

ALDEHYDE, KETONE AND CARBOXILIC ACID

SOLVED SUBJECTIVE EXERCISE

Very Short Answer Type Questions (1 mark)

1.

Draw the structures of the following compounds:

- (i) 3-Bromo-4-phenylpentanoic acid
- (ii) p, p'-Dihydroxybenzophenone

Ans. (i)
$${}^{5}_{CH_3} - {}^{4}_{CH} - {}^{3}_{CH_2} - {}^{2}_{CH_2} - {}^{1}_{C} - OH$$

- 2. Write the IUPAC names of the following ketones and aldehydes. Wherever possible, give also common names.
 - (i) CH₃(CH₂)₅CHO
 - (ii) Ph CH = CH CHO

Ans. (i) IUPAC Name:-

Heptanal

(ii) IUPAC Name :-

3-Phenylprop-2-enal,

Common Name:-

β-Phenylacrolein

3. Name two reagents which can be used to distinguish acetaldehyde from acetone?

Ans. Acetaldehyde reduces Tollens' reagent to produce shining silver mirror and produces red ppt. of Cu₂O with Fehling's solution.

$$CH_{3}CHO + 2\underbrace{Cu^{2+} + 5OH^{-}}_{\text{Fehling's reagent}} \longrightarrow CH_{3}COO^{-} + \underbrace{Cu_{2}O\downarrow}_{\text{Red ppt.}} + 3H_{2}O$$

Acetone, on the other hand, does not give these tests.

4. Write two important uses of formalin.

Ans. It is used (i) In the preservation of anatomical specimens and (ii) In the manufacture of polymers like bakelite, melmac, urea-formaldehyde, etc.

Arrange the following in order of their increasing reactivity towards HCN: CH₃CHO, CH₃COCH₃, HCHO, C₂H₅COCH₃

Ans. (i) Reactivity increases as the +ve charge on carbonyl carbon increases. Since alkyl groups have +I-effect, therefore, reactivity increases as the number of alkyl groups on the carbonyl carbon decreases.

- (ii) Reactivity increases as the number and size of alkyl groups decreases, i.e., steric hindrance decreases. Due to combined effect of these two factors, the reactivity increases in the order:

 C₂H₅COCH₃ < CH₃COCH₃ < CH₂CHO < HCHO.
- Arrange the following compounds in increasing order of their boiling points.
 CH₃CHO, CH₃CH₂OH, CH₃OCH₃, CH₃CH₂CH₃
- Ans. CH₃CH₂CH₃ < CH₃OCH₃ < CH₃CHO < CH₃CH₂OH

Stronger the attractive forces, higher is the boiling point. Hydrocarbons are nonpolar having weakest attractive forces, ethers are polar and aldehydes have strong dipolar interaction. Alcohol have maximum intermolecular forces due to H-bonding.



7. Write the IUPAC name of the following $CH_3 - C - CH_2COCH_3$ Ans. 4-hydroxy-4-methyl pentan-2-one OH

 Arrange the following in decreasing order of acidic strength. CH₂CICOOH, HCOOH, CF₃COOH, CCI₃COOH.

Ans. HCOOH < CH2CICOOH < CCI3COOH < CF3COOH

Short Answer Type Questions (2 mark)

Write a test to differentiate between pentan-2-one and pentan-3-one.

Ans. Pentan-2-one is a methyl ketone (i.e., contains the grouping CH_3CO) and hence undergoes Iodoform test on treatment with I_2 / NaOH to give yellow ppt. of iodoform. In contrast, pentan-3-one is not a methyl ketone and hence does not give yellow ppt. of CHI_3 on treatment with I_2 / NaOH.

$$\begin{array}{c} \bullet & \bigcirc \\ \square \\ \text{CH}_3\text{CH}_2\text{CH}_2 - \text{C} - \text{CH}_3 & \frac{I_2/\text{NaOH}}{\text{(Iodoform test)}} \rightarrow & \text{CHI}_3 & + & \text{CH}_3\text{CH}_2\text{COONa} \\ \hline \text{Pentane-2-one} & \text{Yellow ppt.} & \text{Sod. butanoate} \\ \end{array}$$

$$O$$
 \parallel
 $CH_3CH_2CH_2$ — C — CH_2CH_3 $\xrightarrow{I_2/NaOH}$ No yellow ppt. of CHI_3
 $Pentane.3-one$

10. Name the electrophile produced in the reaction of benzene with benzoyl chloride in the presence of anhydrous AICl₃.
Name the reaction also.

Ans.
$$C_6H_5$$
 C_6 $C_$

The name of the reaction is Friedel-Crafts acylation reaction.

- 11. Predict the products formed when cyclohexane carbaldehyde reacts with following reagents:
 - (i) Tollen's reagent
 - (ii) Zinc amalgam and dilute hydrochloric acid.

Chemistry Chemistry



 pK_a of chloroacetic acid is lower than pK_a of acetic acid. Explain.

Ans. pK_a of chloroacetic acid is lower than pK_a of acetic acid. This means, chloroacetic acid is a stronger acid than acetic acid because of the following two reasons:

(i) Due to –I-effect of Cl atom, the electron density in the O–H bond in chloroacetic acid is much lower than due to + I-effect of CH₃ group in acetic acid. As a result, O-H bond in chloroacetic acid is much weaker than in acetic acid and hence loses a proton more easily than acetic acid.

$$CI \leftarrow CH_2 \leftarrow C \leftarrow O \leftarrow H \quad CH_3 \rightarrow C \rightarrow O \rightarrow H \quad CI \leftarrow CH_2 \leftarrow C \stackrel{O}{\leftarrow} \quad CH_3 \rightarrow C \stackrel{O}{\leftarrow} \stackrel{O}{\leftarrow} \quad CH_3 \rightarrow C$$

- (ii) Due to -I-effect of Cl, dispersal of the -ve charge occurs in chloroacetate ion but due to +I-effect of CH group, intensification of -ve charge occurs in acetate ion. In other words, chloroacetate ion is much mon stable than acetate ion.
- What is Tollens' reagent? Write one usefulness of this reagent.
- Ans. Ammoniacal silver nitrate solution is called tollens' reagent. It is used to test aldehydes. Both aliphatic and aromatic aldehydes reduce Tollens' reagent to shining silver mirror. It is also used to distinguish aldehydes from ketones.

$$2[Ag(NH_3)_2]^+ + RCHO + 3OH^- \xrightarrow{Heat} 2Ag \downarrow + RCOO^- + 4NH_3 + 2H_2O$$

Fluoring is more electron.

- Fluorine is more electronegative than chlorine even then p-fluorobenzoic acid is a weaker acid than p-chlorobenzoic
- Ans. Since halogens are more electronegative than carbon and also possess lone pairs of electrons, therefore, they exer both -I and +R-effects. Now in F, the lone pairs of electrons are present in 2p-orbitals but in Cl, they are present in 3p-orbitals. Since 2p-orbitals of F and C are of almost equal size, therefore, the +R-effect is more pronounced in p-fluorobenzoic acid then in p-chlorobenzoic acid

Thus, in p-fluorobenzoic acid, +R-effect outweighs the -I-effect but is p-chlorobenzoic acid, it is the -I-effect which outweighs the +R-effect. Consequently, p-fluorobenzoic acid is a weaker acid than p-chlorobenzoic acid

- Explain why dialkylcadmium is considered superior to Grignard reagent for the preparation of a ketone from an acid 15.
- $\pmb{Ans.}$ Since Cd (E.N. = 1.7) is less electropositive than Mg (E.N. = 1.2), therefore, dialkylcadmiums are less reactive than Grignard reagents towards nucleophilic addition reactions. As such, dialkylcadmiums react with the more reactive acid chlorides to give ketones but do not react further with the less reactive ketone thus formed to give tert-alcohols In contrast, Grignard reagents being more reactive not only react with the acid chlorides but also with the ketones so

- Aldehydes are more reactive than ketones due to the following two reasons:
- (i) Due to smaller +I-effect of one alkyl group in aldehydes as compared to larger +I-effect of two alkyl groups, the magnitude of positive charge on the carbonyl carbon is more is aldehydes than in ketones. As a result, nucleophilic addition reactions occur more readily in aldehydes than in ketones.
- (ii) Due to presence of a H-atom on the carbonyl group, aldehydes can be more easily oxidised than ketones. As a result, aldehydes act as reducing agents and thus reduce Tollens' reagent, Fehling's solution, etc.



Aldehyde, Ketone and Carboxilic Acid

- 17. Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a acid then phenol. Why?
- Ans. (i) Phenoxide ion has non-equivalent resonance structures in which the negative charge is at the less electronegative carbon atom.
 - (ii) The negative charge is delocalised over two electronegative oxygen atoms in carboxylate ion whereas in phenoxide ion the negative charge less effectively delocalised over one oxygen atom and less electronegative carbon atoms.

$$R - C = 0$$
 δ δ δ δ Carboxylate ion Phenoxide ion

Short Answer Type Questions (3 mark)

- Arrange the following compounds in increasing order of their boiling points: CH₃CH₂CH₂CH₀, CH₃CH₂CH₂CH₂CH₂OH, CH₃CH₂CH₂CH₂CH₂CH₃.
- Ans. The four compounds have comparable molecular masses. CH₃CH₂CH₂CHO (72), CH₃CH₂CH₂CH₂OH (74), CH₃CH₂COCH₃(72) and CH₃CH₂OCH₂CH₃(74). Amongst compounds having comparable molecular masses, alcohols have the highest b.p. due to intermolecular H-bonding, i.e., CH₃CH₂CH₂CH₂OH has the highest boiling point. The boiling points of CH₃CH₂CH₀, CH₃CH₂OCH₂CH₃ and CH₃CH₂COCH₃ depend upon their relative dipole moments. Since dipole moments of these three compounds decrease in the order: ketones > aldehydes > ethers, therefore, their boiling points also decrease in the same order, i.e., boiling point decrease in order: CH₃COCH₂CH₃ > CH₃CH₂CHO > CH₃CH₂OCH₂CH₃.

 Thus, the boiling points of the four compounds decrease in the order: CH₃CH₂CH₂OH > CH₃COCH₂CH₃ > CH₃CH₂CH₂CH₂CHO > CH₃CH₂CH₂CHO > CH₃CH₂CH₂CH₃
- 19. Identity A, B and C in the following reaction

$$HC \equiv CH \xrightarrow{\text{dil. } H_2 \leq O_4} A \xrightarrow{\text{dil. NaOH}} B \xrightarrow{\text{heat}} C$$

$$\begin{array}{c} CH_{3}-CHOH-CH_{2}-CHO & \xrightarrow{\quad \text{ heat } \quad \quad } CH_{3}-CH=CH-CHO \\ \text{ β-Hydroxybutyraldehyde (B)} & \text{ } Dehydration (-H_{2}O) \\ \text{ (An aldol)} & \text{ } But-2-en-1-al (C) \end{array}$$

- 20. An alkene 'A' (Mol. formula C₅H₁₀) on ozonolysis gives a mixture of two compounds 'B' and 'C'. Compound 'B' gives positive Fehling's test and also forms iodoform on treatment with I₂ and NaOH. Compound 'C' does not give Fehling's test but forms iodoform. Identify the compounds A, B and C. Write the reaction for ozonolysis and formation of iodoform from B and C.
- Ans. (i) Since compound 'B' gives Fehling's test, therefore, it must be aldehyde. Further since aldehyde 'B' gives iodoform on treatment with I₂ and NaOH, therefore, 'B' must be acetaldehyde (CH₃CHO).
 - (ii) Since alkene 'A' (MF C₅H₁₀) contains five carbon atoms and one of the products of ozonolysis is 'B' (CH₃CHO) which contains two carbon atoms, therefore, the other product of ozonolysis, i.e., 'C'must contain three carbon atoms.
 - (iii) Since compound 'C' does not give Fehling's test, it must be a ketone, Further since ketone 'C' contains three carbon atoms and gives iodoform on treatment with I_2 and NaOH, therefore, ketone 'C' must be acetone (CH $_3$ COCH $_3$).

22.



(iv) Write the products of ozonolysis, i.e., 'B' (CH₃CHO) and 'C' (CH₃COCH₃) side by side with their C = 0 groups facing each other. Remove the oxygen atoms and join the remaining fragments by a double bond, the structure of alkene 'A' is 2-methylbut-2-ene.

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CH} = \boxed{O} + \boxed{O} = C - CH_3 \\ \text{Acetaldehyde (B)} \end{array} \xrightarrow{\text{CH}_3 \\ \text{(i) O}_3 / \text{CH}_2 \text{Cl}_2} \\ \text{(ii) 2n/H}_2 O \end{array} \qquad \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3\text{CH} = C - CH_3 \\ \text{2-Methylbut-2-ene (A)} \end{array}$$

(v) Formation of iodoform from 'B' and 'C' may be explained as follows:

$$CH_3COCH_3 + 3I_2 + 4NaOH \xrightarrow{\Delta} CHI_3 + CH_3COONa + 3NaI + 3H_2O$$
Acetone (C)
Sod. acetate

- 21. Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.
- Ans. Due to intramolecular H-bonding (chelation), o-hydroxybenzaldehyde exists as discrete

o-Hydroxybenzaldehyde (intramolecular H-bonding)

p-Hydroxybenzaldehyde (intermolecular H-bonding)

molecules while due to intermolecular H-bonding, p-hydroxybenzaldehyde exists as associated molecules. To break these intermolecular H-bonds, a large amount of energy is needed. Consequently, p-hydroxybenzaldehyde has a much higher m.p. and b.p. than that of o-hydroxybezaldehyde. As a result, o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.

- An organic compound with the molecular formula C₉H₁₀O forms 2, 4-DNP derivative, reduces Tollens' reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

 (i) Since the given compound with M.F.C. H. Oforms 2, 2, 4-DNP, doi: 10.1007/j.c. 10.
- Ans. (i) Since the given compound with M.F. C₉H₁₀O forms a 2, 4-DNP derivative and reduces Tollens' reagent, it must an aldehyde.
 - (ii) Since it undergoes Cannizzaro reaction, therefore, CHO group is directly attached to the benzene ring.
 - (iii) Since on vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid, therefore, it must be an ortho-substituted benzaldehyde. The only o-substituted aromatic aldehyde having M.F. $C_9H_{10}O$ is 2-ethylbenzaldehyde. All the reactions can now be explained on the basis of this structure.

$$\begin{array}{c} \text{Ag} \downarrow + \\ \text{Silver} \\ \text{mirror} \end{array} \\ \begin{array}{c} \text{COO} \\ \text{CoOH} \\ \text{Tollens' reagent} \end{array} \\ \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{2-Ethylbenzoate} \end{array} \\ \begin{array}{c} \text{2-Ethylbenzaldehyde} \\ \text{(M.F. C_9H}_{10}\text{O}) \end{array} \\ \text{1, 2-Benzenedicarboxylic acid} \\ \text{2, 4-Dinitrophenylhydrazine} \\ \\ \text{CH} = \text{NNH} \\ \text{NO}_2 \\ \text{CH} = \text{NNH} \\ \text{COOH} \\ \text{2, 4-DNP derivative} \end{array}$$



Aldehyde, Ketone and Carboxilic Acid

How will you convert ethanal into the following compounds?

Ans. (i)
$$2 \overset{\text{CH}_3\text{CHO}}{\text{Ethanal}} \xrightarrow{\text{Dil.NaOH}} \overset{\text{Dil.NaOH}}{\rightarrow} \overset{4}{\text{C}} \overset{\text{H}_3}{\text{H}_3} - \overset{3}{\text{C}} \overset{\text{HOH}}{\text{-CH}_2} - \overset{1}{\text{C}} \overset{\text{HO}}{\text{-CH}_2} \overset{\text{H}_3\text{O}^+/\Delta}{\text{-H}_2\text{O}} \xrightarrow{\text{CH}_3} - \overset{\text{CH}}{\text{CH}} = \overset{\text{CH}}{\text{-CHO}} - \overset{\text{CH}}{\text{-CHO}} \overset{\text{CH}_3}{\text{-H}_2\text{O}} \overset{\text{H}_3\text{O}^+/\Delta}{\text{-H}_2\text{O}} \xrightarrow{\text{CH}_3} - \overset{\text{CH}}{\text{-CHO}} = \overset{\text{CH}}{\text{-CHO}} - \overset{\text{CH}_3}{\text{-CHO}} \overset{\text{CH}_3}{\text{-CH}_3} \overset{\text{CH}_3}{\text{-CH}_3} - \overset{\text{CH}_3}{\text{-CH}_3} \overset{\text{CH}_3$$

(ii)
$$CH_3CHO \xrightarrow{Dil.NaOH} CH_3 - CHOH - CH_2 - CHO \xrightarrow{H_3O^*/\Delta} CH_3CH = CHCHO \xrightarrow{But-2-enal} CH_3CH = CHCHO \xrightarrow{CH_3CHO} CH_3CH = CHCHO \xrightarrow{CHOHO} CH_3CHOHO CH_$$

$$\frac{[A_3(NH_3)_2]^+OH^-}{\text{Tollens' reagent}} \rightarrow CH_3CH = CHCOOH$$
But-2-enoic acid

- (i) Why HCOOH does not give HVZ reaction but CH₃COOH does? 24.
 - (ii) Hydrazones of aldehydes and ketones are not prepared in highly acidic medium. Explain.
- Ans. (i) CH₃COOH contains α-hydrogens and hence gives HVZ reaction but HCOOH does not contain an α-hydrogen and hence does not give HVZ reaction.
 - (ii) In highly acidic medium, the NH2 group of hydrazine gets protonated

$$NH_2$$
— NH_2 + H^+ — NH_2 — NH_3
Hydrazine Protonated hydrazine (non nucleophilic)

Due to strong –I-effect of the TH, group, the lone pair of electrons on the –NH2 group of protonated hydrazine is not available for nucleophilic attack on the C = O group and hence hydrazone formation does not occur.

- An organic compound A (C3H6O) is resistant to oxidation but forms compound B(C3H8O) on reduction. B reacts with HBr to form the compound C. C with Mg forms Grignard reagent D which reacts with A to form a product which on hydrolysis gives E. Identify A to E.
- Ans. The possible structures of the molecular formula C₃H₆O are CH₃COCH₃ (acetone) and CH₃CH₂CHO (propanal), the former one is resistant to oxidation. Thus, A is a ketone, i.e., acetone.
 - (i) A on reduction gives B, thus B is a 2° alcohol, i.e., 2-propanol.

$$\begin{array}{ccc} & & & \text{CH}_3\text{CHCH}_3\\ \text{CH}_3\text{COCH}_3 & \xrightarrow{\text{LIAIH}_4} & \text{OH}\\ & & \text{2-propanol}\\ & & & \text{(B)} \end{array}$$

(ii) 2-propanol reacts with HBr to give 2-bromopropane.

$$\begin{array}{c|c} \text{CH}_3\text{CHCH}_3 & \xrightarrow{\text{HBr}} & \text{CH}_3\text{CHCH}_3 \\ | & & | \\ \text{OH} & & \text{Br} \\ \text{2-propanol} & \text{2-bromopropane} \\ \text{(B)} & & \text{(C)} \end{array}$$

(iii) C (2-bromopropane) gives D (Grignard reagent) with Mg.
$$CH_3CHCH_3 + Mg \xrightarrow{Ether} CH_3CHCH_3$$

Br MgBr (D)

(iv) D reacts with acetone (A) to give on adduct which on hydrolysis gives a 3° alcohol (E)

$$\begin{array}{c} H_{3}C \\ \\ H_{3}C \end{array} \xrightarrow{\delta + \delta} \begin{array}{c} \delta + \delta \\ \\ C = O + (CH_{3})_{2}CHMgBr \end{array} \xrightarrow{H_{3}C} C \xrightarrow{OMgBr} \begin{array}{c} OH \\ \\ H_{3}C \end{array} \xrightarrow{H_{3}C} \begin{array}{c} OH \\ \\ CH(CH_{3})_{2} \end{array} \xrightarrow{H_{3}C} \begin{array}{c} OH \\ \\ CH \end{array} \xrightarrow{\delta + \delta} \begin{array}{c} CH \\ CH \end{array} \xrightarrow{\delta + \delta} \begin{array}{c} OH \\ CH \end{array} \xrightarrow{\delta + \delta} \begin{array}$$

2, 3-dimethyl butan-2-ol (E)

26. Predict the products of the following reactions -

(i)
$$+ HO - NH_2 \longrightarrow H'$$

(iii) RCH = CH
$$-$$
 CHO $+$ NH₂ $-$ C $-$ NH $-$ NH₂ $+$ $+$

Cyclohexanon-2, 4-dinitrophenyl-hydrazone

(ifii)
$$R - CH = CH - CH = N - NH - C - NH2 (iv)$$

- 27. An organic compound with molecular formula C₉H₁₀O forms 2, 4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro reaction. On vigorous oxidation, it give 1, 2-benzene dicarboxylic acid. Identify the compound.
- **Ans.** (i) As the given compound with molecular formula $C_9H_{10}O$ forms a 2, 4-DNP derivative and reduces Tollen's reagent, thus, it must be an aldehyde.
 - (ii) As it undergoes Cannizzaro reaction, hence CHO group is directly attached to the benzene ring.
 - (iii) On vigorous oxidation, it gives 1, 2-benzene-dicarboxylic acid, therefore, it must be an ortho-substituted benzaldehyde. And, the only o-substituted aromatic aldehyde which have $C_9H_{10}O$ molecular formula is o-ethylbenzaldehyde.

Reactions

$$\begin{array}{c|c} CHO & COO^- \\ \hline C_2H_5 & Tollen's reagent & COO^- \\ \hline C_2H_5 & Silver \\ \hline C_2ethylbenzoate & mirror \\ \hline \end{array}$$

1, 2-benzenedicarboxylic acid

CHO
$$C_2H_5$$

$$C_2H_5$$

$$NO_2$$

$$CH=NNH$$

$$C_2H_5$$

$$C_2H_5$$

$$NO_2$$

$$CH=NNH$$

$$C_2H_2O$$

$$C_2H_5$$

$$C_2H_5$$



Describe the following:

- (i) Acetylation
- (ii) Cross aldol condensation
- Ans. (i) Acetylation: Acetylation is the replacement of H atom of alcohol, amines and introduce COCH₃ group in the presence of acetic anhydride.

$$\begin{array}{c} \text{OH} \\ \text{COOH} \\ + \\ \text{CH}_3\text{CO} \\ \text{CH}_3\text{CO} \\ \text{O-Salicylic acid} \end{array} \begin{array}{c} \text{OCOCH}_3 \\ \text{CrO}_3 \\ \text{CrO}_3 \\ \text{Aspirin} \end{array} \begin{array}{c} \text{COOH} \\ + \\ \text{CH}_3\text{COOH} \\ \text{Aspirin} \end{array}$$

(ii) Cross aldol condensation: The condensation of two different carbonyl compounds (one of which must have one α-hydrogen) in the presence of a base is known as cross aldol condensation or mixed condensation.

(b)
$$CH_3CH_2CHO + CH_2 - CHO$$
 CH_3
 CH_3

29. An organic compound contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogensulphite and give positive iodoform test. On vigorous oxidation, it gives ethanoic and propanoic acid. Write the possible structure of the compounds.

147



Ans. The compound is methyl ketone and its probable structure would be :

S.No. 1	Element	Mass Percentage 69.77%	Atomic Mass	Atomic Ratio $\frac{69.77}{12} = 5.8$	Simplest Ratio $\frac{5.8}{1.16} = 5$
2	Н	11.63%	1	$\frac{11.63}{1} = 11.63$	$\frac{11.63}{1.16} = 10$
3	0	18.60%	16	$\frac{18.60}{16} = 1.16$	$\frac{1.16}{1.16} = 1$

Thus, the empirical formula of the compound is $C_5H_{10}O$, it would be $CH_3COCH_2CH_2CH_3$ $CH_3-C-CH-CH_2-CH_3$ Pentan-2-one; Molecular mass = 86

(i) Action with NaHSO,

$$H_3C-C-CH_2-CH_2-CH_3+NaHSO_3$$
 $H_3C-C-CH_2-CH_2-CH_2-CH_3$
 OH
Sodium hydrogen sulphite

(ii) Action with I2 and NaOH

$$\begin{array}{c} \text{H}_{3}\text{C}-\text{C}-\text{CH}_{2}-\text{CH}_{2}-\text{CH}_{3}+3\text{I}_{2}+4\text{NaOH} \xrightarrow{\text{Idoform}} \text{CHI}_{3} + \text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{COONa}+3\text{H}_{2}\text{O}+3\text{Nal}} \\ \text{O} \\ \text{(iii) Vigorous oxidation} \end{array}$$

$$H_3C$$
 $C=O$
 $K_2Cr_2O_7/H_2SO_4$
 $Oxidation$
 CH_3COOH
 CH_3CH_2COOH
 CH_3CH_2COOH
 CH_3COOH
 CH_3COOH

- **30.** State reasons for the following:
 - (i) Monochloroethanoic acid has a higher pk a value than dichloroethanoic acid.
 - (ii) Ethanoic acid is a weaker acid than benzoic acid.
- Ans. (i) Because the stability of conjugate base of monochloroethanoic acid is less due to presence of one electron withdrawing -Cl group than in dichloroethanoic acid.
 - (ii) Because of greater electronegativity of sp² hybridised carbon to which carboxyl carbon is attached.

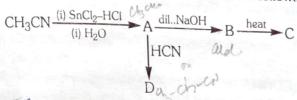


EXERCISE-1

PREVIOUS YEARS BOARD PROBLEMS

CBSE 2016

(a) Write the structures of A, B, C and D in the following reactions:



(b) Distinguish between:

(c) Arrange the following in the increasing order of their boiling points: CH₃CH₂OH, CH₃COCH₃, CH₃COOH

2

- (a) Write the chemical reaction involved in Etard reaction.
- (b) Arrange the following in the increasing order of their reactivity towards nucleophilic addition reaction: CH_3 -CHO, $C_6H_5COCH_3$, HCHO
- (Why pKa of Cl-CH₂-COOH is lower than the pKa of CH₃COOH?
- (d) Write the product in the following reaction.

$$CH_3CH_2CH=CH-CH_2CN \xrightarrow{1.(i-Bu)_2AlH}$$

(e) A and B are two functional isomers of compound C_3H_6O . On heating with NaOH and I_2 , isomer A forms yellow precipitate of iodoform whereas isomer B does not form any precipitate. Write the formulae of A and B.

CBSE 2015

Predict the products of the following reactions:

The Hard the products of the following reactions:

$$CH_3 - C = O \xrightarrow{H_2N-NHCONH_2}? CH_3 - C = N - NM - C - NM$$

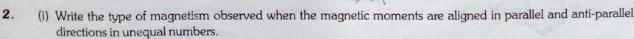
$$\begin{array}{c} \text{(ii)} C_6 H_5 - CH_2 - CH_3 & \text{(a)} KMnO_4 / KOH \\ \text{(b)} H^+ \end{array}? \qquad \begin{array}{c} \text{(b)} H_5 - COUN \\ \text{(b)} H^+ \end{array}$$

, Write the reagents used in the following reactions:

(i)
$$C_6H_5 - CO - CH_3 \xrightarrow{ZO(1/2)} C_6H_5 - CH_2 - CH_3$$

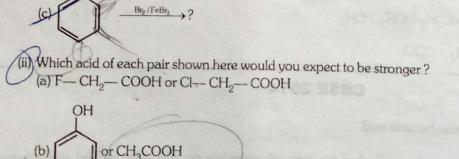
CBSE 2014

Write the structure of 2-hydroxybenzoic acid.



(ii) Which stoichiometric defect decreases the density of the crystal?

Chemistry (a) Write the products formed when CH3CHO reacts with the following reagents : YI) HCN (ii) H.N-OH (iii)CH₃CHO in the presence of dilute NaOH (b) Give simple chemical tests to distinguish between the following pairs of compounds: (i) Benzoic acid and Phenol (ii) Propanal and Propanone (a) Account for the following: (i) Cl – CH₂COOH is a stronger acid than CH₃COOH. (ii) Carboxylic acids do not give reactions of carbonyl group. (b) Write the chemical equations to illustrate the following name reactions : (i) Rosenmund reduction (ii) Cannizzaro's reaction _ ' H- C-n cmc Noon H- C-0 + H-C-n Out of CH₃CH₂ - CO - CH₂ - CH₃ and CH₃CH₂ - CH₂ - CO - CH₃, which gives iodoform test? **CBSE 2013** Rearrange the following compounds in the increasing order of their boiling points. CH₃—CHO CH₃—CH₂—OH CH₃—CH₂—CH₃ (i) How will you convert the following? /(a) Propanone to propan-2-ol (b) Ethanal to 2-hydroxy propanoic acid (c) Toluene to benzoic acid (ii) Give simple chemical tests to distinguish between (a) pentan-2-one and pentan-3-one (b) ethanal and propanal (i) Write the products of the following reactions at CH3 - C - CH3 - Zn-Hg Conc. HCI ? CM3 - Cy cm COOH





CBSE 2012

Write the IUPAC name of the following.

$$CH_3 - CH_2 - CH = CH - C - H$$

1est-2-on-1-al

- (i) An organic compound with molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent and undergoes Cannizzaro's reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.
- (ii) Give the chemical tests to distinguish between
- (a) propanol and propanone
- (b) benzaldehyde and acetophenone
- (iii) Arrange the following compounds in an increasing order of their property as indicated: Acetaldehyde, acetone, methyl tert-butyl ketone (reactivity towards HCN)

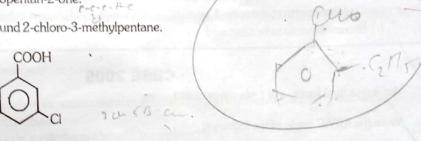


Arrange the following compounds in an increasing order of their property as indicated

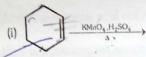
- (i) Benzoic acid, 3, 4-dinitrobenzenzoic acid, 4-methoxy benzoic acid (acid strength)
- (ii) CH₃CH₂CH(Br)COOH, CH₃CH(Br)CH₂COOH, (CH₃)₂CHCOOH (acid strength)

CBSE 2011

- Draw the structure of 4-chloropentan-2-one.
- Write structure of the compound 2-chloro-3-methylpentane.

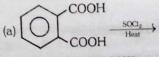


- Wirte IUPAC name of
- Predict the products.

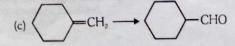


- A compound A(C2H6O) on oxidation by PCC gave B, which on treatement with aqueous alkali and subsequent heating furnished C. B on oxidation by $KMnO_4$, forms a monobasic carboxylic acid with molar mass $60~g~mol^{-1}$. Deduce the structures of A, B and C.
- - (i) Illustrate the following name reactions
 - (a) Cannizzaro's reaction
 - (ii) How would you obtain
 - (a) but-2-enal from ethanal? (c) benzoic acid from ethyl benzene?
- (b) Clemmensen reaction
- (b) butanoic acid from butanol?
- (i) Give chemical tests to distinguish between the following:
- (a) Benzoic acid and ethyl benzoate
- (b) Benzaldehyde and acetophenone

(ii) Complete



(b) C_6H_5CHO — $H_2NCONHNH_2$



153

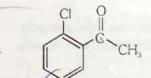
Chemistry



CBSE 2010

What is Tollen's reagent? Write one usefulness of this reagent.

Write the IUPAC name of the following



- (i) Allustrate the following name reactions.
 - (a) Hell Volhard Zelinsky reaction
- (ii) How are the following conversions carried out?
 - (a) Ethylcyanide to ethanoic acid
 - (c) Methyl benzene to benzoic acid
- (b) Wolff-Kishner reduction reaction
- (b) Butan-1-ol to butanoic acid

(i) Illustrate the following name reactions giving a chemical equation in each case:

- (a) Clemmensen reduction
- (b) Cannizzaro's reaction
- (ii) Describe how the following conversions can be brought about:
 - (a) Cyclohexanol to cyclohexan-1-one
- (b) Ethyl benzene to benzoic acid.
- (c) Bromo benzene to benzoic acid

CBSE 2009

Write structural formula of 1-phenyl pentan-1-one.

Write the IUPAC name of the following.

$$(CH_3)_2CH - CH_2 - C - CH (CH_3)_2$$



Write the IUPAC name of the following.

$$O = C - OC_2H_5$$

An organic compound A contains 69.77% carbon, 11.63% hydrogen and rest oxygen. The molecular mass of the compound is 86. It does not reduce Tollen's reagent but forms an addition compound with sodium hydrogen sulphite and gives positive iodoform test. On vigorous oxidation, it gives ethanoic acid and propanoic acids. Derive the structure of compound A.



Give chemical tests to distinguish between

(i) ethanol and propanol

(ii) benzoic acid and ethyl benzoate

An organic compound A (mol. formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid B and alcohol C. Oxidation of C with chromic acid also produced B. On dehydration C gives but-1-ene. Write the equations for the reactions involved.



Indentify A to E in the following sequence.

CH, CH, COOH-



EXERCISE-1

SOLUTION PREVIOUS YEARS BOARD PROBLEMS

ALDEHYDE, KETONE AND CARBOXILIC ACID

CBSE 2016

Ans. (a) A: CH₃CHO

- C: CH₃—CH=CH—CHO
- (b) (i) Heat both the compounds with NaOH and I₂, C₆H₅-CH=CH-COCH₃ gives yellow ppt of iodoform while C₆H₅-CH=CH-CO CH₂CH₃ does not.
 - (ii) Add ammonical silver nitrate solution (Tollens' reagent), HCOOH gives silver mirror while CH₃CH₂COOH does not.
- (c) CH₃COCH₃ <CH₃CH₂OH <CH₃COOH]

- (b) C₆H₅COCH₃ <CH₃CHO< HCHO
- (c) stronger -I effect of Cl, stronger acid less pk_a / strong electron withdrawing power of Cl.
- (d) CH₃CH₂CH=CH—CH₂CHO
- (e) A: CH₃COCH₃ B: CH₃CH₂CHO

CBSE 2015

Sol.1 (i) CH₃-C=N-NH-CO-NH₂
CH₃

(ii)
$$C_6H_5$$
-COOH

Sol.2 (i) Zn-Hg, HCl or H_2N-NH_2 & KOH/Glycol, Δ

(ii) PCl₅ / PCl₃ / SOCl₂ (Any one)

CBSE 2014



Sol.2 Given in solid state chapter

Sol.3 (a) (i) CH₃-CH(OH)CN

(b) (i) NaHCO3 test: Benzoic acid being an acid produces brisk effervescence with NaHCO3 solution while ethylbenzoate does not.

$$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2 \uparrow + H_2O$$

Benzoic acid

Sod. Benzoate

- (ii) By Tollen's test
- (a) Propanal reduces Tollen's reagent, fehling solution, Benedict solution but propanone (ketone) does not reduces.
- (b) Iodoform test:

- Sol.4 (a) (i) Cl is widrawing in nature hence a stablize more carboxylate anion which favours the forward equllibrium.
 - (ii) Becuase of resonance charge sepration with between one carbon and two oxygen atom hence bond polarity reduces so it do not nucleophilic addition reaction.

(b) (i)
$$H_2$$
 CHO
$$Pd-BaSO_4$$

- (ii) HCHO + HCHO

 NaOH → CH₃OH + H COONa Methanol Methanal
- (c) CH, CH, -CH, -CO-CH,

CBSE 2013

Sol.1 CH₃-CH₂-CH₃ < CH₃-CHO < CH₃-CH₂-OH

Sol.2 (a) (i) Ni/H₂

- (ii) HCN, H₃O⁺
- (iii) Alkaline KMnO₄
- (b) (i) Pentan-2-one and pentan-3- one can be distinguished by iodoform test. Pentan-2-one gives iodoform test but pentan-3-one does not.
 - (ii) Ethanal and propanal can be distinguished by iodoform test. Ethanal gives iodoform test but propanal does not.

Sol.3 (a) (i) CH₃-CH₂-CH₃

(ii) CH₃-CHO



(b) (i) F-CH₂-COOH

(ii) CH,COOH

CBSE 2012

Sol.1 Pent-2-en-1-al

- Sol.2 (i) (a) As the given compound with molecular formula $C_9H_{10}O$ forms a 2, 4-DNP derivative and reduces Tollen's reagent, thus, it must be an aldehyde.
 - (b) As it undergoes Cannizzaro reaction, hence CHO group is directly attached to the benzene ring.
 - (c) On vigorous oxidation, it gives 1, 2-benzene-dicarboxylic acid, therefore, it must be an ortho-substituted benzaldehyde. And, the only o-substituted aromatic aldehyde which have C₉H₁₀O molecular formula is o-ethylbenzaldehyde.

Reactions

$$\begin{array}{c|c} CHO & COO \\ \hline \\ C_2H_5 & Tollen's \ reagent \\ \hline \end{array} \\ \begin{array}{c|c} COO \\ \hline \\ C_2H_5 & Silver \\ \hline \\ 2-ethylbenzoate \\ \end{array}$$

$$\begin{array}{c|c} CHO & \hline \\ C_2H_5 & \hline \\ \hline \end{array} \\ Vigrous & \hline \\ COOH \\ \end{array}$$

1, 2-benzenedicarboxylic acid

CHO
$$\begin{array}{c}
O_2N \\
NO_2\\
CH=NNH
\end{array}$$

$$\begin{array}{c}
NO_2\\
NO_2+H_2O\\
C_2H_5
\end{array}$$

$$\begin{array}{c}
C_2H_5
\end{array}$$

$$\begin{array}{c}
C_2H_5
\end{array}$$

(ii) (a) Iodoform test given by propanone. It gives yellow ppt of CHI₃.

$$C-C-CH_3 \xrightarrow{L+NaOH} C-C-ONa + CHI_3 \text{ (yellow ppt)}$$

(b) Tollen's test given by benzaldehyde. It gives silver mirror ppt.

$$\begin{array}{c}
\text{CHO} \\
& \xrightarrow{\text{Ag(NH,)}}
\end{array}$$

Sol.3 (i) methyl tert-butyl ketone < acetone < acetaldehyde

- (ii) (CH₃)₂CHCOOH < CH₃CH(Br)CH,COOH < CH₃CH₂CH(Br)COOH
- (iii) 4-methoxybenzoic acid < Benzoic acid < 3,4-dinitrobenzoic acid



CBSE 2011

Sol.3 3-Brom-5-Chloro Benzene Carboxylic acid

Sol.4 (i) HOOC-C-C-C-COOH

(iii)
$$CH_s - C = N - C - C$$

 C_0H_s

$$\begin{array}{c}
A & Pcc \\
Sol.5 & (C.HO)
\end{array}$$

$$\begin{array}{c}
A & Pcc \\
KnhO_4 \\
C-COOH & 60
\end{array}$$

 $\Lambda \Rightarrow C-C-OH$

B ⇒ C-CHO By oxidation

 $C \Rightarrow C-C=C-CHO$ By Aldol condensation.

Sol.6 (i) (a) Clemmensen reaction: The carbonyl group of aldehyde & ketone is reduced to -CH₂- group on treatment with Zinc amalgam & concentrated hydrochlric acid.

(b) Cannizzaro's reaction: Aldehydes which do not contain any α-hydrogen atom such as formaldehyde, benzaldehyde undergo self oxidations and reduction on treatment with concentrated alkali. A mixture of alcohol & a salt of carboxylic acid are formed.

(1)
$$H - C - H + H - C - H \xrightarrow{NaOH} H - C - OH + H - C - O Na$$

(2) $O - C - H + OH - C - H \xrightarrow{NaOH} OH - C - OH + H - C - O Na$

(ii) (a) Bute-2- enal from ethanal

$$CH_3-C-H \xrightarrow{\text{NaOH}} CH_3-CH=CH-C-H$$
Ethanal
$$Ethanal$$

(Reaction is known as Aldol condensation)



(b)
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 - CH_2 - CH_2 - CH_2 - CH_3 - CH_$$

(c)
$$CH_2$$
- CH_3 $O = C - OH$

$$CH_2$$
- CH_3 $O = C - OH$

$$Oxidation$$
Benzoicacid

Sol.7 (i) (a) Benzoic acid and ethyl benzoate

These two compounds can be distinguished by the following tests:

→ NaHCO₃ test: Benzoic acid being an acid produces brisk effervescence with NaHCO₃ solution while ethylbenzoate does not.

$$C_6H_5COOH + NaHCO_3 \rightarrow C_6H_5COONa + CO_2 \uparrow + H_2O$$

Benzoic acid Sod. Benzoate

CoHoCOOC, Ho Natico, SOLUTION No effervescence due to evolution of CO2 gas.

→ **lodoform test:** Ethylbenzoate on boiling with excess of Na OH solution gives ethyl alchohol which on heating with iodine gives yellow ppt. iodoform.

C₆H₅COOCH₂ CH₃ + NaOH
$$\xrightarrow{\text{Boil}}$$
 C₆H₅COONa + CH₃CH₂ OH
Ethyl benzoate Sod. benzoate Ethyl alcohol
CH₃CH₂OH + 4I₂ + 6NaOH $\xrightarrow{\text{heat}}$ H COONa + CHI₃ + 5NaI + 5H₂O
Ethanol Sod. Idoform
formate (Yellow ppt)

(b) Benzaldehyde and acetophenone

These can be distinguished by the iodoform test.

Iodoform test: Acetophenone being a methyl ketone when treated with NaOI gives yellow ppt of iodoform but benzophenone does not.

$$C_6H_5COOCH_3 + 3 NaOI \rightarrow C_6H_5 COONa + CHI_3 \downarrow + 2NaOH$$

Acetophenone Sodium Iodoform
benzoate (Yellow ppt)

C₆H₅COC₆H₅ No yellow ppt. of CHI₃



CBSE 2010

Sol.1 Ammoniacal silver nitrate solution is called tollens' reagent. It is used to test aldehydes. Both aliphatic and aromatic aldehydes reduce Tollens' reagent to shining silver mirror. It is also used to distinguish aldehydes from ketones.

$$2[Ag(NH_3)_2]$$
 + RCHO + 3OH $\xrightarrow{\text{Heat}}$ + RCOO + 4NH₃ + 2H₂O $\xrightarrow{\text{Silver mirror}}$ RCOO + 4NH₃ + 2H₂O $\xrightarrow{\text{Silver mirror}}$ + RCOO + 4NH₃ + 2H₂O

- Sol.2 2(2-Chloro phenyl) ethanone
- Hell Volhard Zelinsky reaction: Aliphatic carboxylic acids react with bromine or chlorine Sol.3 (i) (a) (but not iodine and fluorine) in the presence of small amount of red phosphorus to give exclusively mono α -halogenated acids. This is known as Hell-Volhard-Zelinsky (HVZ) reacation. The reaction is given by aliphatic acids having α -hydrogen./ Bromine reacts smoothyl.

 $CH_3CH_2COOH + Br_2 \xrightarrow{Red P} CH_3CHBrCOOH + HBr$

(b) Wolff - Kishner reduction reaction: The Carbonyl group of aldehydes and Ketones is reduced to CH, group on treatment with hydrazine followed by heating with potassium hydroxide in high boiling solvent wush as ethylene glycol.

$$\begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \text{C} = \text{O} \\ \begin{array}{c} \text{NH,NH}_{2} \\ -\text{H,O} \end{array} \\ \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \end{array} \\ \text{C} = \text{NNH}_{2} \\ \begin{array}{c} \text{KOH/ethylene glycol} \\ \text{heat} \\ \end{array} \\ \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{2} \\ \end{array} \\ \begin{array}{c} \text{CH}_{2} + \text{N}_{2} \\ \text{CH}_{3} \\ \end{array} \\ \begin{array}{c} \text{CH}_{2} + \text{N}_{2} \\ \text{Propane} \\ \end{array} \\ \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{2} \\ \end{array} \\ \begin{array}{c} \text{CH}_{3} \\ \text{CH}_{3} \\ \end{array} \\ \begin{array}{c} \text{CH}_{3} \\ \end{array}$$

(ii) (a)

(b) CH₃ CH₂ CH₂ CH₂ OH K₂Cr₂O₃/H₂SO₄ CH₃ CH₂ CH₂ COOH Butan-1-ol Butanoic acid

Sol.4 (a) (i) Clemmensen reaction: The carbonyl group of aldehyde & ketone is reduced to -CH, - group on treatment with Zinc amalgam & concentrated hydrochlric acid.

$$\begin{array}{c} CH_3-C-H \xrightarrow{Zn-Hg} CH_3-CH_2-H \\ \text{Ethanal} & \text{Ethane} \end{array}$$

(ii) Cannizzaro's reaction: Aldehydes which do not contain any α- hydrogen atom such as formaldehyde, benzaldehyde undergo self oxidations and reduction on treatment with concentrated alkali. A mixture of alcohol & a salt of carboxylic acid are formed.



(1)
$$H-C-H+H-C-H$$

NaOH

 $H-C-OH+H-C-O$

Na

 $H-C-OH+H-C-OH$

Na

 $H-C-OH+H$

Na

 $H-C-OH+H-C-OH$

Na

 $H-C-OH+H$

N

CBSE 2009

Sol.2 2,5-dimethyl, haxan-3-one

Sol.3 Ethyle-4-Chloro Benzene Carboxylate

Sol.4 C = 69.77%, H = 11.63%, 0 = 100 - (69.77 + 11.63) = 18.6%

Element	%-	Molar Mass	Moles	Simple ratio
С	69,77%	12	5.81	5
Н	11.63	100	11.63	10
0	18.6	16	1.16	1

Empirical formula of given compound = $C_5H_{10}O$ Emplirical formula mass = $5 \times 12 + 10 \times 1 + 16 \times 1 = 86$

$$n = \frac{86}{86} = 1$$

Molecular formula = C₅H₁₀O

Since, it does not give Tollen's test but gives positive iodoform test, hence it is a methyl ketone, ie, have -COCH₃ group. Since, on oxidation, it gives ethanoic acid and propanoic acid, it is pentan-2-one.

$$CH_3-C-CH_2-CH_2-CH_3-CH_3-CH_3-CH_2-COOH$$
[Pentan-2-one]



Test	C-C-OH	C-C-C-OH
	yellow ppt	X

(ii)

	СООН	ÇOOC,H,
NaHCO ₃	0	0
Test	CO, Turns lime water milky	X

Sol.6 (b) The relevant equations for all the reactions involved may be explained as follows:

$$\begin{array}{c} \text{CH}_{3}\text{CH}_{2}\text{CH}_{2} \text{. COCH}_{2}\text{CH}_{2}\text{CH}_{3} & \xrightarrow{\text{Butyl butanoate}} \\ \text{A(m. f. } C_{8}\text{H}_{16}\text{O}_{2}) & \xrightarrow{\text{Hydrolysis}} & \xrightarrow{\text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{OH}} + \xrightarrow{\text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{OH}} \\ \text{C(Butane-1-ol)} & \xrightarrow{\text{CrO}_{4}} & \xrightarrow{\text{Oxidation}} & \xrightarrow{\text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{COOH}} \\ \text{C(Butane-1-ol)} & \xrightarrow{\text{Dehydration}} & \xrightarrow{\text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{COOH}} \\ \text{C(Butane-1-ol)} & \xrightarrow{\text{Dehydration}} & \xrightarrow{\text{CH}_{4}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}} \\ \text{C(Butane-1-ol)} & \xrightarrow{\text{D(But-1-ene)}} & \xrightarrow{\text{D(But-1-ene)}} \end{array}$$

Therefore, (A) Butyl butanoate, (B) Butanoic acid, (C) Butan-1-ol, (D) But-1-ene

Sol.7
$$\Lambda = C-C-CONH_2$$

$$B = C-C-NH$$
,

$$C = C-C-OH$$