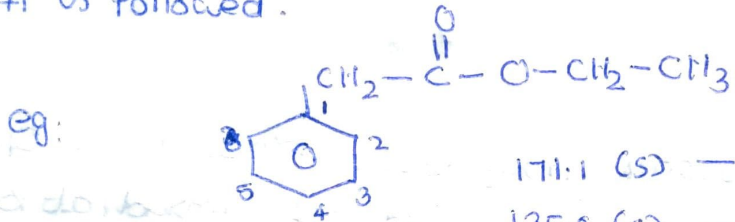


¹³C NMR SPECTROSCOPY ✓ - kalsi

¹³C NMR spectroscopy has following advantages over ¹H NMR.

1. Range of absorption is wide δ 0-200 ppm relative to TMS. Thus fewer peaks overlap.
2. ¹³C isotope has low natural abundance $\sim 1\%$ (¹²C is $\sim 99\%$) in proton decoupled spectra, so ¹³C - ¹³C coupling is negligible and each magnetically non equivalent carbon gives single unsplit peak.
3. In proton coupled spectra, the signal for each carbon is split by the protons bonded directly to the C and n+1 rule is followed.

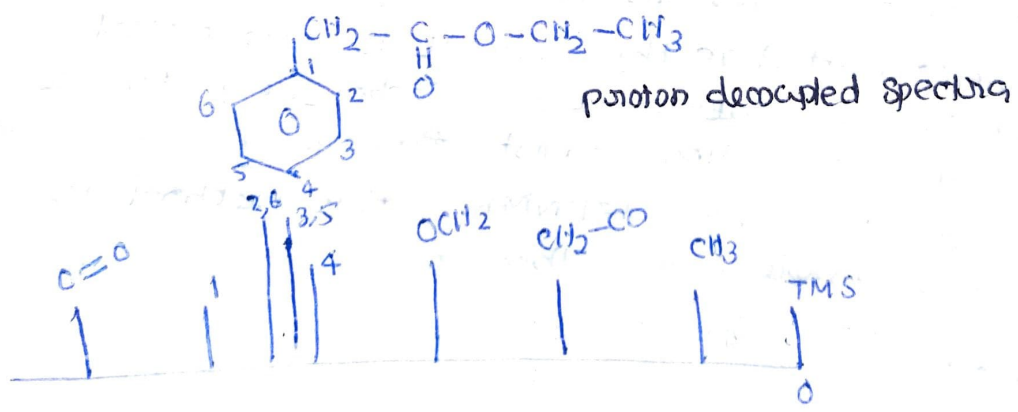


171.1 (s) — C=O	60.6 (t) — OCH ₂
135.0 (s) — C-1	41.4 (t) — Ph-CH ₂
129.6 (d) — C-2,6	14.8 (q) — CH ₃
128.8 (d) — C-3,5	
127.2 (d) — C-4	

4. The areas under the peaks in ¹³C NMR may not be proportional to the no of carbon give rise the signal.

5. In proton coupled spectra the signal for each carbon is split by the proton bonded directly to that C and n+1 rule is followed.

Hydrogen decoupling - Broad band Proton decoupled spectra
Decoupling of protons from the carbons leads to simplification of the spectrum. This will give ^{only} sharp peaks for each carbon



CH ₃	CH ₂	CH ₂	CH ₂	CH ₂	OH
↓	↓	↓	↓	↓	
14.1	22.9	28.5	32.8	62.1	

* Multiplicity - ^1H decoupling - Noise decoupling

^{13}C nucleus and ^1H nucleus both have $I = \frac{1}{2}$, but ^{13}C nucleus is not magnetically active. ^($I=0$) Since the natural abundance of ^{13}C is so low ^{13}C - ^{13}C coupling is very ^{less}, however ^{13}C - ^1H coupling can take place to give multiplets in the spectrum.

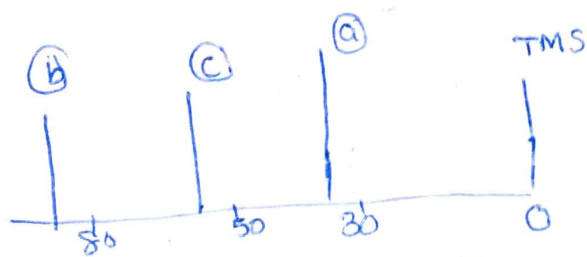
→ Double irradiation of all protons simultaneously and recording ^{13}C spectrum ~~gives~~ eliminates the complication effect of proton couplings. Thus in this technique a decoupling signal is used, which has ^1H frequencies spread around 100 MHz and thus is a form of radiofrequency noise. The spectra thus obtained are decoupled or noise decoupled. The sample is simultaneously irradiated with a band of RF radiation that excite OFF-resonance decoupling ^{all the H atoms so no coupling occurs with ^{13}C nuclei.}

Here the sample is irradiated at a frequency close but not coinciding with the resonance frequency of protons. As a result multiplets becomes narrow, but not removed completely as in fully decoupled spectra. Thus multiplets may still provide useful information without becoming complicated due to overlapping. Thus in off-resonance decoupling ^{13}C nuclei are split by the protons directly bonded to them only.

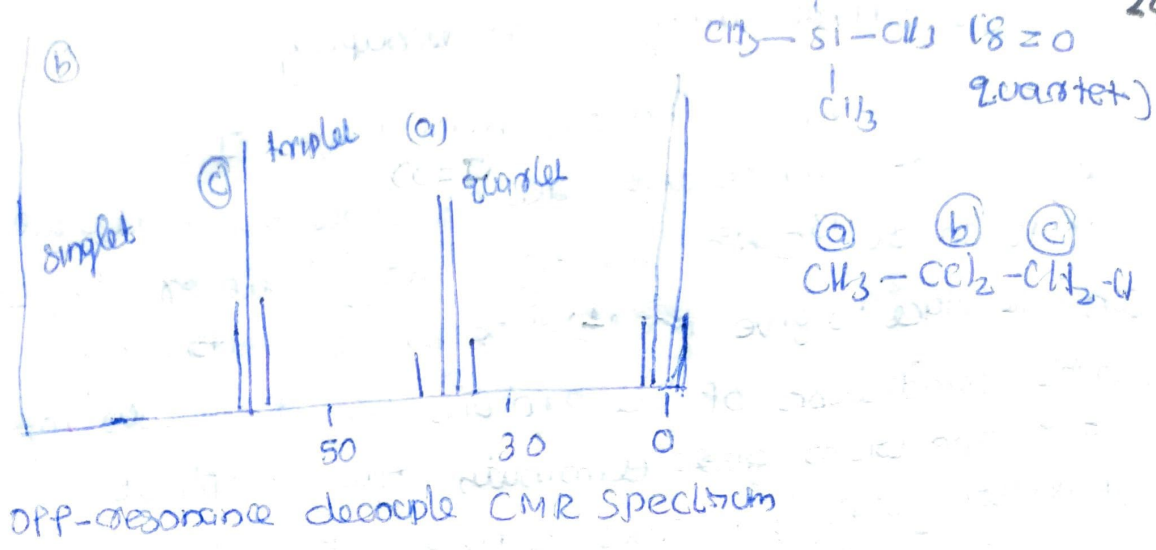
^{13}C -H coupling possible

^{13}C -C-H or ^{13}C -C-C-H are not possible

eg: 1,2,2-trichloropropane



proton-decoupled ^{13}C NMR



→ The carbons which do not bear protons (e.g. C=O) generally have low intensity beca of long relaxation times. The proton bearing carbons have enhanced line intensity beca of NOE. Deuterated solvent like CDCl3 gives CMR signal which are split by coupling to deuterium

For deuterium $I=1$

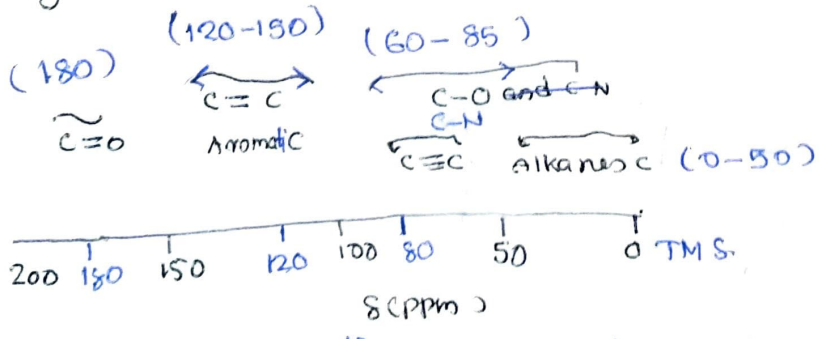
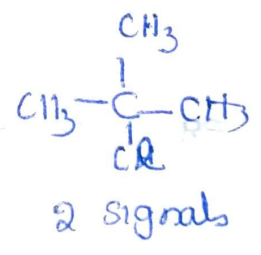
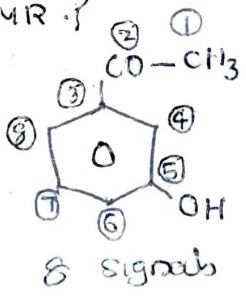
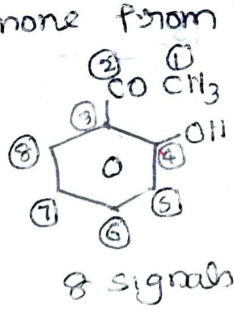
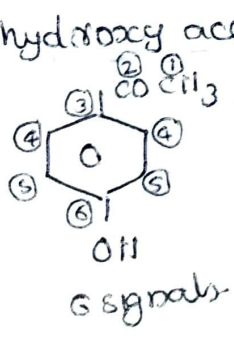
$$\text{multiplicity} = 2nI + 1$$

$$= 2 \times 1 \times 1 + 1 = 3$$

CDCl3 gives triplet signal with 1:1:1 ratio

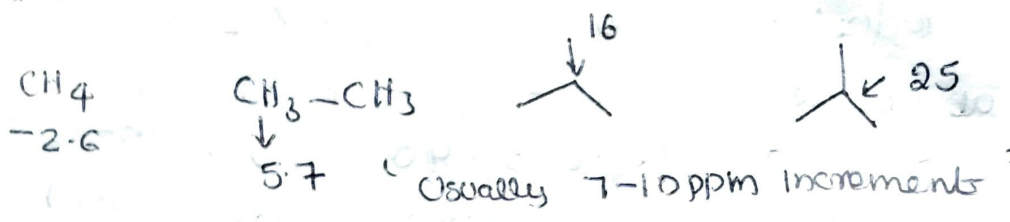
→ Chemical shift equivalences

How can you differentiate ortho, meta and para-hydroxy acetophenone from ^{13}C NMR?



Correlation chart for ^{13}C chemical shift. Chemical shifts δ (ppm) are related to TMS carbon. Majority of absorptions fall in a range of some 200 ppm downfield of TMS.

On moving to quaternary from primary, chemical shift (δ) ppm increases



Usually 7-10 ppm increments

Chemical shift δ can be calculated by eqⁿ for straight chain and branched alkanes

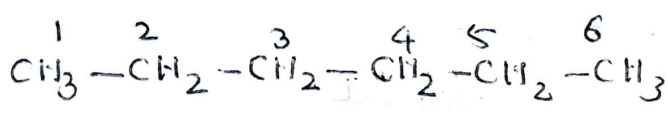
$$\delta_i = -2.6 + 9.1n_\alpha + 9.4n_\beta - 2.5n_\gamma + 0.3n_\delta$$

n_α = no of carbon bonded directly to ith carbon atom.

n_β = " " two bonds away

n_γ = " " three bond away

n_δ = " " four bond away.



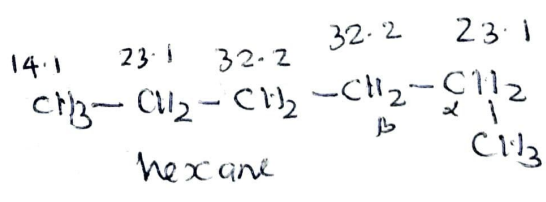
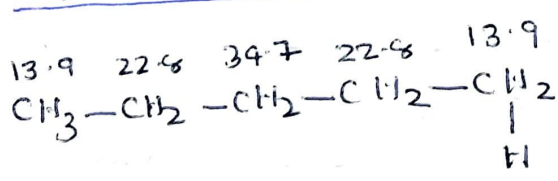
3 signals.

$$\begin{aligned} \text{C-1} &= -2.6 + 9.1 \times 1 + 9.4 \times 1 - 2.5 \times 1 + 0.3 \times 1 \\ &= 13.7 \text{ ppm (13.9)} \end{aligned}$$

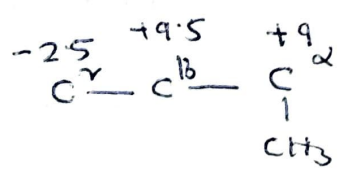
$$\begin{aligned} \text{C-2} &= -2.6 + 9.1 \times 2 + 9.4 \times 1 - 2.5 \times 1 + 0.3 \times 1 \\ &= 22.8 \text{ ppm} \end{aligned}$$

$$\begin{aligned} \text{C-3} &= -2.6 + 9.1 \times 2 + 9.4 \times 2 - 2.5 \times 2 + 0.3 \times 0 \\ &= 31.9 \text{ ppm} \end{aligned}$$

→ α, β, and γ effects



Pentane



Substituents on α, β carbon generally deshield the C nucleus, but γ position shields the nucleus.

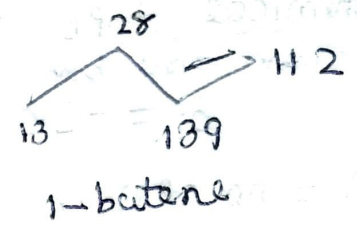
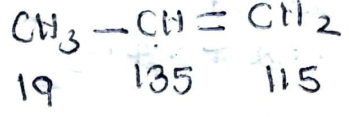
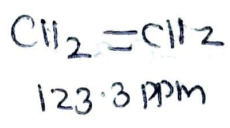
Hybridization of Carbon.

Sp³ hybridized C absorbs at high field - 0-60 ppm from TMS

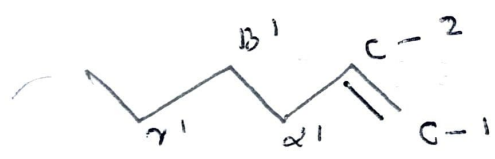
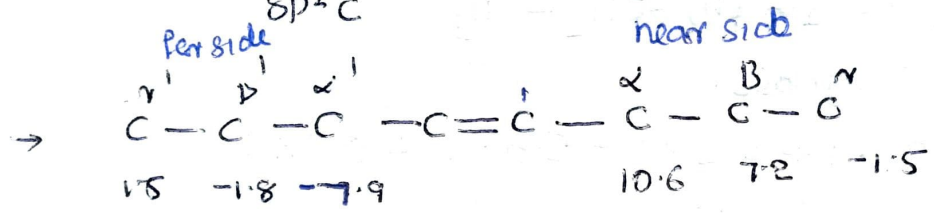
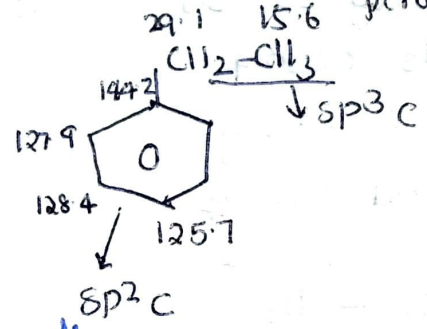
Sp² at low field (~ 110-150 ppm from TMS)

Sp intermediate value (65-90 ppm). Sp² C and

benzenoid C appears in same region (80-140 ppm)



propene



C-1 no substituent near C-1, but substituent on far side α', β', γ'

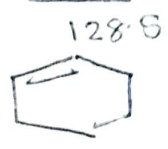
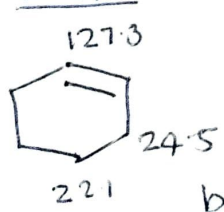
So $128.3 + (-7.9 + -1.8 + 1.5) = 115.1$
δ C₁ = 115.1

C-2 α, β, γ substituents on near side

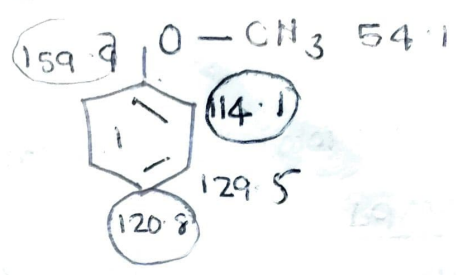
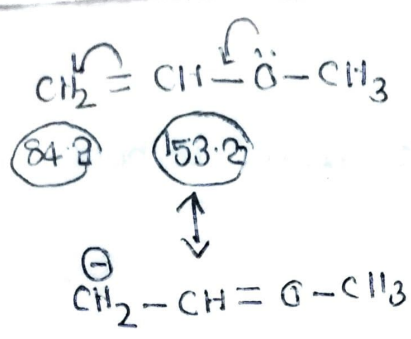
$128.3 + 10.6 + 7.2 - 1.5 = 139.6$
δ C₂ = 139.6 ppm

α terminal =CH₂ absorbs upfield than internal =CH-

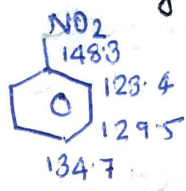
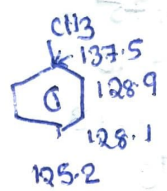
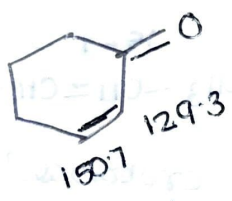
→ polar effects of substituents on unsaturated carbons



both olefinic and aromatic C come in same region.



→ methoxy group deshields the olefinic and aromatic carbon to which it is attached. The other carbons in the ortho/para positions are shielded due to electron donating ability of oxygen.



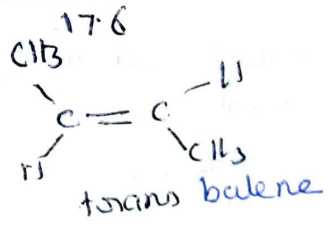
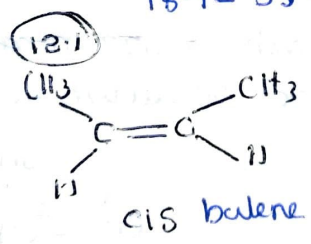
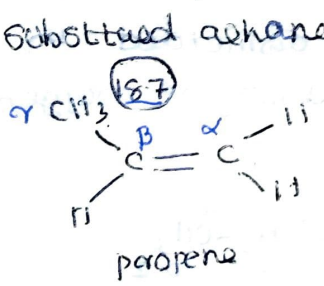
1,3,5 substitution on the benzene ring deshield the carbon.

The benzene carbon absorb at 128.5 ppm. The other correction factor can be applied

sub	C-1	ortho	para
H	0	0	0
CH	+16	+4	+5
CN	-16	+3	-2
Br	-5	+2	+5
COOCH ₃	+3		

γ-effect (stereoisomers of alkenes)

There is upfield shift at the γ carbon in the case of substituted alkene. $18.7 - 5.5 = 13.2$ (calc)



γ-methyl group in the cis isomer exerts a γ effect of -5.5 on the other (upfield)

→ presence of double bond

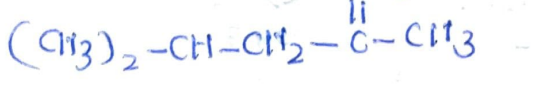
¹H NMR ~ 8 ppm
¹³C NMR 8 ~ 110 - 150 ppm

¹H NMR coupling constant and γ effect in ¹³C NMR are highly useful to deduce the stereoisomers of the alkene.

Carbonyl C

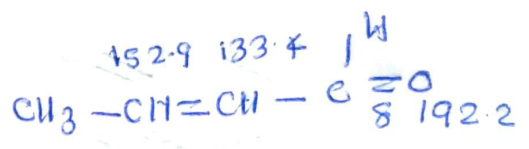
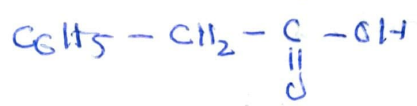
Varry from 150-220ppm. for carbonyl carbon

Compd	δ
ketones	205-220
aldehydes	200-210
carboxylic acid	175-185
1 ^o amide	170-180
ester and anhydride	165-175
2 ^o amide and imide	160-170



4-methyl-pentan-2-one

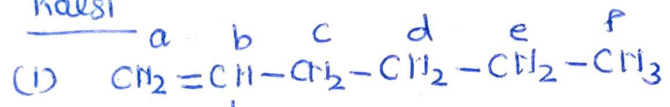
δ - 178.3



crotonaldehyde

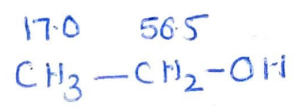
Problems

Kalsi

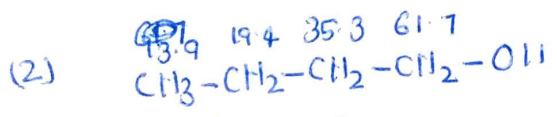


↓ ↓
114.3 139.2
6 signals

$sp^3 C$ δ 14.0 - 33.8
C, d, e, f

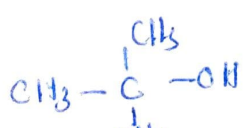


methyl and methylene carbons are more deshielded in ethanol than hex-1-ene bec² of electro negativity of oxygen

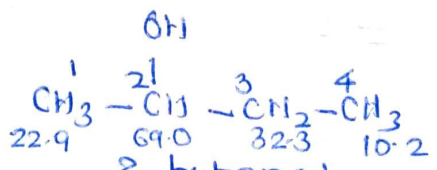


1-butanol
(n-butyl alcohol)

4 signals

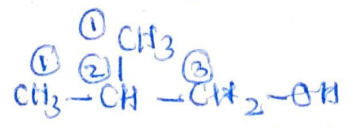


t-butyl alcohol (1 signal)

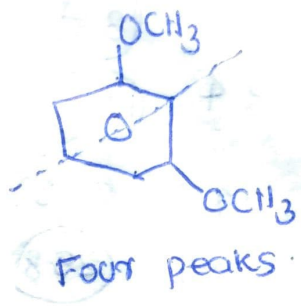
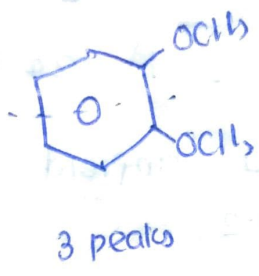
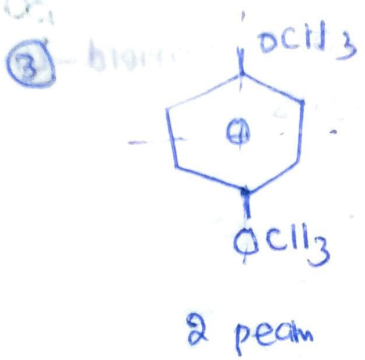


2-butanol
sec-butyl alcohol

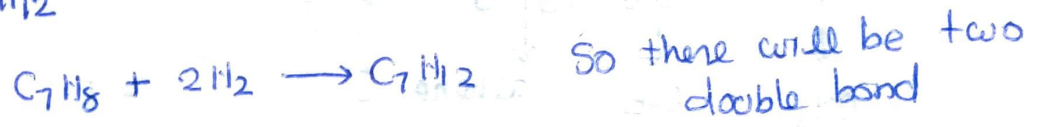
4 signals



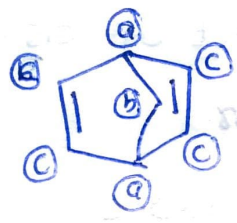
isobutyl alcohol



④ Organic compd C_7H_8 undergo catalytic hydrogenation to get C_7H_{12}

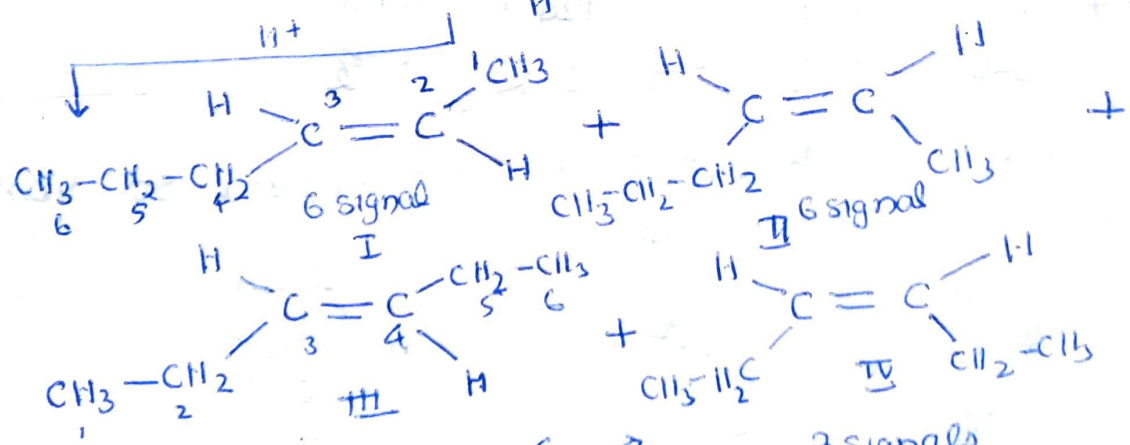
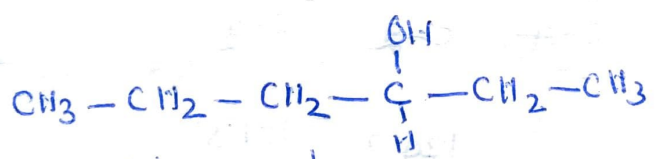


- δ 143 is due to equivalent double bonded carbon
- δ 75 is due CH_2 group
- δ 50 is due to tertiary CH group



- a - δ 50
- b - δ 75
- c - δ 143

⑤

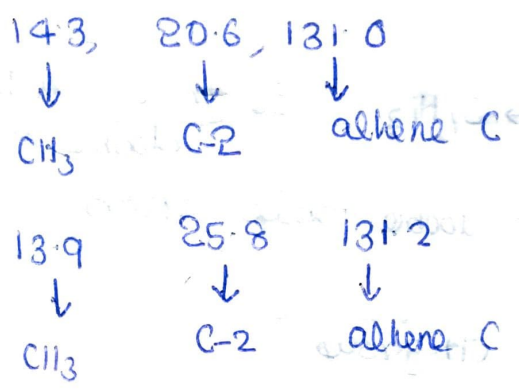


3 signals
14.3, 20.6, 131.0
cis isomer
upfield

3 signals
13.9, 25.8, 131.2
trans isomer

I	12.3	13.5	23.0	29.3	123.7	130.6	upfield - cis
II	13.4	17.5	23.1	35.1	124.7	131.5	
III	14.3	20.6	131.0				upfield - cis
IV	13.9	25.8	131.2				

Isomers III and IV will be 3-hexes, bec2 each shows 3 signals only.

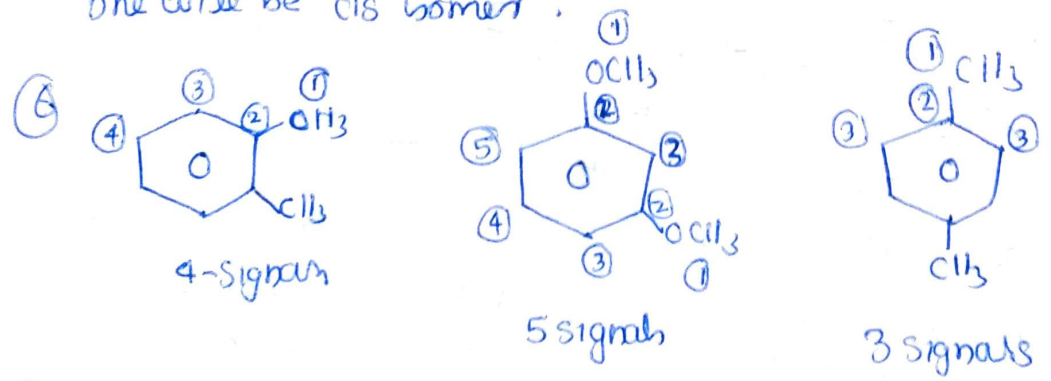


→ C-2 carbon differs by 5ppm (8 effect of cis-trans bond) upfield is III so it will be cis isomer.

2-hexene

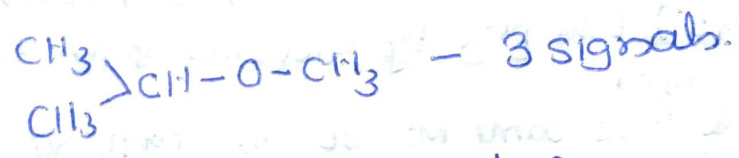
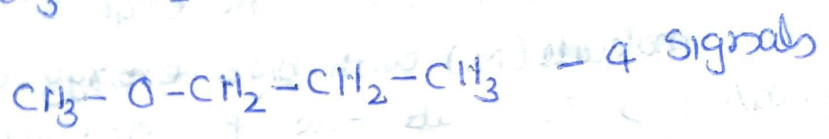
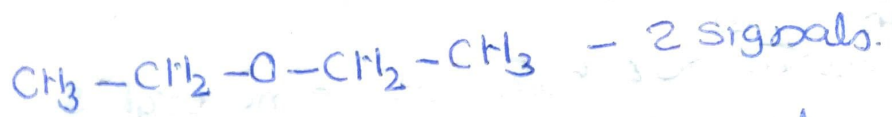
I	12.3	13.5	23.0	29.3	123.7	130.6
	C-1	C-6	C-5	C-4	C-2	C-3
II	13.4	17.5	23.1	35.1	124.7	131.5
	C-1	C-6	C-5	C-4	C-2	C-3

In isomer two signals are about 5ppm upfield so isomer one will be cis isomer.

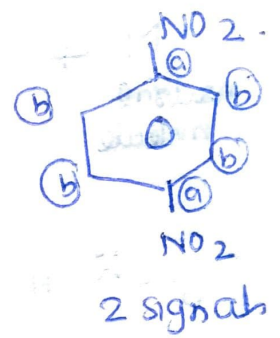
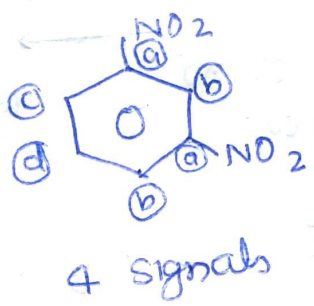
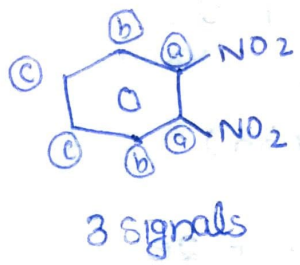


⑦ There are 2 isomeric ethers for molecular formula C₄H₁₀O. Name them how many signals were cause in ¹³C NMR spectrum.

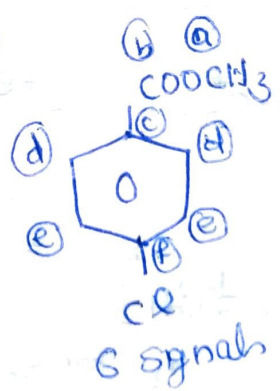
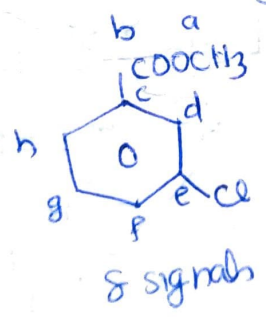
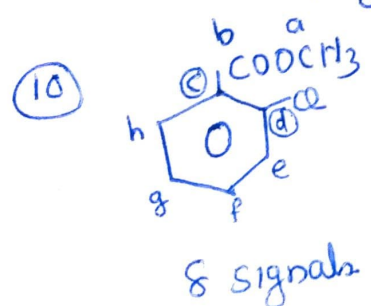
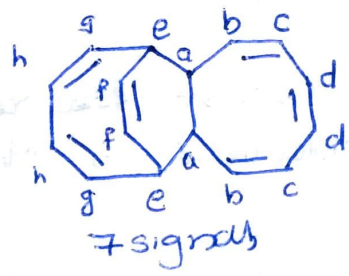
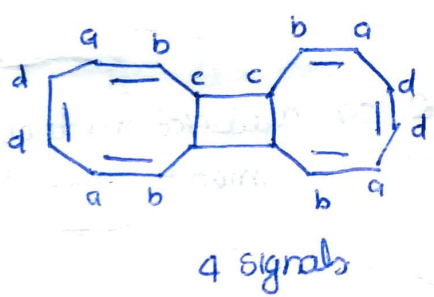
$C_4H_{10}O$



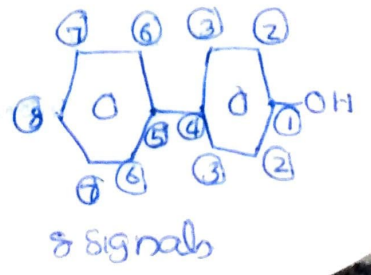
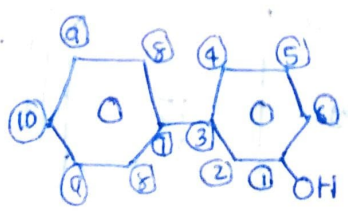
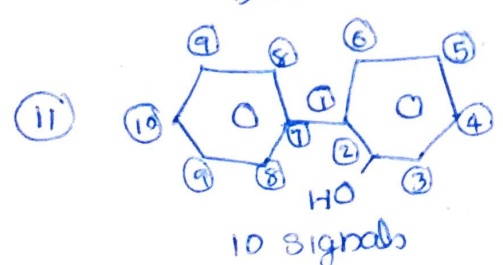
8) How can you differentiate?



9) In the structures given below, represent the dimer of cyclooctatetraene. The actual structure shows 4 signals in ^{13}C NMR spectrum, which is the correct spectrum.



chloro methyl benzene



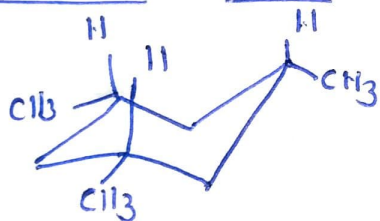
59
9447527465

Carbon-13 NMR Spectroscopy (^{13}C NMR) - Kalsi

^{13}C NMR is less sensitive than ^1H NMR due to the following reasons.

- Most abundant isotope of carbon ^{12}C ($\sim 99\%$) is not detectable by nuclear magnetic resonance (even no. of p and neutron - no magnetic spin), whereas less abundant isotope of C i.e. ^{13}C (1.1%) is having a magnetic spin = $\frac{1}{2}$.
- Magnetic resonance of ^{13}C is much weaker. Thus due to only 1% carbon atoms in a sample being the magnetic isotope, the sensitivity of ^{13}C NMR is ↓ by a factor of 100.
- Gyromagnetic ratio of ^{13}C being only one-fourth that of a proton, the ^{13}C resonance frequency is only one-fourth of that for ^1H NMR (at a given mag field).

Diastereomers of 1,3,5-trimethylcyclohexane - proton decoupled spectra



1-cis, 3-cis, 5-trimethylcyclohexane

All the 3 methyl groups are equatorial and show one signal.
+ all CH_2 carbons are equivalent
+ all CH carbons are equivalent
Total - 3



CH_3
1-cis, 3-trans, 5-trimethylcyclohexane

(6 signals)
C @ equatorial methyl C + 1 axial methyl C + 1 CH_2 groups adjacent to the equatorially sub C + 2 CH_2 groups adjacent to the axially sub C + 2 equatorial C-H carbons + 1-axial CH carbon)

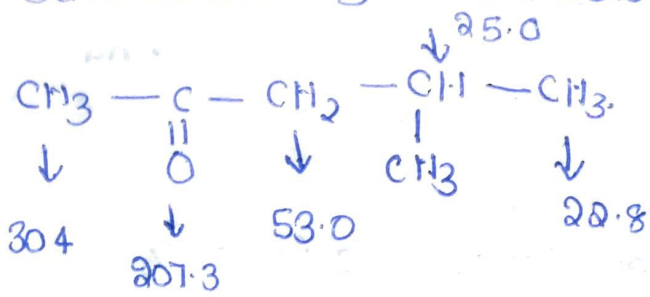
Total - 6

→ Chemical shift is 15-20 times greater than protons.

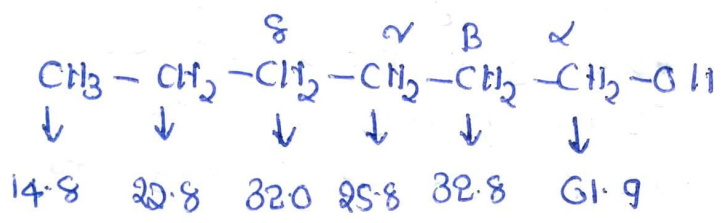
→ Deshielding effect of electronegative moiety

An electronegative substituent, eg: $\text{C}=\text{O}$, halogen atoms on a carbon atom brings downfield shift in resonance relative

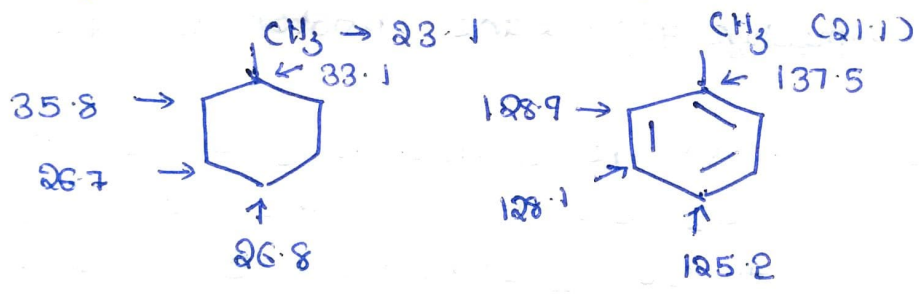
to a saturated hydrocarbon.



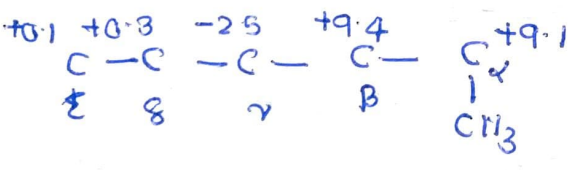
→ a small shielding effect of an electronegative element. An electronegative element brings deshielding shift for α and β carbons, but upfield shift for γ carbon



→ hybridization of C atom

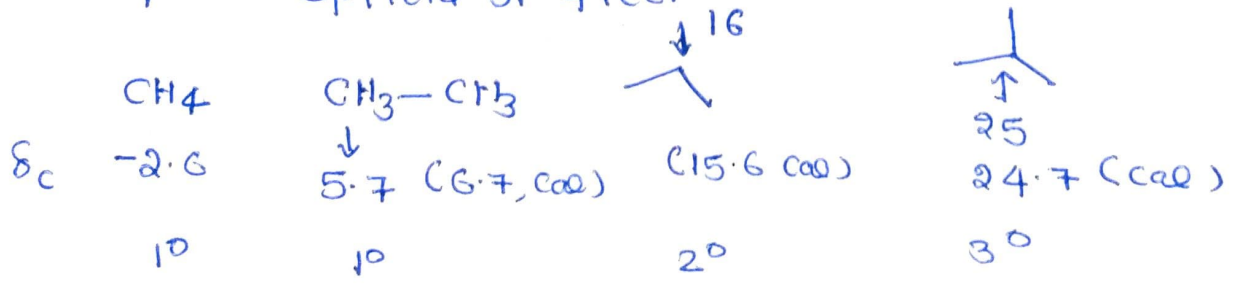


→ α, β, γ effects (straight chain hydrocarbon)



A methyl substituent effect the chemical shift and it is remarkably additive in nature

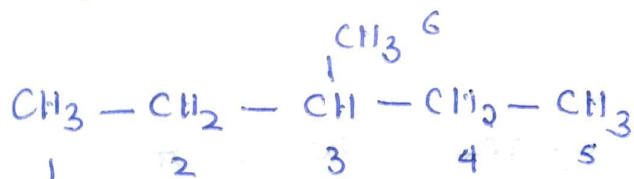
- α, β - downfield effect
- γ - upfield effect



1^o → 3^o (S-increases)

→ Calculation of chemical shift in straight chain alkanes + branched alkanes

$$\delta_i = -2.6 + 9.1 n_\alpha + 9.4 n_\beta - 2.5 n_\gamma + 0.3 n_\delta$$



For C-1 - $1\alpha + 1\beta + 2\gamma + 1\delta$

$$C-1 = -2.6 + 9.1 \times 1 + 9.4 \times 1 + -2.5 \times 2 + 0.3 \times 1 = 11.2 \text{ (11.3)}$$

For C-2 - $2\alpha + 2\beta + 1\gamma$

$$C-2 = -2.6 + 9.1 \times 2 + 9.4 \times 2 + -2.5 \times 1 + -2.5 \times 1 = 29.4 \text{ (29.3)}$$

C-2 is a 2° carbon with attached a 3° carbon. Correction for branching [$2^\circ(3^\circ) = -2.5$].

For C-3 - $3\alpha + 2\beta$

$$C-3 = -2.6 + 9.1 \times 3 + 9.4 \times 2 + -3.7 \times 2 = 36.1 \text{ (36.7)}$$

C-3 is a 3° carbon attached 2° atom. Correction for branching $3^\circ(2^\circ) = -3.7$

For C-6 - $1\alpha + 2\beta + 2\gamma$

$$C-6 = -2.6 + 9.1 \times 1 + 9.4 \times 2 + -2.5 \times 2 + -1.1 \times 1 = 19.2 \text{ (18.6)}$$

C⁶ is a 1° carbon attached 3° atom. Correction $1^\circ(3^\circ) = -1.1$

Corrections for branching ✓

$$1^\circ(3^\circ) = -1.1$$

$$3^\circ(2^\circ) = -3.7$$

$$1^\circ(4^\circ) = -3.4$$

$$3^\circ(3^\circ) = -9.5$$

$$2^\circ(3^\circ) = -2.5$$

$$4^\circ(1^\circ) = -1.5$$

$$2^\circ(4^\circ) = -7.2$$

$$4^\circ(2^\circ) = -8.4$$

γ -effect

γ -effect has been assigned the value (-2.5) which is the weighted average for open chain conformers. A γ carbon could be either gauche or anti to the

