Quadrant II – Transcript and Related Materials

Programme: T. Y. B. Sc.

Subject: Chemistry

Paper Code: CHC 107

Paper Title: Organic Chemistry

Unit: 3- Section A : Spectroscopic Methods in Organic Chemistry

Module Name: Interpretation of NMR spectra of Anisole, Acetic acid, t butylbenzene, 2-Butanone, Propene and Simple problems based on NMR spectral data for identification of molecule.

Module No: 25

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Steps to determine the structure of the compound using the spectroscopic data –

Calculate the Double bond equivalent/degree of unsaturation/Index of hydrogen deficiency from the Mol.Formula to limit the number of possible structures.

Double Bond Equivalence (DBE) = (2a+2)-(b-d)/2

Where, a = No of carbon

b = No of hydrogen/monovalent atom

d = No of Nitrogen/trivalent atom

2. Look at the IR absorption bands/data at wavenumbers above 1500 cm-1 to determine what functional groups are likely present in the compound.

3. Look at the NMR data to determine the connectivity of the compound. 1H NMR tells us the number of neighbouring hydrogens present.

1.C_7H_8O

^1H NMR i) A Singlet (δ 3.75, 3H)

ii) A Triplet (δ 7.26, 2H)

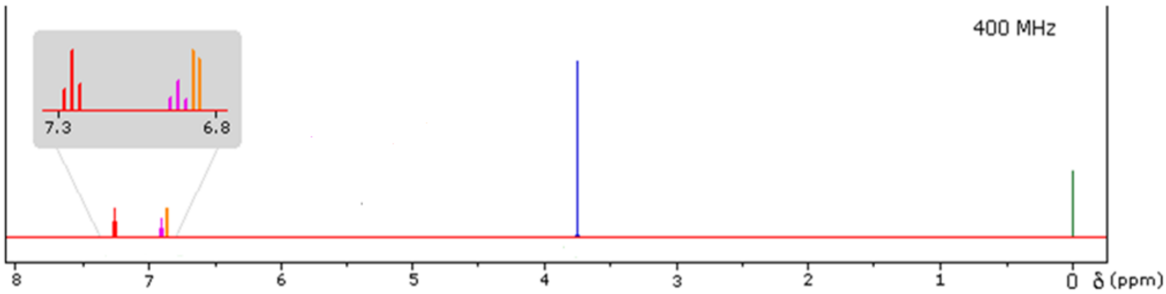
iii)A Doublet (δ 6.88, 2H)

iv) A Triplet (δ 6.92, 1H)

Double Bond Equivalence (DBE) = (2a+2)-(b-d)/2

Where, a = No of carbon, b = No of hydrogen/monovalent atom, d = No of Nitrogen/trivalent atom

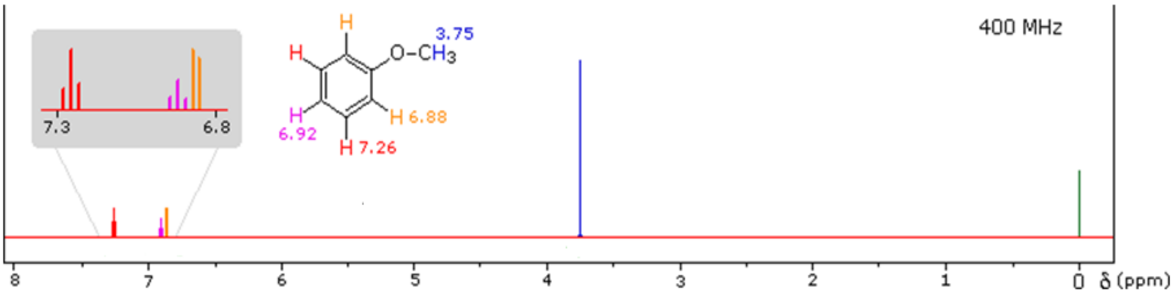
DBE = [2 x 7+2 -8]/2 = 4



Four double bonds equivalence can be due to aromatic ring. This is further confirmed by peaks due to five protons of benzene ring- Monosubstitution.

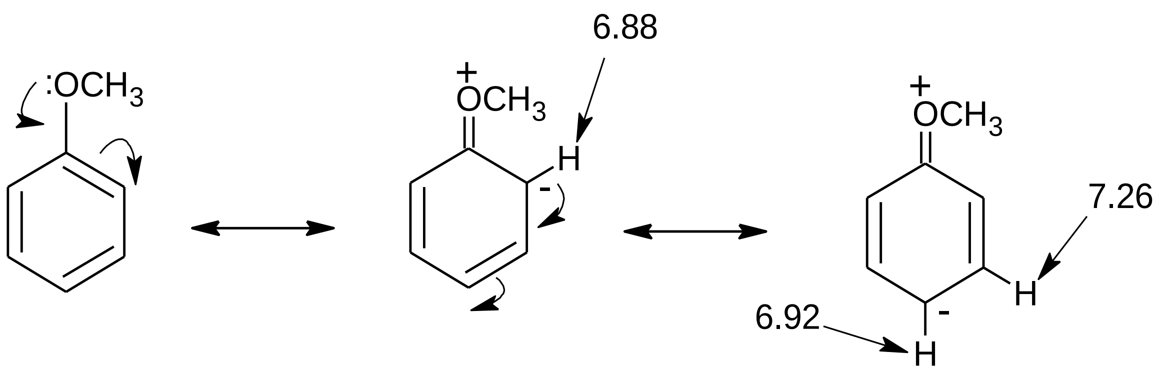
The singlet around δ 3.75, 3H is due to the methyl group attached to the oxygen atom. Thus, the compound is Anisole.

The meta protons are slightly shifted downfield (triplet at δ = 7.26), while the ortho (doublet at δ = 6.88) and para protons (triplet at δ = 6.92) are shifted upfield, because the electron-density increased in these positions.



The methoxy group in anisole donates electrons by resonance to the ortho and para positions, hence ortho and para protons of anisole are shielded–

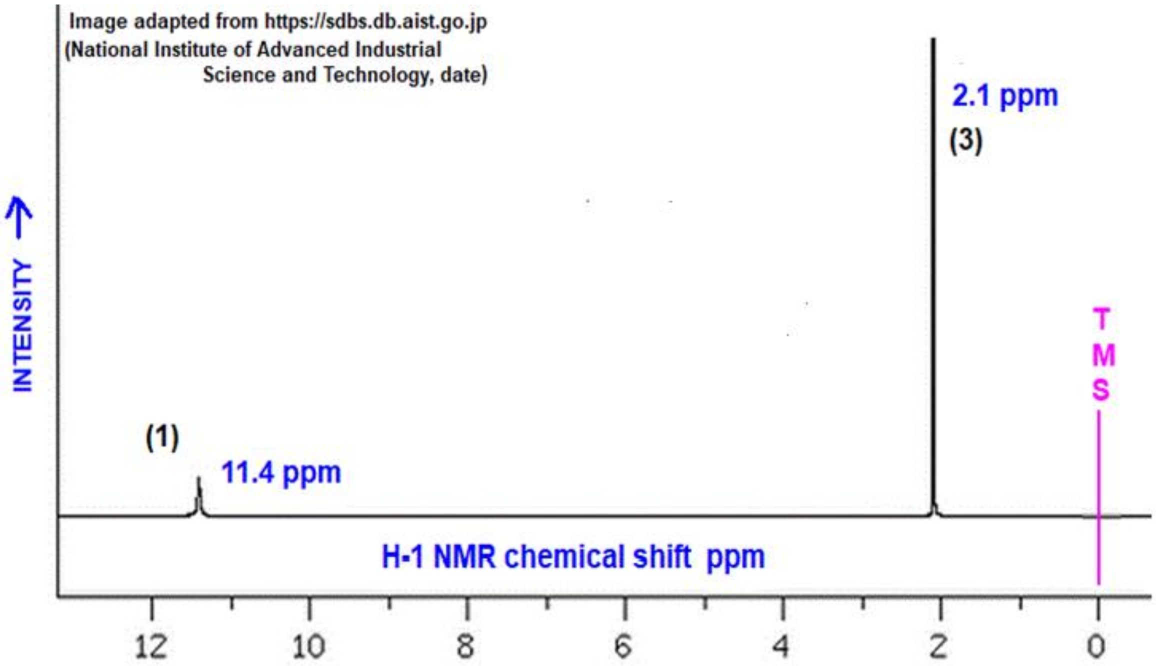
Therefore ortho and para protons show signals in upfield region.



2. $\mathbf{C_2H_4O_2}$

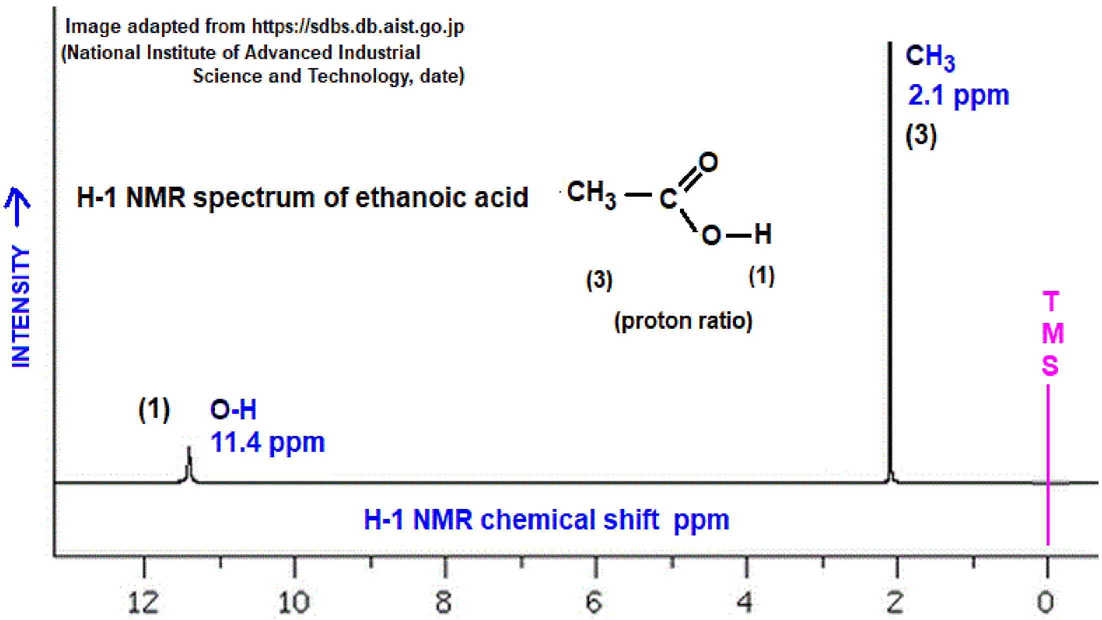
- ^{1}H NMR i) A Broad singlet (δ 11.4, 1*H)*
  ii) A Singlet (δ 2.1, 3*H)*

DBE = [2 x 2+2 -4]/2 = 1



Broad singlet at δ 11.4 is due to the proton of carboxylic acid. Hence, one double bond by DBE is accounted by the C=O of carboxylic acid group.

Singlet at δ 2.1 due to three protons corresponds to hydrogens of methyl group. Thus, the compound is Acetic acid.

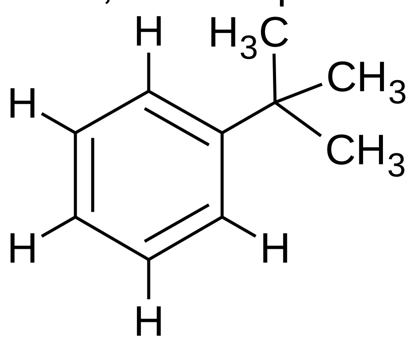


3. $\mathbf{C_{10}H_{14}}$

^{1}H NMR Data

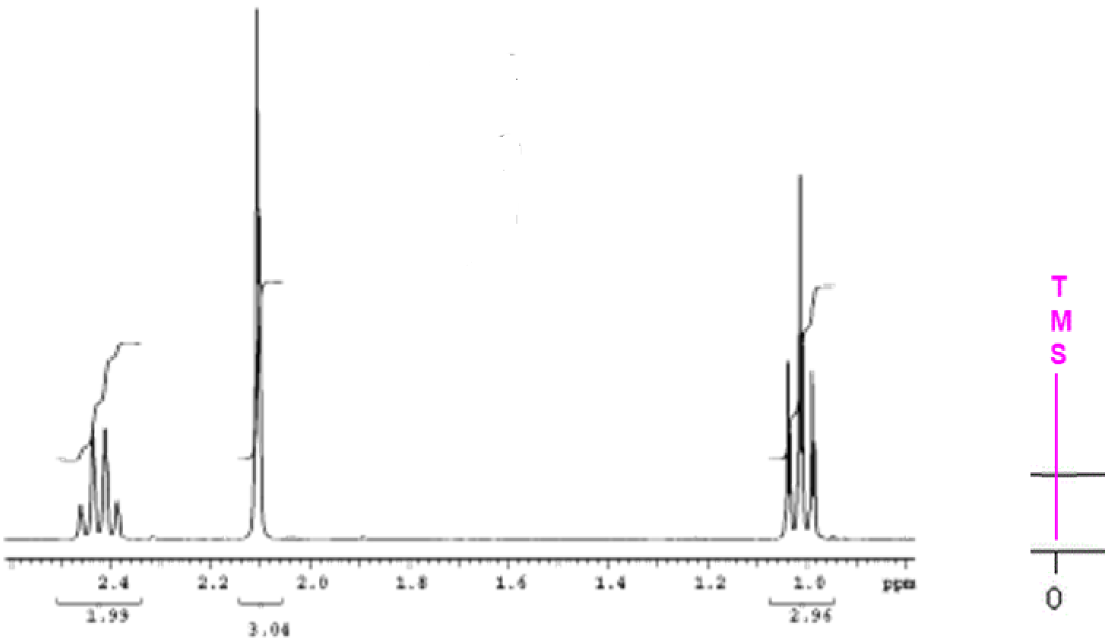
i) Singlet δ 0.88, 9H

ii) Singlet δ 7.28, 5H
DBE = [2 x 10+2 -14]/2 = 4
DBE = 4 corresponds to aromatic compound– General formula C_nH_{2n-6}
- substituted benzene.
Nine protons of one kind and 5 protons of another kind – Mono-substitution in the benzene ring
The two kinds of protons are not spin-spin coupled – Two singlets
The singlet at δ 7.28, 5*H* is due to C_6H_5 *i.e.* phenyl group – Confirms monosubstitution
The singlet at δ 0.88 ppm, 9*H* corresponds to C_4H_9 due to nine equivalent protons of *t*-butyl group.
Thus, the compound is **t-butylbenzene**.



4. **C_4H_8O**

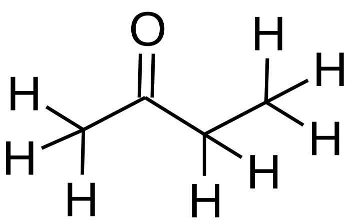
^{1}H NMR
i) A Singlet (δ 2.14, 3*H)*
ii) A Triplet (δ 1.06, 3*H)*
iii) A Quartet (δ 2.45, 2*H)*

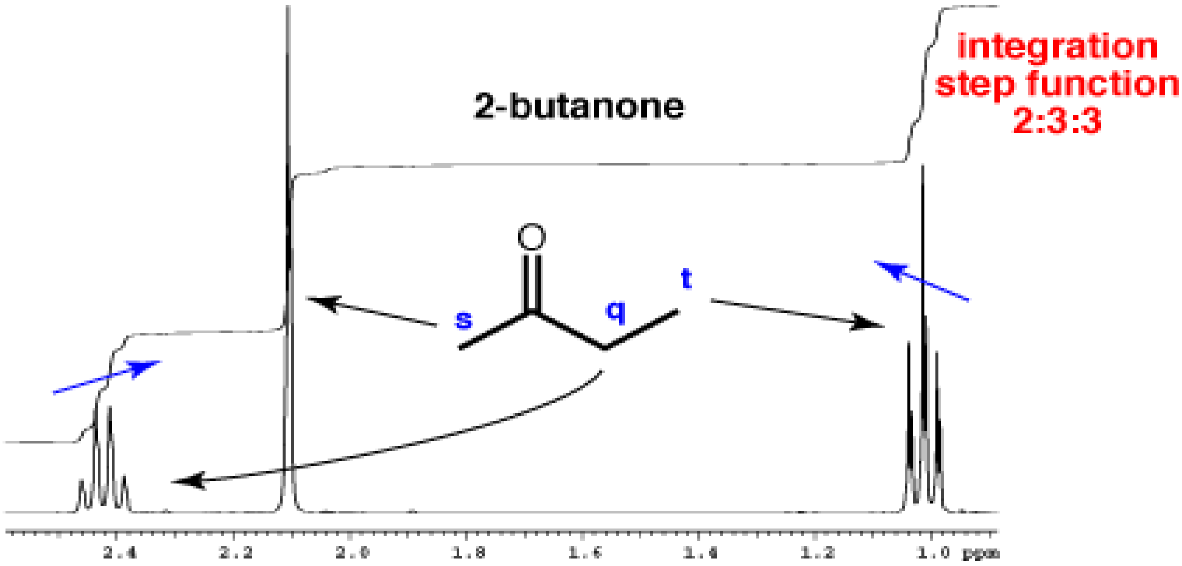


DBE = [2 x 4+2 -8]/2 = 1
Singlet at δ 2.14 due to three protons corresponds to hydrogens of methyl group.
Triplet at δ 1.06 (3*H*) and a Quartet at δ 2.45 (2*H)* is due to the presence of

$-CH_2CH_3$ linkage.

One double bond is accounted by C=O group.
Thus, the compound is **2-butanone.**





5. $\mathbf{C_3H_6}$

^{1}H NMR

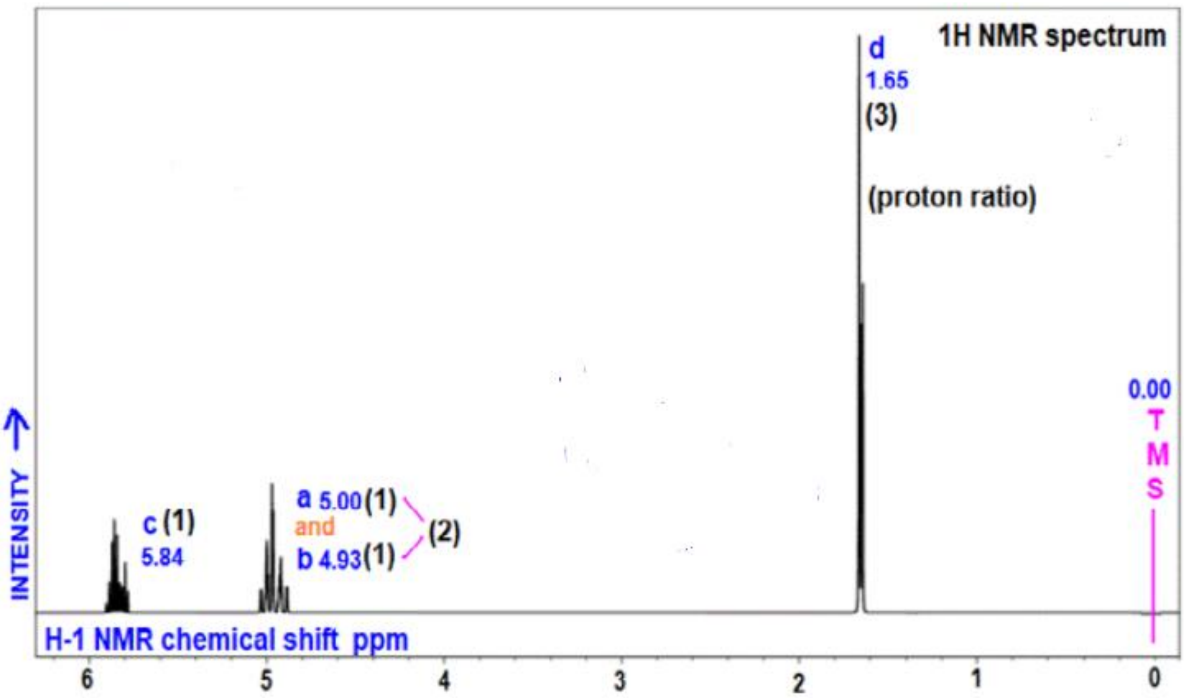
i) Multiplet at δ 5.84 (1*H*)

ii) Triplet at δ 5.00 (1*H*)

iii) Triplet at δ 4.93 (1*H*)

iv) Doublet at δ 1.65 (3*H*)

The high resolution spectrum shows 4 groups of proton resonances in the 1:1:1:3 ratio.



DBE = [2 x 3+2 -6]/2 = 1

The DBE = 1 may be due to the presence of a C=C bond or a ring.

- Triplet at δ 5.00 (1*H*) and Triplet at δ 4.93 (1*H*) is due to the presence of C**H_2**=CH- linkage confirming the presence of C=C bond.

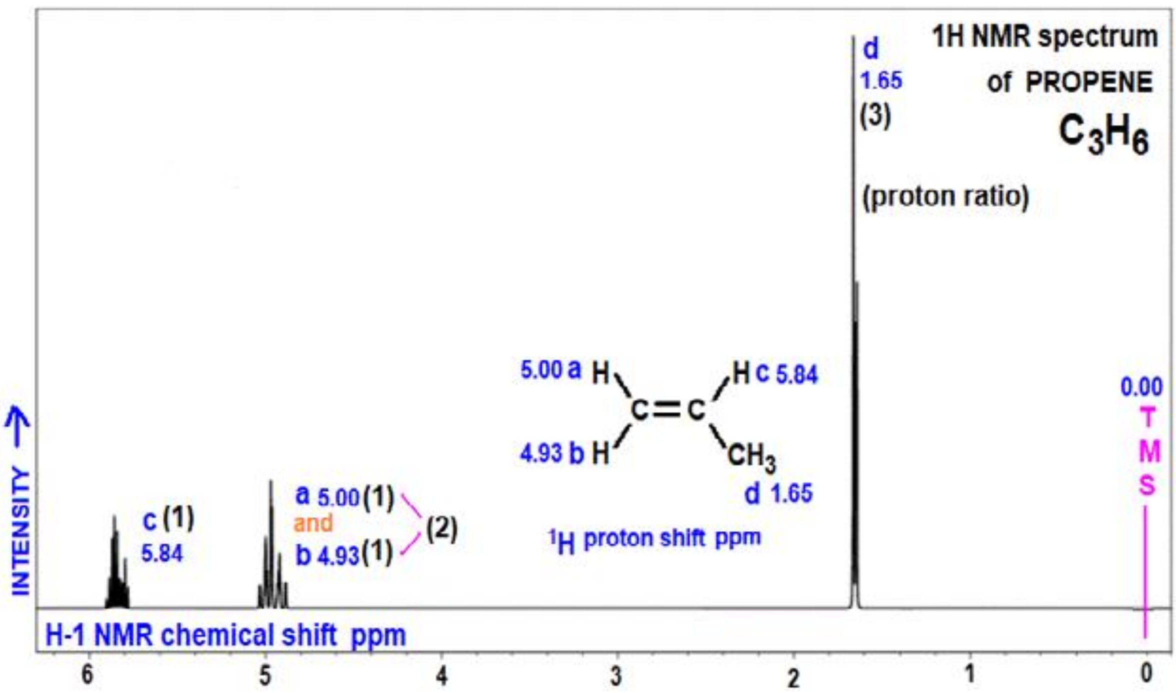
The two resonances for the protons of the end =C**H**$_2$ group are very slightly different due to these two protons experiencing slightly different shielding field effects due to the asymmetric grouping at the other end of the C=C bond Each CH_2 proton is split by the other proton and by the lone CH proton, therefore two triplets are observed overlapping each other (two n+1 = 3)

- Doublet at δ 1.65 (3*H*) is attributed to the presence of =CH-C**H_3** linkage.

The signal is split into a doublet by the adjacent CH group proton (n+1 = 2).

- Multiplet at δ 5.84 (1*H*) is because C**H** proton resonance is split by the CH_3 proton field and also separately by the individual CH_2 protons, to give two overlapping quintets (two n+1 = 5).
- Thus, the compound is Propene.

CH_2=CH-CH_3



- The high resolution spectra of propene shows 4 groups of proton resonances and in the 1:1:1:3 ratio expected from the structural formula of propene.

Problem 1

A monosubstituted aromatic hydrocarbon has molecular formula C_9H_{12}. The ^{1}H NMR data is given below. Identify the structure of the compound.

^{1}H NMR i) A singlet (δ 7.3, 5*H*)
ii) A septet (δ 2.9, 1*H*)
iii) A doublet (δ 1.3, 6*H*)

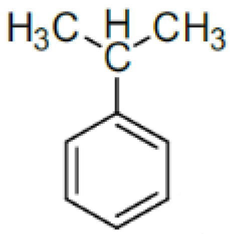
Solution:

DBE = [2 x 9 +2 -12]/2 = 4

The DBE = 4 may be due to an alkene or a aromatic ring. But as given it is an aromatic hydrocarbon, thus four double bonds are accounted by a phenyl ring.

Septet at δ 2.9 for 1*H* and doublet at δ 1.3 for 6*H*, indicate presence of iso-propyl linkage. Peak at δ 7.3 for 5*H*, is due to mono substituted aromatic ring.

Thus, the compound is **Iso-propyl benzene**.



Problem 2

A carboxylic acid $C_4H_7O_2Br$ shows peak at δ 11. The ^1H NMR data is given below. Identify the compound.

^1H NMR i) A singlet (δ 11, 1*H*)
ii) A triplet (δ 4.2, 1*H*)
iii) A quintet (δ 2.1, 2*H*)
iv) A triplet (δ 1.1, 3*H*)

Solution:

DBE = [2 x 4 +2 -8]/2 = 1

The most downfield signal at δ 11 is due to the proton of the carboxylic group.

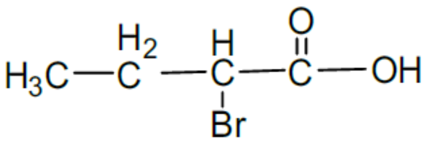
The one double bond by DBE is accounted by the C=O of carboxylic acid group.

Triplet at δ 4.2 for 1*H*, represents -CH_2C**H**- linkage.

Triplet at δ 1.1 for 3*H*, indicate C$\mathbf{H_3}$$CH_2$- linkage.

Quintet at δ 2.1, for 2*H* is due to CH_3C$\mathbf{H_2}$CH- linkage

Thus the structure is **2-Bromobutanoic acid**.



Problem 3

A compound with molecular formula $C_{10}H_{12}O$, shows band near 1715 cm^{-1} and 1600-1450 cm^{-1} in IR spectrum. The ^1H NMR data is given below. Deduce its structure.

^1H NMR i) A multiplet (δ 7.3, 5*H*)
ii) A singlet (δ 3.7, 2*H*)
iii) A quartet (δ 2.45, 2*H*)
iv) A triplet (δ 1.0, 3*H*)

Solution:

DBE = [2 x 10 +2 -12]/2 = 5

Band near 1750 cm^{-1} in IR show presence of keto group (C=O). The DBE is 5, one double bond is accounted by C=O group, the other four double bonds can be due to aromatic ring. This is further confirmed by multiplet at δ 7.3, due to protons of benzene ring.

The triplet and quartet are due to CH_3CH_2- linkage.

A singlet at δ 3.7 is due to protons of the carbon attached to aromatic ring. Thus the structure is **1-Phenyl-2-butanone**.