4. Examine the infrared spectrum of the compound to determine the nature of functional groups and to deduce whether the compound is saturated, unsaturated, aromatic or a composite of these. NMR and UV spectra may also be used for their confirmation.

5. The chemical shift will reveal the chemical environment of the protons present and the spin multiplicity [coupling constant, J (Hz)], the relationship of neighbouring protons. From the integration of various signals in the NMR spectrum in conjunction with the molecular formula, the number of each type of protons can easily be determined. Expand the part structures obtained from infrared.

6. Examine the ultraviolet spectrum either qualitatively (λ_{max} position and application of Woodward-Fieser or Scott rules where appropriate) or quantitatively (λ_{max} and extinction coefficient) to confirm the validity of deductions made in (4) and (5). In some problems, it will play a decisive role in distinguishing between isomeric structures.

7. The mass spectrum fragmentation pattern is very useful when the type of the compound is known. Attempt to determine the mode(s) of fragmentation using known processes. Recognition of fragment ions will confirm earlier predictions.

8. Attempt to assemble all the extracted information into a rational structure.

7.3 COMPOSITE PROBLEMS WITH SOLUTIONS (SET I)

Problem 1

An organic compound A (Mol. formula $C_9H_{10}O_2$) exhibits the following spectral data:
IR: 1745 cm^{-1}(s), 1225 cm^{-1} (br, s), 749(s); 697 cm^{-1}(s);
UV: λ_{max} at 268, 264, 262, 257 nm.
^{1}HNMR: δ 1.96 (3H, s); 5.00 (2H, s); 7.22 (5 H, s)
Deduce the structure of the compound:

Solution

(1) The absorption at 1745 cm^{-1} in the IR spectrum suggests the presence of an ester group.
(2) The broad band at 1225 cm^{-1} is due to C—O—C stretching, characteristic of an acetate.
(3) Absorptions at 749 cm^{-1} and 697 cm^{-1} indicate monosubstituted benzene ring.
(4) λ_{max} values clearly exhibit that the carbonyl group is not conjugated.
(5) Thus, the compound has the partial structure

$$\left. \begin{array}{c} C_6H_5- \\ O \\ \parallel \\ CH_3C-O- \end{array} \right\} \equiv C_8H_8O_2$$
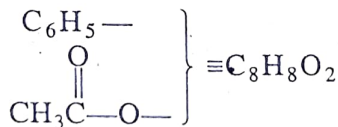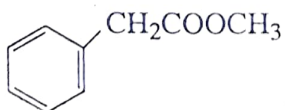
Molecular formula of the compound = $C_9H_{10}O_2$
Molecular formula of the partial structure = $C_8H_8O_2$
The remaining group to be accounted for = CH_2

A two-proton singlet at δ 5.0 suggests that the remaining CH_2 group must be present in between the carbonyl group of the ester and the phenyl ring. Hence the structure of the compound A will be:

The chemical shifts observed in the ^{1}HNMR structure of the comound A are consistent with the above formula.

Problem 2

An organic compound A (molecular formula $C_6H_{12}O_2$) showed the following IR and ^{1}HNMR spectral data. Assign the structure to the compound.

1 R (neat) v_{max} :   2950, 2850, 1730, 1480, 1460, 1400 cm^{-1}
^{1}HNMR : δ :   1.20 (9H, s)
                 3.70 (3H, s)

Solution

(1) Molecular formula of the compound is $C_6H_{12}O_2$

(2) Double bond equivalent will be given by $\smile$

$$6 + 1 - \frac{12}{2} = 1$$

   Thus, the molecule contains either $C=C$ or $C=O$ or one ring.

(3) The absorptions at 2950 and 2850 cm^{-1} indicate the presence of methyl group and the bond at 1730 cm^{-1} exhibits the presence of an ester group.

(4) A singlet at δ 1.20, equivalent to 9H, indicates a tert. butyl group.

(5) A singlet at δ 3.70, equivalent to 3 H, indicates ester methyl group. Hence the possible structure of the compound A is
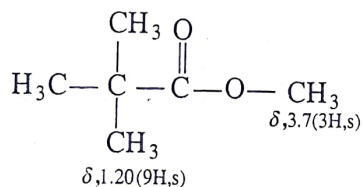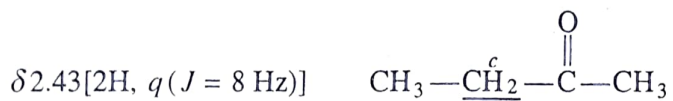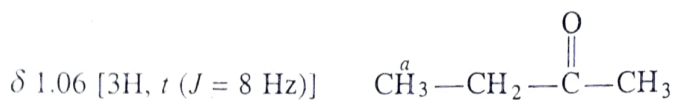

Problem 3

A colourless liquid A (molecular formula C_4H_8O) exhibits the following spectral data:

1R : $v_{max}^{cm^{-1}}$ 1715 cm^{-1} (s)
^{1}HNMR : δ 1.06 [3H, $t(J = 8Hz)$]; 2.14 (3H, s);
2.43 [2H, q $(J = 8$ Hz$)$]

Deduce the structure of the compound A and predict the principal ions in its mass spectrum.

Solution

(1) The infrared absorption at 1715 cm^{-1} indicates that the compound contains a carbonyl group and the molecular formula (C_4H_8O) suggests that the compound is either an aliphatic aldehyde or ketone.

(2) The ^{1}HNMR spectrum completely eliminates the aldehyde group (no resonance near δ 9.5) and confirms the structure as butan -2-one. The integrations, from high to low field, are in the ratio 3: 3: 2 and, therefore, the resonance signals are assigned as follows:

$$\delta\ 1.06\ [3H,\ t\ (J = 8\ Hz)]$$

$$\overset{a}{CH_3}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

$$\delta\ 2.14\ (3H,\ s)$$

$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{b}{CH_3}$$

$$\delta\ 2.43\ [2H,\ q\ (J = 8\ Hz)]$$

$$CH_3-\overset{c}{CH_2}-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

The $\overset{a}{CH_3}$ and $\overset{c}{CH_2}$ groups appear respectively as the expected triplet and quartet. The $\overset{b}{CH_3}$ and methylene protons are deshielded and consequently resonate at lower value of the applied field (higher δ value).

The principal ions formed during fragmentation of butan-2-one are the following:

(i) $CH_3-C\equiv\overset{+}{O}$ (m/z 43) and (ii) $CH_3CH_2-C\equiv\overset{+}{O}$ (m/z 57), the former appearing in greater abundance.

Problem 4

A colourless liquid A (molecular formula $C_9H_{10}O_2$) gives the following spectral data:

IR : $v_{max}^{(cm^{-1})}$ 1720(s), 1602(m), 1581 (m), 1270(s), 1105 (s)

^{1}HNMR (neat): δ 1.29 [3H, $t(J = 8$ Hz)]; 4.35 [2H, q $(J = 8$ Hz)];

7.40 (3H, m); 8.81 (2H, m).

Determine the structure of the compound A.

Solution

(1) The carbonyl absorption at 1720 cm^{-1} in conjunction with the bands at 1270 and 1105 cm^{-1} are compatible with an aromatic ester, the bands at 1602 and 1581 cm^{-1} confirming the presence of an aromatic ring.

(2) The triplet at δ 1.29 (3H, $J = 8$ Hz) and the quartet at δ 4.35 (2H, $J = 8$ Hz) indicate the presence of —O—CH$_2$—CH$_3$ moiety and the compound is, therefore, ethyl benzoate.
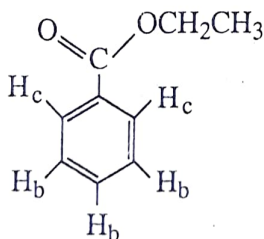
(3) Two separated downfield multiplets centred at δ 7.40 and δ 8.81, exhibit respectively the aromatic protons *b* and *c*. The ortho protons *c* are deshielded by the diamagnetic anisotropic effect of C=O group. The upfield multiplet indicates the three *b* protons.

Problem 5

A hydrocarbon A, containing 85.7% carbon and 14.3% hydrogen, gave the following spectral data:

UV: Transparent above 210 nm

IR: $v_{max}^{(cm^{-1})}$ 3022(m), 1656(m), 965(s);

^{1}HNMR : δ 1.60(d) 5.55 ($\underline{q}$)

Integral ratio 3 : 1

Deduce the structure of the hydrocarbon.

Solution

(1) From the percentage of carbon (85.71%) and hydrogen (14.3%), the empirical formula of the compound is found to be C_4H_8.

(2) Double bond equivalent (DBE) is given by.

$$4 + 1 - \frac{8}{2} = 1$$

Thus, the compound contains either one double bond or one ring.

(3) Since the ultraviolet spectrum is transparent above 210 nm, it indicates the absence of conjugation and carbonyl group.

(4) The C—H stretching absorption at 3022 cm^{-1} in the infrared spectrum is due to the presence of aromatic ring or =C—H unit in the compound. Since the carbonyl group is absent, the band at 1656 cm^{-1} may be due to C=C stretching. Thus, the hydrocarbon must be unsaturated.

(5) Two signals appear in the ^{1}HNMR spectrum:

(i) The doublet at δ 1.60 is due to the methyl group attached to –CH=.

(ii) One proton quartet appearing downfield at δ 5.55. This may be due to deshielding by the presence of double bond. Thus, the partial structure of the compound may be written as

$$CH_3—CH=$$
(Molecular formula = C_2H_4)
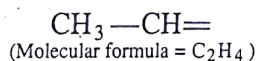
The molecular formula of the compound is exactly double (C_4H_8) to that of the partial structure, hence, the probable structure of the compound is

$$H_3C—CH=CH—CH_3$$
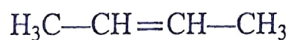
(6) An intense band at 965 cm^{-1} in the infrared spectrum is characteristic of an alkene in which the hydrogen atoms are trans. Thus, the exact structure of the compound is

$$\overset{H_3C}{\underset{H}{}}C=C\overset{H}{\underset{CH_3}{}}$$

trans-2-Butene
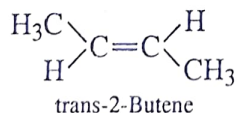
Problem 6

An organic compound containing carbon, hydrogen and oxygen only showed abundant mass spectral peaks at M$^+$ (m/z 136), base peak (m/z 91) and fragment ion (m/z 45). Other spectral data is given below:

UV : λ_{max} 229 nm and 257 nm

IR : $\nu_{max}^{(cm^{-1})}$ 1710 cm^{-1}

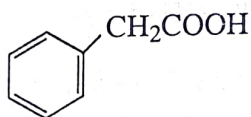^{1}HNMR : δ 7.2 (5H, s) and 3.5 (2H, s).

Deduce the structure of the compound and predict the principal ions in its mass spectrum
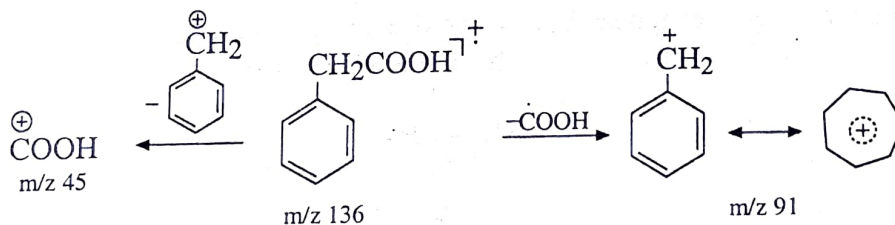
Solution
1. The molecular ion peak at m/z 136 indicates that the molecular weight of the compound is 136.
2. Base peak at m/z 91 indicates the formation of benzyl cation or tropylium ion.
3. The fragment ion at m/z 45 is due to the presence of COOH group.
4. Absorptions at λ_{max} 229 nm (n→π^*) and 257 nm (π→π^*) suggests the presence of keto group and aryl moiety.
5. A singlet at δ 7.2, equivalent to 5H, indicates a phenyl ring.
6. A singlet at δ 3.5, equivalent to 2H, suggests a methylene group in between the phenyl group and – COOH group.

Thus, the possible structure of the compound is

Mass spectral fragmentation pattern of phenylacetic acid is given below.

Problem 7
An organic compound A gave the following spectral data:

Mass (m/z) : 73, 91, 149, 164;

IR $\nu_{max}^{(cm-1)}$: 1730

^{1}HNMR, δ 2.0 (3H, s); 2.93 [2H, t(J = 7Hz)];
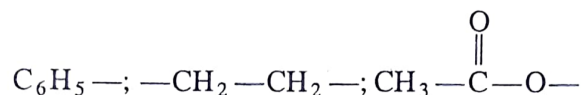4.30 [2H, t(J = 7Hz)]; 7.3 (5H, s).

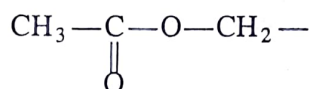Deduce the structure of the compound.

Solution

1. The heaviest peak in the mass spectrum may be assumed to be M$^+$ and hence the molecular weight = 164.
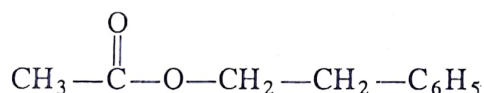
2. The band at 1730 cm^{-1} indicates an ester group or the unit $-\overset{\overset{\displaystyle O}{\|}}{C}-O-$ is present in the compound.

∴ Molecular weight 164 = COO (44) + 12H from NMR (12) + The remaining (108) (The remaining molecular weight (108) is assumed to be equivalent to nine carbon atoms).

3. Since the molecular weight is even, the nitrogen is assumed to be absent and consequently the molecular formula = $C_{10}H_{12}O_2$.

4. The signal positions and the coupling constants display the following structural units,

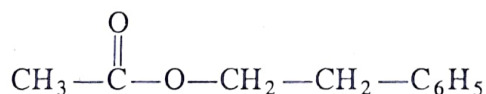$$C_6H_5-; \quad -CH_2-CH_2-; \quad CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-$$

5. The chemical shifts at δ 2.0 (CH$_3$ protons) and δ4.3 (CH$_2$ protons) indicate the presence of the unit

$$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-O-CH_2-$$

On the basis of the chemical shift values of various protons, the structure of the compound is given by

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-C_6H_5$$

On the basis of the chemical shift values of various protons, the structure of the compound is given by

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-C_6H_5$$

Problem 8

An organic compound gives the following spectral data:

UV : The ultraviolet spectrum exhibits no strong band

IR : $\nu_{max}^{(cm-1)}$ 2985 (s), 2950 (s), 1460 (m), 1380 (m)

                 1820 (vs), 1750 (s), 1050 (s)

^{1}HNMR : δ 1.1 [6H, t ($J = 7$Hz)]; 2.4 [4H, q ($J = 7$Hz)].

             Mass (m/zRel.Ab.) : 29 (38), 57(100), 71 (0.6), 73 (0.6), 74(0.7).

Deduce the structure of the compound and explain the principal ions observed in the mass spectrum of the compound.

Solution

1. The UV spectrum shows no strong band and hence there is no conjugation.
2. The aliphatic asymmetric and symmetric C—H stretching vibrations at 2985 and 2950 cm^{-1} in conjunction with aliphatic C—H asymmetric and symmetric in-plane bending vibrations at

UV : λ_{max} 229 nm and 257 nm

IR : $\nu_{max}^{(cm^{-1})}$ 1710 cm^{-1}

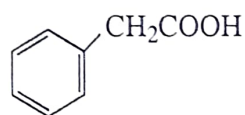^{1}HNMR : δ 7.2 (5H, s) and 3.5 (2H, s).

Deduce the structure of the compound and predict the principal ions in its mass spectrum
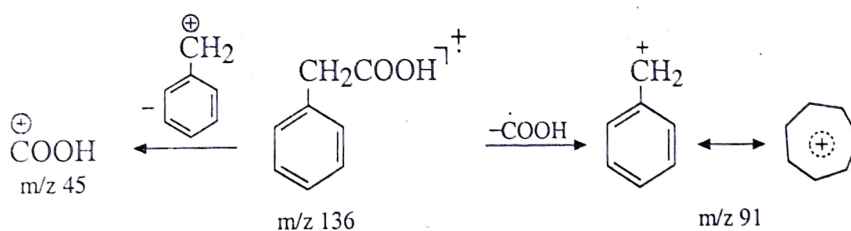
Solution

1. The molecular ion peak at m/z 136 indicates that the molecular weight of the compound is 136.
2. Base peak at m/z 91 indicates the formation of benzyl cation or tropylium ion.
3. The fragment ion at m/z 45 is due to the presence of COOH group.
4. Absorptions at λ_{max} 229 nm (n→π*) and 257 nm (π→π*) suggests the presence of keto group and aryl moiety.
5. A singlet at δ 7.2, equivalent to 5H, indicates a phenyl ring.
6. A singlet at δ 3.5, equivalent to 2H, suggests a methylene group in between the phenyl group and – COOH group.

Thus, the possible structure of the compound is

Mass spectral fragmentation pattern of phenylacetic acid is given below.

Problem 7

An organic compound A gave the following spectral data:

Mass (m/z) : 73, 91, 149, 164;

IR $\nu_{max}^{(cm-1)}$: 1730

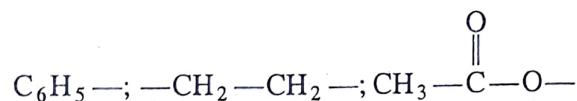^{1}HNMR, δ 2.0 (3H, s); 2.93 [2H, t(J = 7Hz)];
4.30 [2H, t(J = 7Hz)]; 7.3 (5H, s).

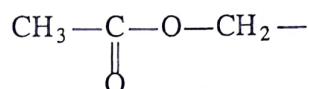Deduce the structure of the compound.

Solution

1. The heaviest peak in the mass spectrum may be assumed to be M$^+$ and hence the molecular weight = 164.
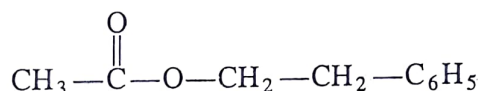
2. The band at 1730 cm^{-1} indicates an ester group or the unit $-\overset{\overset{\displaystyle O}{\|}}{C}-O-$ is present in the compound.

∴ Molecular weight 164 = COO (44) + 12H from NMR (12) + The remaining (108) (The remaining molecular weight (108) is assumed to be equivalent to nine carbon atoms).

3. Since the molecular weight is even, the nitrogen is assumed to be absent and consequently the molecular formula = $C_{10}H_{12}O_2$.

4. The signal positions and the coupling constants display the following structural units,

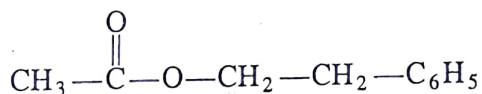$$C_6H_5-; \quad -CH_2-CH_2-; \quad CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-$$

5. The chemical shifts at δ 2.0 (CH_3 protons) and δ4.3 (CH_2 protons) indicate the presence of the unit

$$CH_3-\overset{\underset{\displaystyle \|}{\underset{\displaystyle O}{}}}{C}-O-CH_2-$$

On the basis of the chemical shift values of various protons, the structure of the compound is given by

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-C_6H_5$$

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$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-C_6H_5$$

Problem 8
An organic compound gives the following spectral data:

UV : The ultraviolet spectrum exhibits no strong band

IR : $\nu_{max}^{(cm-1)}$ 2985 (s), 2950 (s), 1460 (m), 1380 (m)
1820 (vs), 1750 (s), 1050 (s)

^{1}HNMR : δ 1.1 [6H, t (J = 7Hz)]; 2.4 [4H, q (J = 7Hz)].

Mass (m/zRel.Ab.) : 29 (38), 57(100), 71 (0.6), 73 (0.6), 74(0.7).

Deduce the structure of the compound and explain the principal ions observed in the mass spectrum of the compound.

Solution

1. The UV spectrum shows no strong band and hence there is no conjugation.
2. The aliphatic asymmetric and symmetric C—H stretching vibrations at 2985 and 2950 cm^{-1} in conjunction with aliphatic C—H asymmetric and symmetric in-plane bending vibrations at

1460 and 1380 cm^{-1} indicate an alkyl group.

3. Prominent absorptions at 1820 and 1750 cm^{-1} represent asymmetric and symmetric C=O stretching vibrations of an acyclic anhydride group, since the higher frequency C=O band is more intense.

4. Strong absorption at 1050 cm^{-1} indicates stretching of $-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-$ unit.

5. A triplet (J = 7Hz) centred at δ 1.1, equivalent to 6H, and a quartet (J = 7Hz) centred at δ 2.4, equivalent to 4H, indicate the presence of two ethyl groups.

6. The peaks at m/z 29 and 57 in the mass spectrums indicate the presence of $C_2\overset{\oplus}{H}_5$ and $C_2H_5\overset{\oplus}{C}O$.

   Even if the molecular ion is taken as 74, both these units cannot be accommodated (29 + 72 = 101 amu). Thus, the isotopic peak at m/z 74 is not the molecular ion peak but a fragment ion and consequently the compound does not give M$^+$ peak.

   This type of fragmentation is possible in t-alcohols, ketals, branched alkanes etc. but IR spectrum eliminates all these possibilities.

7. Thus, the structure of this compound in this case, is to be assembled from the indicated groups alone and then proved by examining the possibility of formation of the base peak.

8. Propionic anhydride is suggested as the structure of the compound on the basis of the fragmentation pattern, as shown below:

9. The very facile α-cleavage shown by carbonyl functions gives the major peak at m/z 57 because the ion is stabilized by resonance involving unshared pair of electrons. Only a minor part of this fragmentation provides m/z 73, $C_2H_5CO\overset{+}{O}$.

10. The McLafferty rearrangement gives a fragment, $C_2H_5C\overset{+\cdot}{O}OH$, m/z 74, which undergoes a
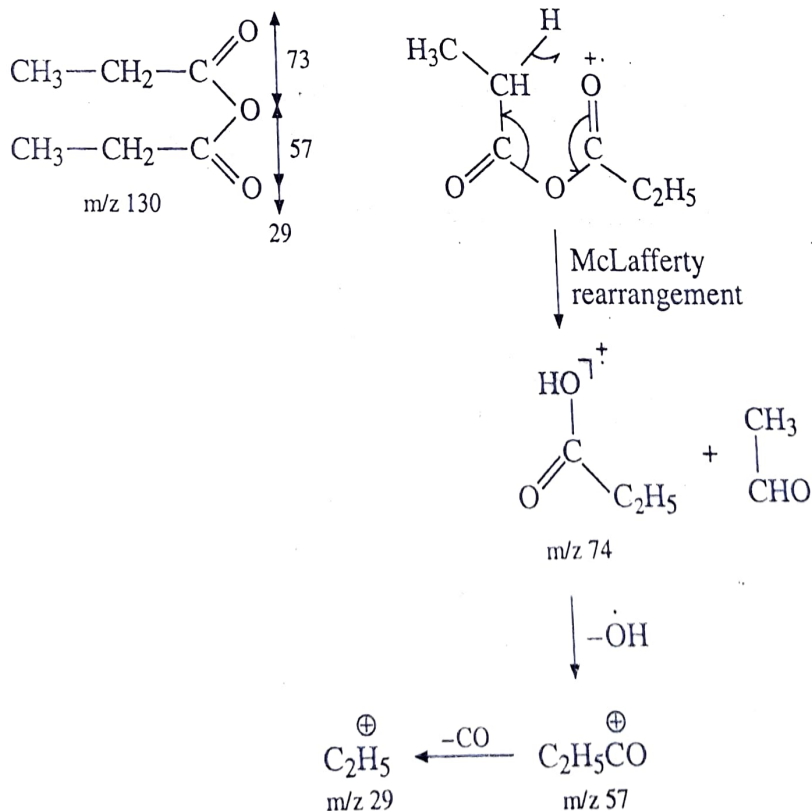
facile loss of $\overset{.}{O}H$ to give the resonace stabilized $C_2H_5C\overset{\oplus}{O}$ ion.

11. Thus, the minor fragments occur at m/z 73 and m/z 74, which might be mistaken for M^{+}, because the propionic anhydride undergoes fragmentation in the ion source and consequently gives no M^{+}.

Problem 9

An organic compound (Molecular weight 108) is not acid, can be easily oxidised to a crystalline compound (m. pt. 122°C). It gives the following spectral data:

UV : λ_{max} 255 mm (ε_{max} = 202)

IR : $v_{max}^{(cm^{-1})}$ 3402 (s, br), 3065 (w), 2888 (m), 1499 (w, sh) 1455 (m);

| ^{1}HNMR : δ	3.90		4.60		7.26
Multiplicity	s		s		s
Integration	1	:	2	:	5

Deduce the structure of the compound and predict the principal ions in its mass spectrum.

Solution

1. The ultraviolet absorption at λ_{max} 255 (ε_{max} = 202) indicates the presence of benzene ring in the compound.
2. The appearance of a strong and broad band at 3402 cm^{-1} indicates N—H or O—H stretching. Since the band is broad, it is more likely to be hydrogen bonded O—H group.
3. The medium intensity band at 3065 cm^{-1} is due to aromatic C—H stretching whereas the medium intensity band at 2888 cm^{-1} indicates C—H stretching of a methyl or methylene group. The bands at 1499 and 1455 cm^{-1} are characteristic of an aromatic ring.
4. The ^{1}HNMR exhibits three singlets with protons in the ratio of 1 : 2 : 5. If the hydroxyl group is present, then one oxygen atom and eight hydrogen atoms (1 + 2 + 5) amounts to 24 mass units. The remainder (108 – 24 = 84 mass units) correspond to seven carbon atoms. Thus, the molecular formula of compound is C_7H_8O.
5. The five proton singlet at δ 7.26 suggests monosubstituted benzene ring. Incorporating OH group, we are left with —CH₂—to get the above molecular formula. Thus, the structure of the compound is

$$CH_2OH$$
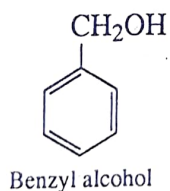
Benzyl alcohol

The structure is strictly in accordance with the given data. The compound can easily be oxidised to benzoic acid which melts at 122°C.

The fragmentation pattern of benzyl alcohol is given on page no. 320.

Thus, the principal ions formed during fragmentation are as follows:

(i)
$CH = O$
m/z 106

(ii)
$C \equiv O$
m/z 105

(iii)
m/z 107

(iv)
m/z 79

(v)
m/z 77

(vi) $C_4H_3^+$
m/z 51
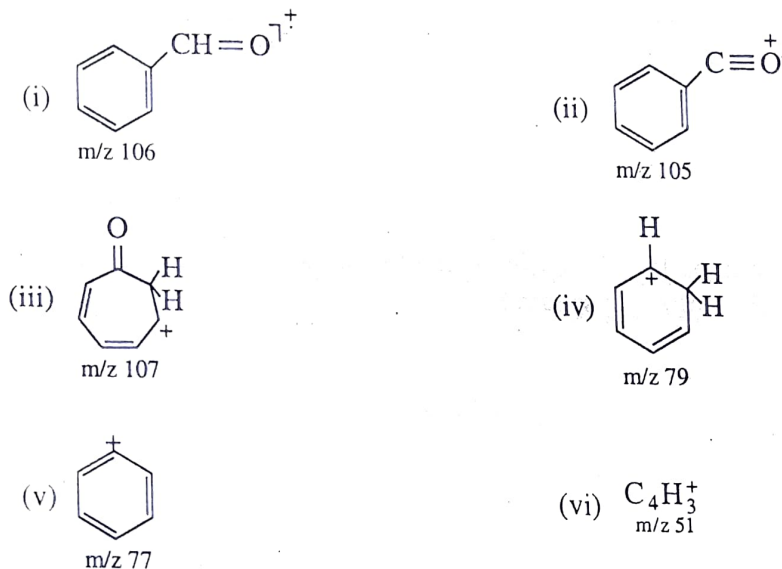
Problem 10

An organic compound (molecular formula C_8H_7Br) yields a primary alcohol on hydroboration and gives the following spectral data:

UV : λ_{max} 282 nm (ε_{max} 450)

IR : $\nu_{max}^{(cm^{-1})}$ 3033 (w), 1646 (m), 1602 (m), 1582 (w), 870 (s), 770 (s), 710 (m).

	(b)		(c)		(a)		
^{1}HNMR : δ	5.14 (dd)		5.70 (dd)		6.70 (dd)		7.26 – 7.38
Integration	1	:	1	:	1	:	4

Deduce the structure of the compound.

Solution

1. The weak absorption at 3033 is assigned to =C—H stretching or aromatic C—H stretching.
2. The bands at 1602 and 1582 cm^{-1} are due to skeletal vibrations of the benzene ring.
3. The strong absorptions at 870 and 770 cm^{-1} (aromatic C—H out-of-plane bending) and 710 (aromatic C—C out-of-plane bending) are typical of a meta-disubstituted benzene ring.
4. The ^{1}HNMR spectrum displays three doublet of doublets. This is possible only if there are three protons and each one of them is in a different environment. Thus, the part of the possible structure is

H^a $C=C$ H^b H^c
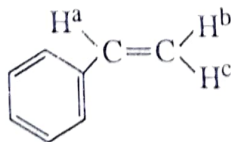
5. Each proton is splited by two other protons in different environments. Thus, three doublet of doublets appear in the ^{1}HNMR spectrum. Each proton is deshielded by the presence of double bond and/or the aromatic ring. The proton 'a', being highly deshielded by the ring appears

most downfield at δ 6.70. The proton 'c' is deshielded more, due to its relative proximity to the ring and appear at δ 5.70 as compared to the proton 'b' which resonates at δ 5.14.

6. The bromine atom must be present in the meta position (aromatic C—H out-of-plane bending bands at 870 and 770 cm^{-1}). It is further confirmed by a four proton asymmetrical pattern observed in the range δ 7.26 – 7.38 in the ^{1}HNMR spectrum.

Hence, the structure of the compound consistent with the given data is:
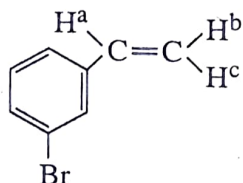
Problem 11

An organic compound A exhibits only a singlet at δ 2.17 in the ^{1}HNMR spectrum and prominent peaks at m/z 58 (M$^+$), 43 (base peak), 39, 27 and 15 in the mass spectrum.

When the compound A is treated with benzaldehyde and dilute ethanolic sodium hydroxide, it yields B. The IR spectrum of B exhibits bands at 3025, 1665, 1630, 1600, 1495, 763 and 705 cm^{-1}. The ^{1}HNMR spectrum of B displays the following signals:

δ :	7.82	7.6	7.05
Multiplicity :	d	m	d
J (Hz) :	18	–	18
Integration of protons :	1	5	1

Deduce the structures of A and B

Solution

1. The molecular ion peak at m/z 58 (molecular weight) indicates that the compound A can accommodate at the maximum four carbon atoms and the possible molecular formulae are:

$$C_4H_{10}, C_3H_6O, C_2H_2O_2, C_2H_6N_2$$
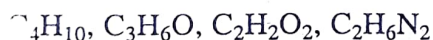
The appearance of prominent peak at M-CH$_3$(M/z 43) in the fragmentation of A eliminates the sulphur compound and $C_2H_2O_2$. No butane can give only a singlet in the ^{1}HNMR spectrum. So, the possible structures for A are CH_3COCH_3 and $CH_3 – N = N – CH_3$.

2. Out of the two possible structures, only CH_3COCH_3 reacts with benzaldehyde (aldol condensation) and hence represents A.

∴ The structure of A is $CH_3 COCH_3$

3. $CH_3COCH_3 \xrightarrow[\text{Base}]{\phi CHO} C_6H_5CH = CHCOCH_3 \xrightarrow[\text{Base}]{\phi CHO} C_6H_5CH = CHCOCH = CHC_6H_5$

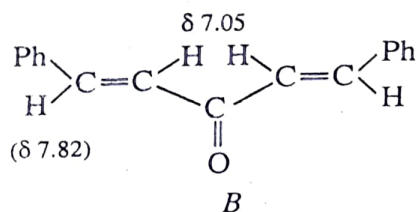$\qquad\qquad\qquad\qquad\qquad$ I $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ II

The compound B can be either of the two products (I or II) mentioned above. The PMR spectral data is helpful in deciding the correct structure:

δ	7.82	7.60	7.05	
multiplicity	d	m	d	
J (Hz)	18	–	18	(trans)
Integration	1 H	5 H	1 H	
	HC =	C$_6$H$_5$–	HC =	

There is no methyl group signal in the PMR spectrum of the compound B and hence the structure of B will be

The IR spectral data of B is consistent with the structure B as shown below: $\nu_{max}^{(cm^{-1})}$ 3025 (aromatic C—H stretching), 1665, (C=O stretching); 1630 (C=C stretching); 1600, 1495 (skeletal vibrations of phenyl ring); 763, 705 (mono-substituted benzene ring).

7.4 INTERPRETATION OF UV, IR, PMR AND MASS SPECTRA FOR THE IDENTIFICATION OF ORGANIC COMPOUNDS (SET II)

Problem 1

Solution

1. The compound contains carbon and hydrogen only. The molecular weight of the compound is 120.09 (MS : M$^+$ 120.0939) and the molecular formula is C$_9$H$_{12}$.
2. The compound contains four DBE.

$$DBE = x + 1 - \frac{y}{2} = 9 + 1 - \frac{12}{2} = 4$$

3. The weak absorption at 3020 cm^{-1} is assigned to aromatic C—H stretching vibration.
4. The aliphatic asymmetric and symmetric C—H stretching vibrational bands at 2920 and 2840 cm^{-1} respectively in conjunction with aliphatic C—H asymmetric and symmetric in-plane bending vibrations at 1470 and 1380 cm^{-1} indicate the presence of methyl group.
5. The bands at 1610 and 1585 cm^{-1} represent skeletal vibrations of the aromatic ring.
6. The strong band at 835 cm^{-1} is consistent with C—H out-of-plane bending vibration of 1, 3, 5-trisubstituted benzene ring.
   Thus, the compound contains a 1,3,5-trisubstituted benzene ring and methyl group (s).
   The PMR and UV spectra of the compound readily establish the structure.
7. A singlet at δ 2.1, equivalent to 9H, represents three methyl groups.
   A singlet at δ 6.3, equivalent to 3H, indicates symmetrical trisubstituted benzene ring.
   Thus, the structure of the compound is 1,3,5-trisubstituted benzene (mesitylene).
9. The absorption at λ_{max} 270 nm ($\varepsilon \approx 300$) substantiates the structure of 1,3,5-trisubstituted benzene.
10. Finally, the structure, 1,3,5-trimethylbenzene, is confirmed by the fragmentation pattern of the compound: