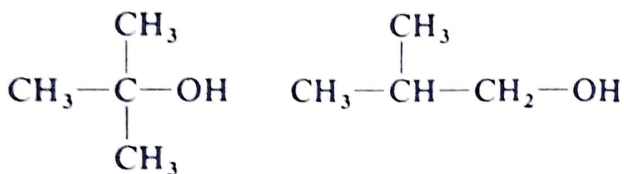


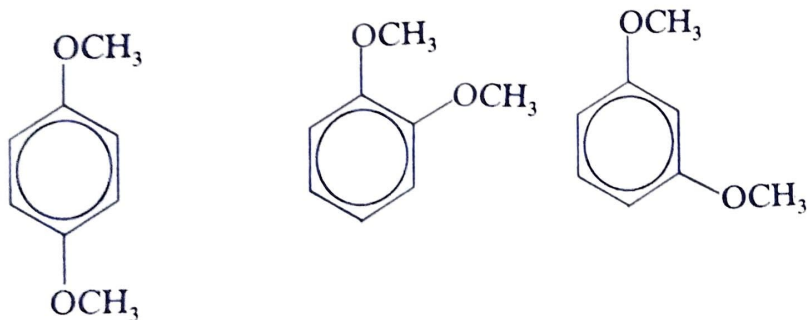
## PROBLEMS AND EXERCISES

- How many distinct absorptions will be observed in the  $^{13}\text{C}$ NMR spectrum of hex-1-ene ( $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ )? How can you compare these positions of absorptions with those in ethanol  $\text{CH}_3\text{CH}_2\text{OH}$  (consult Table 5.3)?
- How the number and position of  $^{13}\text{C}$  NMR signals can help in the identification of the following four isomeric alcohols,  $\text{C}_4\text{H}_{10}\text{O}$ .

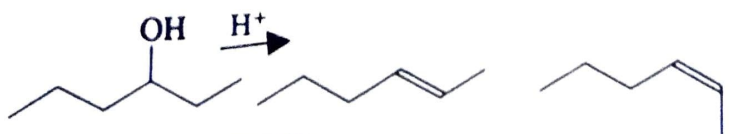
*n*-butyl alcohol*sec*-butyl alcohol*t*-butyl alcohol

isobutyl alcohol

- How will you differentiate among the three following compounds.

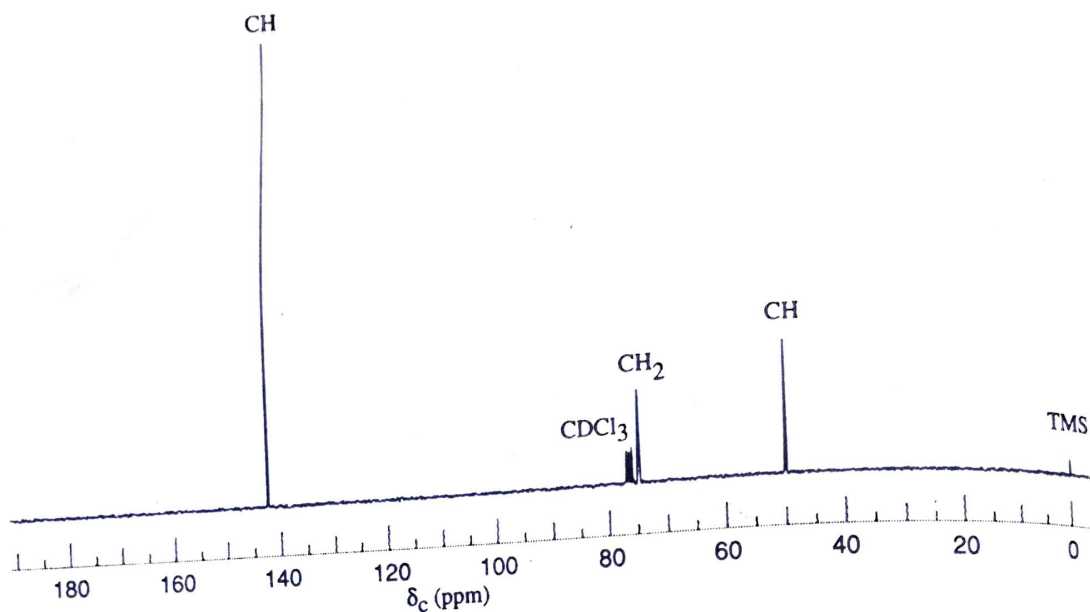


- An organic compound  $\text{C}_7\text{H}_8$  undergoes catalytic hydrogenation to give a tetrahydro product  $\text{C}_7\text{H}_{12}$ . The broadband proton-decoupled  $^{13}\text{C}$  spectrum of the parent compound is depicted (Fig. 5.10C). Make proposals for a possible structure.
- On dehydration 3-hexanol affords a product mixture of four components I-IV. The  $^{13}\text{C}$  NMR data of these are as below. Analyse these data so as to assign structures to the four alkenes.



$\delta_{\text{C}}^{\text{TMS}}$	(I)	(II)	(III)	(IV)
	12.3, 13.5, 23.0, 29.3, 123.7, 130.6	13.4, 17.5, 23.1, 35.1, 124.7, 131.5	14.3, 20.6, 131.0	13.9, 25.8, 131.2

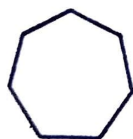
Mixture of isomeric alkenes



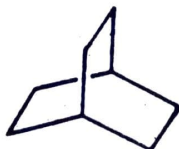
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Fig. 5.10C

- How a cursory examination of CMR spectra helps to know if a compound contains carbon atoms of carbonyls, nitriles, acetylenes and quaternary structures.
- How many peaks you expect in the proton decoupled CMR spectra of:



(I)



(II)



(III)

- How will you differentiate among *o*, *m* and *p*-xylenes on the basis of their proton decoupled CMR spectra.
- Compare the PMR and CMR spectral feature in methyl ethyl ketone. For  $^{13}\text{C}$  NMR consider both proton decoupled and the off-resonance (Sec. 5.1) spectrum.

## ANSWERS TO THE PROBLEMS

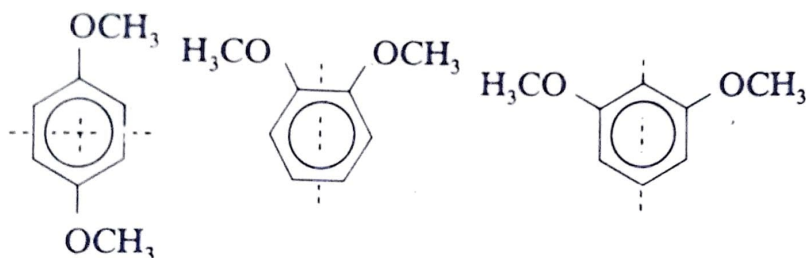
- The four  $sp^3$ -hybridised carbons appear between  $\delta$  14.0 and  $\delta$  33.8 and the two  $sp^2$ -hybridised carbons appear downfield at  $\delta$  114.3 for the terminal carbon and  $\delta$  139.2 for the substituted alkenyl carbon. The chemical shift of methyl carbon in ethanol ( $\delta$  17.0) compared to that in hex-1-ene ( $\delta$  14.0) shows that the effect of an

electro-negative substituent is felt beyond the atom to which the substituent is directly attached. The methylene carbon in ethanol is seen at  $\delta$  56.5 a down field shift of around 35 ppm than the penultimate methylene carbon in hex-1-ene.

2. Both *n*-butanol (*i.e.*, 1-butanol) and 2-butanol will give four signals each. In *t*-butyl alcohol due to equivalence of three methyl groups only two signals will be found, while isobutyl alcohol, *i.e.*, 2-methyl-1-propanol will give three signals. Use of Tables 5.1 and 5.3 will help in making distinction by calculating the values and comparing with the CMR chemical shifts of 1- and 2-butanol ( $\delta$  ppm).

	C—1	C—2	C—3	C—4
1-butanol	61.7	35.3	19.4	13.9
2-butanol	22.9	69.0	32.3	10.2

3. This can be done by the expected peaks in <sup>13</sup>C NMR of aromatic carbons. Consider the symmetry elements for the equivalence of carbons present on these aromatic isomers. The *para* isomer shows only two peaks since the carbons on the aromatic ring are rendered equivalent. The *para* isomer has two simple axes and two planes of symmetry. The *ortho* isomer displays three peaks (consider the plane of symmetry). In the *meta* isomer the plane of symmetry now passes through two carbon atoms and thus it shows four peaks for the ring carbons.



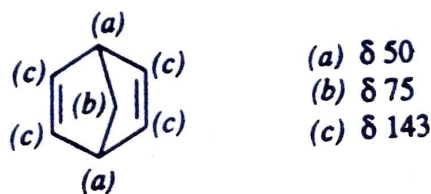
**Two peaks**

**Three peaks**

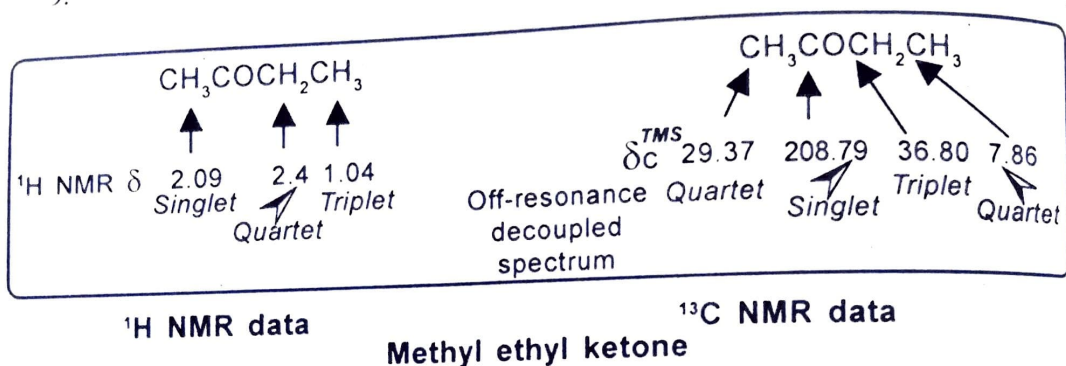
**Four peaks**

The number of peaks in <sup>13</sup>C NMR spectrum in the aromatic region can distinguish one isomer from the other [symmetry considerations].

4. The index of hydrogen deficiency is four. One can detect only one signal around  $\delta$  143 due to doubly bonded carbon, therefore the doubly bonded carbons are all equal. Moreover the signal at  $\delta$  143 is a CH group in the DEPT spectra thus each one of the doubly bonded carbon atoms has a hydrogen attached to it. Further consideration of the DEPT spectra shows that there is a signal at  $\delta$  75 due to a —CH<sub>2</sub>— group a signal at  $\delta$  50 is a tertiary carbon bearing a H. Considering the hydrogenation data, symmetry equivalence of carbons, one may suggest bicyclo [2.2.1] hepta-2,5-diene a structure which fits into index of hydrogen deficiency.



- The isomers III and IV represent two, 3-hexenes since each shows only three signals. In these, the signal around 131 ppm are the  $sp^2$ -hybridised carbons and the signals around 14 ppm are probably the methyl carbons. Significantly the C—2 carbon resonances in III and IV differ by about 5 ppm. This is the  $\gamma$ -effect in a pair of *cis-trans* isomers; so the isomer III (with the upfield C—2) must be the *cis* isomer. Similar arguments can be used to deduce that isomer I, is *cis*-2-hexene and isomer II is *trans*-2-hexene. In isomer I, two of the signals are about 5 ppm upfield of their counterparts in isomer II (35.1 compared to 29.3, 17.5 compared to 12.3).
- Since these carbons do not bear any protons, their signals are relatively smaller in size. The common  $^{13}\text{C}$  nuclear relaxation processes which control signal size depend, at least partly on interaction with attached protons.
- (I) one; (II) two; (III) five.
- Ortho*-xylene, 4 signals; *m*-isomer, 5 signals and *p*-isomer, three signals.



## SUMMARY

- Due to low natural abundance of  $^{13}\text{C}$  and the lower magnetic moment than that of the proton, greater sensitivity is needed to record  $^{13}\text{C}$  NMR spectra compared to that of  $^1\text{H}$  NMR.
- Greater resolution is obtained in  $^{13}\text{C}$  NMR spectra than  $^1\text{H}$  NMR.
- Unlike  $^1\text{H}$  NMR spectra, it is not possible to determine the relative ratio of carbon atoms in a compound by integration of the peak areas. This is due to different relaxation times of carbon atoms in different environments, and due to the Nuclear Overhauser Effect (NOE). Due to these two effects one can identify those peaks in  $^{13}\text{C}$  spectrum which are due to carbon atoms which have no hydrogen attached to them, including those in aromatic rings which carry a substituent.
- Unlike  $^1\text{H}$  NMR spectra where, one normally gets information regarding chemical shift, coupling constant and relative number of absorbing nuclei, the routine information obtained from  $^{13}\text{C}$  NMR spectroscopy is only the chemical shift.
- The values of the chemical shift are normally related to the TMS carbon absorption. In common organic compounds, the absorptions occur in the range of 200 ppm,

between the carbonyl absorptions at low field and the methyl absorption at high field.

6. The <sup>13</sup>C — <sup>1</sup>H coupling constants are large (125-200 Hz for directly bonded protons), thus the resulting multiplets tend to overlap and the spectrum becomes too complicated to analyse. <sup>13</sup>C spectra are thus spin decoupled (noise decoupled) and each absorption then appears as a sharp singlet.
7. The method of off-resonance decoupling allows the coupling of directly bonded carbon and hydrogen to be observed. The separation of the peaks thus obtained however, does not give the true <sup>13</sup>C—<sup>1</sup>H coupling constant. Thus the absorption of a carbon of a methyl, methylene and methine groups appear as quartets, triplets and doublets respectively, provided all the hydrogens are equivalent.
8. The HETCOR (<sup>1</sup>H—<sup>13</sup>C COSY) experiment correlates <sup>13</sup>C nuclei with directly attached (*i.e.*, coupled protons). These are one bond  $J_{CH}$  couplings.
9. A DEPT spectrum is used to distinguish among CH<sub>3</sub> and a CH<sub>2</sub> group and a CH group.



## FURTHER READINGS

1. F.W. Wehrli, A.P. Marchand and S. Wehrli, *Interpretation of Carbon—<sup>13</sup>C NMR Spectra*, 2nd Ed., John Wiley and Sons Ltd., Chichester, UK, 1988.
2. E. Breitmaier and W. Völter, *Carbon—<sup>13</sup>C NMR Spectroscopy*, 3rd Ed., VCH, Weinheim, 1987.