CID PROBLEMS

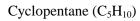
Q1 A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

Answer hydrocarbon with the molecular formula, C_5H_{10} belongs to the group with a general molecular formula C_nH_{2n} . Therefore, it may either be an alkene or a cycloalkane.

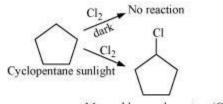
Since hydrocarbon does not react with chlorine in the dark, it cannot be an alkene. Thus, it should be a cycloalkane.

Further, the hydrocarbon gives a single monochloro compound, C_5H_9Cl by reacting with chlorine in bright sunlight. Since a single monochloro compound is formed, the hydrocarbon must contain H–atoms that are all equivalent. Also, as all H–atoms of a cycloalkane are equivalent, the hydrocarbon must be a cycloalkane. Hence, the said compound is cyclopentane.





The reactions involved in the question are:



Mono chlorocyclopentane(C5H10)

Primary alkyl halide C₄H₉Br (a) reacted with alcoholic KOH to give compound (b).Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C₈H₁₈ which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

<u>Answer</u> There are two primary alkyl halides having the formula, C_4H_9Br . They are n – bulyl bromide and isobutyl bromide.

$$CH_3 - CH_2 - CH_2 - CH_2 - Br$$

 $n - Butyl bromide$
 $CH_2 - Br$
 $CH_3 - CH - CH_2 - Br$
 CH_3
 CH_3

Therefore, compound (a) is either n-butyl bromide or isobutyl bromide.

Now, compound (a) reacts with Na metal to give compound (b) of molecular formula, C_8H_{18} , which is different from the compound formed when *n*-butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.

 $2CH_{3}CH_{2}CH_{2}CH_{2}Br \xrightarrow{2Na/dry \text{ ether}} CH_{3}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{2}CH_{3} + 2NaBr$ n - Butyl bromide n - Octane

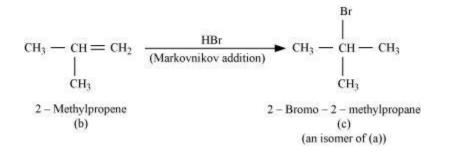
CH ₃ CHCH ₂ Br 2Na/dry ether (Wurtz reaction)	сн ₃ сн сн ₂ с	$CH_2 CH CH_3 + 2NaBr$
CH3	ĊH3	ĊH ₃
Isobutyl bromide (a)	2, 5 – Dimethylhexane (d)	

Thus, compound (d) is 2, 5-dimethylhexane.

It is given that compound (a) reacts with alcoholic KOH to give compound (b). Hence, compound (b) is 2–methylpropene.



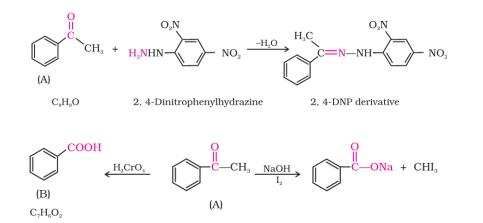
Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a). Hence, compound (c) is 2–bromo–2–methylpropane.



Q3 An organic compound (A) with molecular formula C8H₈O forms an orange-red precipitate with 2,4-DNP reagent and gives yellow precipitate on heating with iodine in the presence of sodium hydroxide. It neither reduces Tollens' or Fehlings' reagent, nor does it decolourise bromine water or Baeyer's reagent. On drastic oxidation with chromic acid, it gives a carboxylic acid (B) having molecular formula C7H6O₂ Identify the compounds (A) and (B) and explain thereactions involved. <u>Answer</u>

(A) forms 2,4-DNP derivative. Therefore, it is an aldehyde or a ketone. Since it does not reduce Tollens' or Fehling reagent, (A) must be a ketone.
(A) responds to iodoform test. Therefore, it should be a methyl ketone. The molecular formula of (A) indicates high degree of unsaturation, yet it does not decolourise bromine water or Baeyer's reagent. This indicates the presence of unsaturation due to an aromatic ring.
Compound (B), being an oxidation product of a ketone should be a carboxylic acid. The molecular formula of (B) indicates that it should be benzoic acid and compound (A) should, therefore, be a monosubstituted aromatic methyl ketone. The molecular formula of (A)

indicates that it should be phenyl methyl ketone (acetophenone). Reactions are as follows:



Q4 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, 2benzenedicarboxylic acid. Identify the compound.

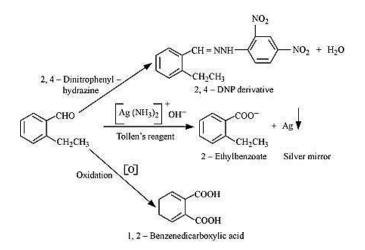
Answer

It is given that the compound (with molecular formula $C_9H_{10}O$) forms 2, 4-DNP derivative and reduces Tollen's reagent. Therefore, the given compound must be an aldehyde.

Again, the compound undergoes cannizzaro reaction and on oxidation gives 1, 2-benzenedicarboxylic acid. Therefore, the –CHO group is directly attached to a benzene ring and this benzaldehyde is ortho-substituted. Hence, the compound is 2-ethylbenzaldehyde.



The given reactions can be explained by the following equations.



Q5An 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). (C) on dehydration gives but-1-ene.Write equations for the reactions involved.

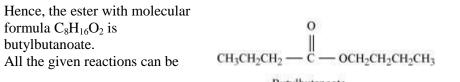
Answer

An organic compound A with molecular formula $C_8H_{16}O_2$ gives a carboxylic acid (B) and an alcohol (C) on hydrolysis with dilute sulphuric acid. Thus, compound A must be an ester. Further, alcohol C gives acid B on oxidation with chromic acid. Thus, B and C must contain equal number of carbon atoms.

Since compound A contains a total of 8 carbon atoms, each of B and C contain 4 carbon atoms.

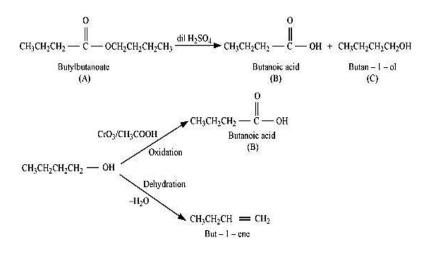
Again, on dehydration, alcohol C gives but-1-ene. Therefore, C is of straight chain and hence, it is butan-1-ol.

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



Butylbutanoate

explained by the following equations.



Q6 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 Tollens' 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.

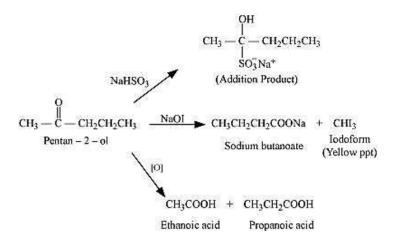
Molecular mass of the compound = 86

 $C_nH_{2n}O$ 12n+2n+16=86 ,i.e. n= 5 Therefore, the molecular formula of the compound is given by $C_5H_{10}O$.

Since the given compound does not reduce Tollen's reagent, it is not an aldehyde. Again, the compound forms sodium hydrogen sulphate addition products and gives a positive iodoform test. Since the compound is not an aldehyde, it must be a methyl ketone.

The given compound also gives a mixture of ethanoic acid and propanoic acid. Hence, the given compound is pentan-2-ol.

Pentan – 2 – ol The given reactions can be explained by the following equations:



Q7 An aromatic compound 'A' on treatment with aqueous ammonia and heating

forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C'

of molecular formula C_6H_7N . Write the structures and IUPAC names of compounds A, B and C.

Answer

It is given that compound 'C' having the molecular formula, C_6H_7N is formed by heating compound 'B' with Br_2 and KOH. This is a Hoffmann bromamide degradation reaction. Therefore, compound 'B' is an amide and compound 'C' is an amine. The only amine having the molecular formula, C_6H_7N is aniline, ($C_6H_5NH_2$).



Therefore, compound 'B' (from which 'C' is formed) must be benzamide, $(C_6H_5CONH_2)$.



Further, benzamide is formed by heating compound 'A' with aqueous ammonia. Therefore, compound 'A' must be benzoic acid.



The given reactions can be explained with the help of the following equations:

