Unit-23 - Organic Compounds Containing Oxygen

Important Points

A Organic compounds containing oxygen - 1

1. Preparation of alcohols:
   → Monohydric alcohols are prepared by the hydrolysis of alkyl halides with aqueous alkali, hydration of alkenes, hydrolysis of ester, reduction of (aldehydes, ketones, acids and acid derivatives). Grignard reagents is also used to prepare monohydric alcohols.

2. Physical properties of alcohols:
   → The boiling points of alcohols are much higher than comparatively same molecular masses of alkanes, ethers and alkyl halides. This is due to intermolecular H-bond. For isomeric alcohols, the boiling points are in the order $1^0 > 2^0 > 3^0$.
   → Due to the formation of H-bond between alcohol and $H_2O$ molecules, alcohol with lower number of carbons are soluble in water.

3. Chemical properties of alcohols:
   → Alcohols exhibit three types of reactions,
     (i) Reaction in which O-H bond cleaves
     (ii) Reaction in which C-O bond cleaves
     (iii) Reaction in which whole molecule of alcohol participate.
   → Victor-Meyer’s test and Lucas reagent are used to distinguish $1^0$, $2^0$ and $3^0$ alcohols. Oxidation reactions are also used to distinguised between $1^0$, $2^0$ and $3^0$ alcohols.

4. Preparation of phenol:
   → Phenol is prepare from cumene, diazonium salt, benzene and coal tar.

5. Physical properties of phenol:
   → Phenols have higher boiling point than the corresponding hydrocarbon and aryl halides. This is due to the presence of intermolecular hydrogen bonding.
   → Phenols are more acidic than alcohols because phenoxide ion is stabilised by resonance. The presence of electron withdrawing group like $NO_2$, increases the acidic strength of phenol and electron donating group like $R$, decreases the acidic strength of phenol.
6. **Chemical properties of phenol:**
   → Reaction of phenols are mainly of two types,
   (i) Reaction involving OH group
   (ii) Reaction involving phenyl group

7. **Preparation of ethers:**
   → Ethers are mainly prepared by Williamson’s synthesis which involves the heating of alkyl halides with sodium or potassium alkoxides or phenoxides. Dehydration of alcohol at 140°c also gives ether.

8. **Chemical properties of ethers:**
   → (i) Reaction involving cleavage of C-O bond with dilute acid or with HX
   (ii) Electrophillic substitution reactions occurring in aromatic ring

**B: Organic compounds containing oxygen - II**

1. **Carbonyl compounds:**
   → Organic compounds containing carbon-oxygen double bond (\(\text{C} = \text{O}\)) are called carbonyl group or carboxy group compounds. In aldehydes, the carbonyl group is attached to one hydrogen atom and one alkyl (or aryl or hydrogen atom) group, while in ketones it is attached to one alkyl and one aryl group or to two alkyl (or aryl) groups, which may be same or different. If carbonyl group is attached to one hydroxyl group, the compounds are known as carboxylic acids. In carboxylic acid compounds, if the hydrogen of hydroxyl group is substituted by alkyl or aryl group the compounds are known as esters, but if it is substituted by acyl group, the compounds are known as acid anhydrides. If the carbonyl group is attached to chlorine and to amino group the compounds are known as acid chlorides and amides respectively. The general formula of these compounds are expressed as

\[
\begin{align*}
\text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O} \\
\text{R} & \quad \text{H} & \quad \text{R} & \quad \text{R}' & \quad \text{R} & \quad \text{O} & \quad \text{OH} & \quad \text{R} & \quad \text{O} & \quad \text{R} & \quad \text{Cl}
\end{align*}
\]

Aldehyde  Ketone  Carboxylic acid  Anhydride  Acid Chloride  Amide

2. **Structure and nature of carbonyl group:**
   → Carbonyl carbon atom is \(sp^2\) hybridised and form three \(\sigma\)-bonds and one \(\pi\) bond. All the three \(\sigma\)-bond lie in same plane having angle 120°. The \(\pi\) bond lies both above and below the C-O \(\sigma\) bond. Thus the carbonyl carbon, oxygen atom and two atoms which are directly bonded to the carbonyl carbon lie in one plane, and is confirmed by electron diffraction and spectroscopic studies.
   → Due to higher electronegativity of oxygen atom relative to carbon atom the carbonyl group is polarized and carbonyl carbon becomes electrophile (Lewis acid) and oxygen becomes nucleophile (Lewis base). Carbonyl group is polar in nature and has dipole moments. Aldehydes and ketones
have dipole moments 2.3-2.8 D. The resonance structures are as shown below:

\[ \text{C}=\text{O} \quad \text{C} \quad \text{C}=\text{O} \]

3. Physical properties of aldehydes and ketones:

- The polar carbonyl groups have dipole-dipole interaction between opposite ends of the \( \text{C}=\text{O} \) group dipoles and hence due to weak intermolecular attraction the melting points and boiling points of aldehydes and ketones are higher than corresponding non-polar compounds.
- The order of boiling points is carboxylic acid > alcohol > isomeric ketone > isomeric aldehyde > ether > hydrocarbon.
- Due to hydrogen bonding with water molecules the aldehydes and ketones upto three carbon are soluble in water.
- The aromatic aldehydes and ketones due to presence of larger hydrocarbon parts (like benzene ring etc.), are insoluble in water.
- All aldehydes and ketones are fairly soluble in organic solvents like benzene, ether, alcohols, chloroform etc.

4. Chemical properties of aldehydes and ketones:

- Due to presence of hydrogen atom, the carbonyl group of aldehyde is much more reactive than ketone.
- Aldehydes and ketones undergo nucleophilic addition reaction because the carbonyl carbon atom is slightly positively charged.
- In nucleophilic addition the first step is reversible and also slow, so it is a rate determining step.
- The second step is reversible.
- Due to steric effect and inductive effect the aldehydes are more reactive than ketones.
- Most of the aldehydes and aliphatic methyl ketones, due to less steric hindrance are more reactive.
- Aldehydes and ketones react with \( \text{NaHSO}_3 \) and give bisulphite addition product which are usually crystalline solids. On hydrolysis they give original aldehydes and ketones, so this reaction is useful for separation and purification of aldehydes and ketones.
- Addition of HCN and Grignard reagent to the aldehyde and ketone which give \( \alpha \)-hydroxy carboxylic acid and \( 1^0, 2^0, 3^0 \) alcohols respectively.
- Addition of alcohol to aldehyde give hemiacetal and further acetal, while ketone give the same product.
- Nucleophilic addition reaction of aldehydes and ketones with \( \text{NH}_3 \) and its derivatives \( (H_2N-Z) \) are catalysed by acids.
- Aldehydes and ketones on reduction give \( 1^0 \) and \( 2^0 \) alcohols respectively.
- Aldehydes and ketones can be reduced to hydrocarbon by using different reagent like Wolff-Kishner reduction, Clemmenses reduction, red phosphorus with HI. Ketones on reduction with magnesium amalgam and water give the product pinacol. Oxidation of aldehydes: Tollens’ test, Fehling’s test and Benedict’s test give the product carboxylic acid. Fehling’s test and Benedict’s test are not given by aromatic aldehydes.
- Oxidation of ketones by strong oxidizing agents like con. \( \text{HNO}_3 \), \( \text{KMnO}_4/\text{H}_2\text{SO}_4 \), \( \text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4 \) give mixture of carboxylic acids.
Oxidation of aldehydes and ketones containing \( CH_3CO \)-group give iodoform test.

Aldol condensation and cross aldol condensation are the reactions given by aldehydes and ketones having \( \alpha \)-hydrogen atom or atoms using dilute alkali as catalyst. Cannizzaro reaction is given by aldehydes and ketones which do not have an \( \alpha \)-hydrogen atom by using con. NaOH or 50\% NaOH.

Electrophilic substitution reactions of aromatic aldehydes and ketones are nitration, sulphonation and halogenation.

5. **Preparation of carboxylic acids:**
Carboxylic acids are prepared from:
- Primary alcohol and aldehyde
- Alkyl benzene and alkenes
- Nitriles and amides.
- Grignard reagents
- Acid halide (chloride) and anhydrides
- Esters

6. **Acidic nature of carboxylic acids:**
Carboxylic acids are stronger acids than phenol and alcohols.

For convenience the strength of an acid is generally indicated by its \( pK_a \) value rather than its \( K_a \) value.

\[ pK_a = -\log K_a \]

Factors affecting strength of acids are
- effect of electron-donating group
- effect of electron withdrawing group
- attachment of phenyl or vinyl group directly to carbonyl group.

7. **Physical and chemical properties of carboxylic acids:**
Carboxylic acid in aqueous solution form intermolecular hydrogen bonding with water molecules.

Carboxylic acids are cyclic dimer in vapour phase or in aprotic solvents.

The reactions of carboxylic acid are
- Reactions involving cleavage of O-H bond.
- Reactions involving cleavage of C-OH bond
- Reaction involving -COOH group

Substitution reaction in hydrocarbon part of carboxylic acid are halogenation and ring substitution as bromination, nitration and sulphonation.

Carboxylic acids are used in different fields.
MCQ

1. Numbers of isomeric alcohols of molecular formula $C_5H_{12}O$ are
   (A) 5     (B) 8     (C) 6     (D) 9

2. Which of the following will produce only one product on reduction with LiAlH$_4$?
   (A) $CH_3COOCH_2CH_3$  (B) $CH_3CH_2OCOCH_2CH_3$
   (C) $CH_3COOCH_3$  (D) $CH_3CH_2OCOCH_2CH_2CH_3$

3. $CH_3CH_2CH_2OH$ can be converted to $CH_3CH_2CH_2COOH$ by the following sequence of steps:
   (A) $PBr_3$, KCN, $H_2/Ni$  (B) $HCN$, $PBr_3$, $H_3O^+$
   (C) $PBr_3$, AgCN, $H_3O^+$  (D) $PBr_3$, KCN, $H_3O^+$

4. $H_2C = CH - COOH \xrightarrow{LiAlH_4} X$. What is "X"?
   (A) $CH_3CH_2 COOH$  (B) $CH_3CH_2 CH_2 OH$
   (C) $H_2C = CH - CH_2OH$  (D) $CH_3CH_2CHO$

5. In the following sequence of reactions, $CH_3CH_2OH \xrightarrow{P+I_2} A \xrightarrow{Mg \text{ ether}} B \xrightarrow{HCHO} C \xrightarrow{H_2O} D$, the compound D is:
   (A) propanal  (B) n-butyl alcohol
   (C) butanal  (D) n-propyl alcohol

6. Acid catalysed hydration of alkenes except ethene leads to the formation of
   (A) primary alcohol
   (B) mixture of primary and secondary alcohols
   (C) secondary or tertiary alcohol
   (D) mixture of secondary and tertiary alcohols

7. During dehydration of alcohol to alkenes by heating with Conc $H_2SO_4$, the initiation step is:
   (A) elimination of water  (B) formation of an ester
   (C) formation of carbocation  (D) protonation of alcohol molecule

8. Which of the following compounds will give positive iodoform test?
   (I) 3- methyl propan-2-ol  (II) 1- phenyl propan-1-ol
   (III) 1- methyl cyclopentan al  (IV) 3- phenyl propan-2-ol.
   (A) I and III  (B) I and IV  (C) II and III  (D) II and IV
9. Which of the following alcohol on heating with conc H₂SO₄ gives product, which show geometrical isomerism?
   (A) 2,4- dimethyl pentan-3-ol   (B) 2- methyl butan -2-ol
   (C) butan-2-ol           (D) all of the above

10. Propan -1-ol and propan-2-ol can be distinguished by
    (A) oxidation with alkaline KMnO₄ 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 conc H₂SO₄ followed by reaction with Fehling Solution

11. Which one of the following will most readily be dehydrated in acidic condition?

12. The best reagent to convert pent - 3 - en-2-ol into pent-3-en-2-one is
    (A) acidic permanganate   (B) acidic dichromate
    (C) chronic anhydride in glacial acetic acid   (D) pyridinium chlorochromate

13. CH₃CH₂OH can not be prepare by which of the following reaction?
    (A) Hydrolysis of ethyl acetate
    (B) Hydroboration of ethene followed by oxidation in basic medium
    (C) Reaction of ethyl chloride with alcoholic potassium hydroxide
    (D) Reaction of ethyl acetate

14. The most suitable reagent for the conversion of primary alcohol into aldehyde with the same number of carbon is
    (A) acidified K₂Cr₂O₇   (B) alkaline KMnO₄
    (C) acidified KMnO₄   (D) pyridinium chlorochromate

15. \( \text{CH₃CHO} \xrightarrow{P₂Br₅} x \xrightarrow{Na} y \) What is \( y \)?

16. An organic compound "X" on treatment with PDC in CH₂Cl₂ gives compound "Y". Compound "Y", reacts with I₂ and alkali to form yellow precipitate. The compound "X" is
    (A) acetone   (B) ethanol   (C) ethanol    (D) acetic acid
17. How many optically active stereoisomers are possible for butan-2,3-diol?
   (A) 1  (B) 2  (C) 3  (D) 4

18. The correct order of boiling points is for
   n-Butyl alcohol  tert-Butyl alcohol
   (I)  (III)
   iso-Butyl alcohol  sec-Butyl alcohol
   (II)  (IV)
   (A) I > II > IV > III  (B) III > IV > II > I
   (C) II > III > I > IV  (D) IV > III > II > I

19. The boiling point of glycerol is more than propanol because of
   (A) hydrogen bonding  (B) hybridization
   (C) arrangement of molecules  (D) size of molecule

20. An organic compound X is oxidised by using acidified K₂Cr₂O₇. The product obtained reacts with
   phenylhydrazine but does not give silver mirror test. The possible structure of X is
   (A) CH₃ CH₂ OH  (B) CH₃ CO CH₃
   (C) (CH₃)₂ CH OH  (D) CH₃ CHO

21. (CH₃)₃ CMgCl on reaction with D₂O produces
   (A) (CD)₃ CD  (B) (CD₃)₃ CH  (C) (CH₃)₃ COD  (D) (CH₃)₃ CD

22. Lucas test is associated with
   (A) alcohols  (B) phenols  (C) aldehydes  (D) carboxylic acids

23. __________ alcohol reacts immediately with anhydrous ZnCl₂ + HCl and gives insoluble chloride
   (A) Methanol  (B) Ethanol
   (C) Isopropyl alcohol  (D) 2-Methyl propan-2-ol,

24. Glycerol is more viscous than ethanol due to
   (A) many hydrogen bonds per molecule  (B) high boiling point
   (C) high molecular weight  (D) Fajer's rule

25. 4.6 gram ethanol when reacts with sodium metal __________ is formed.
   (A) 11.2 litre H₂ at STP  (B) 1.12 litre H₂ at STP
   (C) 1.12 litre O₂ at STP  (D) 11.2 litre H₂ at STP
26. \( P \xrightarrow{(i) B_2, H \overset{\text{D}}{\beta} / OH} \overset{CH_2}{\cdots} \xrightarrow{H,O'} Q \). \( P \) and \( Q \) respectively are
(A) Both \( \bowtie-\text{CH}_2\text{OH} \)
(B) \( \overset{\text{CH}_3}{\cdots} \)
(C) \( \overset{-\text{CH}_2\text{OH}}{\cdots} \)
(D) \( \overset{-\text{CH}_3}{\cdots} \) and \( \overset{-\text{CH}_2\text{OH}}{\cdots} \)

27. \( \text{C}_2\text{H}_5\text{OH} \) and \( \text{C}_6\text{H}_5\text{OH} \) can be distinguished by
(A) \( \text{Br}_2 + \text{H}_2 \text{O} \)
(B) \( \text{I}_2 + \text{NaOH} \)
(C) \( \text{FeCl}_3 \)
(D) Both (B) and (C)

28. In the Lucas test of alcohols, appearance of cloudiness is due to the formation of
(A) aldehyde
(B) alkyl chloride
(C) acid chloride
(D) ketone

29. When ethyl alcohol is treated with \( \text{Cl}_2 \) we get
(A) \( \text{CH}_3 \text{CH}_2 \text{Cl} \)
(B) \( \text{CH}_2 \text{Cl} \text{CH}_2 \text{OH} \)
(C) \( \text{CHCl}_2 \text{CH}_2 \text{OH} \)
(D) \( \text{CCl}_3 \text{CHO} \)

30. When a compound (Molecular formula \( \text{C}_7\text{H}_8\text{O} \)) is treated with acidic sodium dichromate we get compound "X". When "X" is treated with methyl magnesium bromide followed by hydrolysis compound "Y" is formed. The compound "Y" is
(A) isopropyl alcohol
(B) tertiary butyl alcohol
(C) iso butyl alcohol
(D) methyl ethyl ketone

31. Identify \( P, Q \) and \( R \) in the following reactions,
(i) \( \overset{\text{OH}}{\overset{\text{COOH}}{\overset{\Delta}{\underset{P}{\text{OH}}}}} \)
(ii) \( \overset{\text{OH}}{\overset{\text{Zn}}{\overset{\Delta}{\underset{\text{Zn}}{\text{Q}}}}} \)
(iii) \( \overset{\text{C}_2\text{H}_5\text{I}}{\overset{\text{OC}_{2}\text{H}_5}{\underset{\text{R}}{\text{OC}_{2}\text{H}_5}}} \)
(A) Sodium oxide benzene, Sodium phenoxide
(B) Soda lime, benzene, potassium phenoxide
(C) Zn, cyclohexanone, Sodium ethoxide
(D) Sodium cyclohexanone, potassium benzoate

32. Salicylaldehyde and o-nitrophenol are less soluble in water because,
(A) -CHO and -NO\(_2\) groups are not polar.
(B) they are aromatic compounds.
(C) intra molecular H bond is present
(D) their molecular weights are high
33. The final product of the following reaction is / are

\[
\ce{\text{OH}} \xrightarrow{\text{CHCl}_3, \text{KOH}} \times \xrightarrow{50\% \text{KOH}} \]

(A) \ce{\text{OH}} \text{CH} \text{OH} \quad \text{(B)} \ce{\text{OH}} \text{C} \text{COOK}

(C) \ce{\text{OH}} \text{CH}_2\text{OH} + \ce{\text{OH}} \text{COOK} \quad \text{(D)} \ce{\text{CH}_3\text{OH}} + \ce{\text{COOK}}

34. Given I = \(\text{\text{OMe}}\), II = \(\text{\text{NO}_2}\), III = \(\text{\text{OH}}\)

The decreasing order of the acidic character is

(A) I > II > III \quad \text{(B)} II > III > I \quad \text{(C)} II > III > I \quad \text{(D)} II > I > III

35. An organic compound \(\text{`X'}\) with molecular formula, \(\text{C}_8\text{H}_8\text{O}\) is insoluble in aqueous NaHCO₃ but dissolves in NaOH. When treated with bromine water, \(\text{`X'}\) rapidly gives \(\text{`Y'}\) (\(\text{C}_9\text{H}_5\text{OBr}_3\)). The compounds \(\text{`X'}\) and \(\text{`Y'}\) respectively, are

(A) benzyl alcohol and 2,4,6 - tribromo-3-methoxy benzene

(B) benzyl alcohol and 2,4,6 - tribromo-3-methyl phenol

(C) o-cresol and 3,4,5 - tribromo-2- methyl phenol

(D) m-cresol and 2,4,6 - tribromo -3- methyl phenol

36. Williamson's Synthesis is used for the preparation of

(A) acid \quad \text{(B)} ester \quad \text{(C)} ether \quad \text{(D)} alcohol

37. \(\text{P - cresol}\) reacts with chloroform in alkaline medium to give the compound A which adds hydrogen cyanide to form the compound B. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is

(A) \ce{\text{CH}_3} \text{CH(OH)COOH} \quad \text{(B)} \ce{\text{CH}_3} \text{CH(OH)COOH}

(C) \ce{\text{CH}_3} \text{CH(OH)COOH} \quad \text{(D)} \ce{\text{CH}_3} \text{CH}_2\text{COOH}
38. Which of the following has maximum acidic strength?

(A) ![OH](image)  
(B) ![OH](image)  
(C) ![OH](image)  
(D) ![OH](image)  

39. The Structure of the compound that gives a tribromo derivative on treatment with bromine water is

(A) ![OH](image)  
(B) ![OH](image)  
(C) ![OH](image)  
(D) ![OH](image)  

40. (I) Benzene 1,2 - diol  
(II) Benzene 1,3 -diol  
(III) Benzene 1,4 -diol  
(IV) Phenol

The increasing order of boiling points of above mentioned compounds is

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

41. Phenols are more acidic than alcohols because

(A) phenols are more soluble in polar solvents  
(B) phenoxide ion is stabilised by resonance  
(C) phenoxide ion do not exhibit resonance  
(D) alcohols do not lose H atoms at all  

42. The products obtained when benzylic phenyl ether is heated with HI in the mole ratio 1:1 are

1. phenol, 2 benzylic alcohol, 3. benzylic iodide, 4. iodo benzene

(A) 1 and 3 only  
(B) 3 and 4 only  
(C) 1 and 4 only  
(D) 2 and 4 only  

43. The product obtained by the reaction of HBr with phenol is

(A) ![Br](image)  
(B) ![OH](image)  
(C) ![Br](image)  
(D) There is no reaction  

44. H O + N₂Cl⁻ + Base →

(A) ![N = N](image)  
(B) ![OH](image)  
(C) ![OH](image)  
(D) ![OH](image)
45. Which one of the following is reduced with zinc and hydrochloric to give the corresponding hydrocarbon?
(A) Ethyl acetate  (B) Acetic acid  (C) Acetamide  (D) Butan-2-one

46. An organic compound \( x \) with molecular formula \( C_{5}H_{10}O \) yields phenyl hydrazone and gives a negative response to the iodobrom test and Tollen's test. It produces n-pentane on reduction. The compound could be:
(A) pentanal  (B) pentan-2-one  (C) pentan-3-one  (D) amyl alcohol

47. Which of the following on heating with aqueous KOH produces acetaldehyde?
(A) \( CH_{3}COCl \)  (B) \( CH_{3}CH_{2}Cl \)  (C) \( CH_{2}ClCH_{2}Cl \)  (D) \( CH_{3}CHCl_{2} \)

48. The formation of cyanohydrin from a ketone is an example of
(A) electrophilic addition  (B) nucleophilic addition  (C) nucleophilic substitution  (D) electrophilic substitution

49. Which of the following is the best method for making iso-propylmethyl ether?
(A) \( CH_{3}I + (CH_{3})_{2}CHO \rightarrow \)  (B) \( CH_{3}I + (CH_{3})_{2}CHOH \rightarrow \)
(C) \( (CH_{3})_{2}CHI + CH_{3}O^{\cdot} \rightarrow \)  (D) \( (CH_{3})_{2}CHCl + CH_{3}OH \rightarrow \)

50. COC angle would be maximum in
(A) \( CH_{3} - O - CH_{3} \)  (B) \( CH_{3} - O - C_{2}H_{5} \)
(C) \( C_{2}H_{5} - O - C_{2}H_{5} \)  (D) \( (CH_{3})_{2}CH - O - CH(CH_{3})_{2} \)

51. Which of the following reactions does not yield an ether?
(A) Sodium methoxide reacts with dimethyl sulphate
(B) Sodium ethoxide reacts with ethyl bromide
(C) Sodium ethoxide reacts with bromocyclopropane
(D) Ethanol reacts with \( CH_{2}N_{2} \) in presence of HBF_{4}

52. Which of the following reagent is used to convert Butan-2-one into propanoic acid
(A) \( NaOH, I_{2}/H \)  (B) Fehling Solution
(C) Tollen's reagent  (D) NaOH, NaI/H

53. By which of the following procedures can ethyl n-propyl ether be obtained?
(A) \( C_{2}H_{5}OH \xrightarrow{HBr/I} \xrightarrow{Mg/ether} II \xrightarrow{H_{2}O} III \xrightarrow{Na/C_{2}H_{5}Br} \)
(B) \( C_{2}H_{5}OH \xrightarrow{HBr/I} \xrightarrow{Mg/ether} II \xrightarrow{\frac{1}{2}CH_{2}O 2H_{2}O} III \xrightarrow{Na/C_{2}H_{5}Br} \)
(C) \( C_{2}H_{5}OH + H_{2}SO_{4} \xrightarrow{140^\circ C} \)
(D) \( C_{2}H_{5}OH + Conc H_{2}SO_{4} \xrightarrow{180^\circ C} \rightarrow CH_{3}CH_{2}CH_{2}Br \)
54. Oxidation of isopropyl benzene by oxygen in the presence of dilute acid gives_________.
   (A) $\text{C}_6\text{H}_5\text{COOH}$  (B) $\text{C}_6\text{H}_5\text{CH}_3$  (C) $\text{C}_6\text{H}_5\text{CH}_2$  (D) $\text{C}_6\text{H}_5\text{CH}$

55. Cross aldol condensation occurs between
   (A) two same aldehydes
   (B) two same ketones
   (C) two different aldehydes and ketones
   (D) two same acids

56. Pentan-3-one is not obtained from
   (A) 2,2-dichloropentane
   (B) 3,3-dichloropentane
   (C) pentan-3-ol
   (D) pent-2-yne

57. $\text{C}_2\text{H}_5\text{CHO}$ and $(\text{CH}_3)_2\text{CO}$ be distinguished by testing with
   (A) phenyl hydrazine
   (B) hydroxylamine
   (C) Fehling Solution
   (D) sodium bisulphide

58. Which of the following has the most acidic hydrogen?
   (A) hexan-3-one
   (B) hexan 2,4-dione
   (C) hexan 2,5-dione
   (D) hexan 2,3-dione

59. The appropriate reagent for the transformation
   \[
   \begin{array}{c}
   \text{HO-CH}_3 \\
   \text{CH}_3
   \end{array}
   \rightarrow
   \begin{array}{c}
   \text{HO-CH}_2-\text{CH}_3
   \end{array}
   
   (A) $\text{Zn-Hg, HCl}$  (B) $\text{H}_2/\text{N}$  (C) $\text{NH}_2\text{NH}_2, \text{OH}^-$  (D) $\text{NaBH}_4$

60. $\text{CH}_3-\text{CHO} + \text{HCN} \rightarrow A$, compound A on hydrolysis gives
   (A) $\text{CH}_3-\text{CH}_2-\text{COOH}$
   (B) $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{NH}_2$
   (C) $\text{CH}_3\text{CH}_2-\text{CH}_2\text{COOH}$
   (D) $\text{CH}_3\text{CH(OH)}-\text{COOH}$

61. What will be the final product \textit{Z}' of the following reaction?
   $\text{CH}_3\text{CH}_2\text{COOH} \overset{(i) \text{NH}_3, (ii) \Delta}{\rightarrow} X \overset{(i) \text{Br}_2/\text{KOH, (ii) HNO}_3}{\rightarrow} Y \overset{\text{Kmno}_4, \text{H}_2\text{SO}_4}{\rightarrow} Z$
   (A) propan-1-ol
   (B) propan-1-amine
   (C) ethanoic acid
   (D) propanal

62. A compound, containing only carbon, hydrogen and oxygen, has a molecular weight of 44. On complete oxidation it is converted in to a compound of molecular weight 60. The original compound is
   (A) an aldehyde
   (B) an acid
   (C) an alcohol
   (D) an ether

63. The major organic product formed from the following reaction
   \[
   \begin{array}{c}
   \text{CH}_2\text{NH}_2
   \end{array}
   \rightarrow
   \begin{array}{c}
   \text{HO-CH}_3
   \end{array}
   \]
   (i) $\text{CH}_2\text{NH}_2$
   (ii) $\text{LiAlH}_4$
   (iii) $\text{H}_2\text{O}$
64. Which one does not give Cannizaro's reaction?
   (A) benzaldehyde  
   (B) 2- methyl propanal  
   (C) p - methoxy benzaldehyde  
   (D) 2,2- dimethyl propanal

65. A Compound containing molecular formula C₅H₁₀Cl₂ on hydrolysis gives compound containing molecular formula C₅H₁₀O. Which reacts with NH₂OH and also forms iodoform but does not give fehling test.

   Original compound is

   \[
   \begin{align*}
   & Cl \\
   & | \\
   & Cl \\
   (A) & CH₃ - C - CH₂ - CH₂ - CH₃ \\
   & | \\
   & Cl \\
   (B) & CH₃ - CH₂ - C - CH₂ - CH₃ \\
   & | \\
   & Cl \\
   (C) & CH₃ - CH₂ - CH₂ - CH₂ - CH \\
   & | \\
   & Cl \\
   (D) & CH₃ - CH - CH - CH₂ - CH₃ \\
   & | \\
   & Cl
   \end{align*}
   \]

66. Silver mirror test can be used to distinguish between
   (A) ketone and acid  
   (B) phenol and acid  
   (C) aldehyde and acid  
   (D) alcohol and phenol

67. The pair of compounds in which both the compounds give positive test with Töller’s reagent is
   (A) glucose and sucrose  
   (B) fructose and sucrose  
   (C) acetophenone and hexanal  
   (D) glucose and fructose

68. Wolff Kishner reduction reduces
   (A) - COOH group  
   (B) -C≡C- group  
   (C) -O- group  
   (D) - CH₂ group
69. \[ \text{OCH} - \text{CHO} \xrightarrow{[\text{OH}^-]} \text{HOH}_2\text{C} - \text{COOH} \] The reaction given is

(A) Aldol condensation
(B) Cannizzaro reaction
(C) Fehling reaction
(D) Toller's reaction

70. Cyanohydrin of which of the following forms lactic acid

(A) \( \text{CH}_3\text{CH}_2\text{CHO} \)  
(B) \( \text{CH}_3\text{CHO} \)  
(C) \( \text{HCHO} \)  
(D) \( \text{CH}_2\text{COCH}_3 \)

71. The correct order of reactivity of \( \text{pH}_2\text{B} \) with \( \text{pH} - \text{C} - \text{pH}, \text{CH}_3 - \text{C} - \text{H}, \text{CH}_3 - \text{C} - \text{CH}_3 \)

(I) \( \text{O} \)  
(II) \( \text{O} \)  
(III) \( \text{O} \)

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

72. Carboxylic acids are more acidic than phenol and alcohol because of

(A) intermolecular hydrogen bonding  
(B) formation of dimers  
(C) highly acidic hydrogen  
(D) resonance stabilization of their conjugate base

73. When \( \text{CH}_2 = \text{CH} - \text{COOH} \) is reduced with \( \text{LiAlH}_4 \), the compound obtained will be

(A) \( \text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{OH} \)  
(B) \( \text{CH}_2 = \text{CH} - \text{CH}_2\text{OH} \)  
(C) \( \text{CH}_3\text{CO} \text{C}_6\text{H}_5 \)  
(D) \( \text{CH}_3 - \text{CH}_2 - \text{CHO} \)

74. In a set of the given reactions, acetic acid yielded a product C

\[ \text{CH}_3\text{COOH} + \text{PCl}_5 \rightarrow \text{A} \xrightarrow{\text{C}_6\text{H}_4\text{Br}_4, \text{AlCl}_3} \text{B} \xrightarrow{\text{C}_6\text{H}_4\text{MgBr}, \text{ether}} \text{C} \] Product C Would be

(A) \( \text{CH}_3\text{C}(\text{OH})\text{C}_6\text{H}_5 \)  
(B) \( \text{CH}_3\text{CH}-(\text{OH})\text{C}_2\text{H}_5 \)  
(D) \( \text{CH}_2\text{CO} \text{C}_6\text{H}_5 \)  
(D) \( \text{CH}_2\text{CH}(\text{OH})\text{C}_6\text{H}_5 \)

75. Among the following acids which has the lowest \( pK_a \) value

(A) \( \text{CH}_3\text{COOH} \)  
(B) \( \text{HCOOH} \)  
(C) \( (\text{CH}_3)_2\text{CH} - \text{COOH} \)  
(D) \( \text{CH}_3\text{CH}_2\text{COOH} \)

76. One of the following named reaction is an example of “disproportionation reaction”. Identify it.

(A) Brich reduction  
(B) Aldol condensation  
(C) Reimer-Tiemann reaction  
(D) Cannizzaro reaction

77. Acetone and acetaldehyde are differentiated by

(A) \( \text{NaOH} + \text{I}_2 \)  
(B) \( \text{Ag(NH}_3)_2^+ \)  
(C) \( \text{HNO}_2 \)  
(D) \( \text{I}_2 \)
78. Which is not true about acetophenone?
   (A) Reacts to form 2,4-dinitrophenyl hydrazine
   (B) Reacts with Tollen’s reagent to form silver mirror
   (C) Reacts with \( I_2/NaOH \) to form iodoform
   (D) Reacts with alkaline \( KMnO_4 \)

79. Which of the following pairs can be distinguished by sodium hypoiodite?
   (A) \( CH_3CHO \) and \( CH_3COCH_3 \)
   (B) \( CH_3CH_2CHO \) and \( CH_3COCH_3 \)
   (C) \( CH_3CH_2OH \) and \( CH_3CH_2CH(OH)CH_3 \)
   (D) \( CH_3OH \) and \( CH_3CH_2CHO \)

80. \( CH_3CHO \) and \( C_6H_5CH_2CHO \) can be distinguished chemically by
   (A) Benedict test  (B) Iodoform test  (C) Tollen’s test  (D) Fehling solution test

81. Ethanal is treated with excess of ethanol in the presence of hydrochloric acid. The product is

   \[ CH_3 - CH_2 - CH_2 - C - CH_3 \]  \quad \text{(A)}

   \[ (CH_3)\text{C}<\text{OC}_2\text{H}_5 \]  \quad \text{(B)}

   \[ CH_3 - CH_2 - CH_2 - C - CH_2 - CH_2 - CH_3 \]  \quad \text{(C)}

   \[ \text{CH}_3 - \text{C}<\text{OC}_2\text{H}_5 \]  \quad \text{(D)}

82. Predict the product in the given reaction

   \( \text{CHO} \quad \text{Cl} \quad \text{50\% KOH} \)

   \[ \text{(C)} - \text{CH}_2\text{OH} + \text{(CH}_2\text{COO}^- \quad \text{(A)} \text{Cl} \quad \text{OH} \quad \text{OH} \]

   \[ \text{(C)} - \text{CH}_2\text{OH} + \text{COO}^- \quad \text{(C)} \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]

   \[ \text{(D)} - \text{CH}_2\text{OH} + \text{COO}^- \quad \text{(D)} \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \]

83. The number of aldol reaction(s) that occurs in the given transformation is

   \[ \text{CH}_3\text{CHO} + 4\text{HCHO} \quad \text{Con. NaOH}_{(aq)} \]

   \[ \text{OH} - \text{OH} \quad \text{OH} \quad \text{OH} \quad \text{OH} \]

   \[ \text{(A) 1} \quad \text{(B) 2} \quad \text{(C) 3} \quad \text{(D) 4} \]
84. Identify the correct statement.
   (A) Aldehydes on reduction give secondary alcohols.
   (B) Ketones on reduction give primary alcohols.
   (C) Ketones reduce Fehling’s solution and give cuprous oxide.
   (D) Ketones do not react with monohydric alcohol.

85. Arrange the following compounds in increasing order of the reactivity in nucleophilic
addition reactions
   Ethanal (I), Propanal (II), Propanone (III), Butanone (IV)
   (A) III < II < I < IV    (B) IV < III < II < I    (C) II < I < III < IV    (D) I < II < III < IV

86. Ketones reacts with Mg-Hg over water gives
   (A) pinacolone     (B) pinacols     (C) alcohols     (D) none of these

87) In the presence of a dilute base, $C_6H_5CHO$ and $CH_3CHO$ react together to give ______ product.
   (A) $C_6H_5CH_3$     (B) $C_6H_5CH_2CH_2OH$     (C) $C_6H_5CH_2OH$     (D) $C_6H_5CH=CH-CHO$

88) $CH = CH \xrightarrow{H_2SO_4 \text{ dilute}} A \xrightarrow{\text{dilute } NaOH} B$. The compound B is ...
   (A) $\text{CH}_3\text{CH} = \text{CH} - \text{CHO}$     (B) $\text{CH}_3\text{CH} = \text{CH} - \text{C} = \text{CH}_3$
   (C) $\text{CH}_3\text{CH} = \text{CH} - \text{COONa}$     (D) $\text{CH}_3\text{CH} (\text{OH}) - \text{CH} - \text{C} = \text{CH}_3$

89) Choose the weakest acid among the following.
   (A) $\text{F}_3\text{C COOH}$    (B) $(\text{CH}_3)_2\text{CH COOH}$    (C) $\text{CH}_3\text{CH}_2\text{COOH}$    (D) $\text{FCH}_2\text{COOH}$

90) Among the following compounds, the most acidic is
   (A) p-nitrophenol    (B) p-hydroxybenzoic acid
   (C) o-hydroxybenzoic acid    (D) p-toluic acids
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