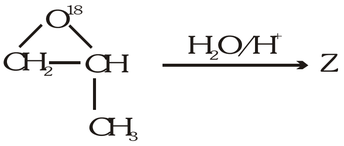
2. 

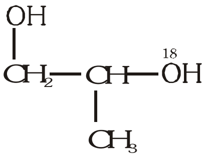
(A) 

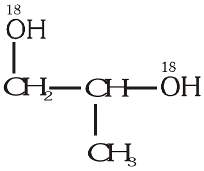
(B) 

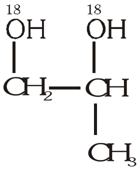
(C) 

(D) None

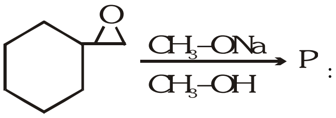
3. 

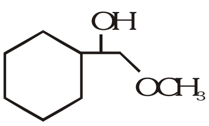
(A) 

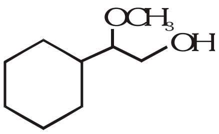
(B) 

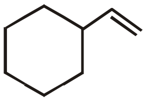
(C) 

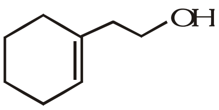
(D) None

4. 

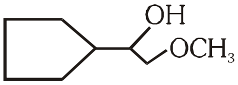
(A) 

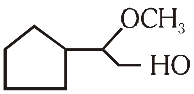
(B) 

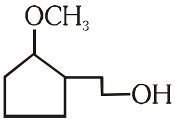
(C) 

(D) 

5. 

(A) 

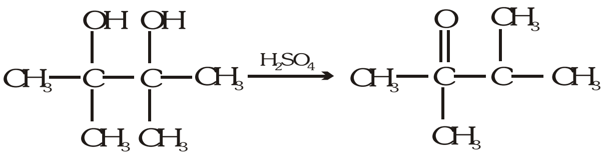
(B) 

(C) 

(D) None

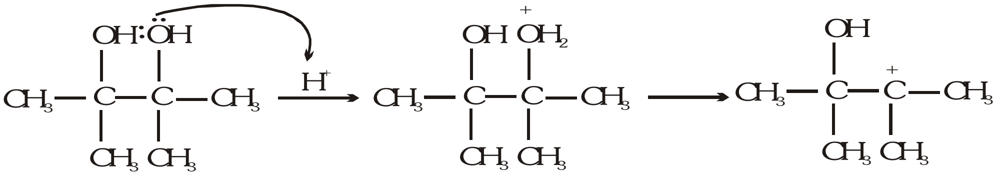
Comprehension # 3

When pinacol is treated with dilute H_2SO_4, a re-arrangement reaction takes place which leads to the formation of a ketone.



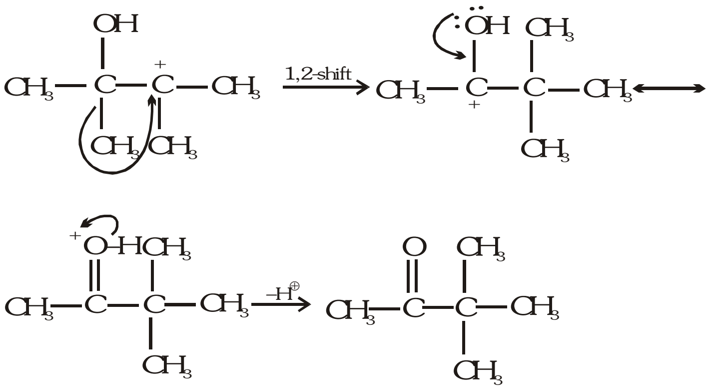
This reaction involves re-arrangement of carbocation.

Step 1:

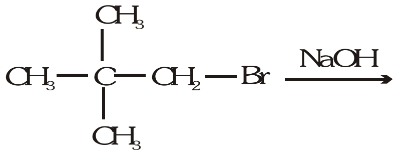


Step 2 :

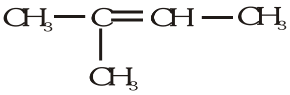
Carbocation rearrange by hydride, alkyl or aryl shift to get as stable as they can. Stability is the driving force for re-arrangement migration of bond may also occur. Where by ring expansion and ring contraction takes place. The relief of strain can provide a powerful driving force for re-arrangement.



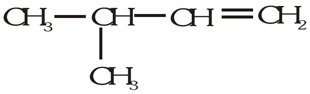
1. What will be the product of following reaction



$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-Br \xrightarrow{NaOH} P$, P is :

(A) 

$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_3$

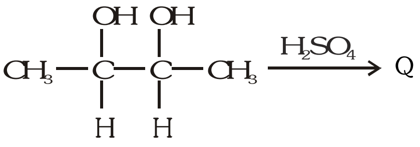
(B) 

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

(C) Both of these

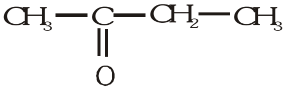
(D) None of these

2. What will be the product of following reaction

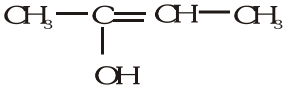


$CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xrightarrow{H_2SO_4} Q$

Q is :

(A) 

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

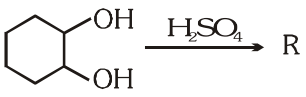
(B) 

$CH_3-\underset{\underset{OH}{|}}{C}=CH-CH_3$

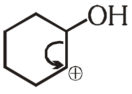
(C) Both

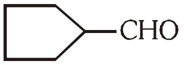
(D) None

3. What will be the product of following reaction



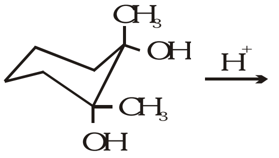
R is :

(A) 

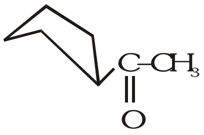
(B) 

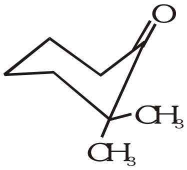
(C) Both

(D) None

4. What will be the product of following reaction  S,

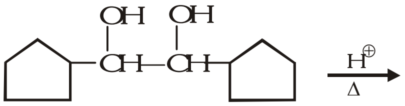
S is :

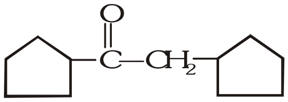
(A) 

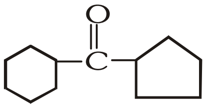
(B) 

(C) Both

(D) None

5. What will be the product of following reaction  ?

(A) 

(B) 

(C) both

(D) None

MISCELLANEOUS TYPE QUESTION

ANSWER KEY

EXERCISE -3

- ***True / False***

1. T 2. T 3. T 4. F 5. T

6. T 7. T 8. T

- ***Fill in the Blanks***

1. H-bonding
2. coupling reaction
3. azeotropic
4. phenolphthalein, indicator
5. dehydriation, alkene
6. formaldehyde, formic acid
7. resonance stabilisation
8. vicinal, adjacent
9. phenoside ion
10. O-nitrophenol

- ***Match the Column***

1. (A) → q ; B → p ; (C) → r ; (D) → q
2. (A) → s ; (B) → p ; (C) → r ; (D) → q

- ***Assertion - Reason Questions***

1. C 2. A 3. A 4. B 5. A

- ***Comprehension Based Questions***

Comprehension #1 : 1. (A) 2. (B) 3. (B) 4. (D) 5. (C)
Comprehension #2 : 1. (A) 2. (A) 3. (B) 4. (A) 5. (B)
Comprehension #3 : 1. (A) 2. (A) 3. (B) 4. (A) 5. (B)

EXERCISE–04 [A]

CONCEPTUAL SUBJECTIVE EXERCISE

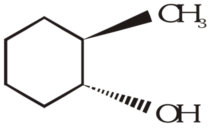
1. $C_2H_5OH \xrightarrow{PCl_5} (A) \xrightarrow{KCN} (B) \xrightarrow{H_3O^+} (C) \xrightarrow{NH_3} (D) \xrightarrow{heat} (E)$

2. $CH_3CH_2CH_2OH \xrightarrow{PBr_5} (A) \xrightarrow{KOH(Alc.)} (B) \xrightarrow{HBr} (C) \xrightarrow{NH_3} (D)$

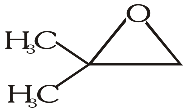
3. t-butyl alcohol reacts less rapidly with metallic sodium than the primary alcohol. Explain why?

4. Explain why ArOR ethers are cleaved to give RI and ArOH rather than ArI and ROH.

5. Complete tthe following reactions :

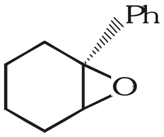
(a) 

$\xrightarrow{SOCl_2}$

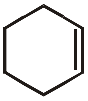
(b) 

$\xrightarrow[H_2O]{CH_3MgBr}$

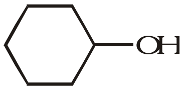
6. Complete tthe follofing reactions :

(a) 

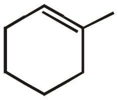
$\xrightarrow{HI}$

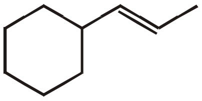
(b) 
$\xrightarrow[NaHSO_3]{OsO_4}$

7. Provide products in the following reactions :

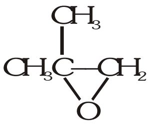
(a) 

$\xrightarrow[Pyridine]{SOCl_2}$

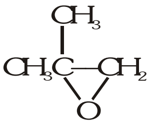
(b) 
$\xrightarrow[CH_3OH]{Hg(OAc)_2} \xrightarrow{NaBH_4}$

(c) 
$\xrightarrow{mCPBA}$

8. Identify the products A and B giving proper explanation :



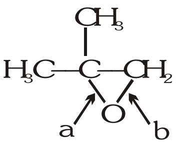
$+ H_2O^{18} \xrightarrow{H^+}$ A,



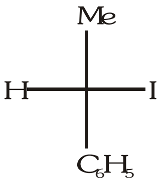
$+ CH_3OH \xrightarrow{CH_3ONa}$ B

9. Indicate bonds which are cleaved

I : in basic conditions II : in acidic conditions



10. In the following S_N2 reaction



(dextro)

$\xrightarrow[S_N2]{OH^-}$ (A) is .... (stereoisomer)

CONCEPTUAL SUBJECTIVE EXERCISE

ANSWER KEY

EXERCISE -4(A)

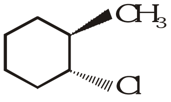
1. (A) C_2H_5Cl; (B) C_2H_5CN; (C) C_2H_5COOH; (D) $C_2H_5COONH_4$; (E) $C_2H_5CONH_2$

2 (A) C_3H_7Br; (B) $CH_3CH{=}CH_2$; (C) $CH_3CHBrCH_3$; (D) $CH_3CHNH_2CH_3$

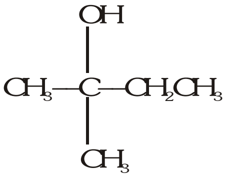
3. The +I.E. of three methyl groups on central C-atom of tert-butyl alcohol makes is partially negative with the result that it pushes the electron pair of –OH bond towards H-atom and thus H-atom is not replaced easily.

4. S_N2 attack on a carbon of benzene ring does not occur nor does the high energy $C_6H_5^+$ form by an S_N1 reaction. Hence ArI cannot be a product even in an excess of conc. HI.

5. (a)

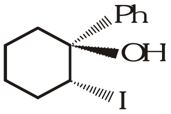


(b)

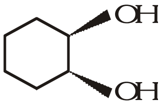


$CH_3-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_2CH_3$

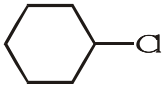
6. (a)



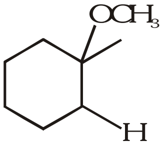
(b)



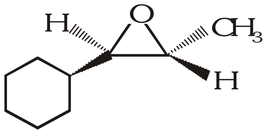
7. (a)



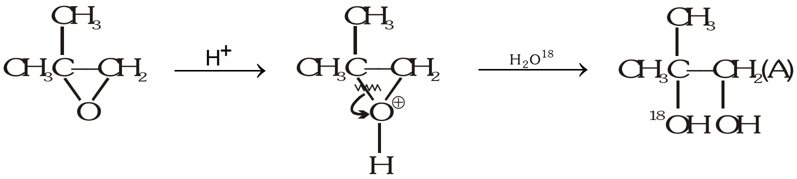
(b)



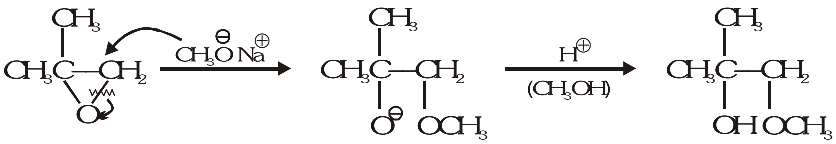
(c)



8.



(nucleophile attacks the more substituted carbon in acid-catalysed reaction)



(nucleophile attacks the less substituted carbon in base-catalysed reaction)

9. I : bond b ; II : bond a

10. A is laevo - isomer

EXERCISE–04 [B] BRAIN STORMING SUBJECTIVE EXERCISE

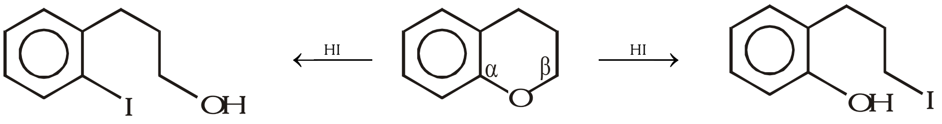
1. A compound (X) reacts with thionyl chloride to give a compound (Y). (Y) reacts with Mg to form a Grignard reagent, which is treated with acetone and the product is hydrolysed to give 2-methyl-2- butanol. What are structural formulae of (X) and (Y) ?

2. Compound (A) $C_4H_{10}O$ reacts rapidly with metallic sodium, but undergoes almost no reaction with Lucas reagent. When (A) is treated with hot concentrated sulphuric acid, a new compound (B) C_4H_8 is formed. If C_4H_8 is hydrated with sulphuric acid a new compound (C) C_4H_9OH is formed, which is almost inert to metallic sodium but reacts rapidly with Lucas reagent. What are (A), (B) and (C) ?

3. Give the product of the reaction of Ph_2CHCH_2OH with HBr and explain its formation.

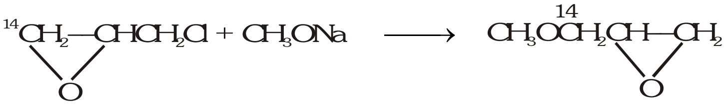
4. Hydration of 3-phenyl-1-butene in dilute H_2SO_4 is not a satisfactory method for preparing 3-phenyl-2-butanol, because 2-phenyl-2-butanol is obtained instead. Explain.

5. When A (given below) reacts with HI products is B and not C. Explain.



(C) (A) (B)

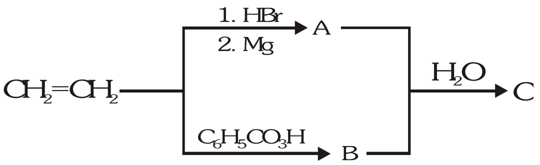
6. Isotopic carbon-14 in (A) appears at new position (as in B) when (A) reacts with CH_3ONa. Explain.



$^{14}CH_2—CHCH_2Cl + CH_3ONa \longrightarrow CH_3OCH_2\overset{14}{C}H—CH_2$

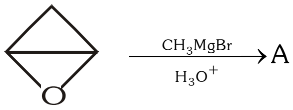
(A) (B)

7. Complete the following reaction



8. Complete the following reactions

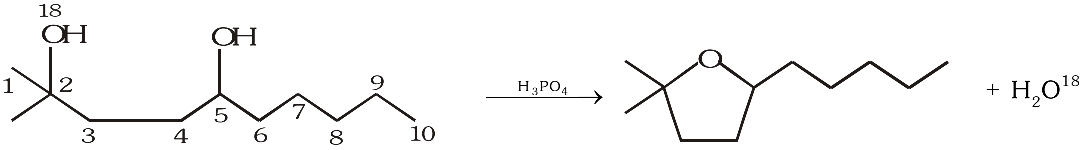
(a)



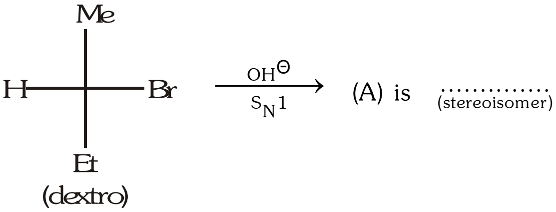
(b)

(c) $CH_3CH=CH_2 \xrightarrow{mCPBA} A \xrightarrow[H_3O^+]{C_2H_5MgBr} B$

9. In the following dehydration of diol with H_3PO_4, following product is formed such that isotopic ^{18}O goes with H_2O. Explain.



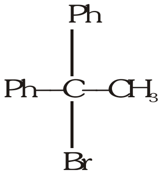
10. In the following S_N1 reaction :



1. C_2H_5OH C_2H_5Cl
Ethyl alcohol Ethyl chloride
(X) (Y)

2. $(CH_3)_2CHCH_2OH$; $(CH_3)_2C{=}CH_2$; $(CH_3)_3COH$
(A) (B) (C)

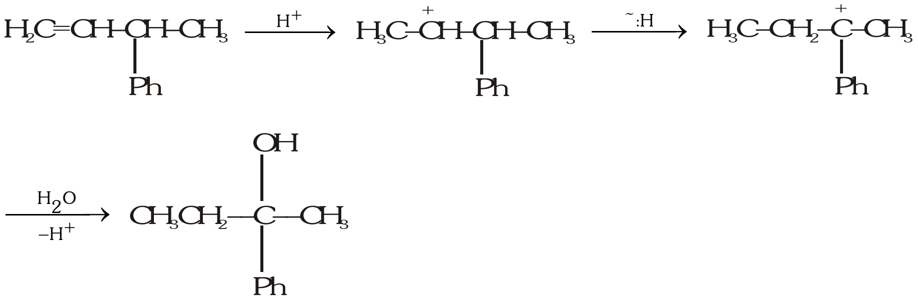
3.



$Ph-\overset{\overset{\large Ph}{|}}{\underset{\underset{\large Br}{|}}{C}}-CH_3$

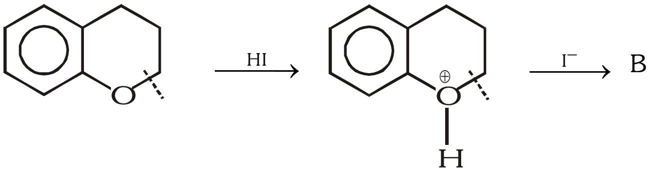
Synchronous migration of Ph provides greater assistance in the removal of H_2O form the protonated alcohol than does a methyl group.

4.

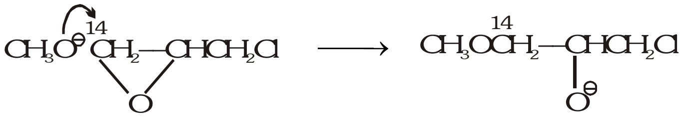


(Hydration gives an intermediate 2 C$^+$, which undergoes a hydride shift Although phenyl is a better migrator than H, migration of H occurs leading to a more stable 3 benzylic carbocation.)

5. Bond energy of C (vinylic)––O bond (α) is greater than that of C(alkylic)––O bond (β). Hence, when A reacts with HI, bond β breaks forming B.

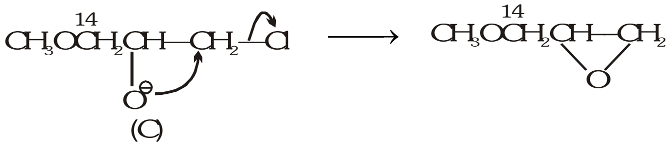


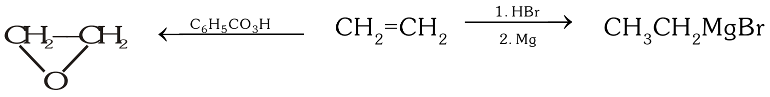
6. CH_3O^- (nucleophile) attacks less submituted carbon (which is C-14 in this case) forming intermediate (C).



(A) (C)

(C) will displace Cl^- forming (B)

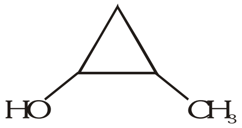


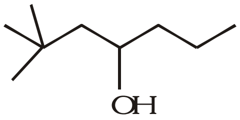
7. 

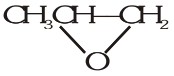
(B) (A)

$A + B \xrightarrow{H_2O} CH_3CH_2CH_2CH_2OH$

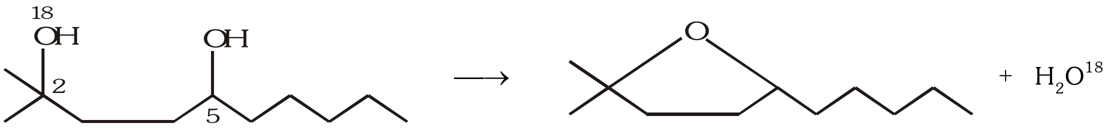
(C)

8. (A) 

(B) 

(C) 

9. 3 alcohol at C_2 is more basic than 2 alcohol at C_5. Hence, intramolecular dehydration takes place such that H of 2 alcoholic group at C_5 eliminates OH of 3 alcoholic groups at C_2 (with isotopic ^{18}O) to form cyclic ether



10. A is a mixture of d- and 1- and thus racemic mixture.

EXERCISE–05 PREVIOUS YEARS QUESTIONS

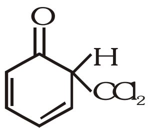
1. The products of combustion of an aliphatic thiol (RSH) at 298 K are - [IIT-92]

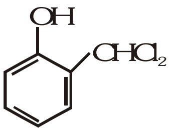
(A) CO_2 (ℓ), H_2O (g) and SO_2 (g)
(B) CO_2 (g), H_2O (g) and SO_2 (g)
(C) CO_2 (ℓ), H_2O (ℓ) and SO_2 (g)
(D) CO_2 (g), H_2O (ℓ) and SO_2 (ℓ)

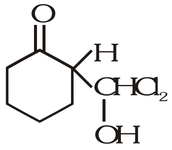
2. An organic compound C_3H_6O does not give a precipitate with 2, 4-dinitrophenyl hydrazine reagent and does not react with sodium metal. It could be - [IIT-93]

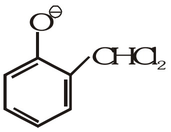
(A) $CH_3 - CH_2 - CHO$
(B) $CH_3 - CO - CH_3$
(C) $CH_2 = CH - CH_2OH$
(D) $CH_2 = CH - OCH_3$

3. When phenol is reacted with $CHCl_3$ and NaOH followed by acidification, salicylaldehyde is obtained which of the following species are involved in the above mentioned reaction as intermediates ? [IIT-95]

(A) 

(B) 

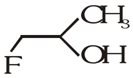
(C) 

(D) 

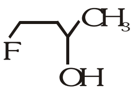
4. The reaction products of, $C_6H_5OCH_3 + HI \xrightarrow{\Delta}$ are : [IIT-95]

(A) $C_6H_5OH + CH_3I$
(B) $C_6H_5I + CH_3OH$
(C) $C_6H_5CH_3 + HOI$
(D) $C_6H_6 + CH_3OI$

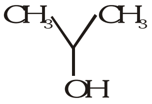
5. The order of reactivity of the following alcohols - [IIT-97]



(I)



(II)



(III)

(IV)

towards conc. HCl is -

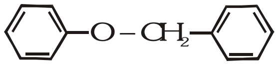
(A) I > II > III > IV
(B) I > III > II > IV
(C) IV > III > II > I
(D) IV > III > I > II

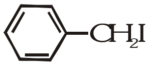
6. Among the following compounds, the strongest acid is - [IIT-98]

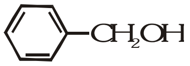
(A) $HC \equiv CH$
(B) C_6H_6
(C) C_2H_6
(D) CH_3OH

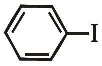
7. Benzenediazonium chloride on reaction with phenol in weakly basic medium gives - [IIT-98]

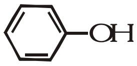
(A) Diphenyl ether
(B) p-hydroxyazobenzene
(C) Chlorobenzene
(D) Benzene

8. The ether  when treated with HI produces [IIT-99]

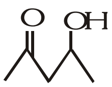
(A) 

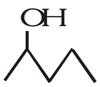
(B) 

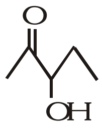
(C) 

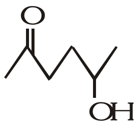
(D) 

9. Which one of the following will most readily be dehydrated in acidic condition - [IIT-2000]

(A) 

(B) 

(C) 

(D) 

10. 1-propanol & 2-propanal can be best distinguished by - **[IIT-01]**

(A) Oxidation with alkaline $KMnO_4$ followed by reaction with Fehling solution

(B) Oxidation with acidic dichromate followed by reaction with Fehling solution

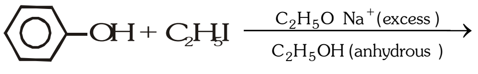
(C) Oxidation by heating with copper followed by reaction with fehling solution

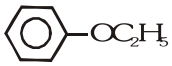
(D) Oxidation with concentrated H_2SO_4 followed by reaction with Feheling

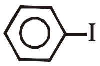
11. Identify the corect order of boiling point of the following compounds - **[IIT-02]**

(A) $CH_3CH_2CH_2CH_2OH$; (B) $CH_3CH_2CH_2CHO$; (C) $CH_3CH_2CH_2COOH$

(A) A > B > C (B) C > A > B (C) A > C > B (D) C > B > A

12.  **[IIT-03]**

(A) 

(B) 

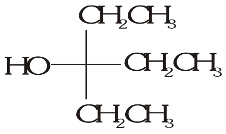
(C) $C_6H_5OC_6H_5$ (D) $C_2H_5OC_2H_5$

13. Reaction of entainomerically pure acid with 1 chiral carbon and racemic alcohol with 1 chiral carbon gives an ester which is : **[IIT-03]**

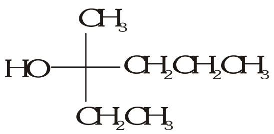
(A) Meso (B) Optically active

(C) Racemic mixture (D) Enantionmerically pure

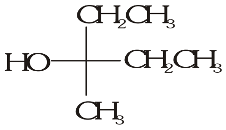
14. CH_3MgBr + Ethyl ester → which can be formed as product (excess) : **[IIT-03]**

(A) 

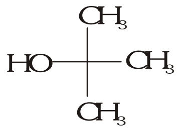
$HO-\overset{CH_2CH_3}{\underset{CH_2CH_3}{|}}-CH_2CH_3$

(B) 

$HO-\overset{CH_3}{\underset{CH_2CH_3}{|}}-CH_2CH_2CH_3$

(C) 

$HO-\overset{CH_2CH_3}{\underset{CH_3}{|}}-CH_2CH_3$

(D) 

$HO-\overset{CH_3}{\underset{CH_3}{|}}-CH_3$

15. On acid catalysed hydration, 2-phenyl propene gives : **[IIT-04]**

(A) 3-phenyl-2-propanol (B) 2-phenyl-1-propanol

(C) 1-phenyl-3-propanol (D) 2-phenyl-2-propanol

16. Conversion of cyclohexanol into cyclohexene is most effective in : **[IIT-05]**

(A) concentrated H_3PO_4 (B) concentraated HCl

(C) concentrated HCl / $ZnCl_2$ (D) concentrated HBr

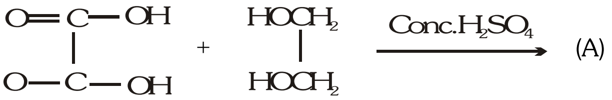
17. When t-butanol and n-butanol are separately treated with a few drops of dilute $KMnO_4$ in one case only, purple colour disappears and a brown precipitate is formed. Which of the two alcohols gives the above reaction and what is the brown precipitate ? **[IIT-94]**

18. 3,3-Dimethylbutan-2-ol loses a molecule of water in the presence of a concentrated sulphuric acid to give tetramethyl ethylene as a major product. Suggest a suitable mechanism. **[IIT-96]**

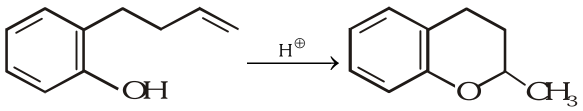
19. A compound $D(C_8H_{10}O)$ upon treatment with alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid (E) $(C_7H_6O_2)$. Write the structures of (D) and (E) and explain the formation of (E). **[IIT-96]**

20. Which of the following is the correct method for synthesising methyl-t-butyl ether and why?

(i) $(CH_3)_3CBr + NaOMe \rightarrow$ (ii) CH_3Br + tert-BuONa $\rightarrow$ [IIT- 97]

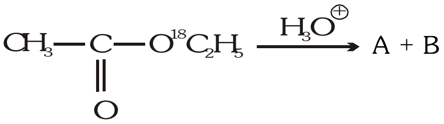
21.  [IIT-97]

22. Write the intermediate steps for the following reaction: [IIT- 98]

(i) 

23. Discuss why o-hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid? [IIT-99]

24. Write the structures of the product A & B



$$CH_3-\underset{\underset{O}{\|}}{C}-O^{18}C_2H_5 \xrightarrow{H_3O^{\oplus}} A + B$$

[IIT-2000]

25. Cyclobutyl bromide on treatment with magnesium in dry ether forms an organometallic A. The organometallic reacts with ethanal to give an alcohol B after mild acidification. Prolonged treatment of alcohol B with an equivalent amount of HBr gives 1- bromo-1-methylcyclopentane (C). Write the structures of A, B and explain how C is obtained from B. [IIT-2001]

26. How would you synthesis 4- methoxyphenol from bromobenzene in NOT more than five steps? State clearly the reagents used in each step and show the structures of the intermediate compounds in your synthetic scheme. [IIT-2001]

27. Identify X, Y and Z in the following synthetic scheme and write their structure. Explain the formationof labelled formaldehyde (H_2C^*O) as one of the products when compound Z is treated with HBr and subsequently ozonolysed. Mark the C* carbon in the entire scheme.

$BaC^*O_3 + H_2SO_4 \rightarrow X$ (gas) [C* denotes C^{14}]

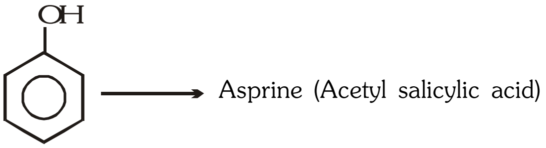
$CH_2 = CH - Br \xrightarrow[\text{(ii) X, (iii)}H_3O^+]{\text{(i)Mg / ether}} Y \xrightarrow{LiAlH_4} Z$ [IIT-2001]

28. Compound X on reduction with $LiAlH_4$ gives a hydride Y containing 21.72% hydrogen along with other products. The compound Y reacts with air explosively resulting in boron trioxide. Identify X and Y. Give balanced reactions involved in the formation of Y and its reaction with air. Draw the structure of Y.

[IIT-2001]

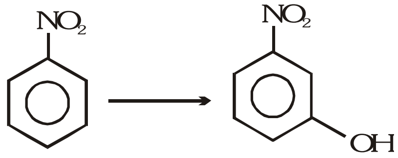
29. Mention two esters produced when a racemic mixture of 2- phehyl propanoic acid is treated with (+) 2- butanol. What is the stereochemical relationship between these esters? [IIT-2003]

30. Carry out following conversion in 3 or less steps.

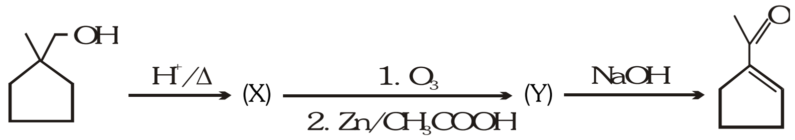


[IIT-2003]

31. Carry out following conversion in four or less steps. Also mention all the reagents used and reaction conditions.

 [IIT-2004]

32. An organic compound P($C_5H_{10}O$) reacts 10^{15} times faster then ethylene with dilute H_2SO_4 to give two products Q and R. Both Q and R give positive iodoform test. Identify P, Q and R and also give reason for very high reactivity of P. **[IIT-2004]**

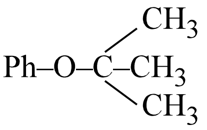
33. 

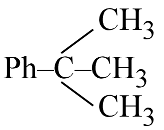
Identify (X) and (Y). **[IIT-2004]**

34. Phenyl magnesium bromide reacting with t-Butyl alcohol gives **[JEE 2005]**

(A) Ph – OH

(B) Ph – H

(C) 
$Ph–O–C(CH_3)_3$

(D) 
$Ph–C(CH_3)_3$

35. **Statement-1**: p-Hydroxybenzoic acid has a lower boiling point than o-hydroxybenzoic acid. **[JEE 2007]**

because

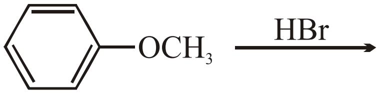
Statement-2 : o-Hydroxybenzoic acid has intramolecular hydrogen bonding.

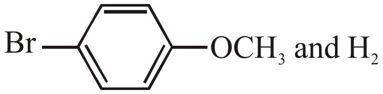
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

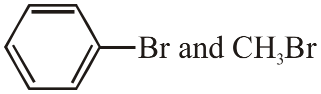
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False.

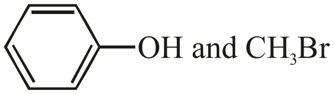
(D) Statement-1 is False, Statement-2 is True.

36. In the reaction  the products are **[JEE 2010]**

(A) 

(B) 

(C) 

(D) 

PREVIOUS YEARS QUESTIONS ANSWER KEY EXERCISE -5

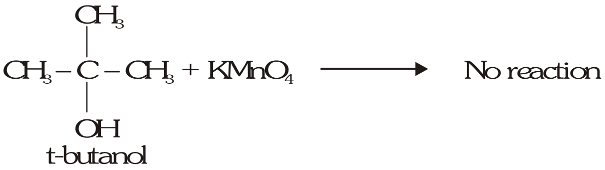
1. (B) 2. (D) 3. (D) 4.(A) 5. (C) 6. (D) 7.(B) 8. (D) 9. (A)

10. (C) 11. (B) 12. (A) 13. (C) 14. (C) 15. (D) 16. (A)

17. n-butanol is oxidised by $KMnO_4$ and not t-butanol as the latter does not contain H atom attached to carbinol carbon atom.

$$CH_3CH_2CH_2CH_2OH + KMnO_4 \rightarrow CH_3CH_2CH_2COO\overset{-}{O}\overset{+}{K} + MnO_2 + KOH$$

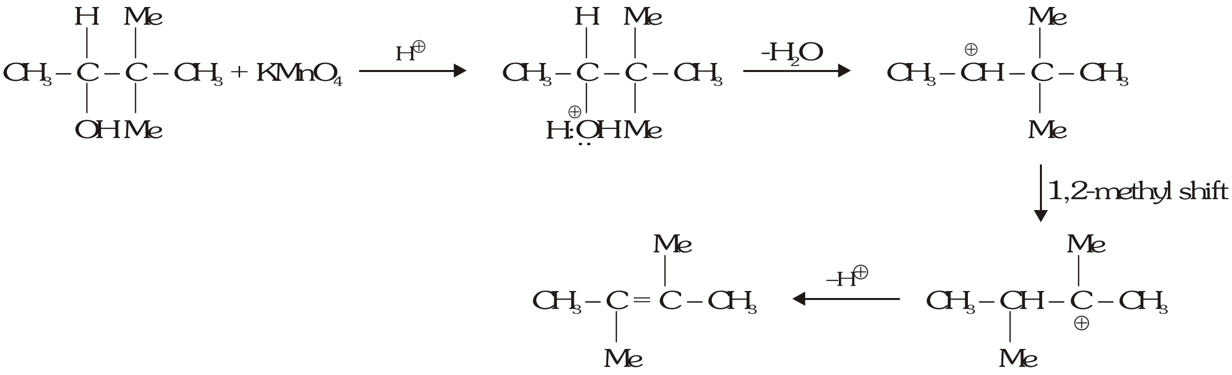
n-Butanol Brown



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 + KMnO_4 \longrightarrow \text{No reaction}$$

t-butanol

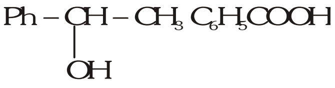
18.



$$CH_3-\underset{OH}{\overset{H}{C}}-\underset{Me}{\overset{Me}{C}}-CH_3 + KMnO_4 \xrightarrow{H^{\oplus}} CH_3-\underset{H\overset{\oplus}{O}H}{\overset{H}{C}}-\underset{Me}{\overset{Me}{C}}-CH_3 \xrightarrow{-H_2O} CH_3-\overset{\oplus}{C}H-\underset{Me}{\overset{Me}{C}}-CH_3$$

$$\xrightarrow{\text{1,2-methyl shift}} CH_3-\underset{Me}{CH}-\underset{\oplus}{\overset{Me}{C}}-CH_3 \xrightarrow{-H^{\oplus}} CH_3-\underset{Me}{C}=\overset{Me}{C}-CH_3$$

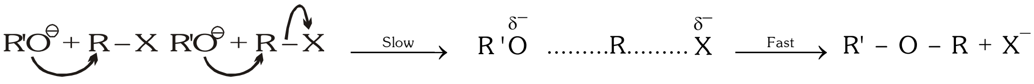
19. (D)



$$Ph-\underset{OH}{CH}-CH_3 \quad C_6H_5COOH$$

(D) (E)

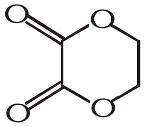
20. The ether formation involves nucleophilic substitution of alkoxide ion for halide ion.



$$R'\overset{\ominus}{O} + R-X \quad R'\overset{\ominus}{O} + R-X \xrightarrow{\text{Slow}} R'\overset{\delta-}{O}\text{.........}R\text{.........}\overset{\delta-}{X} \xrightarrow{\text{Fast}} R'-O-R+X^-$$

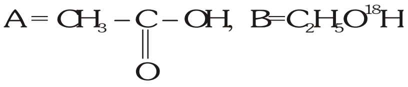
3 alkyl halide can also involve elimination of HX to give alkene in the presence of a base. So, it is better to start with 3 alkoxide and 1 alkyl halide, i.e., equation (b).

21.



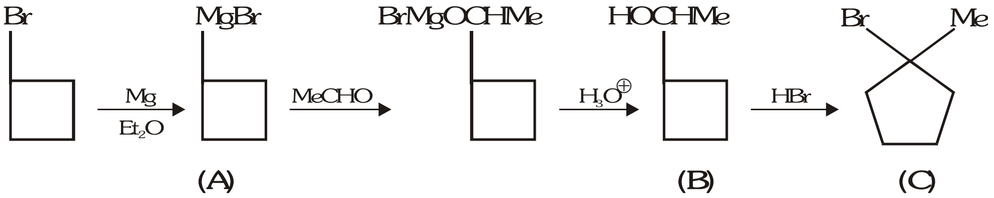
23. Due to intermolecular H-bonding

24.

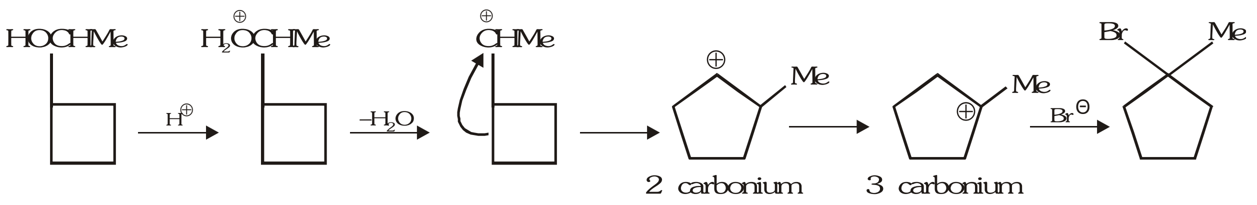


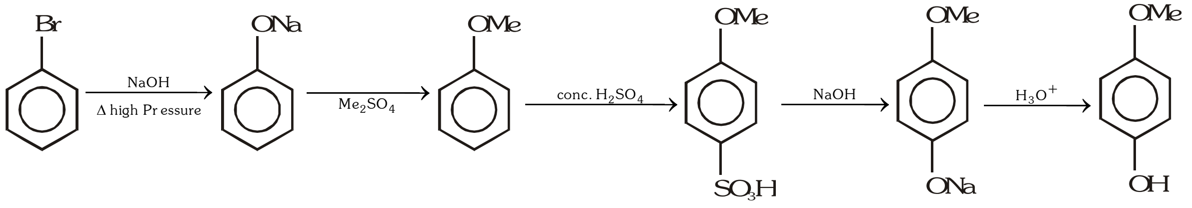
$$A = CH_3-\underset{\|\atop O}{C}-OH, \; B = C_2H_5O^{18}H$$

25.

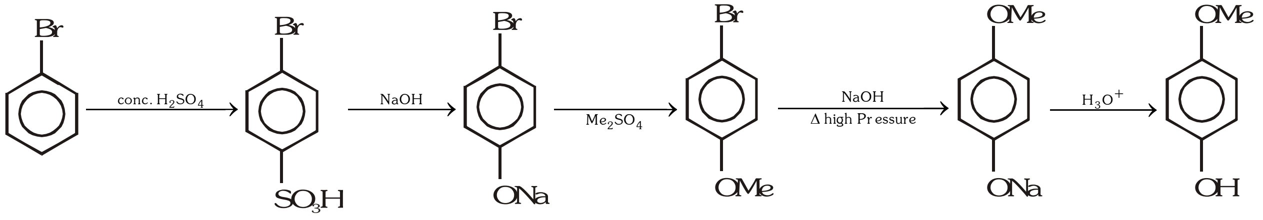


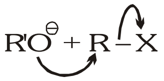
Meachnism



26. 

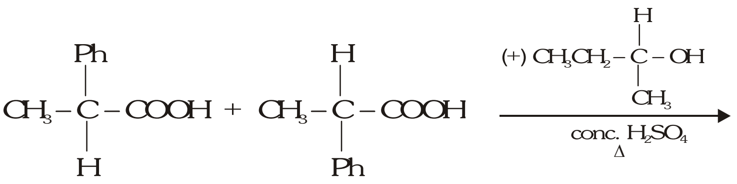
Alternative rout



27. $\dot{C}O_2$; $CH_2=\dot{C}OOH$; $CH_2=CH.\dot{C}H_2OH$; $\dot{C}H_2O$ 

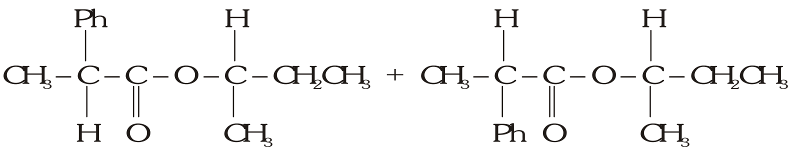
(X) (Y) (Z)

28. X = BCl_3 ; Y = B_2H_6

29. 

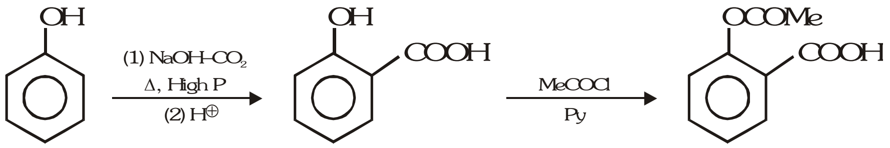
$$CH_3-\underset{H}{\overset{Ph}{C}}-COOH + CH_3-\underset{Ph}{\overset{H}{C}}-COOH \xrightarrow[\text{conc. } H_2SO_4,\ \Delta]{(+)\ CH_3CH_2-\underset{CH_3}{\overset{H}{C}}-OH}$$

(racemic mixture)

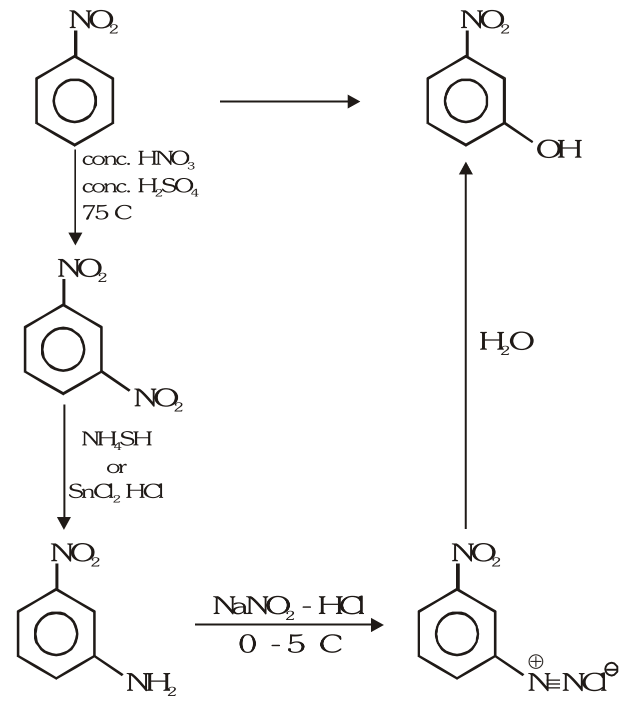


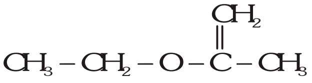
$$CH_3-\underset{H}{\overset{Ph}{C}}-\underset{\|}{C}\!\!\!\!\underset{O}{}-O-\underset{CH_3}{\overset{H}{C}}-CH_2CH_3 + CH_3-\underset{Ph}{\overset{H}{C}}-\underset{O}{\overset{}{\underset{\|}{C}}}-O-\underset{CH_3}{\overset{H}{C}}-CH_2CH_3$$

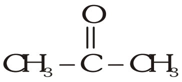
during esterification reaction only –COOH and –OH participates. There is no effect on structure or configuration of carbon adjacent to these groups. So when (±) acid reacts with pure (+) alcohol two esters are produced which are diastereoisomers of each other.

30. 

31.

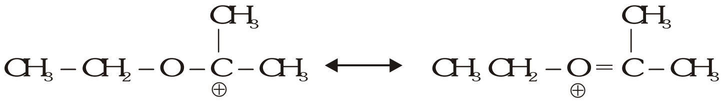


32. (P) 

$CH_3-CH_2-O-\overset{\overset{\displaystyle CH_2}{\|}}{C}-CH_3$; (Q) CH_3CH_2OH ; (R) 

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

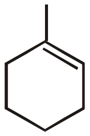
When ethylene reacts with dil. H_2SO_4 $CH_3CH_2^{\oplus}$ is produced during rate determining step, whereas P gives resonance stabilized intermediate.



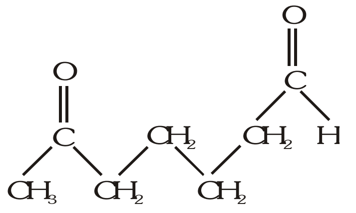
$$CH_3-CH_2-O-\underset{\oplus}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3 \longleftrightarrow CH_3\,CH_2-\underset{\oplus}{O}=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH_3$$

Due to extra stability of intermediate the rate of reaction is very fast.

33.



(X)



(Y)

34. B 35. D 36. D