Chapter 12

Alcohols, Phenols and Ethers

Solutions

SECTION - A

Objective Type Questions (One option is correct)

1. Product obtained in following reaction is

OH
$$CH_2$$

 \downarrow \parallel \parallel $CH_3-CH-CH_2-C-CH_2-OH \xrightarrow{MnO_2}$ Product

(1)
$$CH_3 - C - CH_2 - C - CH_2OH$$

Sol. Answer (3)

$$\begin{array}{c|cccc} OH & CH_2 & OH & CH_2 \\ I & II & II & II \\ CH_3 - CH - CH_2 - C - CH_2OH \xrightarrow{MNO_2} CH_3 - CH - CH_2 - C - CHO \end{array}$$

2. Isobutyl alcohol is treated with PCI₅ to give A which is treated with Magnesium in ether to give B.

$$O$$
 + Compound B \rightarrow X H_2O/H^+ Product

Final product of reaction sequence is

OH
$$(4) (CH_3)_2 CH - CH - (CH_2)_2 - CH_3$$

Sol. Answer (3)

$$(CH_3)_2CH-CH_2MgCI+CH_2-CH_2$$

$$(CH_3)_2CH-CH_2-CH_2-CH_2OMgCI$$

 $\downarrow H_2O/H^{\dagger}$
 $(CH_3)_2CH-CH_3-CH_3-CH_3OH$

3. Following reaction is taking place

Compound A
$$\xrightarrow{\text{HIO}_4}$$
 2Q

Product is two moles of cyclohexanone, then compound A is

$$(1) \bigcirc OH \qquad (2) \bigcirc OH \qquad (3) \bigcirc OH \qquad (4) \bigcirc OH \qquad (4)$$

Sol. Answer (3)

$$\frac{\text{HIO}_{4}}{\text{OH OH}} \rightarrow 2$$

4. During a synthesis, cyclohexanol is used as

Reaction I :
$$PCC \rightarrow A \xrightarrow{CH_3MgBr} B \xrightarrow{H_2SO_4} C \xrightarrow{BH_3} D$$

OH

OH

Reaction II:
$$\frac{\text{Conc}}{\text{H}_2\text{SO}_4} P \frac{(1) \text{Hg}(\text{CH}_3\text{COO})_2}{(2) \text{NaBH}_4} Q$$

Select correct statement.

- (1) Compound Q and compound D have different molecular formula
- (2) Compound D and Q are enantiomers
- (3) Compound D and Q on reaction with HCl give same product
- (4) Compound D is ether

Sol. Answer (3)

$$\begin{array}{c}
OH \\
PCC \\
\hline
\end{array}
\begin{array}{c}
CH_3MgBr \\
H_3O^{\dagger}
\end{array}
\begin{array}{c}
OH \\
\hline
\end{array}
\begin{array}{c}
Conc. \\
H_2SO_4 \\
\hline
\end{array}
\begin{array}{c}
BH_3 \\
\hline
H_2O_2/OH \\
\hline
\end{array}
\begin{array}{c}
OH \\
\hline
\end{array}$$

$$\begin{array}{c}
OH \\
\hline
\end{array}
\begin{array}{c}
OH \\
\end{array}$$
\begin{array}{c}
OH \\
\end{array}

5. In following sequence of reactions, final product Z is

Reaction I :
$$\frac{\text{NaOH}}{\text{(High T, High P)}} X$$

Reaction II: $X + CH_2 = CH - CH_2CI \rightarrow Y$

Reaction III: $Y \xrightarrow{200^{\circ}C} Z$

(1)
$$CH_2-CH=CH_2$$

$$CH_2-CH=CH_2$$

$$CH_2-CH=CH_2$$

$$CH_2-CH=CH_2$$

$$CH_2-CH=CH_2$$

$$O-CH_2-CH=CH_2$$
4)

Sol. Answer (3)

$$\begin{array}{c|c}
CI & ONa \\
\hline
ONa & O-CH_2-CH=CH_2 \\
\hline
O+CH_2=CH-CH_2CI \rightarrow OH \\
\hline
O-CH_2-CH=CH_2 & OH \\
\hline
CH_2-CH=CH_2
\end{array}$$

6. Aniline is treated with NaNO₂/HCl under ice-cold conditions to give Q then Q is hydrolysed with water to give A which is then treated with NaOH and then with CO₂ under pressure to give B.

$$B \xrightarrow{H_3O^+} C \xrightarrow{Ac_2O} D$$

Incorrect statement about above reaction is

- (1) Compound A reacts with sodium bicarbonate
- (3) Compound D is used as medicine
- (2) Compound C is acid
- (4) Compound A can undergo coupling reaction

Sol. Answer (1)

$$\begin{array}{c|c}
NH_2 & N_2^+CI^- & OH \\
\hline
NaNO_2 & OH & OH \\
OH & OH & COONa
\end{array}$$

$$\begin{array}{c|c}
OH & OH & COONa \\
\hline
OCOCH_3 & C
\end{array}$$

$$\begin{array}{c|c}
COOH & Asprin
\end{array}$$

- 7. Hydrogen chloride does not react with primary or secondary alcohol unless Anhydrous ZnCl2 or some Lewis acid is added to the reaction mixture. The role of ZnCl₂ in this reaction is
 - (1) ZnCl₂ react with HCl to form ZnCl₃ and H⁺ so number of free H⁺ increase, they attack on oxygen atom to become a good leaving group
 - (2) ZnCl₂ form a complex with the alcohol so leaving group ability of hydroxyl group increases
 - (3) ZnCl₂ attack on the carbon atom that is bonded with oxygen and replace the hydroxyl group
 - (4) $ZnCl_2$ convert into Zn and Cl^{\ominus} then Cl^{\ominus} replaces the OH^{\ominus}

Sol. Answer (2)

$$\begin{array}{c} \text{R-O-H} + \text{ZnCl}_2 \xleftarrow{\text{HCl}} & \text{R-O}^{(+)} - \text{ZnCl}_2 + \text{H}^{\oplus} \\ & \text{Cl}^{\ominus} \mid \\ & \text{H} \\ & \downarrow \\ & \text{R-Cl} + [\text{Zn (OH) Cl}_2]^{-} \end{array}$$

In which of the following reaction, 2° alcohol is formed as major product? 8.

(1)
$$CH_3$$

O

(i) $LiAlH_4$

(ii) H_3O^+

(2) O

NaBH₄ / C_2H_5OH

(3) O

HI

(4) O

HBr

Sol. Answer (1)

(1)
$$CH_3$$
 O
 CH_3
 CH_3
 CH_3
 CH_3
 CH_2
 CH_3
 CH_3
 CH_3
 CH_3
 CH_4
 CH_5
 CH_5
 CH_5
 CH_5
 CH_5
 CH_7
 CH_7

(2)
$$\xrightarrow{\text{NaBH}_4}$$
 No Reaction

$$(3) \qquad O \qquad HI \qquad CH_2 - CH_2 - OH_2 -$$

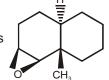
(4)
$$\longrightarrow$$
 $CH_3 - C - CH_2 - OH$

$$CH_3 - C - CH_3 -$$

9. The correct statement, about the reaction given below is

(Here MCPBA → Meta Chloroperoxybenzoic Acid)

(1) Major product of the reaction is



(2) Major product of the reaction is



(3) Major product is 2° alcohol

(4) Major product is 3° alcohol

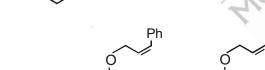
Sol. Answer (2)

Due to steric repulsion.

10. Correct statement about the product P.

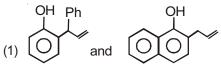
- (1) Degree of unsaturation of P is 1
- (2) Product P can show cis as well as trans isomer
- (3) Product P is optically active
- (4) One molecule of product P contain even number of H atom

Sol. Answer (4)



11. If a mixture of and and

is heated in a container then products are



Sol. Answer (1)

Claisen rearrangement is an example of pericyclic reaction and it is concerted mechanism. Claisen rearrangement is completed via six membered transition state and no chance of cross product in the reaction.

12. Consider the structure given below and the labelled alcoholic groups

Select the correct statement about the reagent mentioned.

S₁: PCC in CH₂Cl₂ can oxidise only 'C'.

S₂: Cu/573 K will cause aromatisation in the compound.

 $\rm S_3$: Acidic $\rm KMnO_4$ will oxidise B as well as D.

(1) Only S_1 and S_2 (2) Only S_1 and S_3

Only S_2 and S_3 (4) S_1 , S_2 and S_3 (3)

Sol. Answer (3)

PCC will oxidise B, C and D. Cu/573 K will form

Major products (A) and (B) are respectively.

(3)
$$OH$$
 SO_3H NO_2 NO_2 NO_2

(4)
$$OH$$
 OH OH OH OO_2 OO_3H OO_2 OO_3H OO_2

Sol. Answer (3)

Phenol is converted into phenol-2, 4-Disulphonic Acid on reaction with conc. H₂SO₄ and then with Nitric Acid, it yields Picric Acid.

14.
$$\xrightarrow{SOCl_2} \xrightarrow{RO} \xrightarrow{RO} \xrightarrow{O_3} \xrightarrow{H_2O}$$

Consider the statements related to the above reaction sequence and choose the incorrect option.

- (1) Starting with the cis isomer, if R = Et, then the end product is a dicarboxylic acid
- (2) Starting with the trans isomer, if R = Et, then the end product is a keto acid
- (3) Starting with the cis isomer, if R = tBu, then the end product is a keto acid
- (4) Starting with the trans isomer, if R = tBu, then the end product is a dicarboxylic acid

Sol. Answer (3)

The major product obtained is

$$(1) \qquad \qquad (2) \qquad \qquad (2) \qquad \qquad (3) \qquad \qquad (4) \qquad \qquad (4) \qquad \qquad (4) \qquad \qquad (5)$$

Sol. Answer (3)

16. Consider the following reaction sequence:

$$SO_3H$$

$$\longrightarrow NaOH$$

$$\Delta (X) \xrightarrow{H^+/H_2O} (Y) \xrightarrow{Zn} (Z)$$

The degree of unsaturation of organic compound Z is

(1) 1

(2) 2

(3) 3

(4) 4

Sol. Answer (4)

17. A hydrocarbon X(C₆H₁₂) is first allowed to react with dil. H₂SO₄ to form product (A). (A) On reaction with conc. H_3PO_4/Δ forms (B). Reductive ozonolysis of (B) forms Acetone as the only product.

Select the correct statements out of the following.

- S₁. X cannot have a quaternary carbon
- S₂. X cannot show cis-trans isomerism
- S₃. B cannot have a secondary hydrogen
- S₄. B must be symmetric alkene
- (1) S_1 and S_2 only
- (2) S_3 and S_4 only
- (3) S_2 , S_3 and S_4 only (4) S_1 , S_2 , S_3 and S_4

Sol. Answer (3)

X can be

B is
$$CH_3$$
 $C=C$ CH_3 CH_3

18.
$$CH_3$$
 CH_3
 A
 CH_3
 A
 CH_3
 A
 CH_2
 CH_2
 CH_3
 A
 CH_2
 CH_3
 C

The major product obtained in the above reaction sequence is

(3)
$$CH_3$$
 CH_3 CH_3 CH_2 CH_2 CH_3 CH_3

$$O-CH-CH_2-\mathring{C}H_3$$
 $O-CH_3$

Sol. Answer (1)

$$CH_{3} \xrightarrow{OH} CH_{3} \xrightarrow{OH^{\odot}} CH_{3} \xrightarrow{CH_{2} = CH - CH_{2} - CI} CH_{3} \xrightarrow{CH_{3} \leftarrow CH_{3} \leftarrow CH_{3}} CH_{3} \xrightarrow{CH_{2} - CH = CH_{2}} CH_{3} \xrightarrow{CH_{3} \leftarrow CH_{3} \leftarrow CH_{3}} CH_{3} \xrightarrow{CH_{3} \leftarrow CH_{3} \leftarrow CH_{3}} CH_{3} \xrightarrow{CH_{3} \leftarrow CH_{3} \leftarrow CH_{3} \leftarrow CH_{3}} CH_{3} \xrightarrow{CH_{3} \leftarrow CH_{3} \leftarrow CH_{3}$$

Which of the following will not lead to formation of ether?

(1)
$$PhO + CH_3 - CI \longrightarrow$$

(2)
$$CH_3 \xrightarrow{C} CH_3 + CH_3 - X \longrightarrow CH_3$$

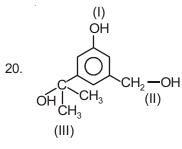
(3)
$$CH_3 - CH_2 = CH - CH_2 - CI \longrightarrow$$
 (4) $CH_3 - CH_2 = CH - CI \longrightarrow CH_3$ $CH_3 - CH_2 = CH - CI \longrightarrow CH_3$

(4)
$$CH_3 \xrightarrow{I} O + CH_2 = CH - CI \longrightarrow CH_3$$

$$CH_3 \xrightarrow{I} CH_3$$

Sol. Answer (4)

CH₂=CH—CI has partial double bond between CI and C.



The correct order of acidity of the alcohols is

(1) | 1 > | 1 > | | |

(2) ||| > || > |

(3) | > | | > | |

(4) || > || > |

Sol. Answer (1)

SECTION - B

Objective Type Questions (More than one options are correct)

- 1. Synthesis of cyclohexane 1, 2-diol from cyclohexene may be accomplished in two ways :
 - I. $Mn\overline{O}_4$ dilute, $\overline{O}H$, $O^{\circ}C$ dihydroxylation.
 - II. Peracid epoxidation followed by NaOH opening of the epoxide ring.
 Which of the following statements about the products from these reactions is correct?
 - (1) Methods I and II give same product
 - (2) Method I gives resolvable racemic mixture while method II will give non-resolvable achiral product
 - (3) Method I gives non resolvable optically inactive compound while method II gives resolvable racemic mixture
 - (4) Products obtained through method I and II will have diasteriomeric relationship

Sol. Answer (3, 4)

In method (I), Syn addition occurs and the product is obtained is Meso form which is non resolvable optically inactive compound. In method (II), anti addition occurs and product is resolvable Recemic mixture (equimolar amount of d and I-form). d-form and Meso form or I-form and Meso form are diastereomers.

2. Which of the following convert a primary hydroxyl group into a good leaving group for a S_N2 reaction?

(1)
$$H_3C$$
 \longrightarrow S \longrightarrow CI

(3) PCI₅

(4) Nal (5 molar solution)

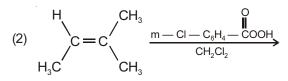
Sol. Answer (1, 2, 3)

Fact.

□ is better nucleophile in dilute solution not is concentrated solution.

3. Which of the following reaction or reaction sequence can be used to prepare epoxides?

(1)
$$C - CH_3 \xrightarrow{1. Br_2(1 \text{ eq})} \xrightarrow{2. NaBH_4}$$



(3)
$$CH = CH_2 \xrightarrow{1. Br_2/H_2O} \xrightarrow{2. NaOH (1 eq)}$$

(4)
$$H_2C = C$$

$$CH_3$$

$$CH_3$$

$$1. Br_2/CCl_4$$

$$2. NaOH (1 eq)$$

$$CH_3$$

Sol. Answer (1, 2, 3)

(1)
$$C - CH_3 \xrightarrow{Br_2(1 \text{ eq.})} C - CH_3 \xrightarrow{O} CH_2 \xrightarrow{O} CH_2$$
Epoxide

(2)
$$H_3C = C \xrightarrow{CH_3} \frac{O}{M_3 - CI - C_6H_4 - C - O - OH} \xrightarrow{H_3C} CH_3$$
 $CH_3C = C \xrightarrow{CH_3} \frac{O}{CH_3} \xrightarrow{CH_2CI_2} H_3C \xrightarrow{CH_3} CH_3$

(3)
$$CH = CH_2 \xrightarrow{Br_2/H_2O} CH - CH_2 \xrightarrow{NaOH} CH - CH_2 \xrightarrow{OO-H} CH_2 \xrightarrow{OO$$

Which of the following compounds will dissolve in aq.NaOH?

(1)
$$\sim$$
 SH (2) \sim CH₃ \sim CH₃ (3) \sim (4) \sim CH₃ \sim CH₃

Sol. Answer (1, 4)

NaOH reacts with those compounds which give more stable conjugate base than OH ion.

- 5. Which of the following reagents can be used to distinguish phenol from Anisole?
 - (1) FeCl₃
- (2) Aqueous NaOH
- (3) Br₂

(4) NaHCO₃

Sol. Answer (1, 2)

Phenol gives violet colour with FeCl₃ and also reacts with aqueous NaOH but Anisole react with FeCl₃ as well as NaOH. So, FeCl₃ and aqueous NaOH can be used to distinguish phenol from Anisole.

Which sequence of reactions can be used to perform the given transformation? 6.

$$CH = CH_2 \xrightarrow{?} CH_2 - CH_2 - OH$$

- (1) (i) B₂H₆. THF
- (ii) OH/H2O2
- (2) (i) Conc. H_2SO_4 (ii) H_2O , Δ
- (3) (i) Hg(OAC) / H₂O (ii) NaBH₄
- (4) (i) HBr/Peroxide, hv
- (ii) NaOH

Sol. Answer (1, 4)

(1)
$$CH = CH_{\frac{1}{2}} \xrightarrow{B_2H_6/THF} \left[CH_2 - CH_2 \xrightarrow{B_3} B \xrightarrow{H_2O_2/OH} CH_2 - CH_2 - OH_3 \right]$$

$$(4) \quad \bigcirc -CH = CH_2 - CH_2 - CH_2 - CH_2 - Br \quad \xrightarrow{NaOH} \bigcirc -CH_2 - CH_2 - OH_2 - CH_2 - OH_2 - CH_2 - OH_2 - OH$$

7. Consider the following reaction

Probable products of the above reaction are

Sol. Answer (3, 4)

OR
$$\begin{array}{c}
CH_{3} \\
OH
\end{array}$$

$$\begin{array}{c}
H_{2}SO_{4} \\
OH
\end{array}$$

$$\begin{array}{c}
H_{2}OH
\end{array}$$

8. Which of the following reactions will not occur?

Sol. Answer (2, 3)

Five or Six membered cyclic ether can't cleaved by a base or nucleophile. Only three membered cyclic ether can cleaved due to high strain.

9. Ortho salicylic acid is frequently used as precursor for the preparation of Aspirin. Which of the following reactions can be used to prepare o-salicylic acid from phenol?

(1)
$$\longrightarrow$$
 OH $\xrightarrow{\text{NaOH/CHCI}_3}$ $\xrightarrow{\text{H}_3\text{O}^+}$ (2) \longrightarrow OH $\xrightarrow{\text{(1) NaOH}}$ $\xrightarrow{\text{H}_3\text{O}^+}$ (3) \longrightarrow OH $\xrightarrow{\text{(1) NaOH}}$ $\xrightarrow{\text{Hydrolysis}}$ (4) \longrightarrow OH $\xrightarrow{\text{(1) NaOH}}$ $\xrightarrow{\text{H}_3\text{O}^+}$

Sol. Answer (2, 3)

(2)
$$(i)$$
 NaOH ONa COOH H_3O^+ COOH O-Salicylic Acid

(3)
$$NaOH/CCI_4$$
 ONa OH COOH
Reimann Tiemann
Reaction ONa
OH
COOH
OH
COOH
OH
COOH
OH
COOH
OH
COOH
OH
COOH

10. What would be the products of the given reaction?

$$(1) \qquad \begin{array}{c} NH_2 & NH_2 & OH \\ NH_2 & OH \\ N & N & N \end{array}$$

$$(2) \qquad \begin{array}{c} H & H \\ N & N & N \end{array}$$

$$(3) \qquad \begin{array}{c} OH \\ N & N & N \end{array}$$

$$(4) \quad HO \qquad \begin{array}{c} N & N & N \\ N & N & N \end{array}$$
Answer (3, 4)

Sol. Answer (3, 4)

Benzene diazonium Chloride shows coupling reaction with phenol in basic medium.

11. Which of the following reactions can be used to prepare cyclic ethers?

(1)
$$HO$$

(2) HO

(3) HO

(4) HO

(1) HO

(1) HO

(2) HO

(3) HO

(4) HO

(5) HO

(6) HO

(7) HO

(8) HO

(9) HO

(1) HO

(1) HO

(2) HO

(3) HO

(4) HO

(5) HO

(6) HO

(7) HO

(8) HO

(9) HO

(9) HO

(1) HO

(1) HO

(1) HO

(2) HO

(3) HO

(4) HO

(4) HO

(5) HO

(6) HO

(7) HO

(8) HO

(9) HO

(9) HO

(9) HO

(10) HO

(11) HO

(12) HO

(13) HO

(14) HO

(15) HO

(16) HO

(17) HO

(17) HO

(17) HO

(18) HO

(19) HO

(19)

Sol. Answer (1, 3, 4)

(1)
$$H_{\bullet}$$
 $OH HSO$ OH_{\bullet} OH_{\bullet}

In alkaline medium, this reaction does not occur.

- 12. Which of the following chemical tests can be used to distinguish primary, secondary and tertiary alcohol from each other?
 - (1) Hinsberg Test
- (2) Haloform Test
- (3) Lucas Test

Cyclic ether

(4) Victor-Meyer's Test

Sol. Answer (3, 4)

Fact

13. Which reaction or sequence of reactions can be used to prepare catechol in good yield?

(1)
$$OH$$
Catechol

CHO
OH
(1) $NaOH/H_2O_2$
(2) H_3O^+
(3)

Br
OMe
(3) OH
(4) OH
(1) OH
(1) OH
(1) OH
(2) OH
(2) OH
(3) OH
(4) OH
(5) OH
(6) OH
(7) OH
(8) OH
(9) OH
(9) OH
(1) OH
(1) OH
(1) OH
(1) OH
(2) OH
(2) OH
(3) OH
(4) OH
(4) OH
(5) OH
(6) OH
(7) OH
(8) OH
(9) OH
(9) OH
(1) OH
(1) OH
(1) OH
(1) OH
(2) OH
(2) OH
(3) OH
(4) OH
(4) OH
(5) OH
(6) OH
(7) OH
(7) OH
(8) OH
(9) OH
(9) OH
(1) OH
(1) OH
(1) OH
(1) OH
(2) OH
(2) OH
(3) OH
(4) OH
(4) OH
(5) OH
(6) OH
(7) OH
(8) OH
(9) OH
(9) OH
(9) OH
(1) OH
(1) OH
(1) OH
(1) OH
(2) OH
(1) OH
(2) OH
(3) OH
(4) OH
(4) OH
(4) OH
(5) OH
(6) OH
(7) OH
(8) OH
(9) OH
(9)

Sol. Answer (1, 2, 3)

$$(1) \qquad O \qquad H_3O^+ \qquad OH$$
Catechol

(2)
$$NaOH/H_2O_2$$
 ONa ONA H_3O^+ OH Catechol

(3) Br O Me Mg/Ether
$$O Me O_2$$
 O Me $O_2 O Me$ O Me $O_3 O Me$ OH OH

Catechol

- 14. Which of the following statement is/are correct?
 - (1) $CH_3-CH_2-CH_2-OH > CH_3-CH_2-O-CH_3$ (Boiling Point)
 - (2) In Chlorobenzene, CI is deactivating group but compound show Friedel-Craft Reaction
 - (3) Phenol reacts with concentrated sulfuric acid and under kinetic control major product is ortho sulfonated product
 - (4) Boiling point of ortho nitrophenol is less than para nitrophenol

Sol. Answer (1, 2, 3, 4)

Alcohol have higher B.P than ether.

15. Consider the following sequence of reaction

A
$$C_4H_6$$
 C_4H_8O C_4

Select the correct statement(s).

 CH_3 — $C\equiv C$ — CH_3 —Cindlar's Catalyst

- (1) A is an alkyne while D is cyclic ether
- (2) B is lindlar catalyst
- (3) If B is Na/NH₃ and all other reagent are same (as given in sequence) then final product will be same
- (4) If B is Na/NH₃ and E is H₃O⁺ then (if all other remain same) then final product is meso

Sol. Answer (1, 2, 3, 4)

$$\begin{array}{c|c}
 & O & OH & H \\
\hline
H_{IIII} & CH_3OH/H^{\uparrow} & Racemic mixture & + H | | | | | | | \\
\end{array}$$

If Na/NH₃ is used in place of Lindlar's catalyst trans alkene is formed.

If H₃O⁺ is used then meso will be formed as the major product.

16. Which of the following method(s) produce 3° alcohol as product?

(1)
$$CH_3-C-CH_3 \xrightarrow{(i) CH_3MgBr}$$
 O

(3)
$$O-CH_2-CH_2-CH_3 \xrightarrow{HI}$$

(4)
$$CH_3-CH_2-C-O-CH_3$$
 (i) CH_3MgBr (Excess)
 $(ii) H_3O^{\oplus}$

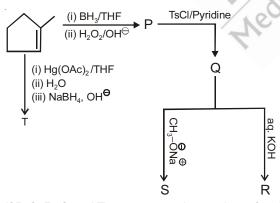
Sol. Answer (1, 4)

(1)
$$CH_3$$
- C - CH_3 $\xrightarrow{(i) CH_3MgBr}$ CH_3 - C - CH_3
 CH_3

(2)
$$CH_3$$
 CH_3 CH_3

(4)
$$CH_3-CH_2-C-O-CH_3$$
 (i) CH_3MgBr (Excess) (ii) H_3O^{\oplus} (ii) H_3O^{\oplus} CH₃ $CH_3-CH_2-C-CH_3+CH_3-OH$ OH

17. Following sequence of reactions was performed.



If P, Q, R, S and T represent major product of various reactions, which of the following statement (s) is/are correct?

- (1) Compound P is 2° alcohol and show stereoisomerism
- (2) Compound T is 3° alcohol and show geometrical isomerism
- (3) Compound P and R have same molecular mass
- (4) Reaction of S with dilute acid give R as one of product

Sol. Answer (1, 3, 4)

SECTION - C

Linked Comprehension Type Questions

Comprehension-I

Phenols are more acidic than aliphatic alcohols, acidity of phenols can be further increased by the introduction of electron withdrawing groups in aromatic ring. Acidic nature of phenol is because of the resonance stabilization of phenoxide ion.

1. Which of the following will evolve CO₂ gas with aqueous NaHCO₃?

Sol. Answer (3)

Only 2, 4, 6-trinitrophenol (Picric acid) will evolve CO_2 gas with aqueous $NaHCO_3$ due to high acidic nature.

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2. Arrange the given phenols in the increasing order of acidic strength.

- (2) || < | < || < |V
- $(3) | < | \lor < | | < | |$
- (4) $|| < | \lor < | < | ||$

Sol. Answer (1)

-CN group increases the acidity of phenol. When electron releasing group like MeO- is present on mposition w.r.t. —OH group then it acts as —I effect group and increases the acidity. MeO— is good electron releasing group in comparison to -Me. So, order of acidity becomes.

3. Consider the following reactions

$$\begin{array}{c|c}
NO_2 & C = C - H \\
\hline
NAOH (1 eq) & Major \\
NH_2 & product
\end{array}$$

Major product of the above reaction would be

ÓН

OH

So. Answer (1)

$$\begin{array}{c|c} NO_2 & C \equiv C - H \\ \hline \\ OH & OH \\ \end{array} \begin{array}{c} NaOH \\ \hline \\ ONa & OH \\ \end{array} \begin{array}{c} C \equiv C - H \\ \hline \\ NH_2 \\ \end{array}$$

In which NaOH reacts with only —OH group which is directly attached to the benzene ring. Other groups can't give H⁺ in aqueous medium.

Comprehension-II

Attack by a strong nucleophile such as CH_3O^{\ominus} (Methoxide ion) on an epoxide occurs at the least hindered carbon, similar to an S_N2 reaction.

Attack by a weak nucleophile such as MeOH can occur only when the epoxide has been protonated so that a better leaving group is formed, under acidic condition weak nucleophile attacks more substituted carbon to give final product.

- 1. Which statement is true about base ring opening reaction of epoxide?
 - (1) Base catalyzed epoxide opening is nonstereo selective reaction
 - (2) Both acid catalyzed and base catalyzed ring opening is regioselective
 - (3) In acidic medium attack of nucleophile take place at less substituted carbon of epoxide
 - (4) Epoxides are less reactive than oxetanes

Sol. Answer (2)

Both acid catalyzed and base catalyzed ring opening is regioselective.

2. Given synthetic transformation can be performed by

(2) (i) OsO₄ (ii) Hydrolysis

(3) (i)
$$KMnO_4$$
, $\overset{\ominus}{O}H$, 0°C (ii) Hydrolysis

(4) (i) Br₂ / H₂O (ii) OH

Sol. Answer (1)

Formation of epoxide and then ring opening is the anti addition.

$$\begin{array}{c}
O \\
\parallel \\
O \\
\hline
O \\
O \\
\end{array}$$

$$\begin{array}{c}
O \\
H_2O \\
O \\
O \\
\end{array}$$

$$\begin{array}{c}
O \\
O \\
O \\
O \\
\end{array}$$

3. What would be the major product of the given transformation?

$$(1) \begin{array}{c} Ph \\ \hline \\ H \end{array}$$

$$(2) \begin{array}{c} Ph \\ \hline \\ H \end{array}$$

$$(3) \begin{array}{c} Ph \\ \hline \\ H \end{array}$$

$$(4) \begin{array}{c} MeO \\ \hline \\ H \end{array}$$

$$(4) \begin{array}{c} Ph \\ \hline \\ H \end{array}$$

Sol. Answer (3)

In the 1st step CH_3O^- attacks on least hindered carbon similar to S_N^2 reaction. If acidic medium is taken together than reverse reaction occurs.

Comprehension-III

$$\begin{array}{c}
O \\
\hline
 & (1) OH^{-} \\
\hline
 & (2) H^{+}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{+}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}
\end{array}$$

$$\begin{array}{c}
A \\
\hline
 & (2) H^{-}$$

$$\begin{array}{c}
A \\
 & (2) H^{-}$$

$$\begin{array}{c}
A \\
 & (2) H$$

1. Product (B) is



Sol. Answer (2)

2. Product (D) is more acidic than



Sol. Answer (4)

Column-II

Hydroboration oxidation

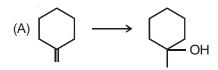
Markovnikov's product

SECTION - D

Matrix-Match Type Questions

Match the Column-I (Chemical transformation) with Column-II (Name of reaction).

Column-I



$$(B) \longrightarrow OH$$

$$(C) \longleftrightarrow CH_2 - Br \longrightarrow C$$

(D)
$$CH_3 - C = C - CH_3 \longrightarrow CH_3 - C - C - CH_3$$

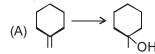
OH H

(s) Carbocation intermediate

Oxymercuration

demercuration

Sol. Answer A(q, r), B(p), C(s), D(r, s)



The reaction is oxymercuration—demercuration. The net result of this reaction is the addition of H₂O according to Markownikoff's rule.

$$(B) \longrightarrow \bigcirc OH$$

The reaction is hydroboration oxidation. The net result of this reaction is the addition of H₂O according to Anti-Markownikoff's rule.

(C)
$$CH_2 - Br \xrightarrow{NaOH} OH CH_2 \xrightarrow{Ring} CH_2 \xrightarrow{Ring} OH$$

The reaction proceeds through carbocation intermediate.

The reaction proceeds through carbocation intermediate and H₂O is added according to Markownikoff's rules.

2. Match the Column-I with Column-II

Column-I

Column-II

Product/s gives test

(p) With neutral FeCl₃ test

$$\begin{array}{c|c} & O - O - H \\ & \downarrow & CH_3 \end{array}$$

$$(B) \qquad \xrightarrow{+H^{\oplus}}$$

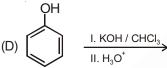
(q) With NaHCO₃

(C)
$$N = N - C$$

$$PH = 9$$

$$OH$$

(r) With Na



(s) With 2, 4 DNP reagent

Sol. Answer: A(p, q, r), B(p, r, s), C(p, r), D(p, r, s)

Salicylic acid gives purple colour with neutral FeCl_3 due to presence of —OH group and reacts with NaHCO $_3$ and Na.

(B)
$$H_3C$$
 CH_3 $C=C$

Phenol can give purple colour with neutral FeCl₃ and also reacts with Na but not with NaHCO₃. Acetone reacts with 2, 4, DNP.

Azo dye gives purple colour with neutral FeCl₃ and also reacts with Na due to —OH group

(D)
$$(i)$$
 KOH/CHCI₃ OH CHO
$$(ii)$$
 H₃O⁺ Salicyldehyde

Product reacts with neutral ${\sf FeCl}_3$ and Na due to —OH group and reacts with 2, 4-DNP due to —CHO group.

3. Match the following.

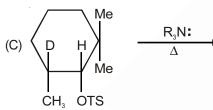
Column-II Column-II

(A)
$$Me$$
 CH_3
 CI
 $P = O$
 CI
 CI

(p) Isotopic effect

(B)
$$H$$
 CH_3 Δ Δ Me

(q) Saytzeff product



r) Rearrangement

(D)
$$Ph - CH_2 - CH - CH$$

$$CH_3$$

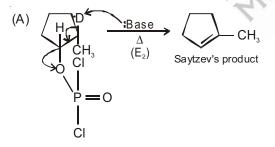
$$Ch_3$$

$$Conc. H^*$$

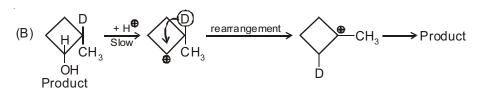
$$\Delta$$

s) Bimolecular elimination

Sol. Answer A(p, s), B(q, r), C(p, q, s), D(r)



It also involves isotopic effect.



(D) Also involve carbocationic formation followed by rearrangement.

4. Match the following.

Column-I

$$C \equiv N \qquad CH_2 - NH_2$$

$$(B)$$
 C
 CH_3
 CH_3

$$(C)$$
 CN CHO

$$(D) \bigvee_{N-H} \longrightarrow \bigvee_{N-H}$$

Column-II

(p) LiAIH,

(q) NaBH₄

(r)
$$H_2/Pd - C$$

- DIBAL-H (1 eq)
- (t) Reduction

Sol. Answer A(p, r, t), B(p, q, r, s, t), C(s, t), D(p, r, t)

$$-\text{CN} \xrightarrow{\quad \text{x} \quad} -\text{CH}_2 \xrightarrow{\quad \text{NH}_2 \quad} (\text{x may be LiAlH}_4 \text{ and H}_2/\text{Pd-C})$$

All are reducing agents.

5. Match the following.

Column-I

(A)
$$CH_3$$
— CH — CH_2 CH_3^-O/CH_3OH

(C)
$$CH_3$$
 C O_2H_5 H_3O^+

(D)
$$CH_3$$
— C — O — C_2H_5 — H_3O^+

Column-II

- (s) O¹⁸ is present in alcoholic group
- (t) O¹⁶ is present in alcoholic group

Sol. Answer A(q), B(p), C(t), D(s)

SECTION - E

Assertion-Reason Type Questions

1. STATEMENT-1: Victor-Meyer's test can be used to distinguish primary and secondary alcohols.

and

STATEMENT-2: Under Victor-Meyer's condition these alcohols give different colouration.

Sol. Answer (1)

In Victor Meyer's test, primary alcohol gives Red Colouration while secondary alcohol gives blue colouration.

2. STATEMENT-1: Solubility of alcohols decreases with increasing molecular weight.

and

STATEMENT-2: Increase in hydrophobic group decreases proportion of hydrogen bonding.

Sol. Answer (1)

Fact.

STATEMENT-1: Phenols cannot be converted into esters by direct reaction with carboxylic acids whereas alcohols can be.

and

STATEMENT-2: This is due to the fact that the esterification reaction is exothermic for alcohols but slightly endothermic for phenols.

Sol. Answer (1)

Fact.

4. STATEMENT-1: Secondary alcohols react faster than primary alcohols with Na.

and

STATEMENT-2: O—H bond in secondary alcohol is less polar than primary alcohol.

Sol. Answer (4)

O—H bond is less polar in secondary alcohol than primary alcohol. So, primary alcohol reacts faster with Na than secondary alcohol.

5. STATEMENT-1: Resorcinol turns FeCl₃ solution purple.

and

STATEMENT-2: Resorcinol is a dihydric phenol.

Sol. Answer (2)

OH (Resorcinol) turns FeCl₃ solution purple and it is dihydric phenol also.

6. STATEMENT-1: The C — O bond length of aliphatic alcohols is less than phenols.

and

STATEMENT-2 : In phenols C — O bond acquires π bond character.

Sol. Answer (4)

In phenols, C—O bond acquires π bond character. So, C—O bond length in phenols is less than aliphatic alcohol.

7. STATEMENT-1: POCl₃ can be used to dehydrate alcohols.

and

STATEMENT-2: This reaction proceeds by formation of carbocation in 1st step

Sol. Answer (3)

In the dehydration, no carbocation is formed. The reaction takes place by E_2 mechanism. In CS_2 solvent, I^- acts as weak nucleophile and it gives elimination reaction.

8. STATEMENT-1: In phenylbenzoate, Frie's rearrangements is faster than ethylbenzoate.

and

STATEMENT-2: Phenyl acylium cation is more stable than ethylacylium cation.

Sol. Answer (1)

9. STATEMENT-1: When phenol is treated with PBr₃, it gives bromobenzene.

and

STATEMENT-2: It is an example of nucleophilic substitution.

Sol. Answer (3)

10. STATEMENT-1: Phenol and benzoic acid can be distinguished by NaHCO₃.

and

STATEMENT-2: Phenol releases CO₂ gas from NaHCO₃.

Sol. Answer (3)

11. STATEMENT-1: Hydration of alkenes may give more than one type of alcohol.

and

STATEMENT-2: Carbocation intermediate may show rearrangement.

Sol. Answer (1)

Hydration of alkenes starts with formation of carbocation which may undergo rearrangement.

12. STATEMENT-1: Phenols are more acidic than carboxylic acid.

and

STATEMENT-2: Acidity depends on resonance stabilisation of the conjugate base formed.

Sol. Answer (4)

Phenoxide ion is resonance stabilized therefore phenol can lose H⁺ ion showing acidic behavior, but carboxylate ion has identical resonance structures hence is more stabilized making R—COOH more acidic.

SECTION - F

Integer Answer Type Questions

1. CH_2OH $\xrightarrow{H^{\dagger}} Product$ CH_2-OH

The degree of unsaturation of product is

Sol. Answer (4)

$$CH_3NH_2$$
, $CH_3 - C - CH_3$, OH and $H - C = C - H$ are less acidic than C_2H_5OH .

2.

In final product, the number of aromatic rings in the product is/are

Sol. Answer (2)

$$\begin{array}{c|c} O & OH \\ \hline \\ CH_3 & C_2H_5 \end{array} \begin{array}{c} OH \\ \hline \\ CH_2CH_3 \end{array}$$

3. The number of isomers (including stereoisomers) of ${\rm C_5H_{12}O}$ which can give positive haloform test is

Sol. Answer (4)

4.
$$CH_3$$
 C_2H_5 Product

In final product, the number of π electrons involved in aromaticity is 2x. The value of x is

Sol. Answer (5)

OH
$$CH_3$$

$$2x = 10$$

$$x = 5$$

Trans - 2-methyl cyclopentanol undergoes dehydration using POCl₃ in pyridine the major product is x-methyl
 cyclopentene. X is the locant number of methyl in IUPAC naming the value of (x + 4)² is

Sol. Answer (49)

Dehydration with POCI₃ is E₂ mechanism so answer is 3-methylcyclopentene.

so,
$$x = 3$$

$$x + 4 = 7$$

$$(x + 4)^2 = 49$$

6. Some statement are given below out of which x is correct, then value of $(x + 2)^2$ is

(i)
$$CH_3 \xrightarrow{\text{(i) BH}_3, T.H.F}$$
 This reaction has syn stereoselectivity.

(ii)
$$NaOH \rightarrow No$$
 epoxide is observed in this reaction.

- (iv) When anisole react with Br₂ in ethanoic acid form p-Bromoanisole as the major product
- (v) CH₃OH is called wood spirit
- (vi) 3° alcohol on reaction with Cu at 573 K form alkene.

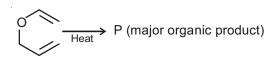
(vii)
$$CH_3 - CH = CH - CH_2 - OH \xrightarrow{P.C.C} (A)$$
, then A is $CH_3CH_2 - CH_2 -$

Sol. Answer (64)

$$x = 6$$

Only statement (vii) is incorrect because P.C.C does not affect the double bond.

7. Consider the following reaction

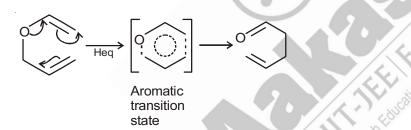


How many below statement(s) are correct about P or this reaction?

- (i) P on reduction with NaBH₄/H₂O given primary alcohol
- (ii) The transition state of this reaction is aromatic
- (iii) P is aromatic
- (iv) 1 mol of P has deficiency of 3 mol of $\rm H_2$
- (v) IUPAC name of P is pent-4-enal
- (vi) Compound P is ketone
- (vii) Compound P on reaction with CH_3MgBr and H_3O^+ form 3° alcohol as major product
- (viii) Compound P is optically active
- (ix) Transition state of reaction has six delocalised electrons
- (x) Carbocation is formed as intermediate
- (xi) This reaction is example of nucleophilic substitution
- (xii) Compound P is ether

Sol. Answer (4)

Statement (i), (ii), (v), (ix) are correct



This is Claisen rearrangement.

8. The total number of reactions in which major aromatic products formed, are more acidic than phenol are 'X' then value of (X)² is

(a)
$$OH$$

$$(ii) NaOH$$

$$(iii) CO_{2}$$

$$(iiii) H^{(i)}$$
NO₂

$$NO_{2}$$

$$NO_{2}$$

$$NO_{2}$$

$$NO_{2}$$

$$NO_{2}$$

$$NO_{2}$$

$$NO_{2}$$

$$NAOH/\Delta$$

$$OH$$

$$(c)$$

$$OH$$

$$Br_{2}/H_{2}O$$

(d)
$$OH$$
Conc. HNO_3
OH
(i) $NaOH$
(ii) CH_3CI
OH
(f) OH
 $CH_3 - CH_2 - CI$
Anhy . $AICI_3$

Sol. Answer (16)

9. Consider the following acidic dehydration reaction of alcohols, identify only those reactants which provide the alkene through rearrangement.

Sol. Answer (8)

10. Bromine water is added to phenol. Bromine get substituted at certain sites the sum of these sites (locants) in product formed is Z. The value of $\frac{Z}{3}$ is

Sol. Answer (4)