Organic Chemistry Important Questions // Lecture 10 //Pattern Classes

Question 1 : Give simple chemical tests to distinguish between the following pairs of compounds.

(i) Propanal and Propanone
(ii) Acetophenone and Benzophenone
(iii) Phenol and Benzoic acid
(iv) Benzoic acid and Ethyl benzoate
(v) Pentan-2-one and Pentan-3-one
(vi) Benzaldehyde and Acetophenone
(vii) Ethanal and Propanal

Ans. :

(i) Propanal and propanone can be distinguished by the following tests.

(a) Tollen's test

Because propanal is an aldehyde, it reduces Tollen's reagent. However, because propanone is a ketone, Tollen's reagent is not reduced.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2[\,\underset{\text{Tollen's reagent}}{Ag(NH_3)_2}\,]^+ + 3OH^- \longrightarrow \underset{\text{Propanoate ion}}{CH_3CH_2COO^-} + \underset{\text{Silver mirror}}{Ag\downarrow} + 4NH_3 + 2H_2O$$

(b) Fehling's test

Ketones do not respond to Fehling's test, while aldehydes do.

Propanone is a ketone, therefore it does not reduce Fehling's solution to a red-brown Cu_2O precipitate, but Propanal is an aldehyde, so it does.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2Cu^{2+} + 5OH^- \longrightarrow \underset{\text{Propanoate ion}}{CH_3CH_2COO^-} + \underset{\substack{\text{Cuprous oxide}\\ \text{(Red - brown ppt)}}}{Cu_2O\downarrow} + 3H_2O$$

(ii) Acetophenone and Benzophenone can be distinguished using the iodoform test.

Test for iodoform:

When methyl ketones are oxidised by sodium hypoiodite, a yellow ppt. of iodoform is formed.

Because acetophenone is a methyl ketone, it responds to this test, but not benzophenone.

$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + \underset{\substack{\text{Sodium}\\ \text{hypoiodite}}}{3\,NaOI} \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + \underset{\substack{\text{Iodoform}\\ \text{(yellow ppt)}}}{CHI_3} + 2NaOH$$

$$\underset{\text{Benzophenone}}{C_6H_5COCH_3} + NaOI \longrightarrow \text{No yellow ppt of } CHI_3$$

(iii) Phenol and benzoic acid can be distinguished by ferric chloride test.

Test for ferric chloride:

Phenol interacts with $FeCl_3$ to generate an iron-phenol complex, which results in a violet colour.

$$\underset{\text{Phenol}}{6C_6H_5OH} + FeCl_3 \longrightarrow \underset{\substack{\text{Iron-phenol complex}\\ \text{(violet coloration)}}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3Cl^-$$

A buff coloured ppt of ferric benzoate is produced when benzoic acid reacts with neutral $FeCl_3$.

$$\underset{\text{Benzoic acid}}{3C_6H_5OH} + FeCl_3 \longrightarrow \underset{\substack{\text{Ferric benzoate}\\ \text{(Buff coloured ppt)}}}{(C_6H_5COO)_3Fe} + 3HCl$$

(iv) Benzoic acid and Ethyl benzoate can be distinguished by sodium bicarbonate test.

Test for sodium bicarbonate:

When acids react with $NaHCO_3$ and CO_2 gas is formed, a brisk effervescence is produced.

This test responds to benzoic acid since it is an acid, but not to ethylbenzoate.

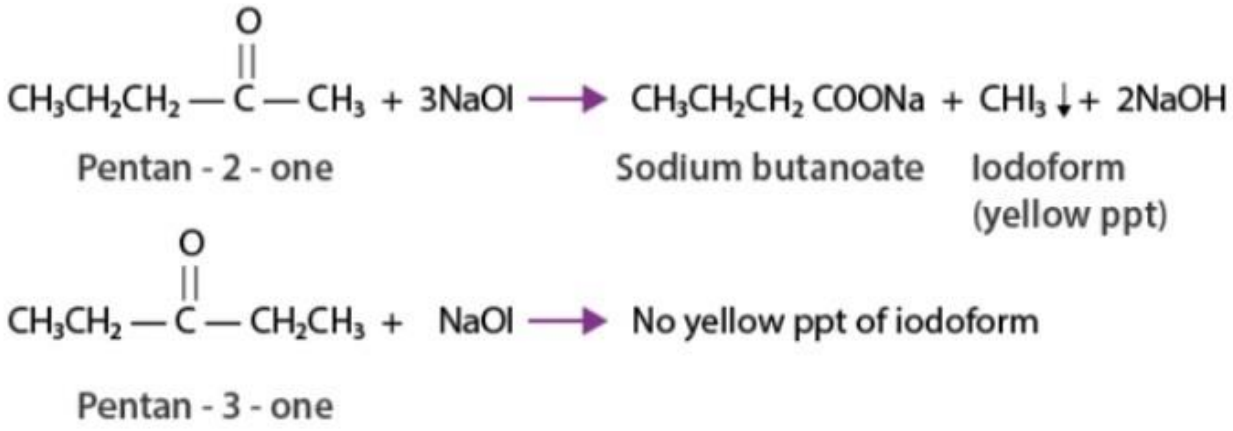
$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + NaHCO_3 \longrightarrow \underset{\text{Sodium benzoate}}{C_6H_5COONa} + CO_2\uparrow + H_2O$$

$$C_6H_5COOC_2H_5 + NaHCO_3 \longrightarrow \text{No effervescence due to evolution of } CO_2 \text{ gas}$$

(v) Pentan-2-one and pentan-3-one can be distinguished by iodoform test.

Iodoform test:

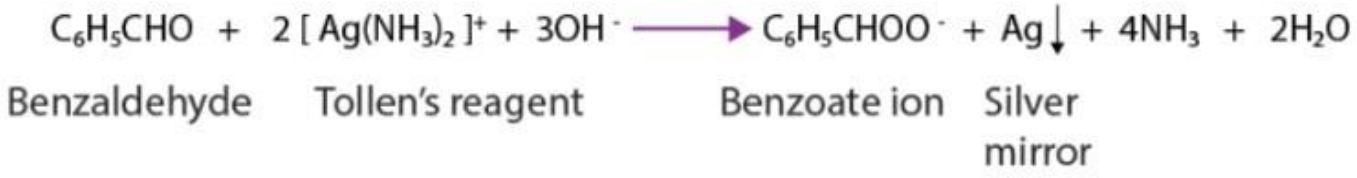
Because pentan-2-one is a methyl ketone, it responds to this test. Pentan-3-one, however, does not respond to this test since it is not a methyl ketone.



(vi) Benzaldehyde and acetophenone can be distinguished by the following tests.

(a) Tollen's Test

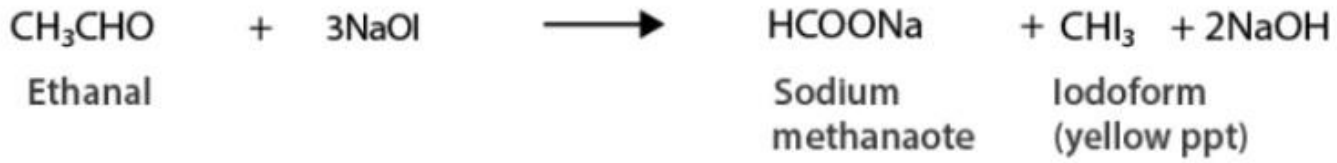
Tollen's test has an effect on aldehydes. Red-brown precipitate of Cu_2O is produced by Benzaldehyde reducing Tollen's reagent, but acetophenone being a ketone does not.



(vii) Ethanal and propanal can be distinguished by iodoform test.

Iodoform test

The iodoform test holds for aldehydes and ketones that have at least one methyl group attached to the carbonyl carbon atom. This test also holds for ethanal, which has one methyl group attached to the carbonyl carbon atom. Propanal, on the other hand, lacks a methyl group attached to the carbonyl carbon atom and hence does not respond to this test.



Question 2 :
Give one chemical test to distinguish between the following pairs of compounds.
(i) Methylamine and dimethylamine
(ii) Secondary and tertiary amines
(iii) Ethylamine and aniline
(iv) Aniline and benzylamine
(v) Aniline and N-methylaniline.

(i) Methylamine and dimethylamine can be distinguished by the carbylamine test.

Carbylamine test: Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form foul-smelling isocyanides or carbylamines. Methylamine (being an aliphatic primary amine) gives a positive carbylamine test, but dimethylamine does not.

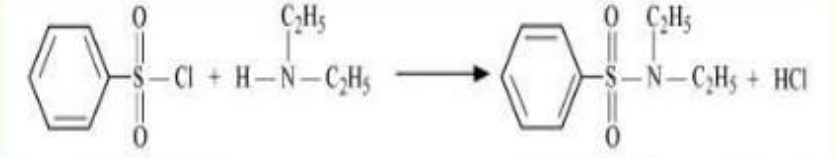
$$CH_3-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} CH_3-NC + 3KCl + 3H_2O$$

Methylamine (1^0) Methylisocyanide (foul smell)

$$(CH_3)_2NH + CHCl_3 + 3KOH \xrightarrow{\Delta} \text{No reaction}$$

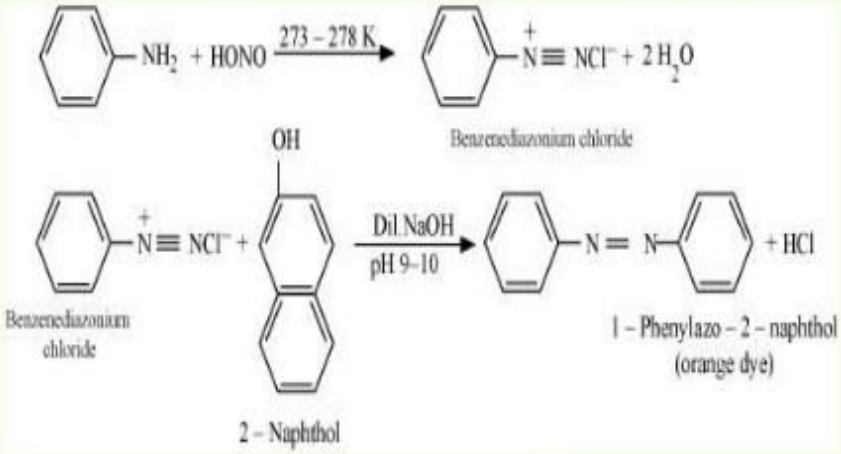
(ii) Secondary and tertiary amines can be distinguished by allowing them to react with Hinsberg's reagent (benzenesulphonyl chloride, $C_6H_5SO_2Cl$).

Secondary amines react with Hinsberg's reagent to form a product that is insoluble in an alkali. For example, N, N−diethylamine reacts with Hinsberg's reagent to form N, N−diethylbenzenesulphonamide, which is insoluble in an alkali. Tertiary amines, however, do not react with Hinsberg's reagent.



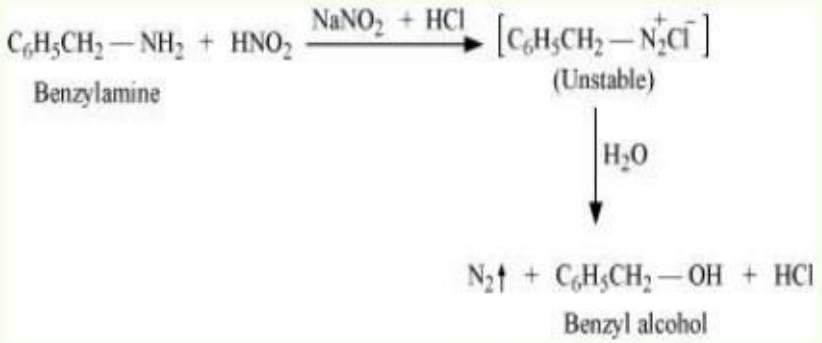
Benzenesulphonyl chloride N, N − Diethylbenzenesulphonamide

(iii) Ethylamine and aniline can be distinguished using the azo-dye test. A dye is obtained when aromatic amines react with HNO_2 ($NaNO_2$ + dil.HCl) at 0-5°C, followed by a reaction with the alkaline solution of 2-naphthol. The dye is usually yellow, red, or orange in colour. Aliphatic amines give a brisk effervescence due (to the evolution of N_2 gas) under similar conditions.

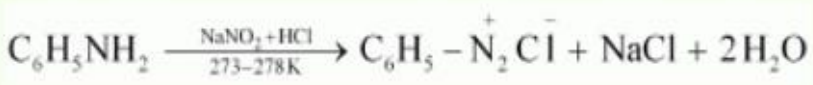


$$CH_3CH_2 - NH_2 + HONO \xrightarrow{0\text{-}5^\circ C} C_2H_5OH + N_2\uparrow + H_2O$$

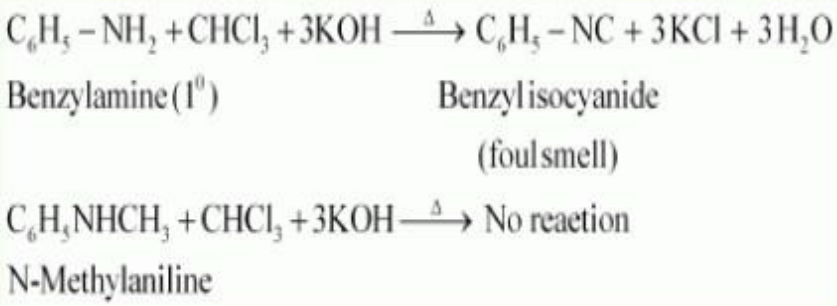
(iv) Aniline and benzylamine can be distinguished by their reactions with the help of nitrous acid, which is prepared in situ from a mineral acid and sodium nitrite. Benzylamine reacts with nitrous acid to form unstable diazonium salt, which in turn gives alcohol with the evolution of nitrogen gas.



On the other hand, aniline reacts with HNO_2 at a low temperature to form stable diazonium salt. Thus, nitrogen gas is not evolved.



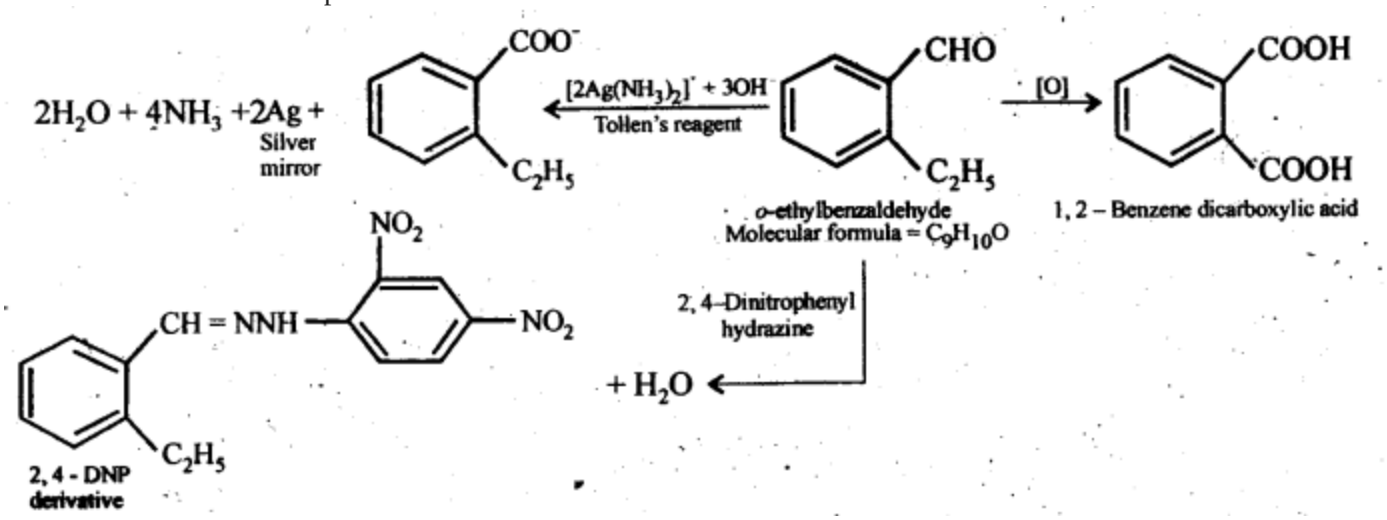
(v) Aniline and N-methylaniline can be distinguished using the Carbylamine test. Primary amines, on heating with chloroform and ethanolic potassium hydroxide, form foul-smelling isocyanides or carbylamines. Aniline, being an aromatic primary amine, gives positive carbylamine test. However, N-methylaniline, being a secondary amine does not.



Question 3.: An organic compound with the molecular formula $C_9H_{10}O$ forms 2,4-DNP derivative, reduces Tollen's reagent, and undergoes Cannizzaro reaction. On vigorous oxidation, it gives 1,2-benzenedicarboxylic acid. Identify the compound.

Ans: Since the given compound with molecular formula $C_9H_{10}O$ forms a 2,4-DNP derivative and reduces Tollen's reagent, it must be an aldehyde. Since it undergoes Cannizzaro reaction, therefore, CHO group is directly attached to die benzene ring.

Since on vigorous oxidation, it gives 1, 2-benzene dicarboxylic acid, therefore, it must be an ortho- substituted benzaldehyde. The only o-substituted aromatic aldehyde having molecular formula $C_9H_{10}O$ is o-ethyl benzaldehyde. Ail the reactions can now be explained on the basis of this structure.



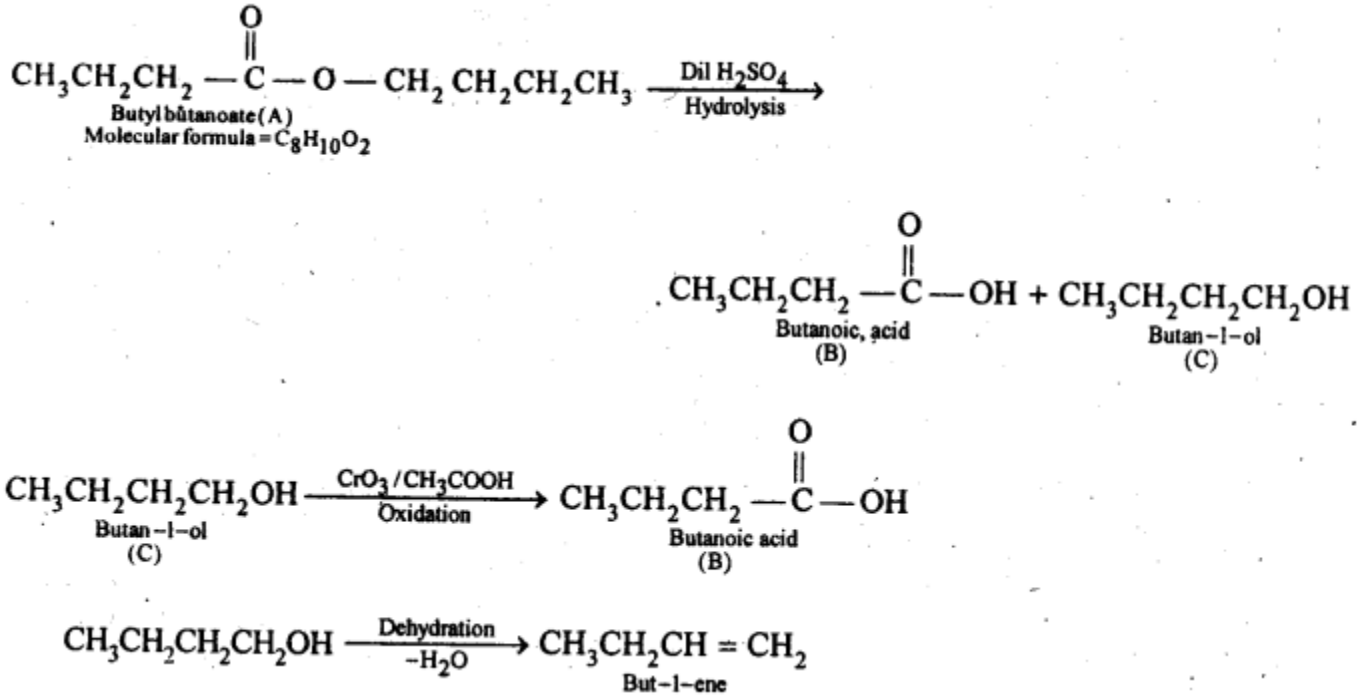
Question 4 . An organic compound (A) (molecular formula $C_8H_{16}O_2$) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B} and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (Q on dehydration gives but-l-ene. Write equations for the reactions involved.

Ans: Since an ester A with molecular formula $C_8H_{16}O_2$ upon hydrolysis gives carboxylic acid B and the alcohol C and oxidation of C with chromic acid produces the acid B, therefore, both the carboxylic acid B and alcohol C must contain the same number of carbon atoms.

Further, since ester A contains eight carbon atoms, therefore, both the carboxylic acid B and the alcohol C must contain four carbon atoms each.

Since the alcohol C on dehydration gives but-l-ene, therefore, C must be a straight chain alcohol, i.e., butan-l-ol.

If C is butan-l-ol, then the acid B must be butanoic acid and the ester A must be butyl butanoate.The chemical equations are as follows:



Question 5. 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 Tottens' 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 compound.

Ans:

$C = 69{\cdot}77\%, H = 11{\cdot}67\%$

$\therefore \quad O = 100 - (69{\cdot}77 + 11{\cdot}63)\% = 18{\cdot}6\%$

$$\therefore \quad C : H : O = \frac{69{\cdot}77}{12} : \frac{11{\cdot}63}{1} : \frac{18{\cdot}6}{16} = 5{\cdot}88 : 11{\cdot}63 : 1{\cdot}16 :: 5 : 10 : 1$$

The empirical formula of the given compound = $C_5H_{10}O$

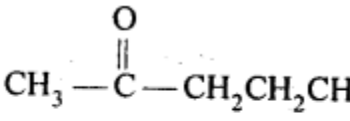
Empirical formula mass = $5 \times 12 + 10 \times 1 + 1 \times 16 = 86$

Molar mass = 86 (given)

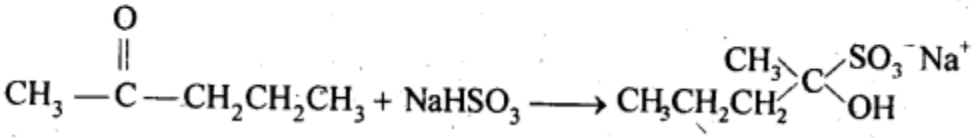
$\therefore$ Molecular formula = $C_5H_{10}O$

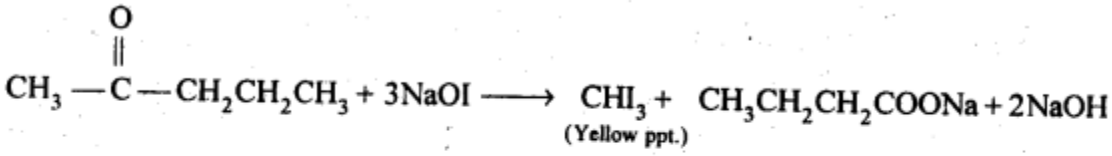
Since the compound form sodium hydrogen sulphite addition product, therefore, it must be either an – aldehyde or methyl/ cyclic ketone. Since the compound does not reduce Tollens' reagent therefore, it cannot be an aldehyde. Since the compound gives positive iodoform test, therefore, the given compound is a methyl ketone. Since the given compound on vigorous oxidation gives a mixture ofethanoic acid and propanoic acid,

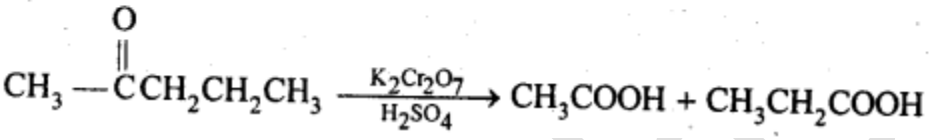
therefore, the methyl ketone is pentan-2-one, i.e.,



. The reactions involved are:







Question 6: An organic compound (A) (molecular formula C8H16O2) was hydrolysed with dilute sulphuric acid to give a carboxylic acid (B) and an alcohol (C). Oxidation of (C) with chromic acid produced (B). (C) on dehydration gives but-1-ene. Write equations for the reactions involved.

Ans. : According to the question, A is an organic compound having molecular formula $C_8H_{16}O_2$. This gives a carboxylic acid (B) and an alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester.

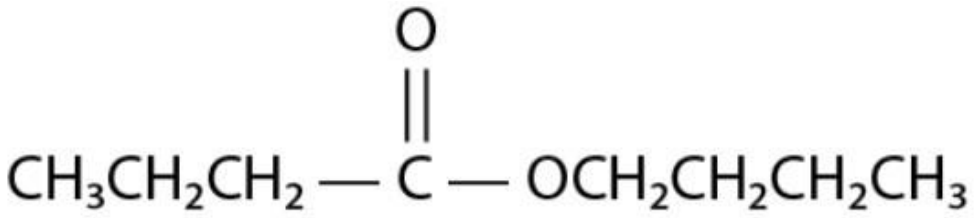
Further, oxidation of alcohol (C) with chromic acid gives acid B. Thus, B and C must contain an equal number of carbon atoms.

A total of 8 carbon atoms are present in compound A, each of B and C contain 4 carbon atoms.

Again, alcohol C gives but-1-ene on dehydration. Therefore, C is a straight-chain and hence, it is butan-1-ol.

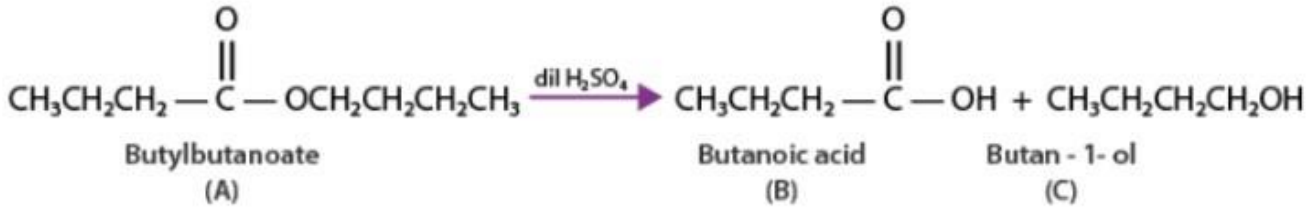
On oxidation, Butan-1-ol gives butanoic acid. Hence, acid B is butanoic acid.

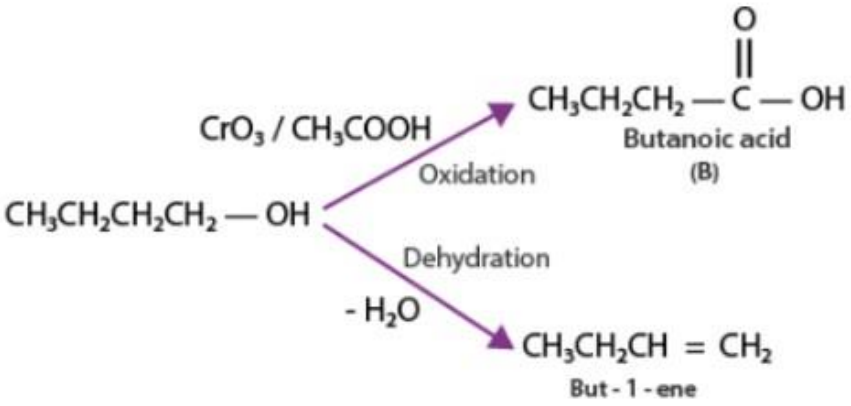
Hence, the ester with molecular formula $C_8H_{16}O_2$ is butylbutanoate.



Butylbutanoate

All the mentioned reactions can be illustrated by the following equations.





Question 7 : A compound (X) having molecular formula $C_4H_8O_2$ is hydrolysed by water in presence of an acid to give a carboxylic acid (Y) and an alcohol (Z). (Z) on oxidation with chromic acid gives (Y). (X), (Y) and (Z) are:

Solution

$$\underset{\text{Ethyl ethanoate (x)}}{CH_3COOC_2H_5} \xrightarrow{H_2O/H^+} \underset{(Y)}{CH_3COOH} + \underset{(Z)}{C_2H_5OH} \xrightarrow{CrO_3} \underset{(Y)}{CH_3COOH}$$

Question

A neutral organic compound X of molecular formula C_2H_6O on oxidation with acidified potassium dichromate gives an acidic compound Y. Compound X reacts with Y on warming in the presence of conc. H_2SO_4 to give a sweet-smelling substance Z. What are X, Y and Z?

Solution

The neutral organic compound 'X' having the molecular formula C_2H_5OH is ethanol (alcohol with functional group -OH).

When ethanol undergoes oxidation reaction (controlled combustion) with acidified potassium dichromate, it gets oxidised to form an acidic compound, Y, called ethanoic acid ($CH_3 - COOH$).

$$CH_3 - CH_2 - OH + 2[O] \xrightarrow{KMnO_4} CH_3 - COOH + H_2O.$$

Ethanol reacts with ethanoic acid in the presence of concentrated sulphuric acid to release a sweet smelling ester, Z, called ethyl ethanoate (CH3 – COO – CH2 – CH3).

$$CH_3 - COOH + CH_3 - CH_2OH \xrightarrow{Conc.H_2SO_4} CH_3 - COO - C_2H_5 + H_2O$$

Question

An organic compound [A] having molecular formula C_2H_7N on treatment with nitrous acid gives a compound [B] having molecular formula C_2H_6O. [B] on treatment with an organic compound [C] gives a carboxylic acid [D] and a sweet smelling compound [E] . Oxidation of [B] with acidified potassium dichromate also gives [D]
Identify [A], [B], [C], [D] and [E]

Solution

A is $C_2H_5NH_2$ ethylamine
B is C_2H_5OH ethanol
C is $CH_3CO-O-CO-CH_3$ acetic anhydride
D is CH_3COOH Acetic acid
E is $CH_3COOC_2H_5$ ethyl acetate

Ethylamine on treatment with nitrous acid gives ethanol.

$$C_2H_5NH_2 \xrightarrow{HNO_2} C_2H_5OH$$

Ethanol on treatment with acetic anhydride gives acetic acid and sweet-smelling ethyl acetate.

$$C_2H_5OH + CH_3CO-O-CO-CH_3 \rightarrow CH_3COOH + CH_3COOC_2H_5$$

Oxidation of ethanol with acidified potassium dichromate also gives acetic acid.

$$C_2H_5OH \xrightarrow{K_2Cr_2O_7} CH_3COOH$$

Question

An organic compound (A) with molecular formula C_8H_8O forms an orange-red precipitate with 2,4 DNP and gives a yellow precipitate of compound (B) on treatment with iodine and sodium hydroxide solution. Compound (A) does not give Tollen's or Fehling test but on drastic oxidation with potassium permanganate, it gives (C) which on reaction with thionyl chloride gives a compound (D) having formula C_7H_5OCl. (D) on reaction with compound (E) having general formula R_2Cd gives back (A)/ Identify (A), (B), (C), (D) and (E). Also, give chemical equations for the reaction involved.

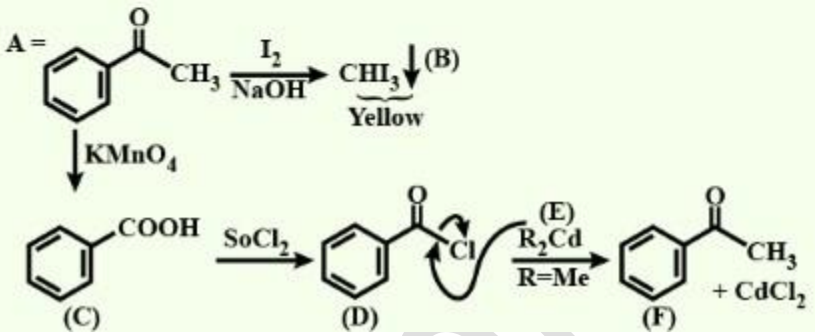
Compound A is acetophenone.

It on reaction with $I_2 + NaOH$ undergoes haloform reaction to form yellow coloured iodoform as a product.

When compound A reacts with $KMnO_4$ it undergoes oxidation to form benzoic acid (C).

When benzoic acid reacts with $SoCl_2$ it forms benzoyl chloride (D) as a product.

When Benzoyl chloride reacts with (R_2Cd) it gives corresponding ketone (acetophenone) (A) as a product.



Question

An organic compound A of molecular formula C_2H_6O is a constituent of wine and beer. This compound on heating with alkaline potassium permanganate forms another organic compound B which turns blue litmus to red. Identify the compounds A and B.

Solution

An organic compound A of molecular formula C_2H_6O is a constituent of wine and beer, so it must be an alcohol containing molecule, i.e. ethanol (CH_3CH_2OH).

When ethanol is treated with alkaline potassium permanganate, it oxidizes ethanol and forms compound "B" which is ethanoic acid.

$$C_2H_5OH + KMnO_4 \xrightarrow{\text{alkaline}} CH_3COOH + H_2O$$

Due to the formation of ethanoic acid, blue litmus turns red.