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Introduction to Spectroscopy: Spectroscopic Identification of Organic Compounds

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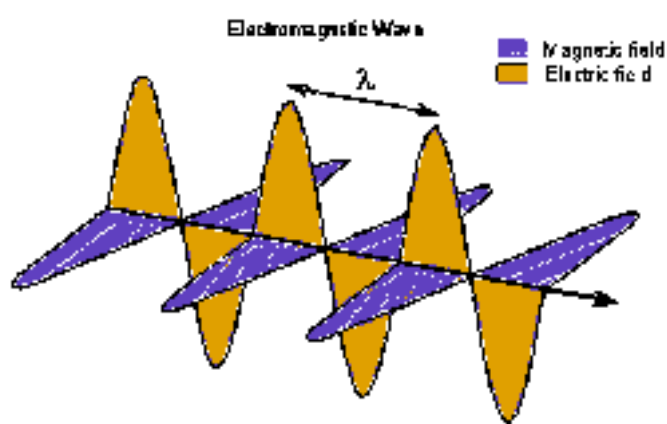
By Mutasem Z. Bani-Fwaz
Introduction to Spectroscopy

Spectroscopy:

The study of the interaction of electromagnetic radiation with atoms or molecules to determine their structures.

Electromagnetic Radiation:

A propagating wave of electrical energy with an orthogonal magnetic component oscillating with exactly the same frequency.



$$C = \lambda \nu$$

C: Speed of light 3×10^8 m/s λ : Wavelength of radiation

ν : Frequency of electromagnetic radiation

$$E = h\nu = hc/\lambda$$

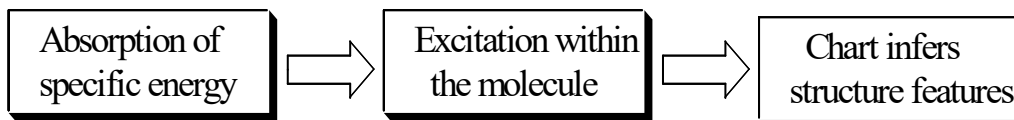
E: Energy of electromagnetic Radiation, h: Plank's constant 6.62×10^{-34} Js

As the energy increase, the wavelength decrease and vice versa

Regions of Electromagnetic Radiation Spectrum

| X-Ray | Ultraviolet | Visible | | Infrared | Micro wave | Radio frequency |
|-------|-------------|---------------|-------------|------------|---------------|--------------------|
| | 200 nm | 400 nm 800 nm | 2.5 μ m | 15 μ m | 1m | 3m |

The Wavelength increase, The Energy decrease



Types of Energy Transition in Each Region of the Electromagnetic Radiation

| Region of Spectrum | Energy Trasitions |
|----------------------|----------------------------|
| X-Rays | Bond Braking |
| Ultraviolet/ Visible | Electronic Transition |
| Infrared | Vibrational |
| Microwave | Rotational |
| Radiofrequency | Nuclear Magnetic Resonance |

Empirical Formula:

The simplest ratio between the atoms in the molecule



Molecular Formula

The exact ratio between the atoms in the molecule

The Index of Hydrogen Deficiency (IHD)

(Degree of Unsaturation)

$$IHD = \frac{2C + 2 - H + N - X}{2}$$

IHD = zero i.e. Saturated compound

IHD = 1 i.e. the compound contains **C=O**, or **C=C**, or **one ring**

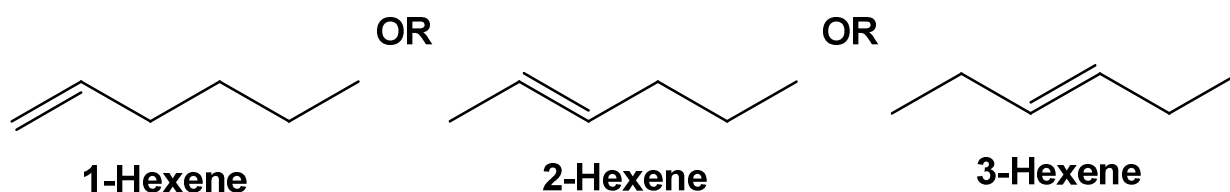
IHD = 2 i.e. the compound contains a **triple bond**; or **two double bonds**; or **two rings**; or one of each

IHD = 3 (2+1) or (1+1+1)

IHD = 4 i.e. the compound contains **benzene ring**

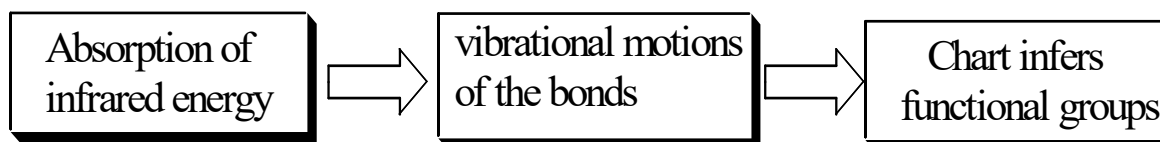
IHD = 5 (4 + 1).....

Example: A hydrocarbon has a molecular formula of C_6H_{12} It will react with one mole of hydrogen in the presence of palladium catalyst to give a compound of formula C_6H_{14} Give a possible structure. (IHD = 1)



Infrared Spectroscopy

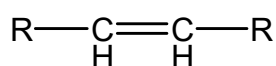
Spectroscopic tool used for identification of the functional groups (with covalent bonds) in organic compounds



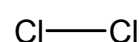
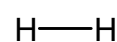
Only those bonds, which have a dipole moment, are capable of absorbing infrared radiation. Symmetric bonds like H-H or Cl-Cl will not absorb infrared radiation. The bond must be unsymmetric.



Symmetric Alkynes

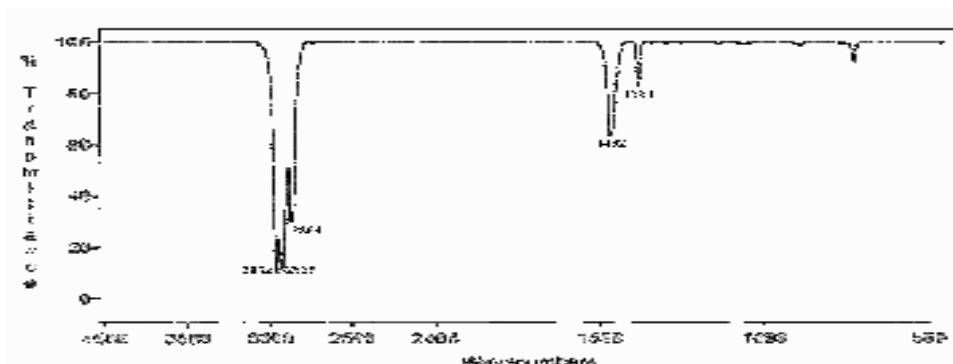


Symmetric Alkenes



The Chart (Spectrum) of the IR is a relation between % of Transmittance (% T) and the Wavenumber $\bar{\nu}$ (reciprocal of wavelength) The range of spectrum extends from 4000 to 650 cm^{-1}

$$\bar{\nu} = \frac{1}{\lambda} \quad (\text{cm}^{-1})$$

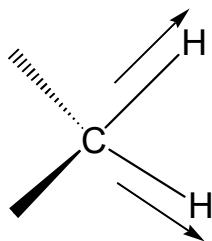


Finger Print Region

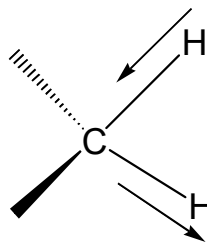
The region, which is specific for each compound (650-1430 cm^{-1})

The Modes of Vibration

1- Stretching Vibrations: Change in the bond length

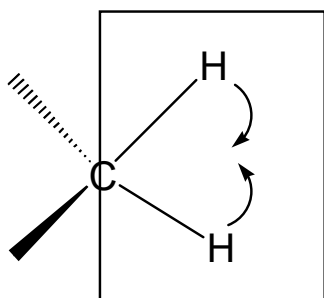


Symmetric Stretching

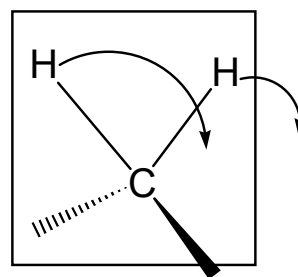


Asymmetric Stretching

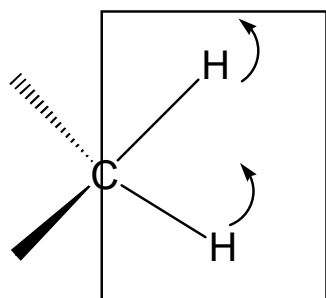
2- Bending Vibrations: Change in the bond angle



Scissoring

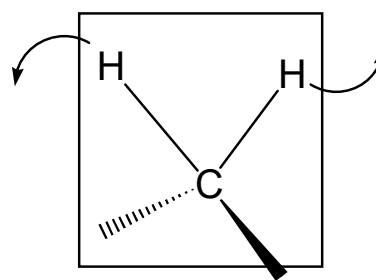


Wagging



Rocking

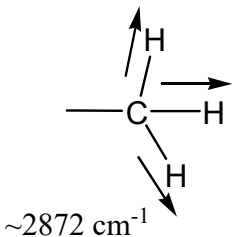
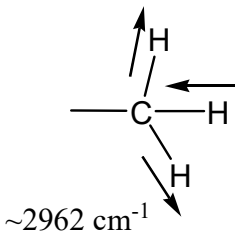
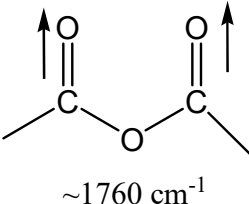
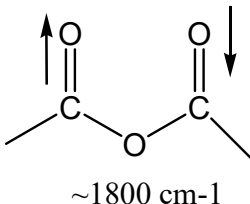
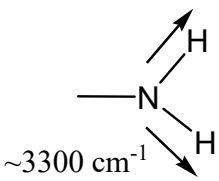
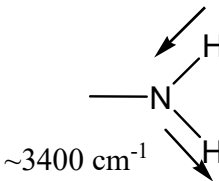
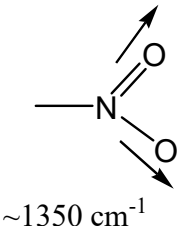
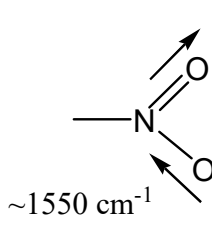
In Plane



Twisting

Out of Plane

For the groups of three or more atoms (at least two atoms are identical) they have two modes of stretching (symmetric and asymmetric) as shown in the given Table.

| | Symmetric Stretching | Asymmetric Stretching |
|-----------|---|--|
| Methyl |  ~2872 cm ⁻¹ |  ~2962 cm ⁻¹ |
| Anhydride |  ~1760 cm ⁻¹ |  ~1800 cm ⁻¹ |
| Amino |  ~3300 cm ⁻¹ |  ~3400 cm ⁻¹ |
| Nitro |  ~1350 cm ⁻¹ |  ~1550 cm ⁻¹ |

Overtone bands: resulted from excitation of the molecule from ground state to higher energy states (multiple integer of fundamental frequencies 2ν , 3ν , ... etc).

Combination band: coupling of two vibrational frequencies ($\nu_{\text{comb.}} = \nu_1 + \nu_2$).

Difference band: difference of two vibrational frequencies ($\nu_{\text{diff.}} = \nu_1 - \nu_2$).

Fermi Resonance: Coupling of fundamental frequency with an overtone or combination band

Calculation of Vibrational Frequencies

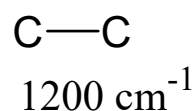
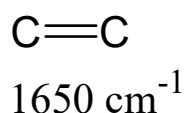
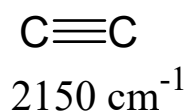
Hook's Law

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{K/\mu}$$

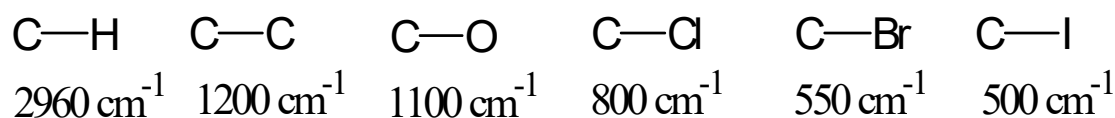
K : Force constant = 5×10^5 dyne/cm of single bond
 = 10×10^5 dyne/cm of double bond
 = 15×10^5 dyne/cm of triple bond

μ ; reduced mass

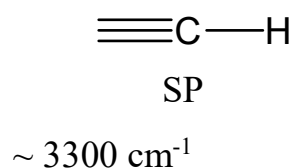
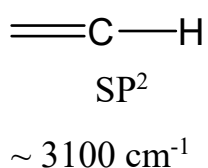
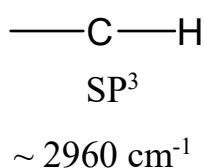
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$



As the atom bonded to carbon increase in mass, μ will increase and $\bar{\nu}$ will decrease

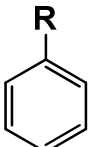
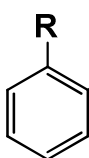
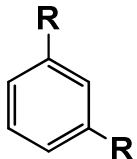
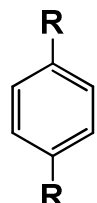


The bond is stronger in the order $\text{SP} > \text{SP}^2 > \text{SP}^3$

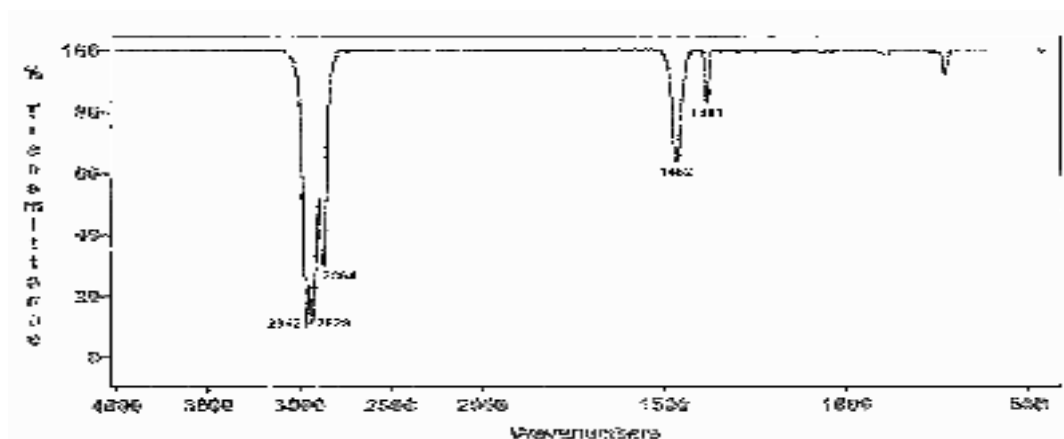


Wavenumber ($\bar{\nu}$) of Functional Groups

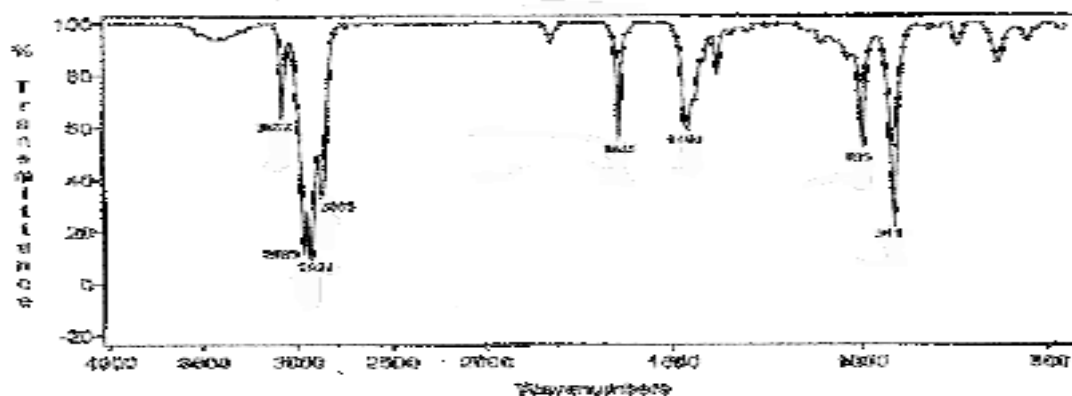
| | | | |
|---|--|--------------------------|------------------------------------|
| Alkanes $\text{R-CH}_2\text{-CH}_3$ | $\text{C-H} \sim 2960 \text{ cm}^{-1}$ $\text{CH}_2 = \sim 1450 \text{ cm}^{-1}$ $\text{CH}_3 = \sim 1375 \text{ cm}^{-1}$ | | |
| Alkenes RHC=CH_2 | $=\text{C---H} \sim 3100 \text{ cm}^{-1}$ | C=C | $1660\text{-}1600 \text{ cm}^{-1}$ |
| Alkynes $\text{RC}\equiv\text{CH}$ | $\equiv\text{C---H} \sim 3300 \text{ cm}^{-1}$ | $\text{C}\equiv\text{C}$ | $\sim 2150 \text{ cm}^{-1}$ |

| | | |
|---------------------------------------|---|---|
| Aromatic | $\text{=C—H} \sim 3100 \text{ cm}^{-1}$ | $\text{C=C} \quad 1600, 1475 \text{ cm}^{-1}$ |
| |  $\sim 3100 \text{ cm}^{-1}$ $1600, 1475 \text{ cm}^{-1}$ $\sim 690, 750 \text{ (s)} \text{ cm}^{-1}$ |  $\sim 3100 \text{ cm}^{-1}$ $1600, 1475 \text{ cm}^{-1}$ $\sim 750 \text{ (s)} \text{ cm}^{-1}$ |
| |  $\sim 3100 \text{ cm}^{-1}$ $1600, 1475 \text{ cm}^{-1}$ $\sim 690, 780, 880 \text{ (s)} \text{ cm}^{-1}$ |  $\sim 3100 \text{ cm}^{-1}$ $1600, 1475 \text{ cm}^{-1}$ $\sim 800\text{-}850\text{(s)} \text{ cm}^{-1}$ |
| | | |
| Alcohols $\text{R-CH}_2\text{-OH}$ | O-H (Free of H-bond) $3650\text{-}3600 \text{ cm}^{-1}$ C-O $1250\text{-}1000 \text{ cm}^{-1}$ | |
| Phenols Ar-OH | O-H (H-bond) $3500\text{-}3200 \text{ cm}^{-1}$ C-O $1250\text{-}1000 \text{ cm}^{-1}$ | |
| Ethers R-C-O-C-R | C-O $1300\text{-}1000 \text{ cm}^{-1}$ Aryl ether, Vinyl ether, Epoxides, Acetals, Ketals | |

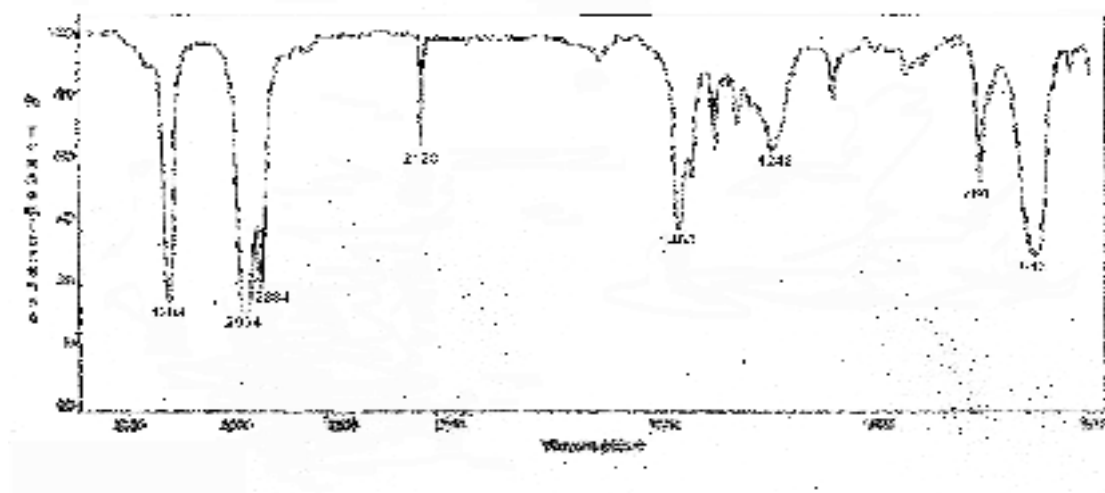
Hexane (C_6H_{14})



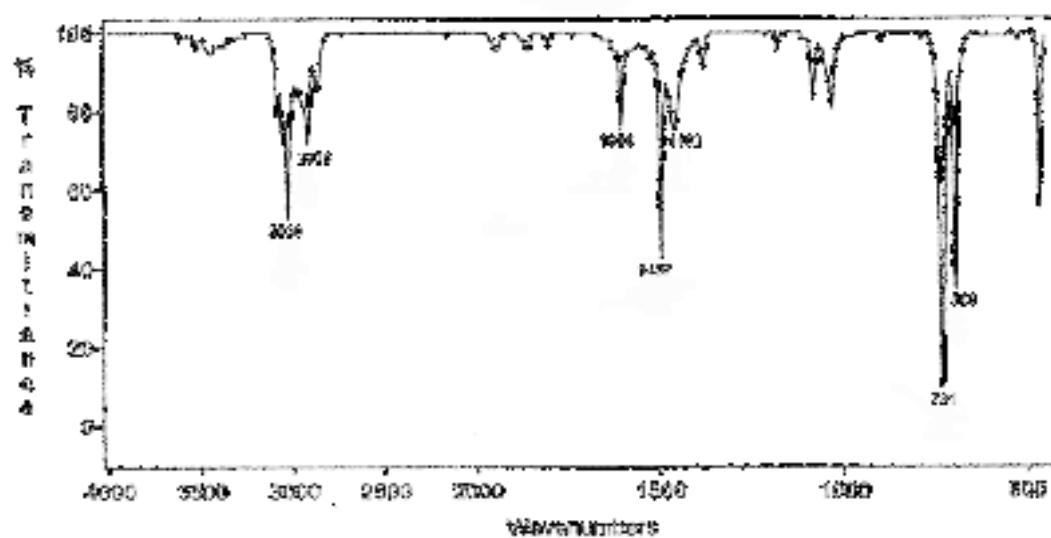
1-Hexene (C_6H_{12})



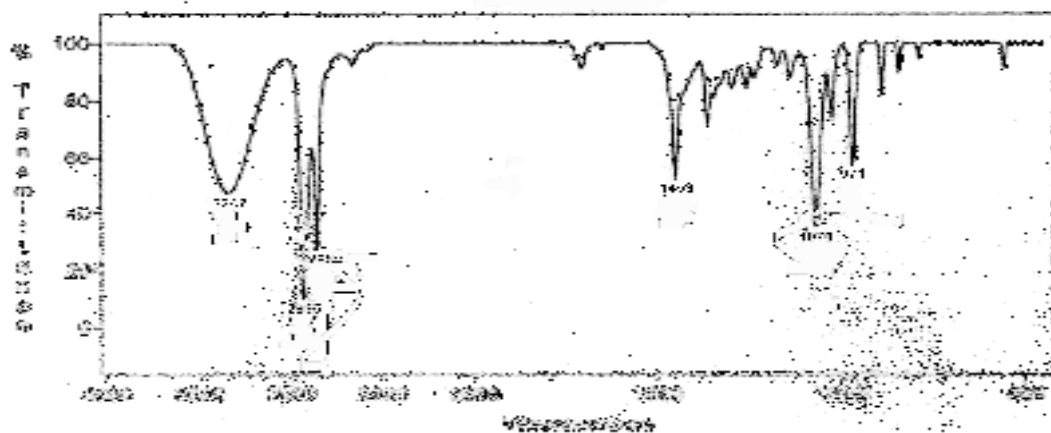
1-Hexyne (C_6H_{10})



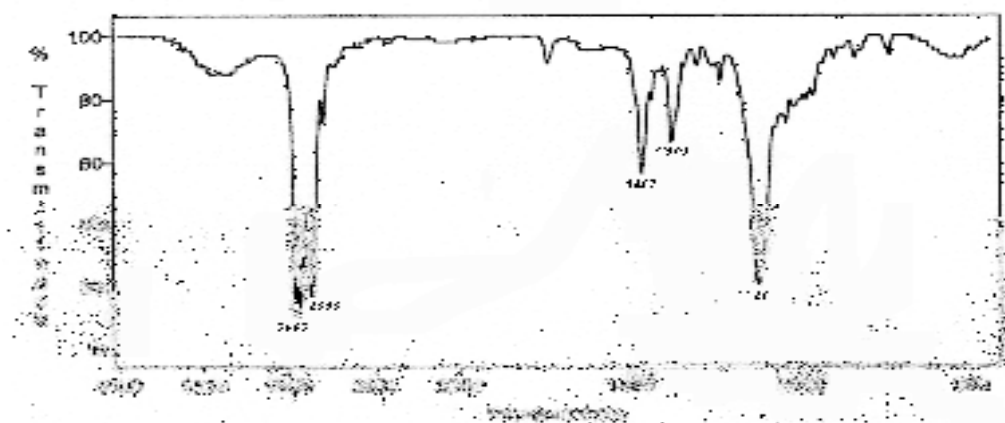
Toluene (C_7H_8)



Cyclohexanol



Dibutyl ether

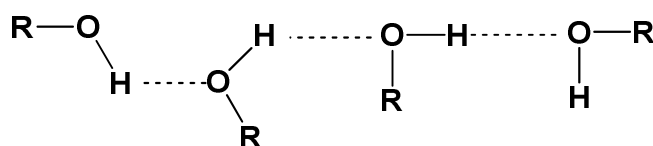


Types of Hydrogen Bonds

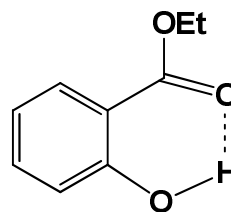
1- Intermolecular H-bond: Between one molecule and other molecule. Many kinds of OH bonds of different lengths and strengths leads to a **broad absorption**.

This type of bands are largely decreases by dilution and the peak of (OH) group changes from broad into sharp.

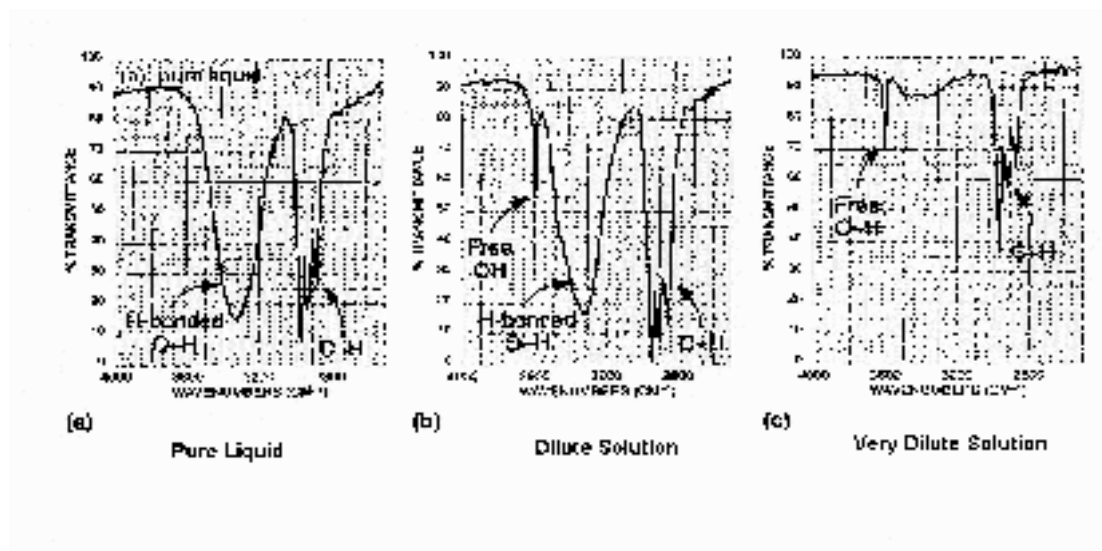
2- Intramolecular H-bond: Within the same molecule and the shape of the peak not affected by dilution



Intermolecular H-bond



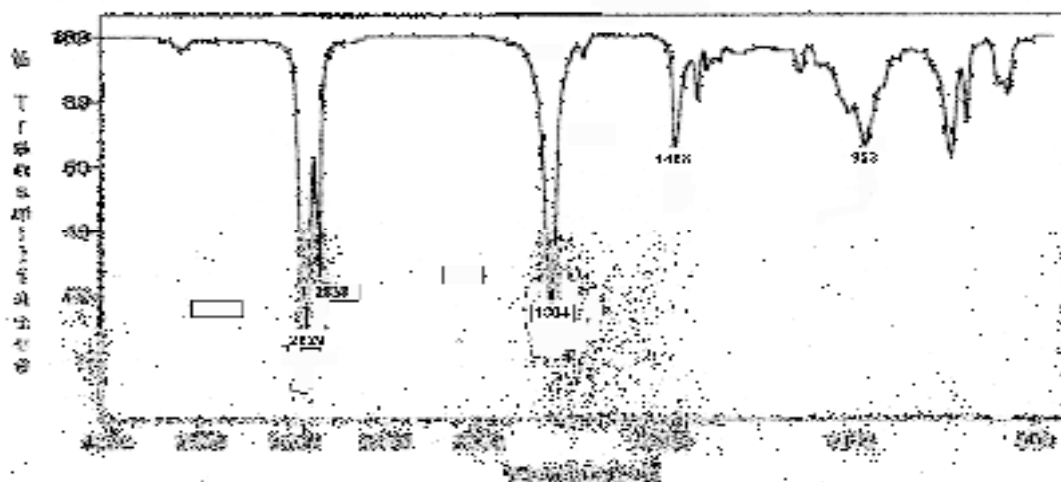
Intramolecular H-bond



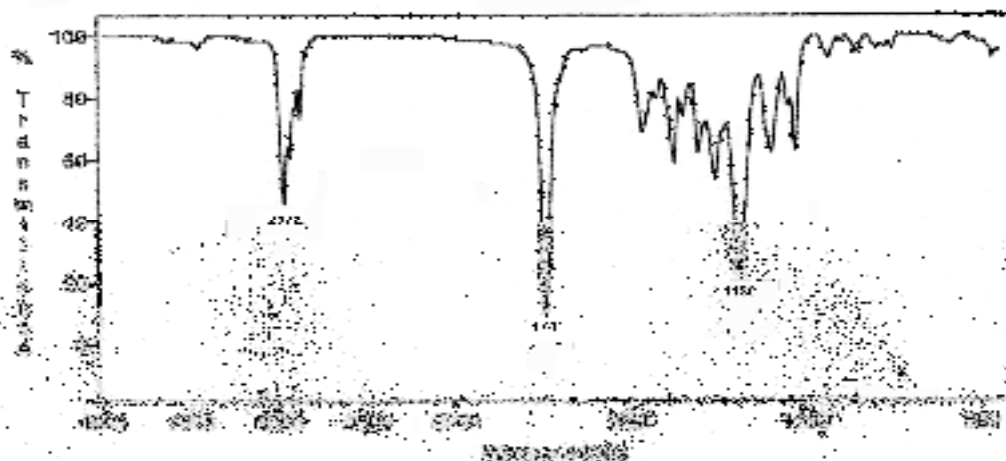
Wave numbers of carbonyl compounds (C=O)

| | | | |
|---|--|--|---|
| a) Anhydride $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}$ | C=O two bands at 1830-1800 cm^{-1} and 1775-1740 cm^{-1} C-O 1300 ~1000 cm^{-1} | e) Aldehydes $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ | C=O at ~1725 cm^{-1} C-H of (CHO) has two weak bands at 2750 and 2850 cm^{-1} |
| b) Acid Chloride $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$ | C=O ~ 1800 cm^{-1} | f) Ketones $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R}'$ | C=O ~ 1715 cm^{-1} |
| c) Esters $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{R}'$ | C=O ~ 1735 cm^{-1} C-O 1300 ~1000 cm^{-1} | g) Amides $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2$ | C=O at ~1690-1640 cm^{-1} and for NH_2 (1ry amide) has two bands at ~3400 and 3100 cm^{-1} |
| d) Carboxylic acid $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$ | C=O 1730-1700 cm^{-1} and O-H very broad band at 3400-2400 cm^{-1} C-O 1300 ~1200 cm^{-1} | $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHR}'$ | for NH (2ry amide) has one band at ~3200 cm^{-1} |

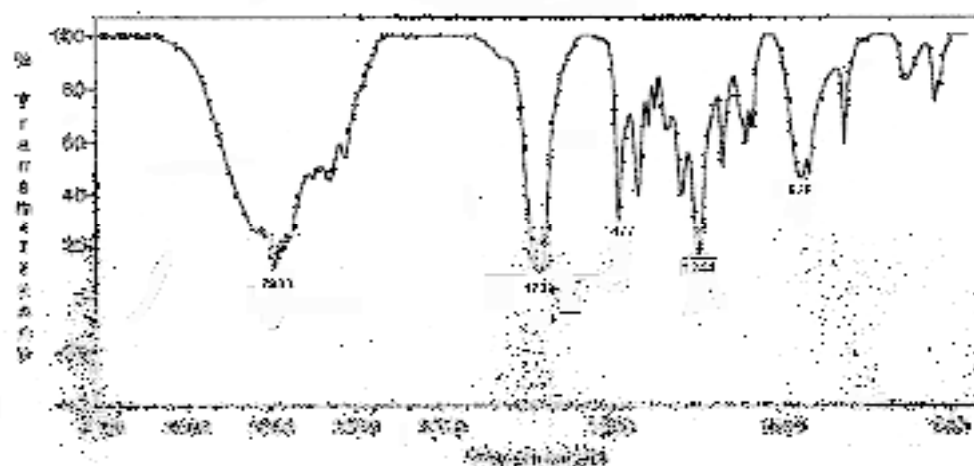
Acid Chloride



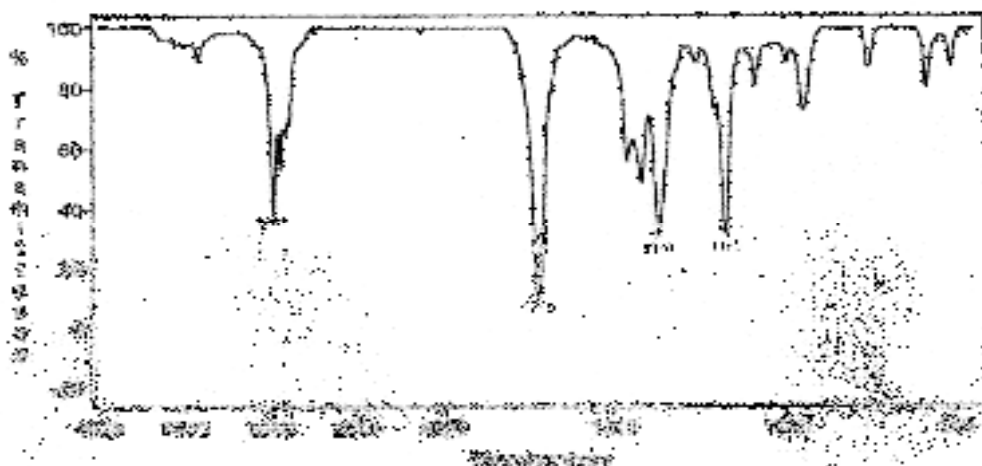
Ester



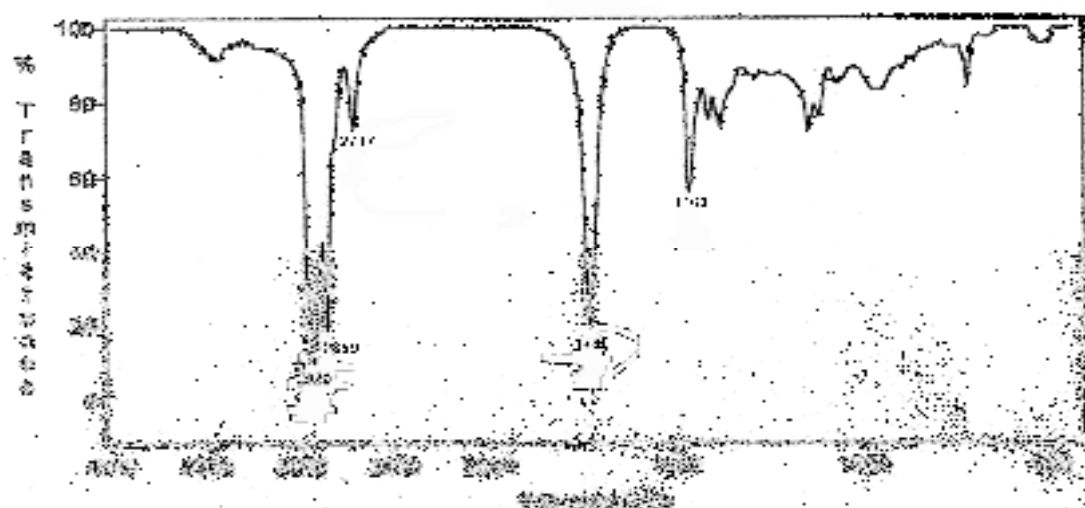
Carboxylic Acid



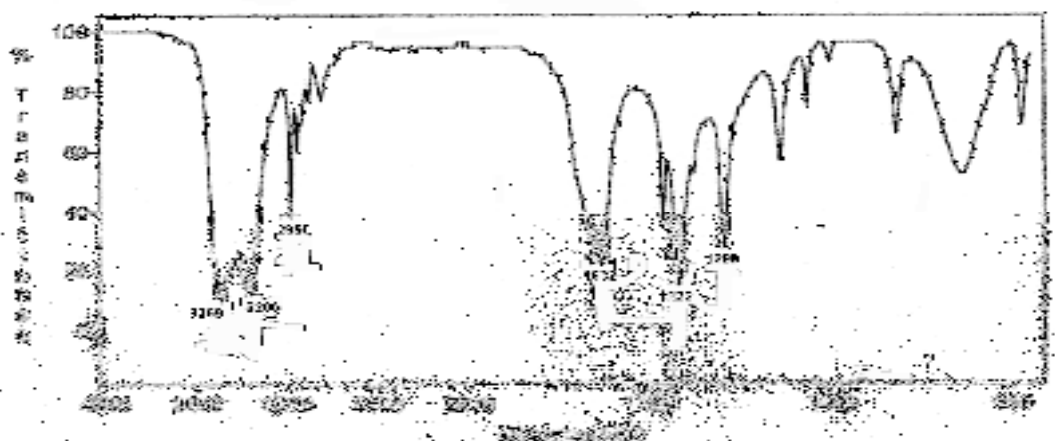
Ketone



Aldehyde



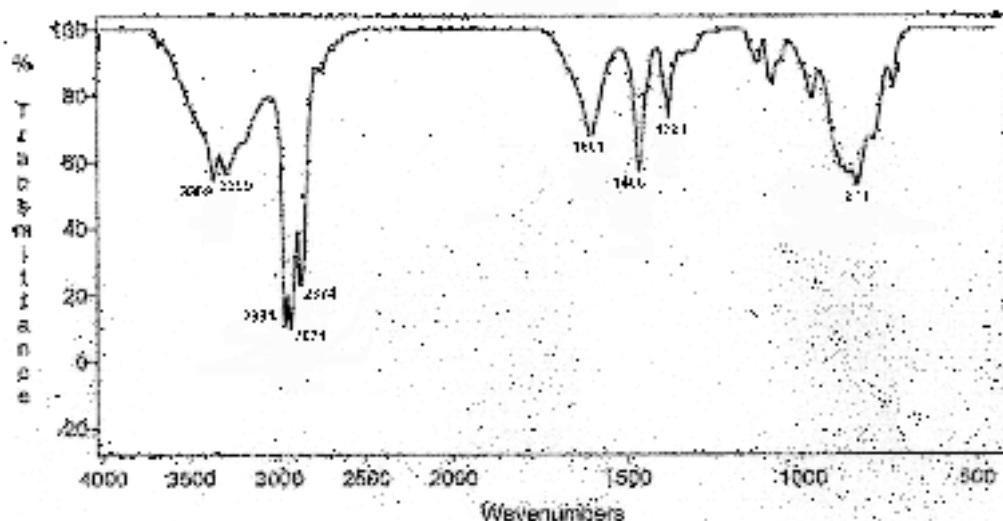
Amide



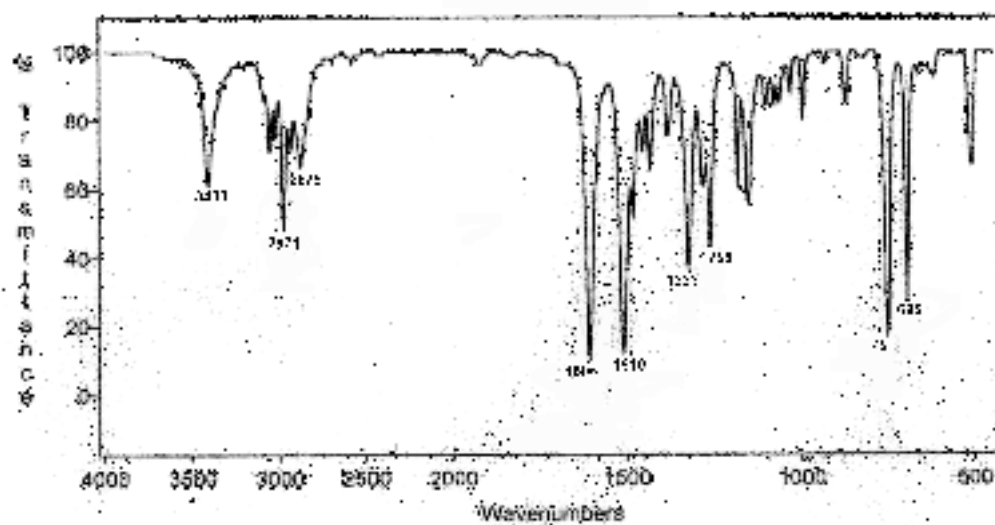
Wave numbers of other functional groups

| | |
|--|---|
| Amines $R-NH_2$ (1ry amines) $RNHR'$ (2ry amines) $RNR'R''$ (3ry amines) | NH_2 has two bands at $3500 - 3300\text{ cm}^{-1}$ NH has one band at $\sim 3200-3100\text{ cm}^{-1}$ has no band |
| Nitrile RCN | $C\equiv N$ one band at $\sim 2250\text{ cm}^{-1}$ |
| Isocyanates $R-NCO$ | $N=C=O$ one band at $\sim 2270\text{ cm}^{-1}$ |
| Isothiocyanates $R-NCS$ | $C=N$ one band at $\sim 1690-1640\text{ cm}^{-1}$ |
| Nitro Compounds RNO_2 $ArNO_2$ | NO_2 has two bands at $\sim 1600-1500\text{ cm}^{-1}$ and $\sim 1390-1350\text{ cm}^{-1}$ |

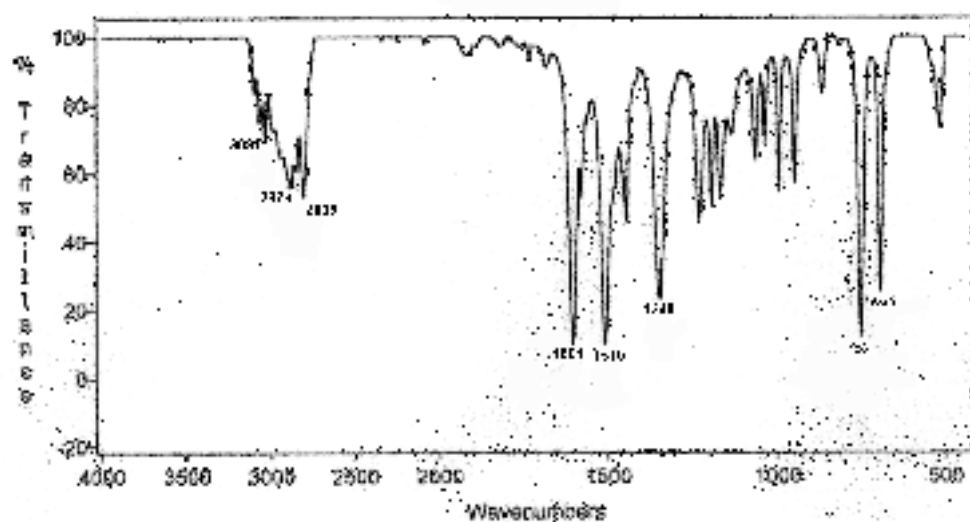
Primary Ammonies



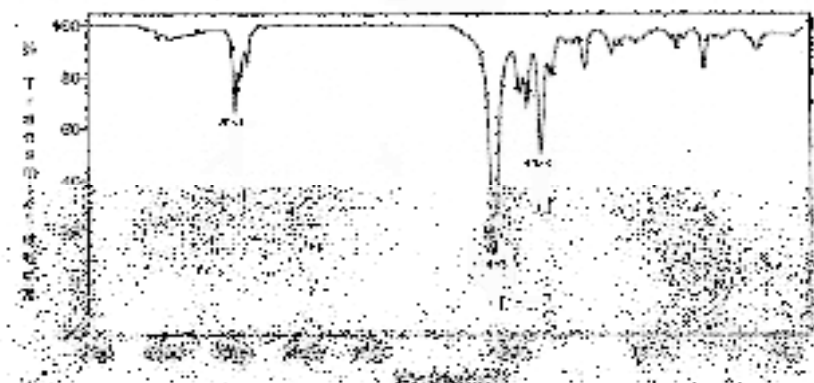
Secondary Amines



Tertiary Amines



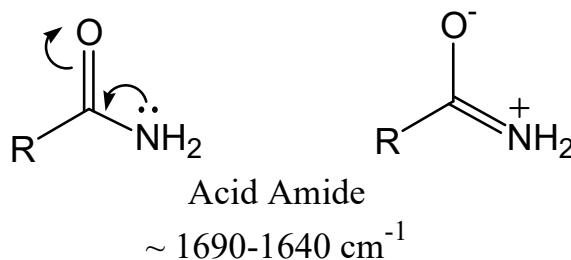
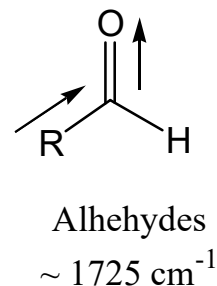
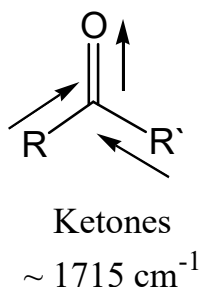
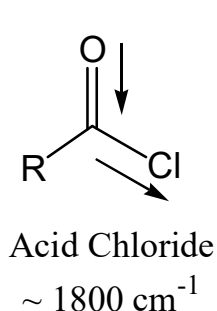
Nitro Compound



Factors Affecting on Vibrational Frequency ($\bar{\nu}$) on (C=O)

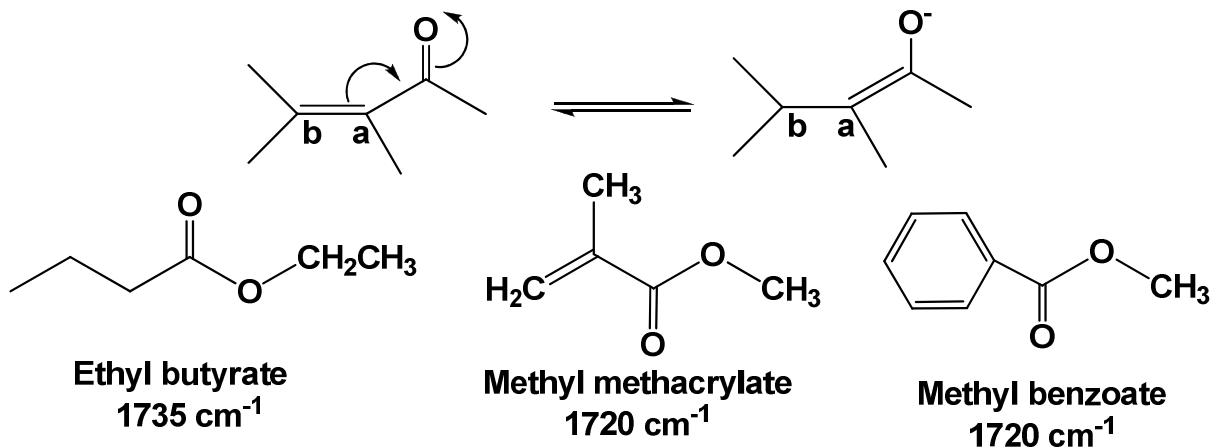
1. Inductive (I) and Resonance (R) Effect

The groups with (-I) will shift the electrons and increase the **double bond character** (the force constant will increase) and thus ($\bar{\nu}$) will increase. On the other hand, the groups with (+I) or (+R) will enhance the polarization and decrease the **double bond character** (the force constant will decrease) and thus ($\bar{\nu}$) will decrease.

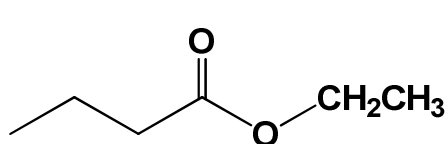


2. Effect of Conjugation

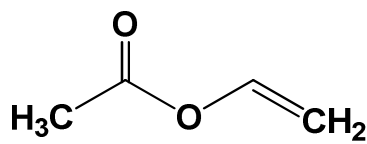
Conjugation of (C=O) or (C=C) with α,β -unsaturation or aryl group leads to polarization of the double bond, thus decrease double bond character and decrease ($\bar{\nu}$)



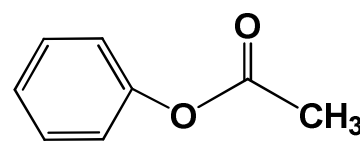
In case of ester, conjugation of oxygen atom with α,β -unsaturation or aryl group leads to increase ($\bar{\nu}$) of (C=O) group.



Ethyl butyrate
1735 cm^{-1}



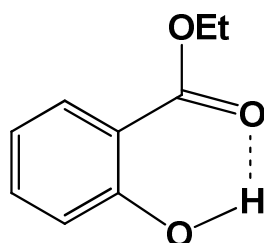
Vinyl acetate
1770 cm^{-1}



Phenyl acetate
1770 cm^{-1}

3. Effect of Hydrogen Bond

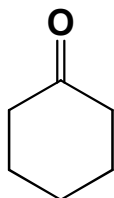
H-bond increase the length of (C=O) group and decrease the force constant, thus decrease the ($\bar{\nu}$)



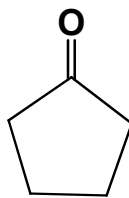
Ethyl salicylate ($\bar{\nu}$) = 1680 cm^{-1}

4. Effect of Ring Strain

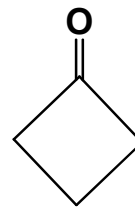
In case of cyclic ketones, cyclic esters (Lactones) and cyclic amides (Lactams) as the ring size decrease the ($\bar{\nu}$) increase due to the increasing of s-character of (C=O) group.



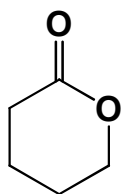
Cyclohexanone
1715 cm^{-1}



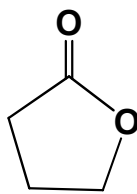
Cyclopentanone
1750 cm^{-1}



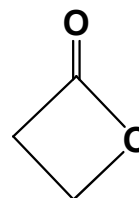
Cyclobutanone
1775 cm^{-1}



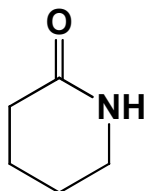
d-Valerolactone
1735 cm⁻¹



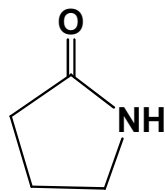
g-Butyrolactone
1770 cm⁻¹



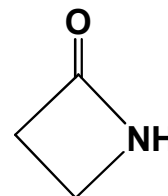
b-Propionolactone
1785 cm⁻¹



d-Valerolactame
1660 cm⁻¹



g-Butyrolactame
1705 cm⁻¹



b-Propionolactame
1745 cm⁻¹

Interpretation for IR Chart

Is (C=O) group is present

1640 - 1830 cm⁻¹

IF YES

| | | |
|--|---|---------------|
| If 2 signals for (C=O) | → | Anhydride |
| If Broad band 3400-2400 cm ⁻¹ | → | Acid |
| If NH signals at 3400-3200 cm ⁻¹ | → | Acid Amide |
| If two weak signals at 2850, 2750 cm ⁻¹ | → | Aldehyde |
| If C-Cl band at 800 cm ⁻¹ | → | Acid chloride |
| If C-O band at 1000-1250 cm ⁻¹ | → | Ester |
| No other signal | → | Ketone |

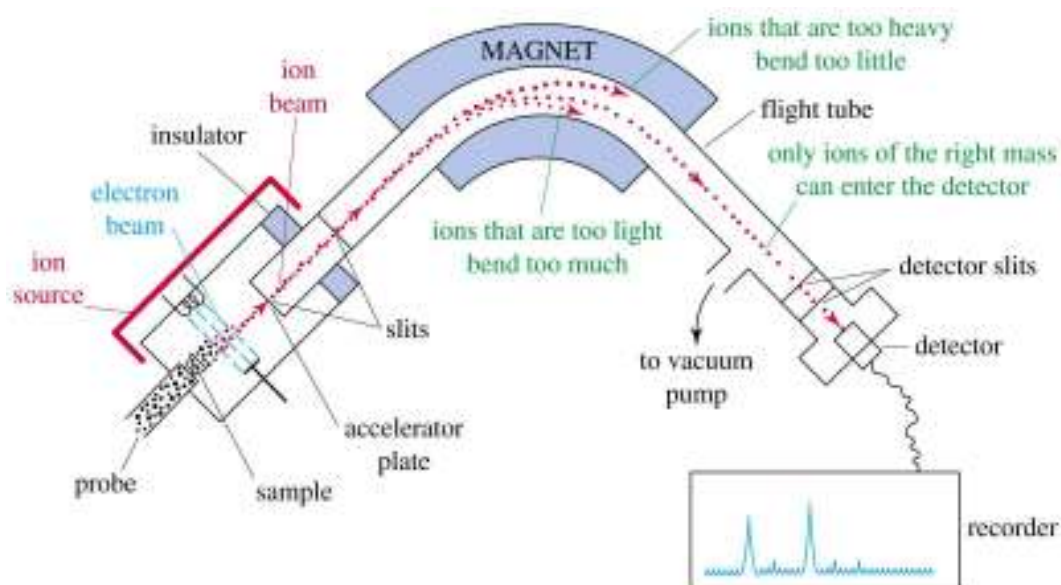
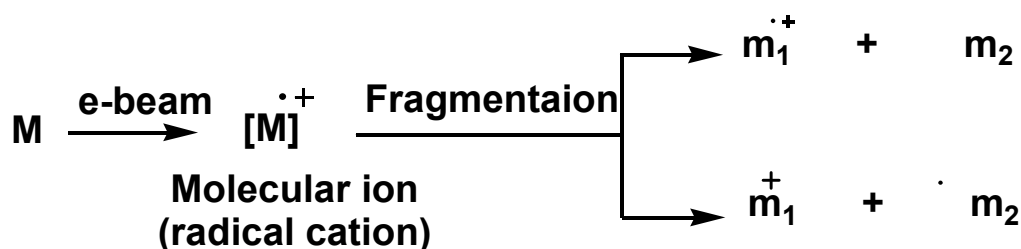
IF NO

| | |
|--|----------------------|
| Signal at 3600-3200 cm ⁻¹ | Amines or Alcohols |
| signal at 1000-1250 cm ⁻¹ | Ethers |
| signal at 2200-2400 cm ⁻¹ | Nitriles or Alkynes |
| signal at 1500-1660 cm ⁻¹ | Alkenes or Aromatics |
| two signals at 1450, 1350 cm ⁻¹ | Nitro compounds |
| only signal at 2950 cm ⁻¹ | Alkanes |

MASS SPECTROMETRY

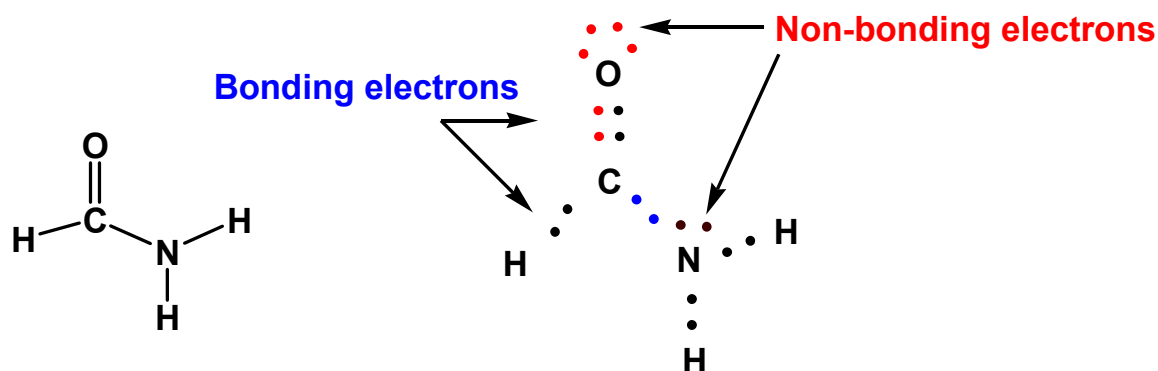
Another tool of spectral data which depends on bombardment of organic compound by electron beam with high energy leads to ionization of this compound (molecular ion or parent ion) followed by fragmentation

From these data **we can measure the exact molecular mass (molecular weight) of organic compounds** and also **we can predict the fragmentation pattern.**



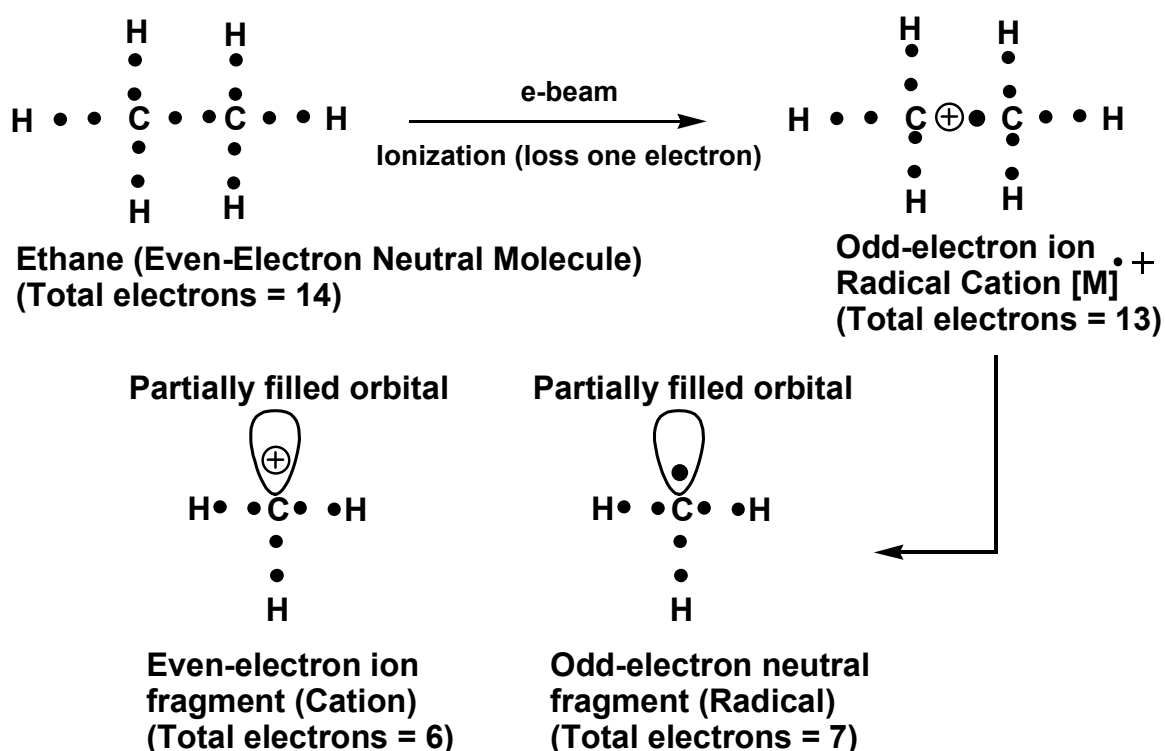
Even-Electron Neutral Species (EE⁰):

Nearly all electrically neutral organic molecules have an even number of electrons in their ground state. Most (EE⁰) species have all their electrons paired either in single, double, or triple bonds or as nonbonding (lone) pairs.



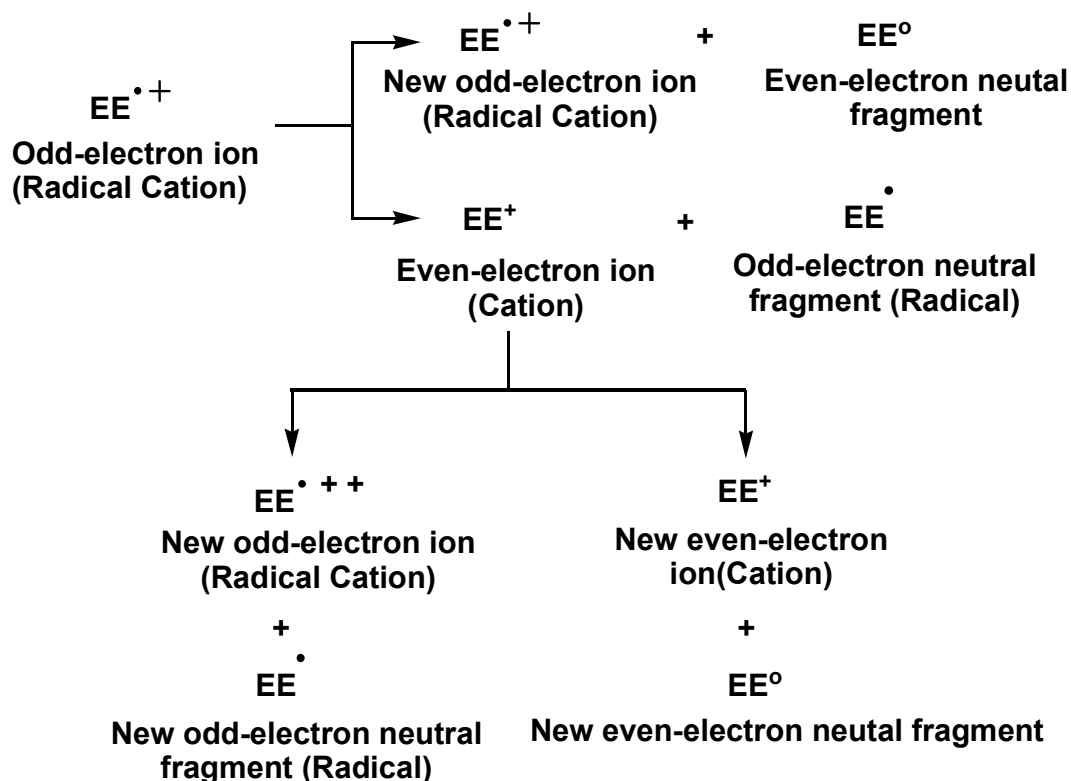
Odd-Electron Ion (Radical Ion; $OE^{+\bullet}$):

Ejection of one electron from an **Even-Electron Neutral molecule (EE^0)** produces an **odd-electron ion** (the molecular ion; $M^{+\bullet}$) in which the single electron remaining in partially filled orbital and become unpaired as shown in ethane molecule (C_2H_6).

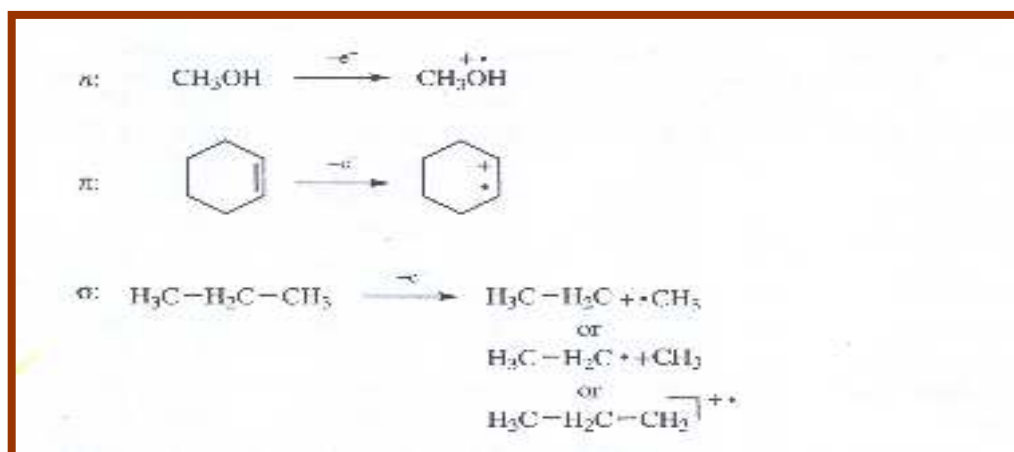


The central bond of the $M^{+\bullet}$ of ethane, weakened by the loss of one electron from the C—C σ -bond, breaks apart to give **Odd-electron neutral** methyl

radical which contains one unpaired electron in nonbonding Sp^3 orbital of carbon atom. This fragment is electrically neutral not a charged species, it is not detected by the mass spectrometer. Another fragment is **Even-electron cation (EE^+)** [methyl carbenium or methyl carbocation] which contains empty electron in nonbonding Sp^3 orbital of carbon atom. This fragment is detected by the mass spectrometer.

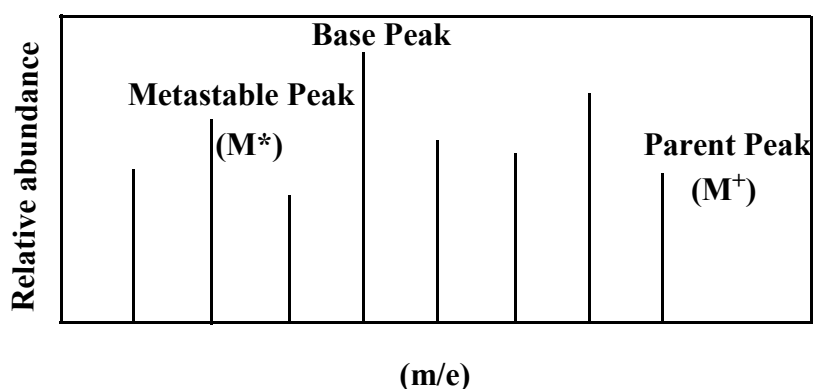


Normally, ionization will occur by removal of an electron from the atom which contains at least lone pair of electrons (non-bonding electron). If the molecule does not contain lone pair of electron it will carry out ionization from (π) electrons (if the molecule is unsaturated). If the molecule is saturated and has no lone pair of electron it will carry out ionization from (σ) electrons. The general trend observed in ionization is ($n > \pi > \sigma$). Where (n) is a non-bonding electron, (π) is a pi-bonding electron and (σ) is a sigma-bonding electron.



Mass Spectrum

The mass spectrum is a plot of relative abundance of the fragments (radical cations or cations) and their m/e (its molecular weight)



Parent Peak (Molecular ion Peak) $[\text{M}^+]$

The largest (m/e) peak in the mass spectrum which represents the molecular weight of the compound

Base Peak

The tallest peak in the mass spectrum which represents the most stable fragment

Metastable Peak (M^*)

The peak which links two peaks, the original fragment (m_1) and new fragment (m_2)

$$(\text{M}^*) = (m_2)^2 / m_1$$

Nitrogen Rule

If the compound has an odd molecular weight it must contain an odd number of nitrogen atom(s). On the other hand, if the compound has an even M. Wt. it either has no nitrogen atom or even number of nitrogen atoms

e.g. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ (M. Wt. = 59 and contains one nitrogen atom)

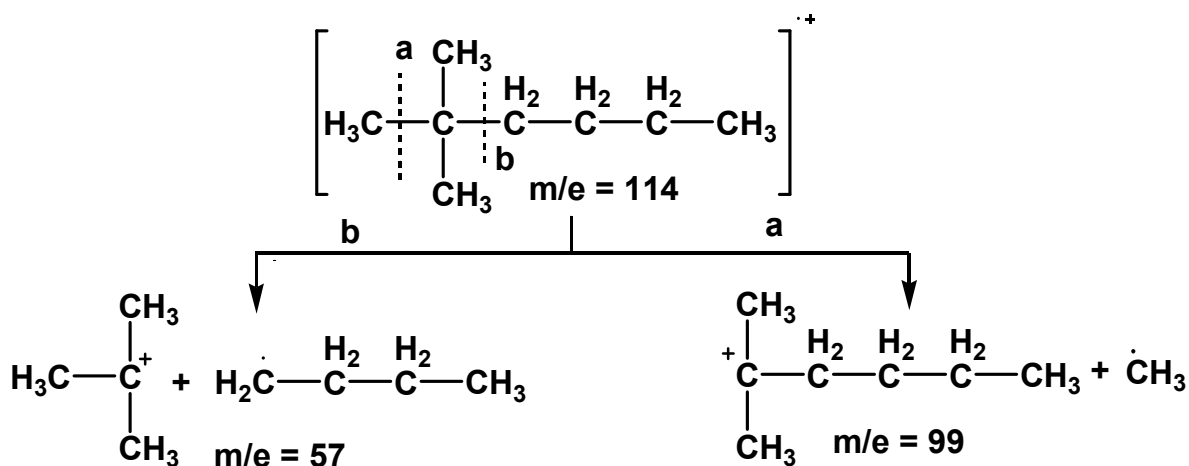
CH_3CH_3 (M. Wt. = 30 and number of nitrogen atoms = zero)

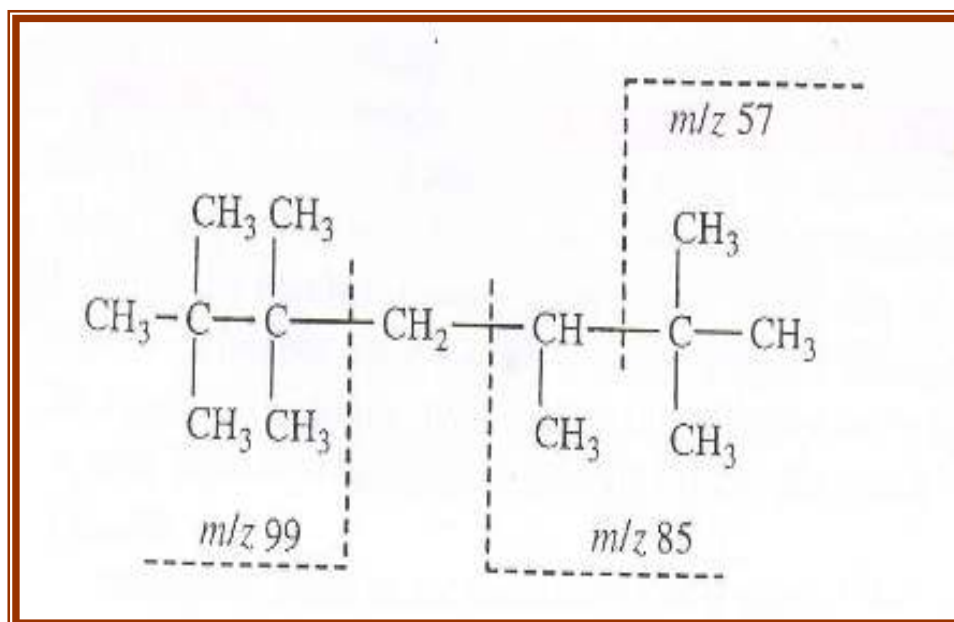
$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (M. Wt. = 74 and contains two nitrogen atoms)

Fragmentation Pattern of Organic Compounds

1. Alkanes: In general, linear alkanes will show significant intensity for the molecular ion peak. As the amount of branching increases, the intensity of the molecular ion peak will decrease, and when the molecule has significant branching the molecular ion may be undetectable

Cleavage of alkanes occurs at most branched carbon atom to give stable carbocation ($3^\circ > 2^\circ > 1^\circ$).





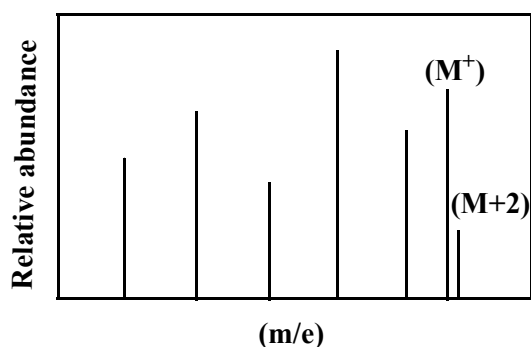
2. Halogenated Hydrocarbons

We can start our study of the halogenated compounds by dividing them into two convenient groups; those that contain F and I (**A elements**) and those that contain Cl and Br (**A + 2 elements**).

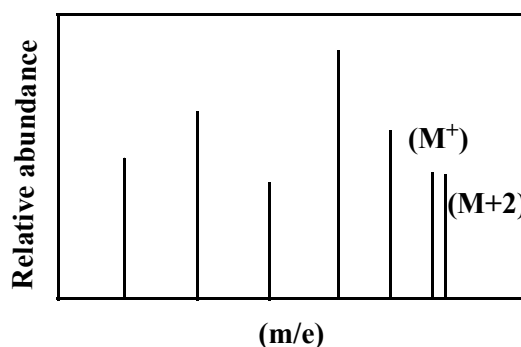
(M+2) Peaks

Chlorine has 2-isotopes $^{35}_{17}\text{Cl}$, $^{37}_{17}\text{Cl}$ in a ratio 3:1 so in the mass spectrum if we have (M^+), ($M+2$) peaks with the ratio 3:1 indicating that we have one chlorine atom in the molecular formula

Bromine has 2-isotopes $^{79}_{35}\text{Br}$, $^{81}_{35}\text{Br}$ in a ratio 1:1 so in the mass spectrum if we have (M^+), ($M+2$) peaks with the ratio 1:1 indicating that we have one bromine atom in the molecular formula

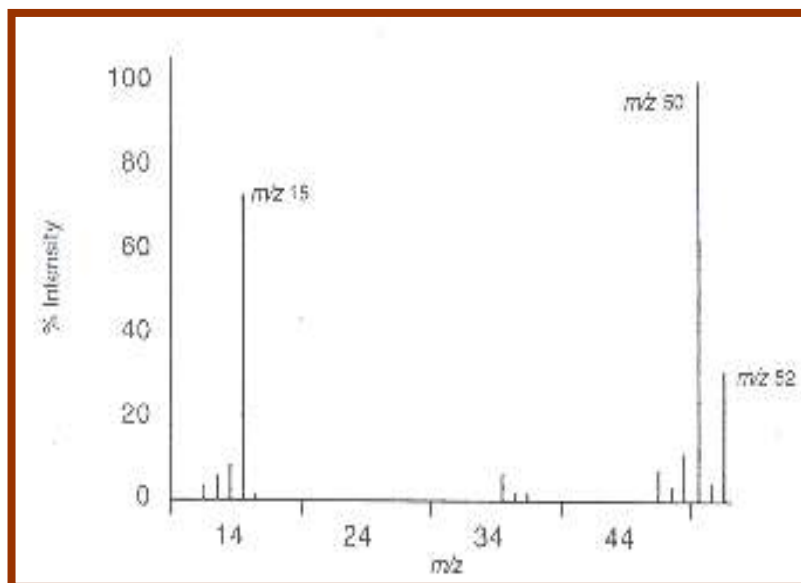


The compound has one Cl atom



The compound has one Br atom

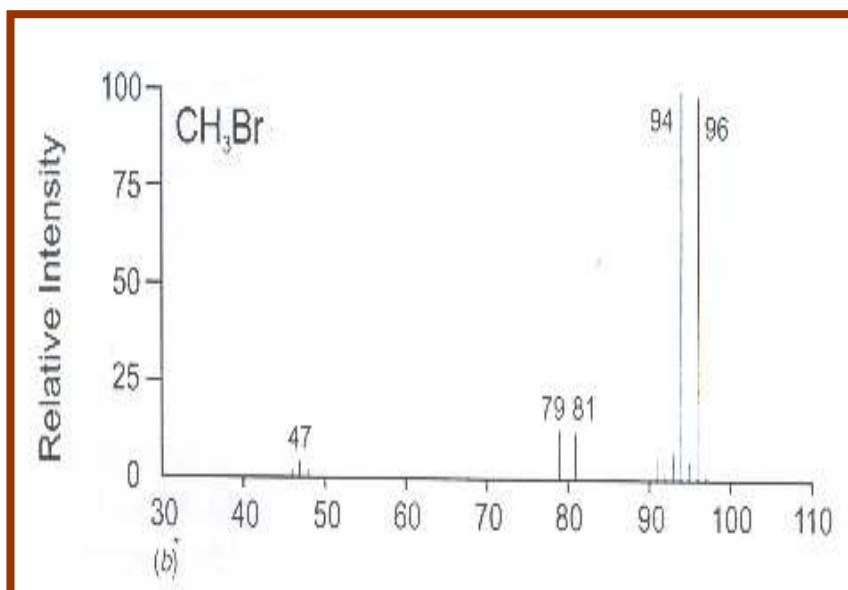
Methyl Chloride (CH_3Cl , M. Wt. = 50)



The ratio of intensities of the two peaks that result because of the presence of this Cl atom is given by the equation

$$\frac{[M]}{[M + 2]} = \frac{\text{relative abundance of } ^{35}\text{Cl}}{\text{relative abundance of } ^{37}\text{Cl}} = \frac{P(^{35}\text{Cl})}{P(^{37}\text{Cl})} = \frac{0.75}{0.25} = \frac{3}{1} = \frac{100}{33.3}$$

Methyl Bromide (CH_3Br , M. Wt. = 94)



The ratio of intensities of the two peaks that result because of the presence of this Br atom is given by the equation

$$[M] / [M + 2] = \text{relative abundance of } ^{79}\text{Br} / \text{relative abundance of } ^{81}\text{Br} =$$

$$P(^{79}\text{Br}) / P(^{81}\text{Br}) = 0.5 / 0.5 = 1/1 = 100/100.$$

When two Br atoms occur in the same ion, three combinations of isotopes are possible,

$$P(2\ ^{79}\text{Br}) = P(^{79}\text{Br}) P(^{79}\text{Br}) = (0.5)(0.5) = 0.25 [M]$$

$$P(^{79}\text{Br}\ ^{81}\text{Br}) = P(^{79}\text{Br}) P(^{81}\text{Br}) = (0.5)(0.5) = 0.25 [M+2]$$

$$P(2\ ^{81}\text{Br}) = P(^{81}\text{Br}) P(^{81}\text{Br}) = (0.5)(0.5) = 0.25 [M+4]$$

The relative intensities for the three peaks due to the presence of two Br atoms are therefore

$$\begin{aligned} [M] / [M + 2] / [M + 4] &= P(2\ ^{79}\text{Br}) / [P(^{79}\text{Br}\ ^{81}\text{Br}) + P(^{81}\text{Br}\ ^{79}\text{Br})] / P(2\ ^{81}\text{Br}) \\ &= (0.25) / [(0.25) + (0.25)] / (0.25) = (0.25) / (0.5) / (0.25) = 50/100/50 \\ &= 1/2/1 \end{aligned}$$

When two Cl atoms occur in the same ion, three combinations of isotopes are possible,

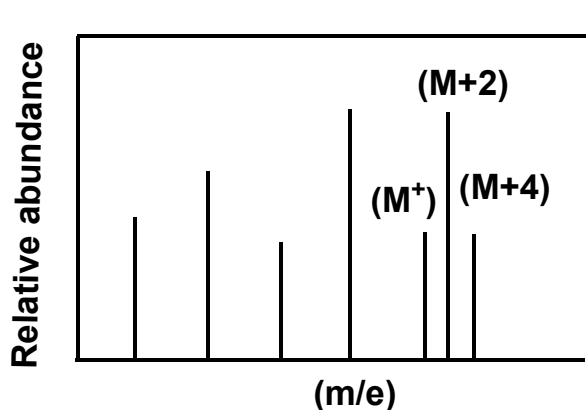
$$P(2\ ^{35}\text{Cl}) = P(^{35}\text{Cl}) P(^{35}\text{Cl}) = (0.75)(0.75) = 0.5625 [M]$$

$$P(^{35}\text{Cl}\ ^{37}\text{Cl}) = P(^{35}\text{Cl}) P(^{37}\text{Cl}) = (0.75)(0.25) = 0.1875 [M+2]$$

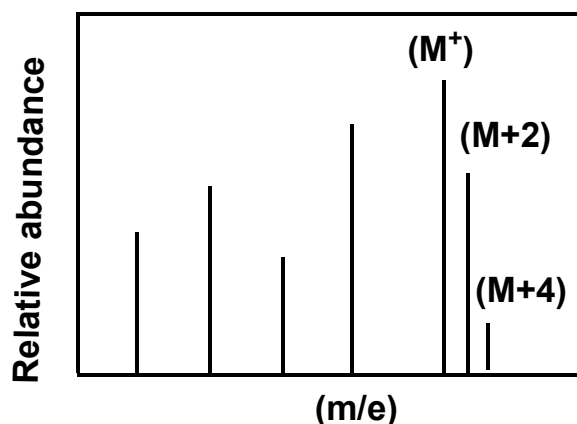
$$P(2\ ^{37}\text{Cl}) = P(^{37}\text{Cl}) P(^{37}\text{Cl}) = (0.25)(0.25) = 0.0625 [M+4]$$

The relative intensities for the three peaks due to the presence of two Cl atoms are therefore

$$\begin{aligned} [M] / [M + 2] / [M + 4] &= P(2\ ^{35}\text{Cl}) / [P(^{35}\text{Cl}\ ^{37}\text{Cl}) + P(^{37}\text{Cl}\ ^{35}\text{Cl})] / P(2\ ^{37}\text{Cl}) \\ &= (0.5625) / [(0.1875) + (0.1875)] / (0.0625) = (0.5625) / (0.375) / (0.0625) = \\ &= 9 / 6 / 1 \end{aligned}$$



The compound has two Br atoms



The compound has two Cl atoms

When one Cl atom and one Br atom occur together in an ion,

$$P(^{35}\text{Cl } ^{79}\text{Br}) = (0.75)(0.5) = 0.375, p(^{37}\text{Cl } ^{79}\text{Br}) = (0.25)(0.5) = 0.125$$

$$P(^{35}\text{Cl } ^{81}\text{Br}) = (0.75)(0.5) = 0.375, P(^{37}\text{Cl } ^{81}\text{Br}) = (0.25)(0.5) = 0.125$$

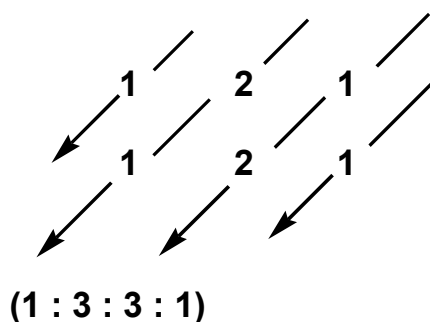
$$[M] / [M + 2] / [M + 4] = P(^{35}\text{Cl } ^{79}\text{Br}) / [p(^{37}\text{Cl } ^{79}\text{Br}) + p(^{35}\text{Cl } ^{81}\text{Br})] / P(^{37}\text{Cl } ^{81}\text{Br}) = (0.375) / [(0.125) + (0.375)] / (0.125) = (0.375) / (0.5) / (0.125) = 3 / 4 / 1$$

Determining relative intensities when three Br atoms are present in an ion is approachable by extending the concepts developed so far:

$$\text{Br}_2 \times \text{Br} = (1 : 2 : 1) \times (1 : 1) =$$

$$(1 : 2 : 1) \times 1 = (1 : 2 : 1)$$

$$(1 : 2 : 1) \times 1 = (1 : 2 : 1)$$

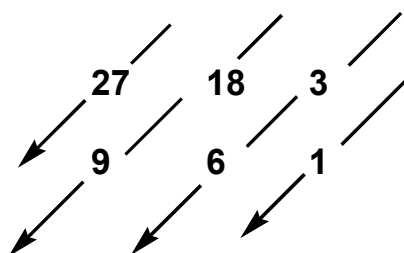


Determining relative intensities when three Cl atoms are present in an ion

$$\text{Cl}_2 \times \text{Cl} = (9 : 6 : 1) \times (3 : 1) =$$

$$(9 : 6 : 1) \times 3 = (27 : 18 : 3)$$

$$(9 : 6 : 1) \times 1 = (9 : 6 : 1)$$



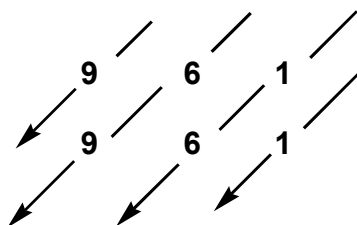
$$(27 : 27 : 9 : 1)$$

Q/ predict the pattern produced by two chlorine atoms and one bromine atom?

$$\text{Cl}_2 \times \text{Br} = (9 : 6 : 1) \times (1 : 1) =$$

$$(9 : 6 : 1) \times 1 = (9 : 6 : 1)$$

$$(9 : 6 : 1) \times 1 = (9 : 6 : 1)$$



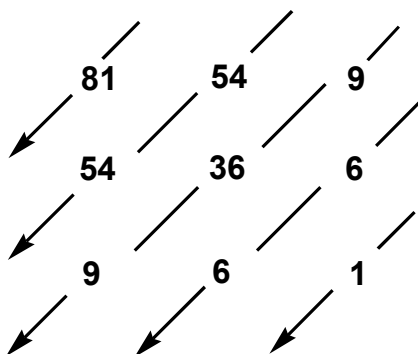
$$(9 : 15 : 7 : 1)$$

Q. predict the pattern produced when a molecule containing four chlorine atoms?

can be viewed as $\text{Cl}_2 \times \text{Cl}_2$

$$(9 : 6 : 1) \times (9 : 6 : 1)$$

$$(9 : 6 : 1) \times 9 = 81 : 54 : 9, (9 : 6 : 1) \times 6 = 54 : 36 : 6, (9 : 6 : 1) \times 1 = 9 : 6 : 1$$



$$(81 : 108 : 54 : 12 : 1)$$

Relative distribution of isotope lines for polyhalogenated compounds.

| Compounds contain | M | M+2 | M+4 | M+6 | M+8 | M+10 |
|-------------------|-----|-----|-----|-----|-----|------|
| Cl ₂ | 9 | 6 | 1 | - | - | - |
| ClBr | 3 | 4 | 1 | - | - | - |
| Br ₂ | 1 | 2 | 1 | - | - | - |
| Cl ₃ | 27 | 27 | 9 | 1 | - | - |
| ClBr ₂ | 3 | 7 | 5 | 1 | - | - |
| Br ₃ | 1 | 3 | 3 | 1 | - | - |
| Cl ₄ | 81 | 108 | 54 | 12 | 1 | - |
| Br ₄ | 1 | 4 | 6 | 4 | 1 | - |
| Cl ₅ | 243 | 405 | 270 | 90 | 15 | 1 |
| Br ₅ | 1 | 5 | 10 | 10 | 5 | 1 |

How many chlorine atoms are actually present?

| m/z | % Abundance | Re-Normalized |
|-----------|-------------|---------------|
| 290 [M] | 38% | 50.7% |
| 292 [M+2] | 75% | 100% |
| 294 [M+4] | 62% | 82.7% |
| 296 [M+6] | 28% | 37.3% |
| 298 [M+8] | 7% | 9.3% |

Suppose we have 4 chlorine atoms

| m/z | Relative Distribution | Re-Norm -alized |
|-----------|-----------------------|-----------------|
| 290 [M] | 81 | 75% |
| 292 [M+2] | 108 | 100% |
| 294 [M+4] | 54 | 50% |
| 296 [M+6] | 12 | 11.1% |
| 298 [M+8] | 1 | 0.9% |

Not matched with standard values

Suppose we have 5 chlorine atoms

| m/z | Relative Distribution | Re-Norm -alized |
|------------|-----------------------|-----------------|
| 290 [M] | 243 | 60% |
| 292 [M+2] | 405 | 100% |
| 294 [M+4] | 270 | 66.7% |
| 296 [M+6] | 90 | 22.2% |
| 298 [M+8] | 15 | 3.7% |
| 300 [M+10] | 1 | 0.2% |

Not matched with standard values

Suppose we have 6 chlorine atoms

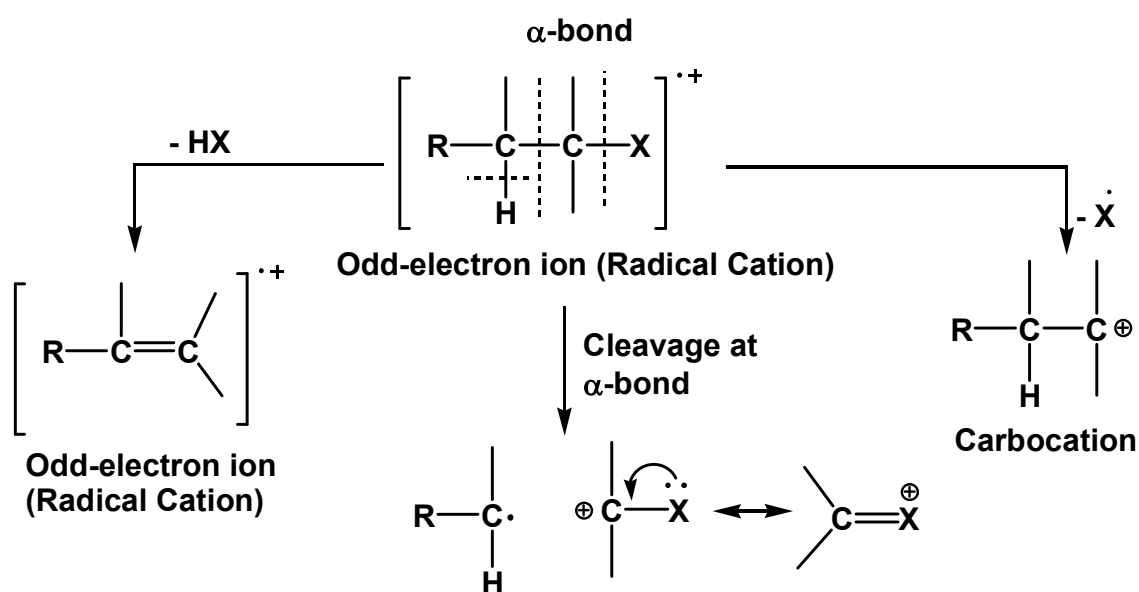
| m/z | Relative Distribution | Re-Norm-alized |
|------------|-----------------------|----------------|
| 290 [M] | 729 | 50% |
| 292 [M+2] | 1458 | 100% |
| 294 [M+4] | 1215 | 83.3% |
| 296 [M+6] | 540 | 37% |
| 298 [M+8] | 135 | 9.3% |
| 300 [M+10] | 18 | 1.2% |
| 302 [M+12] | 1 | 0.06% |

matched with standard values

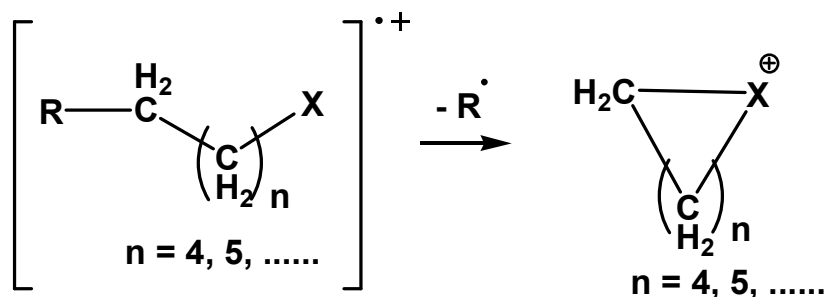
Thus, the compound contains 6-chlorine atoms.

Fragmentation pattern of halogenated hydrocarbons

a) Elimination of (X) atom to give the corresponding carbocation. b) Cleavage at α -bond to give carbocation which stabilized by resonance. c) Elimination of HX [Compounds containing F and Cl tend to show loss of HF (loss of 20 amu) and HCl (loss of 36 and 38 amu), while loss of HBr and HI is relatively rare].



If the alkyl group which carries out the halogen atom contains more than 5 carbon atoms it will lose alkyl radical and give the corresponding cyclic product as shown.



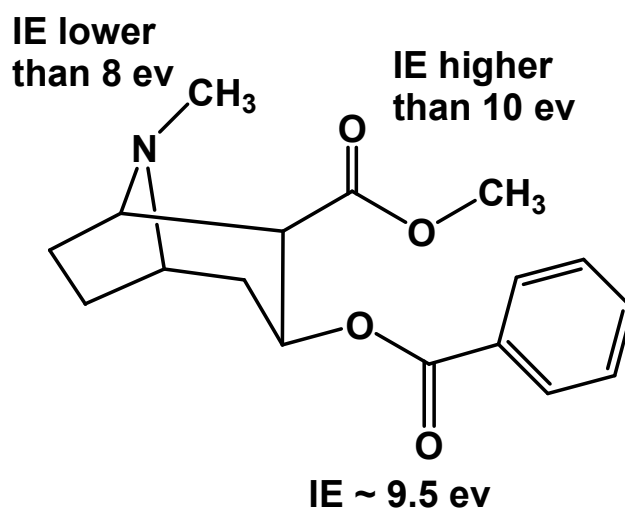
Ionization energy (IE) or ionization potential of the molecule.

"The energy required to remove one electron from a molecule". A list of ionization energies for a number of molecules and radicals is found in Table, in order to devise realistic mechanisms for how molecules fragment the site of initial ionization must be defined.

| Hydrocarbons | | O/S/ N Compounds | | | | Radicals | |
|-------------------------------------|-------|-----------------------------------|-------|----------------------|-------|---|------|
| HC=CH | 11.4 | CO | 14.0 | N ₂ | 15.6 | F• | 17.4 |
| CH ₂ =CH ₂ | 10.5 | CO ₂ | 13.6 | HCN | 13.6 | Cl• | 13.0 |
| n-Alkanes | ~10.4 | H ₂ O | 12.5 | NH ₃ | 10.2 | Br• | 11.8 |
| R ₂ CHCHR ₂ ' | ~10.2 | H ₂ C=O | 10.9 | RCONH ₂ | ~9.8 | I• | 10.5 |
| Cyclohexane | 9.9 | RCO ₂ R' | ~10.2 | RCH=NH | ~9.6 | SH• | 10.4 |
| Benzyne | 9.7 | n-ROH | ~10.1 | Pyridine | 9.3 | CH ₃ • | 9.8 |
| n-Alkenes | ~9.6 | RCHO | ~9.8 | RCH=NR' | ~9.1 | CH ₂ =CH• | 8.8 |
| Benzene | 9.2 | CH ₃ COCH ₃ | 9.7 | RCONR ₂ ' | ~8.8 | ROCO• | 8.6 |
| RCH=CHR' | ~9.1 | ArCO ₂ H | 9.7 | n-RNH ₂ | ~8.7 | CH ₃ O• | 8.6 |
| 1,3-Butadiene | 9.1 | CH ₂ C=O | 9.6 | Pyrrole | 8.2 | Ar• | 8.1b |
| ArCH ₃ | 8.9 | R ₂ O | ~9.5 | R ₂ NH | ~8.0 | CH ₂ =CHC H ₂ • | 8.1 |
| Cyclohexene | 8.8 | ArCOR | ~9.4 | ArNH ₂ | 7.7 | HCO• | 8.1 |
| Ar-CH=CH ₂ | 8.4 | n-RSH | ~9.1 | | | n-Bu• | 8.0 |
| Naphthalene | 8.1 | Thiophene | 8.9 | | | HOCH ₂ • | 7.6 |
| | | Furan | 8.9 | n-RF''' | ~12.5 | HSCH ₂ • | 7.5 |
| | | ArOH | 8.5 | n-RCI'' | ~10.7 | s-Bu• | 7.3 |
| | | R ₂ S | ~8.4 | n-RBr''' | ~10.1 | ArCH ₂ • | 7.1 |
| | | ArOR | ~8.2 | n-RI | ~9.2 | CH ₃ CO• | 7.0 |
| | | CH ₃ SSCH ₃ | 7.2 | ArCl | 9.1 | ROCH ₂ • | ~6.9 |
| | | | | ArBr | 9.0 | t-Bu• | 6.7 |
| | | | | | | Cyclic C ₃ H ₃ • | 6.6 |
| | | | | | | Cyclic C ₇ H ₇ • | 6.2 |

- First, the IEs for groups containing electronegative atoms are higher than those for other species.
- Second, the addition of a double or triple bond in a structure generally lowers the IE, because π -orbitals are generally found at higher energies than σ -orbitals.
- Third, the IEs for the radicals listed at the right side of the table reflect the stabilities of the ions that are formed by removal of the unpaired electron that is, the, lower the IE, the more stable the resulting ion.
- Fourth, The IEs for isomeric alkyl radicals also conform to this trend, with that of the tert-butyl radical being the lowest, that of n-butyl the highest, and that for sec-butyl falling in between.
- Finally, the IEs of small double and triple bonded molecules such as CO, CO₂, N₂, and HCN are all quite high, so that these molecules resist taking a positive charge.

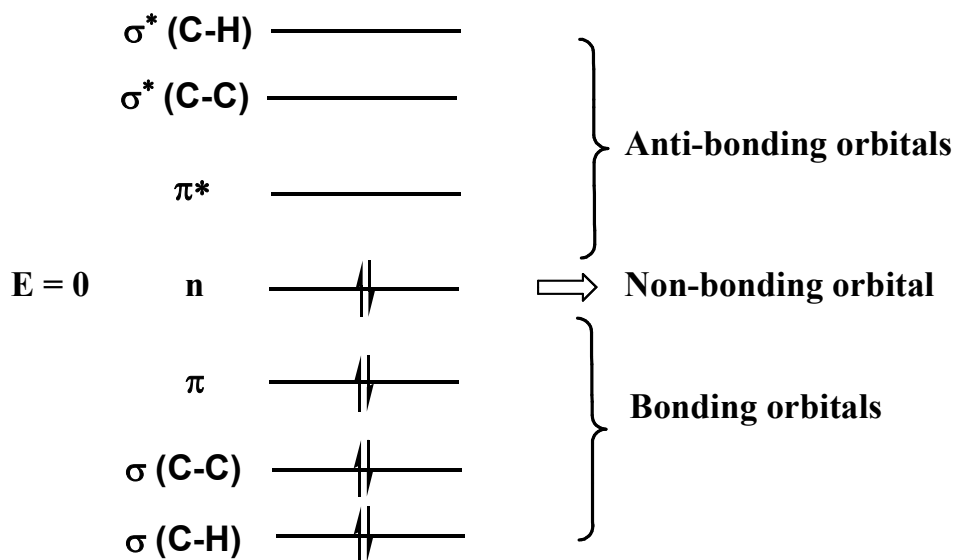
Q. Determine the most likely initial ionization site for cocaine, whose structure is given below?



The initial ionization will be at (N-CH₃) group

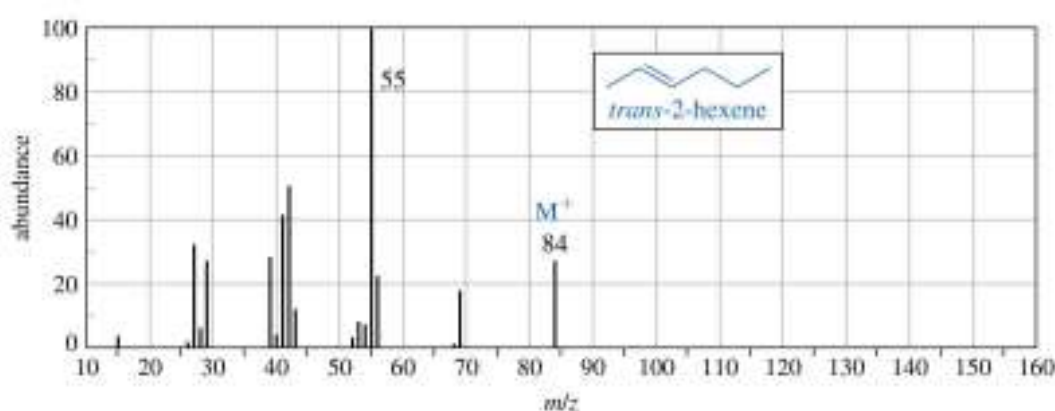
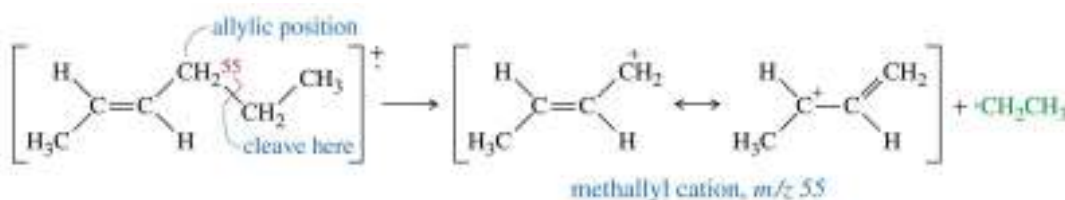
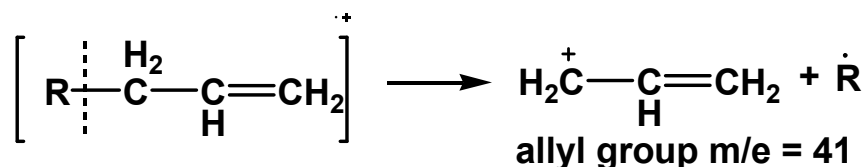
SITE OF INITIAL IONIZATION:

The electrons most susceptible to ejection are those in molecular orbitals having the highest energy. Figure shows the relative energies of different types of molecular orbitals found in organic compounds. Basically, these molecular orbitals fall into five categories σ , π , n , π^* , and σ^* .

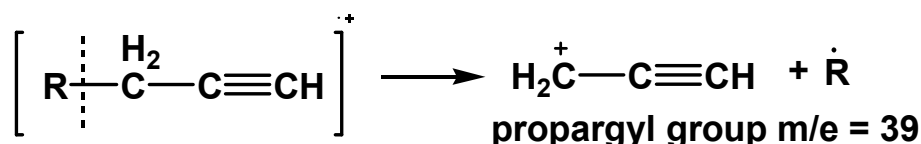


Relative energies of molecular orbitals in organic molecules

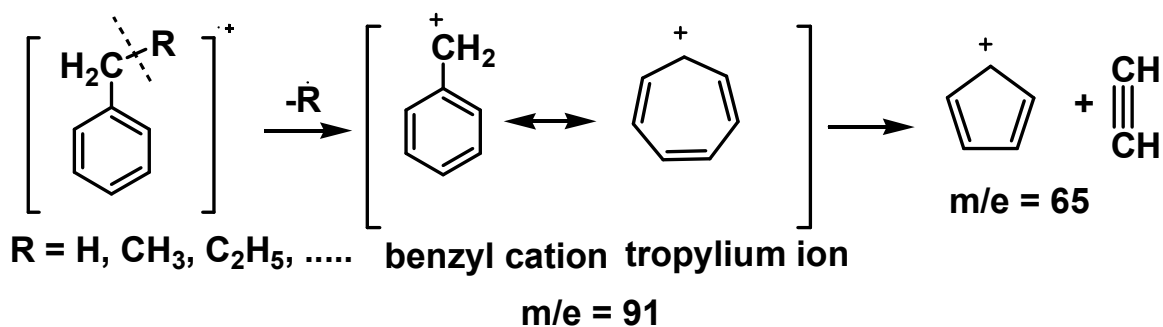
3. Alkenes Cleavage after the α -bond to give allyl group (stabilized by resonance)

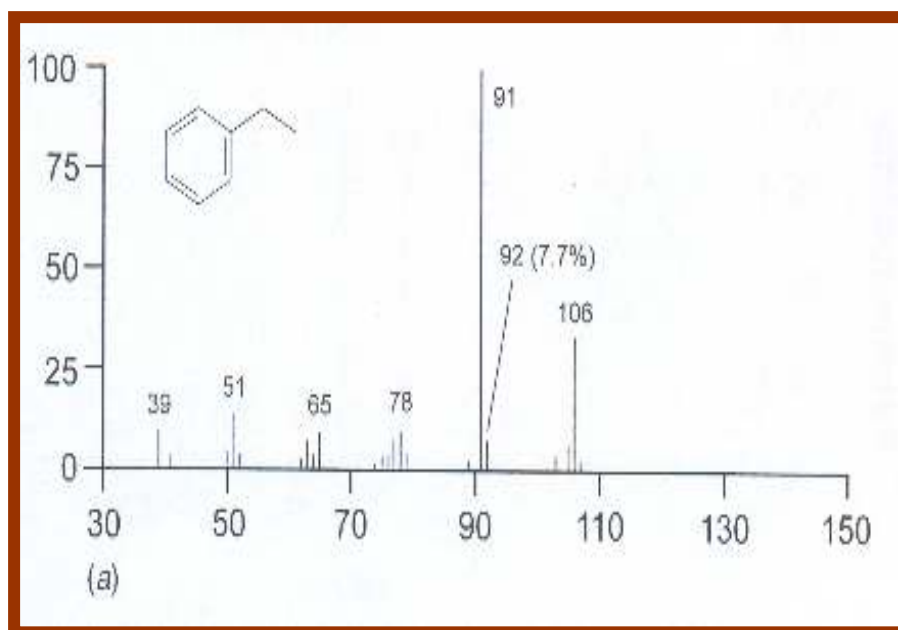


4. Alkynes: Cleavage after the α -bond to give propargyl group (stabilized by resonance)



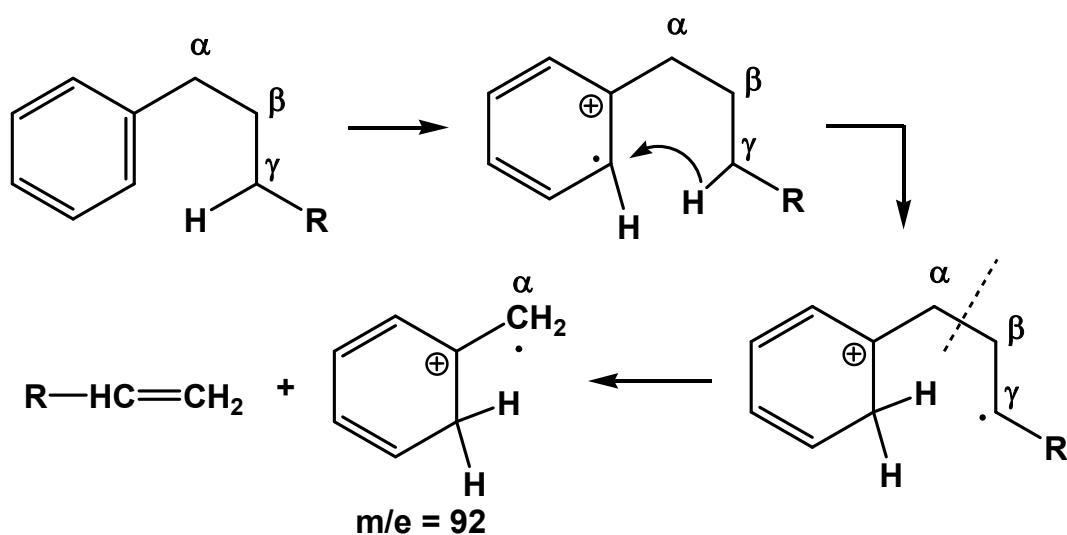
5. Aromatic Hydrocarbons (Alkyl substituted benzene): Cleavage at β -bond with respect to benzene ring to give benzyl cation which undergo rearrangement to give tropylium ion

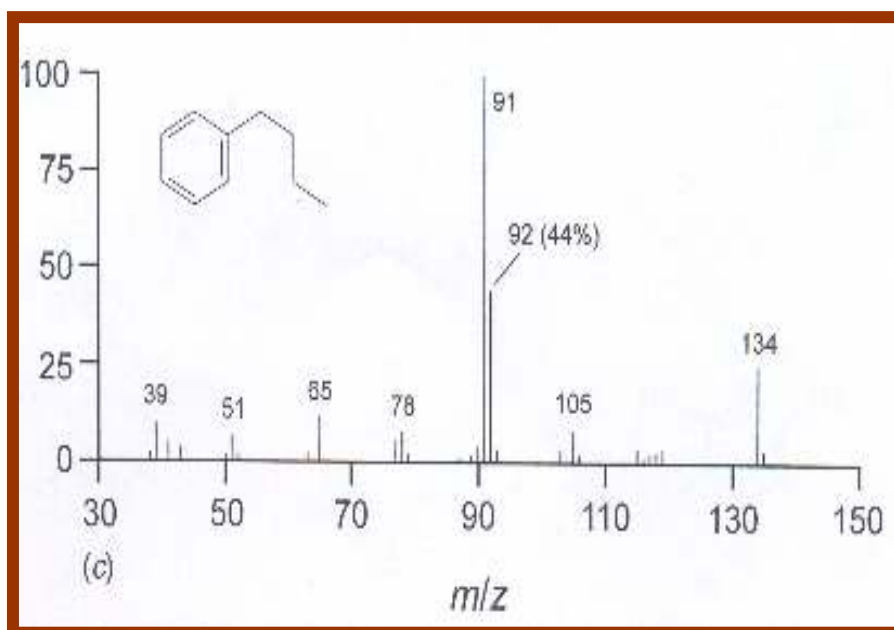




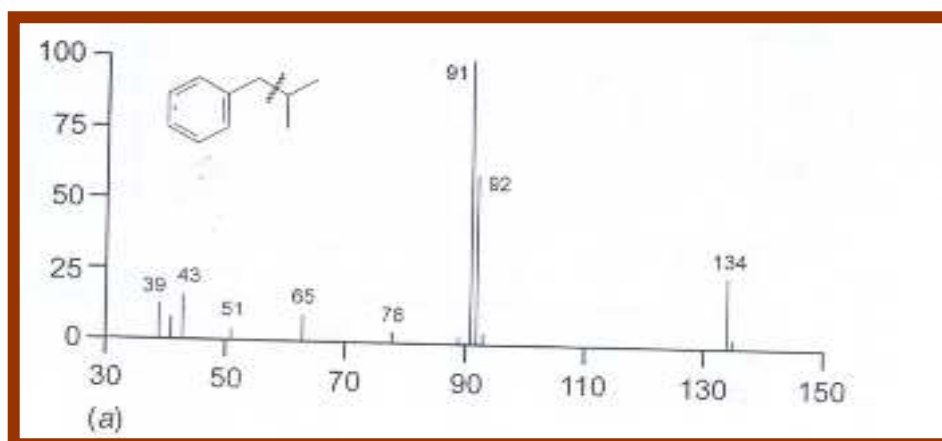
γ -Hydrogen Rearrangement

If the alkyl group on benzene ring (side chain) contain at least **3 carbon atoms** (α , β , γ) it will carry out **γ -hydrogen rearrangement** to give peak at $m/e = 92$ beside benzyl cation at $m/e = 91$ as shown

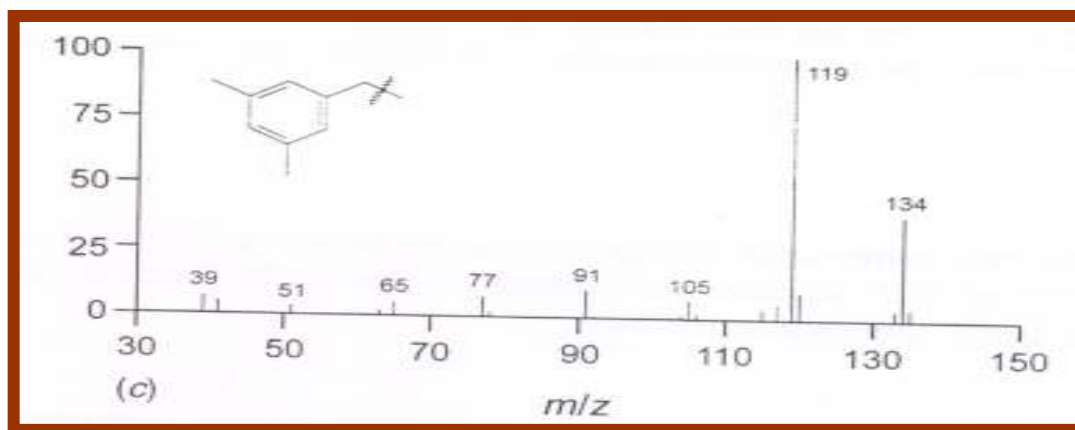




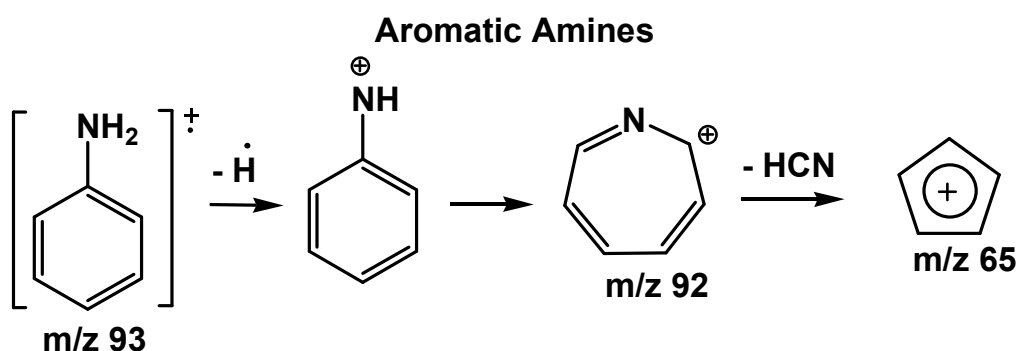
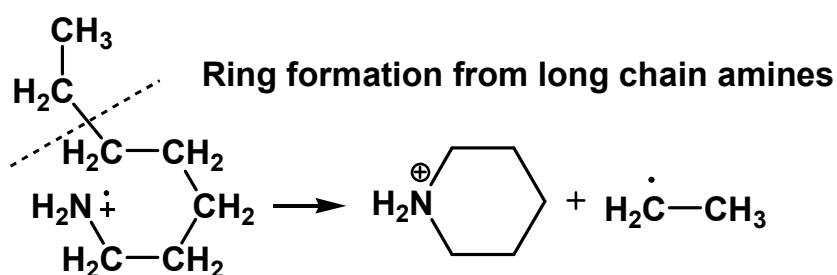
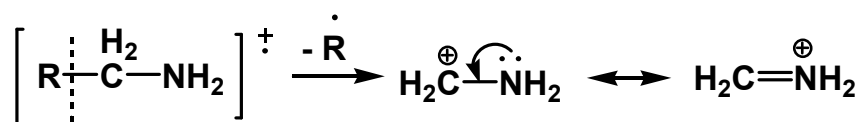
In the mass spectrum of isobutylbenzene, the stability of (H^\bullet) cannot compete with that of ($\text{CH}_3\text{C}^\bullet\text{HCH}_3$), so that the $M - 1$ peak is not observed.



On the other hand, loss of any of the eight benzylic H atoms on the three benzylic C atoms of 3,5-dimethylethylbenzene competes somewhat more effectively with loss of the single methyl group, so that the $[M - 1]$ peak is observed. Loss of ($^\bullet\text{CH}_3$) from the $[\text{M}]^{+\bullet}$ of this compound is still preferred by a factor of about 20.



6. Amines : a) Cleavage at α -bond to give carbocation which stabilized by resonance. b) If the alkyl group which carries out the nitrogen atom contains more than 5 carbon atoms it will loss alkyl radical and give the corresponding cyclic product. c) Aromatic amines has fragmentation pattern as shown.

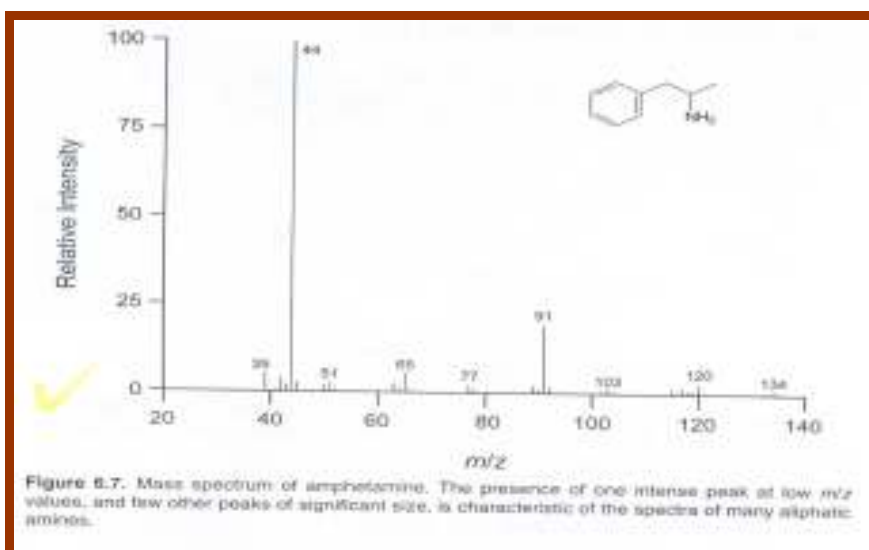
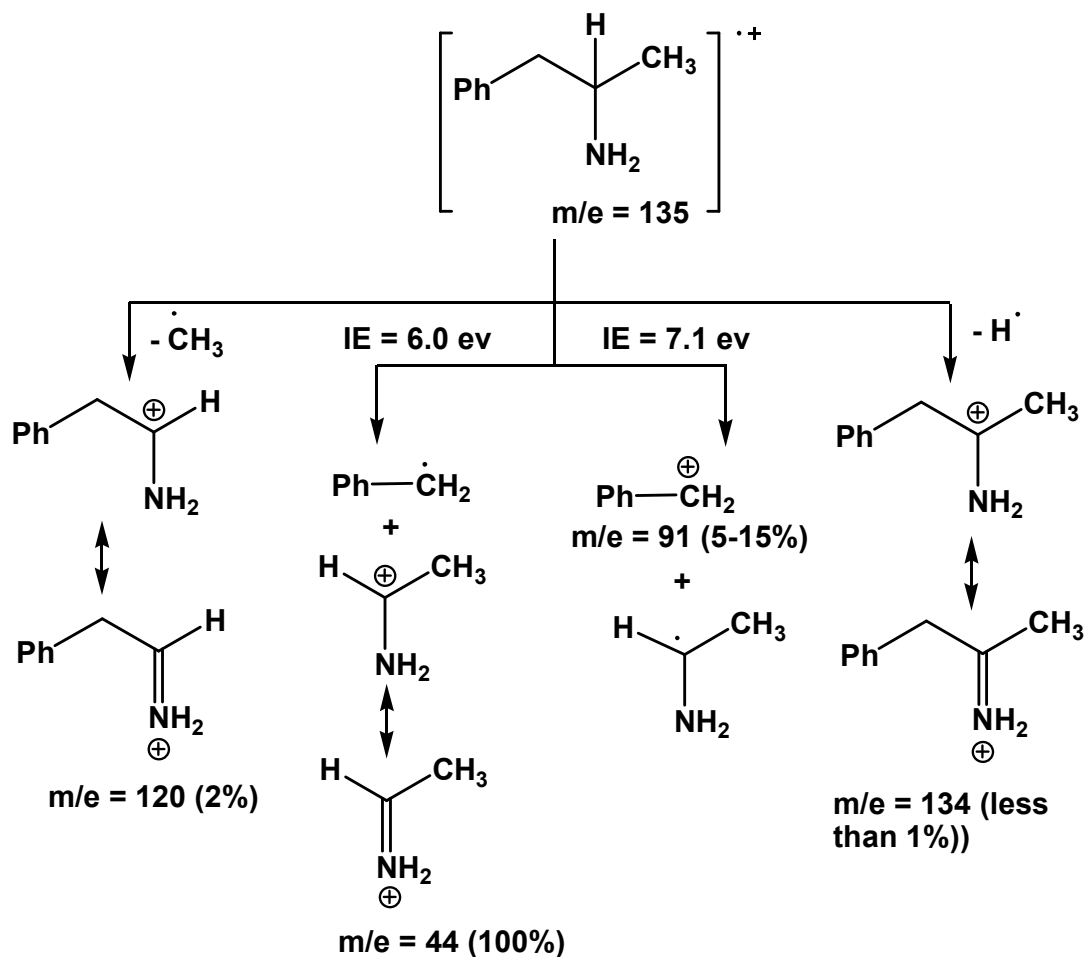


Fragmentation of 1-phenyl-2-amino propane (Amphetamine)

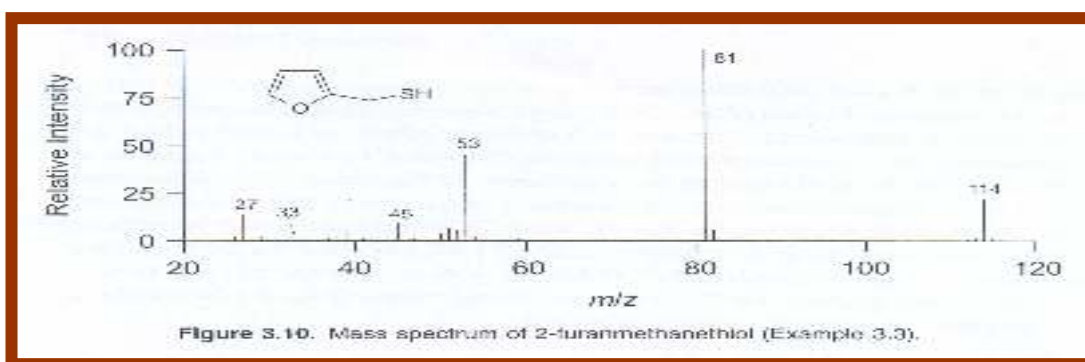
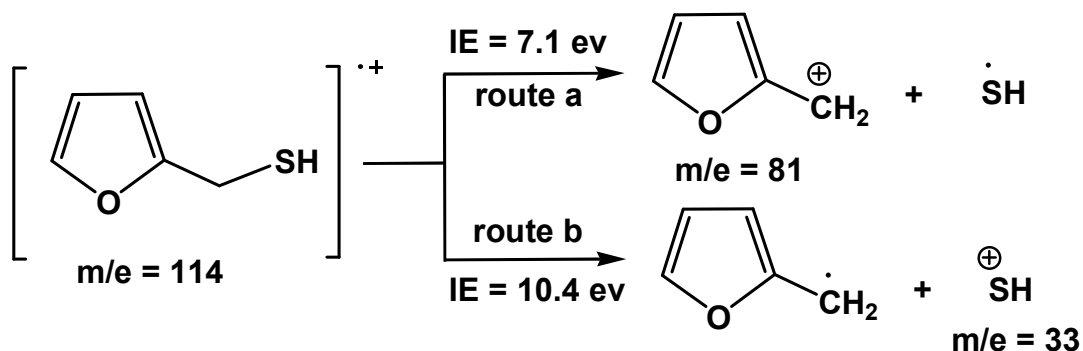
Cleavage of σ -bond gave benzyl cation & N-containing radical (IE of this bath = 7.1 eV) or benzyl radical & N-containing cation (IE of this bath = 6.0 eV). To determine the pathway of the fragmentation pattern we must apply

Stevenson's Rule

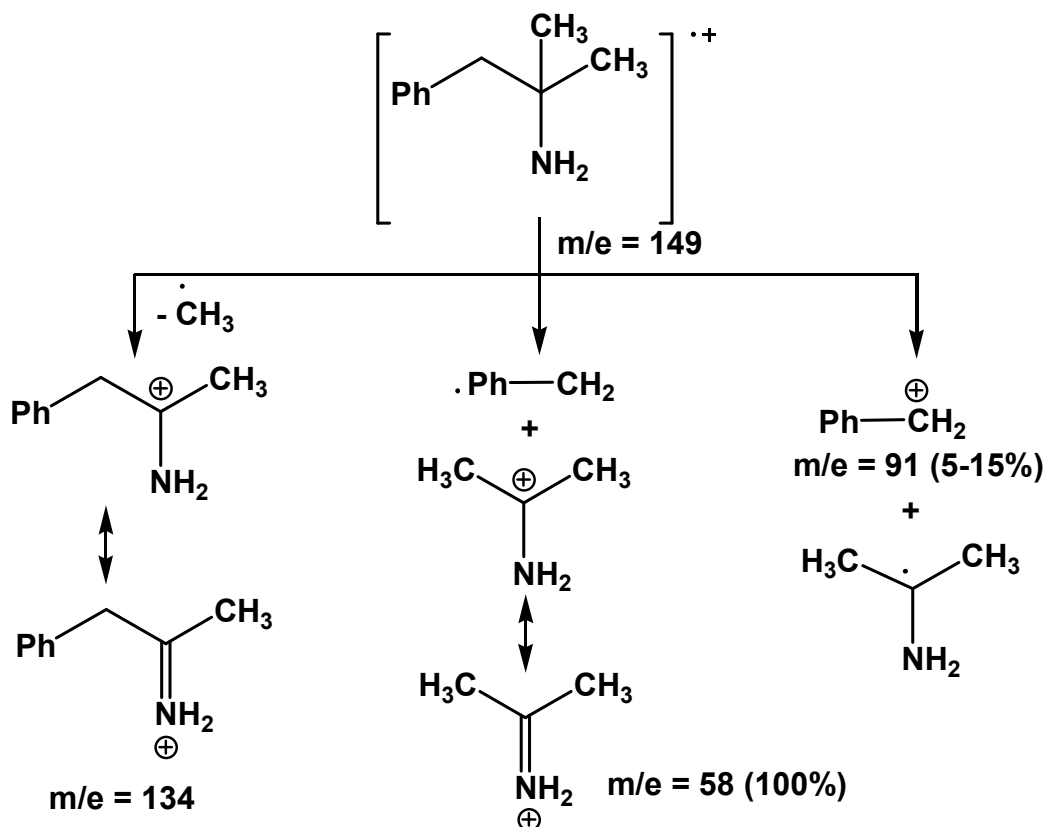
"If we have two pathways for cleavage of σ -bond, it will proceed with the route of lower ionization energy" so Stevenson's rule predicts that the charge will reside primarily on the N-containing fragment (m/e 44), which is what is observed.



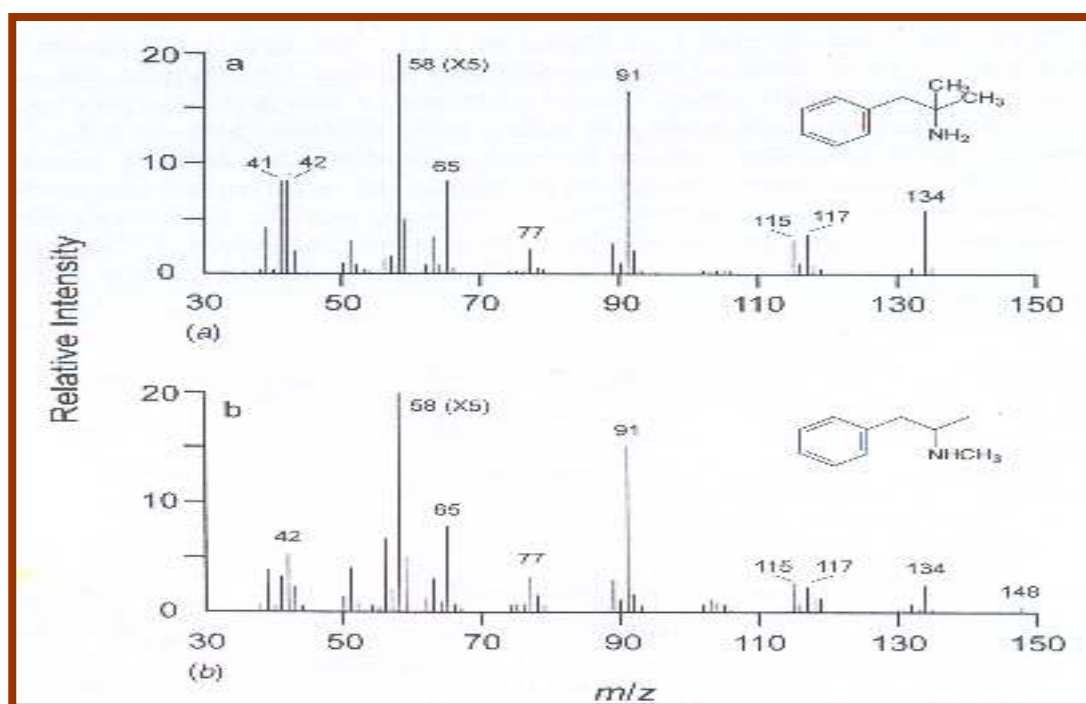
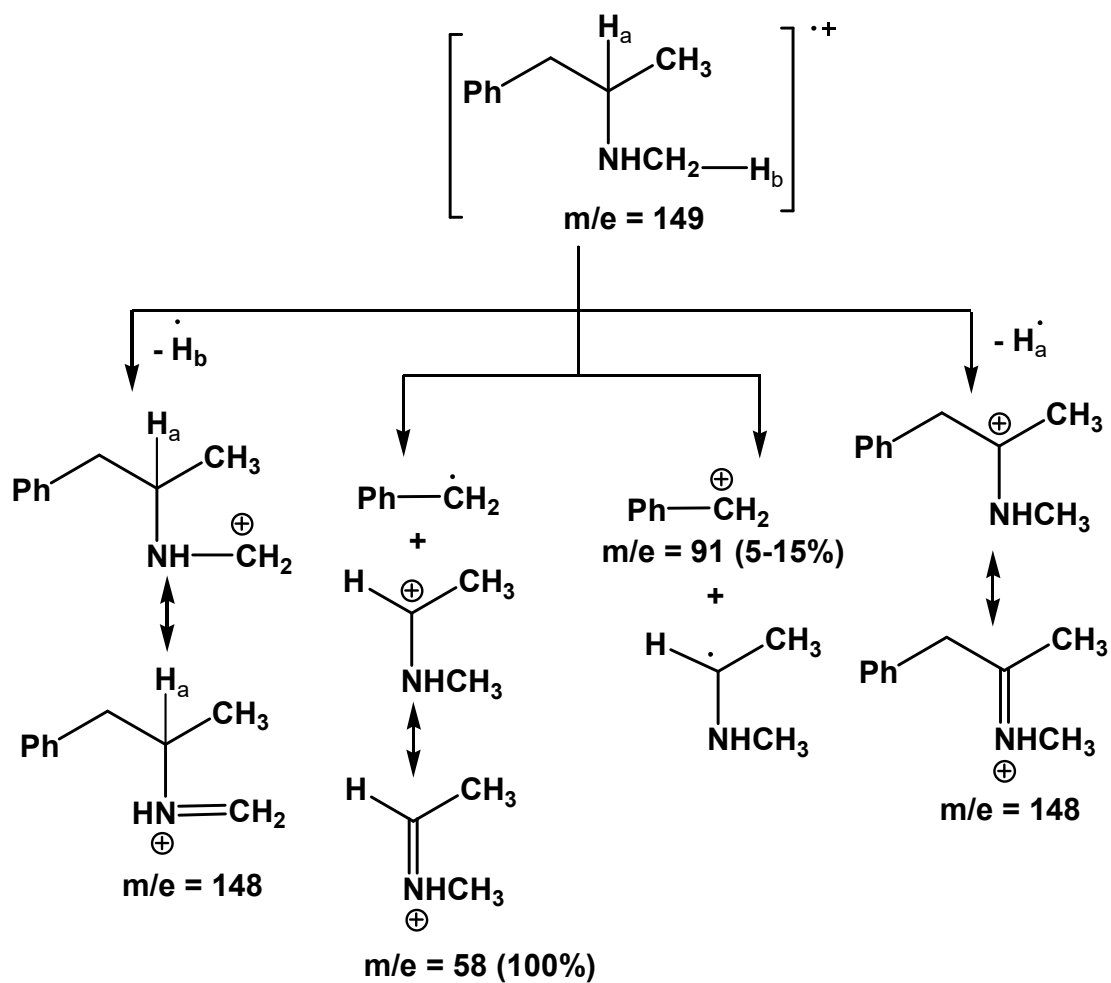
Another example of 2-thiomethyl furan in which the fragmentation pattern prefers route a (lower IE)



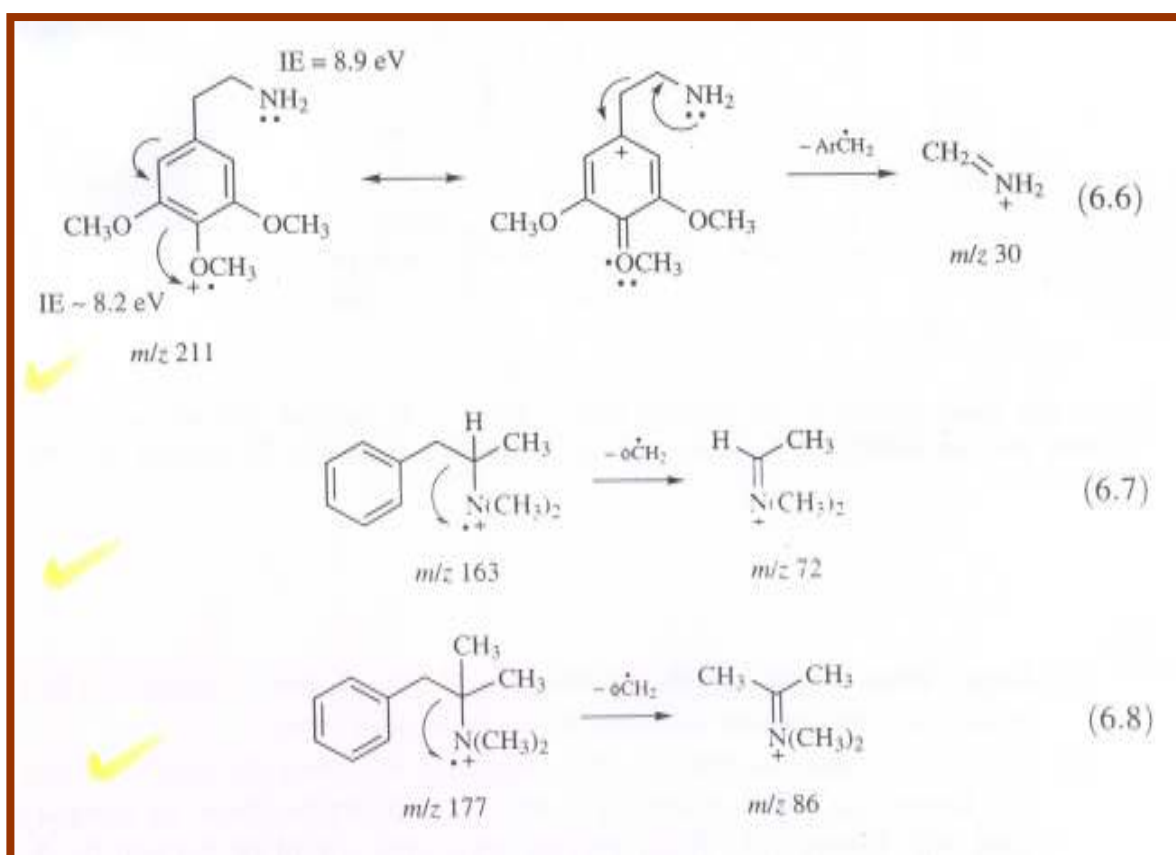
Fragmentation of 1-phenyl-2-amino-2-methyl propane (Phentermine)



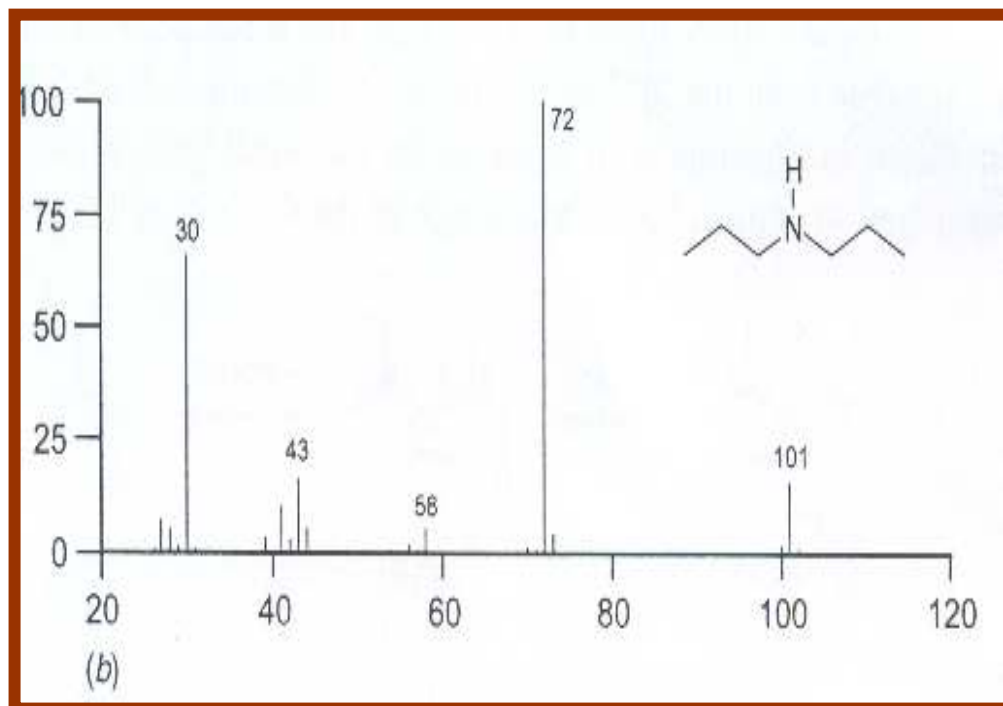
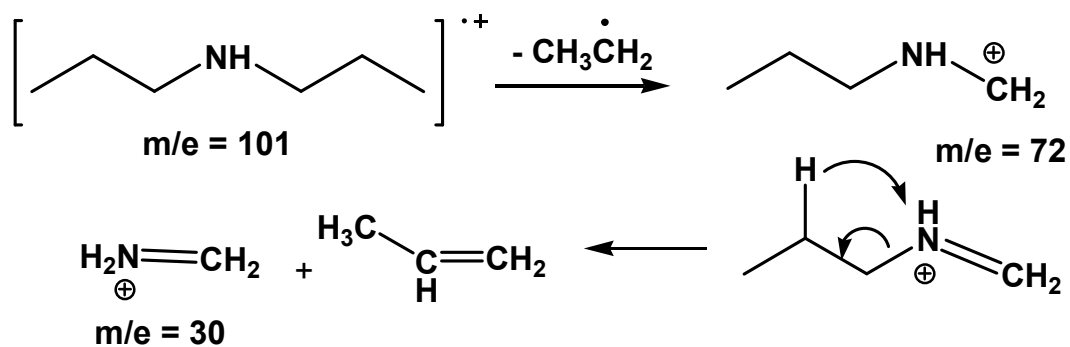
Fragmentation of 1-phenyl-2-(methylamino) propane (Methamphetamine)



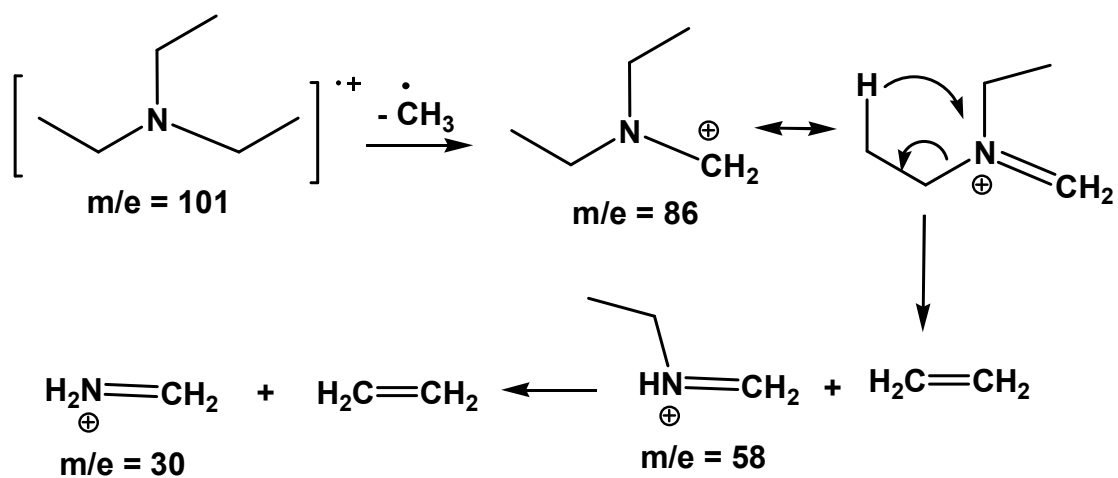
Compounds having long aliphatic groups attached to the N atom lose this largest aliphatic radical and produce an intense peak (usually the base peak) of the remaining N-containing cation. Thus, the spectrum of **3,4,5-trimethoxy- β -phenethylamine (Mescaline)** shows a base peak at $m/e = 30$, **N,N-dimethylamphetamine** [$C_6H_5CH_2CH(CH_3)N(CH_3)_2$] produces a base peak at $m/e = 72$; and **N,N-dimethylphenentermine** [$C_6H_5CH_2-C(CH_3)_2N(CH_3)_2$] gives a base peak at $m/e = 86$.

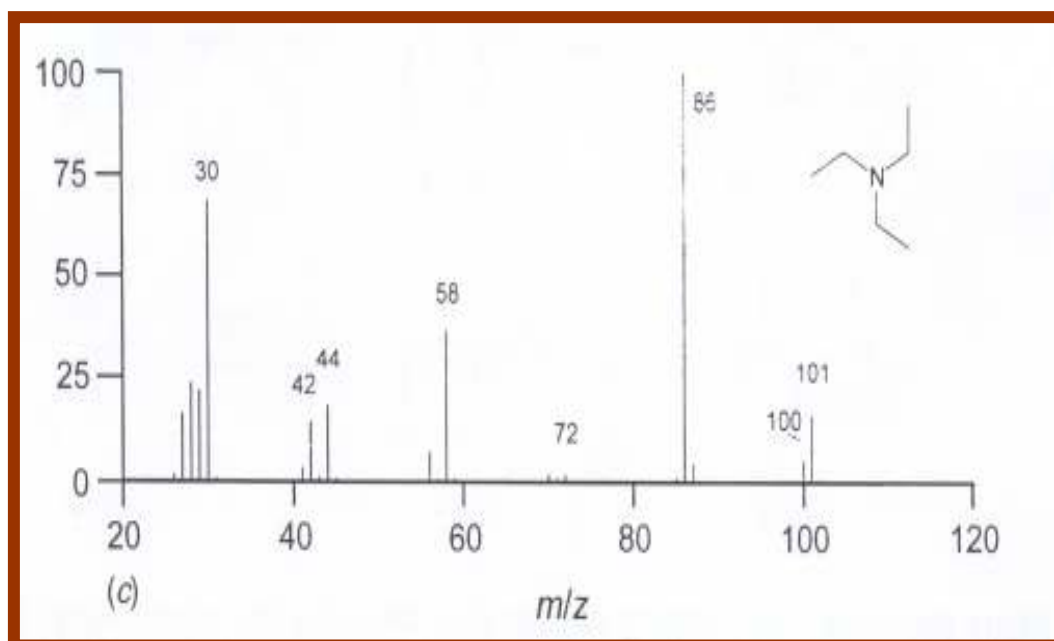


Many secondary and tertiary amines undergo α -cleavage followed by elimination of alkene molecule through hydride (H^-) shift. The spectra of di-*n*-propylamine exhibit the expected peaks from α -cleavage at $M - 29$ ($m/e = 72$), and another intense fragment ion peak also occurs at ($m/e = 30$) due to secondary elimination of a molecule of propylene. Same behavior was observed in case of primary amines in which the amino group is internal as shown in case of 3-aminopentane.

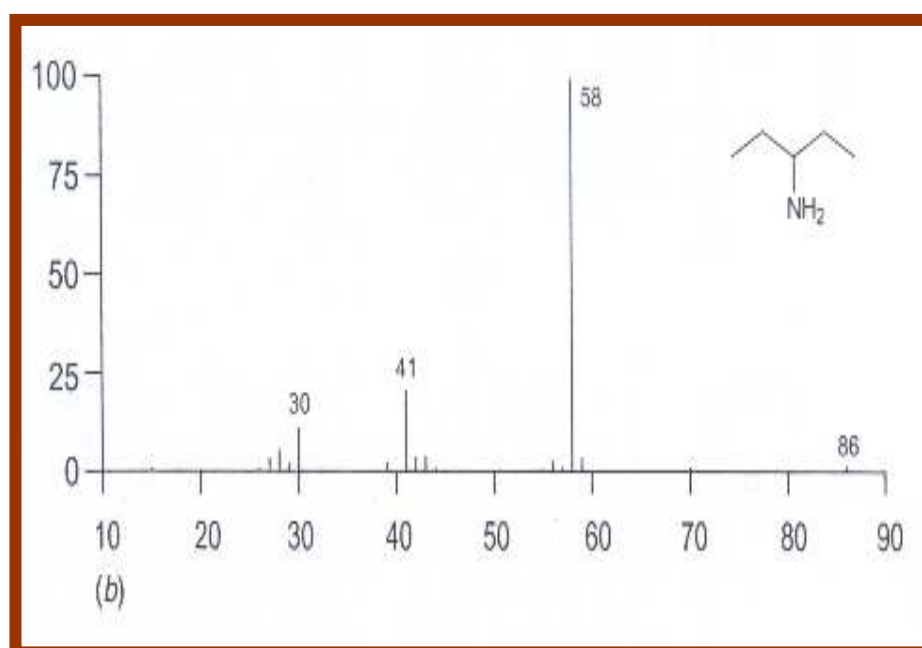
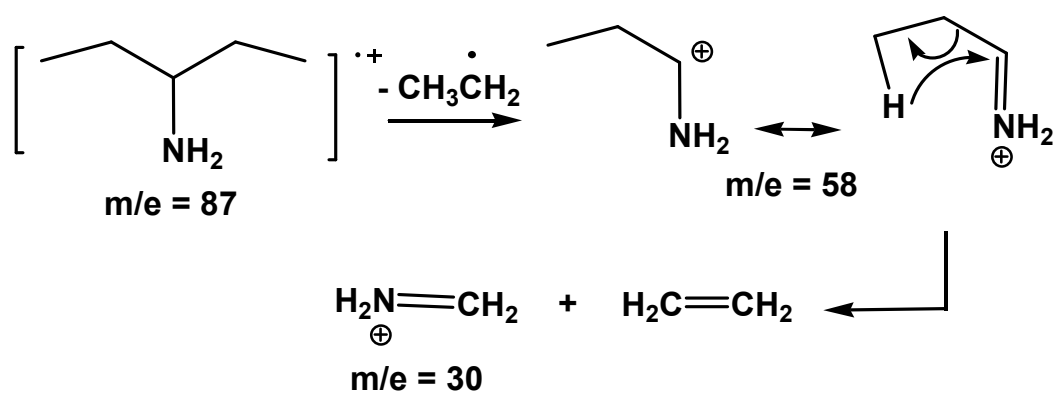


Triethyl amine

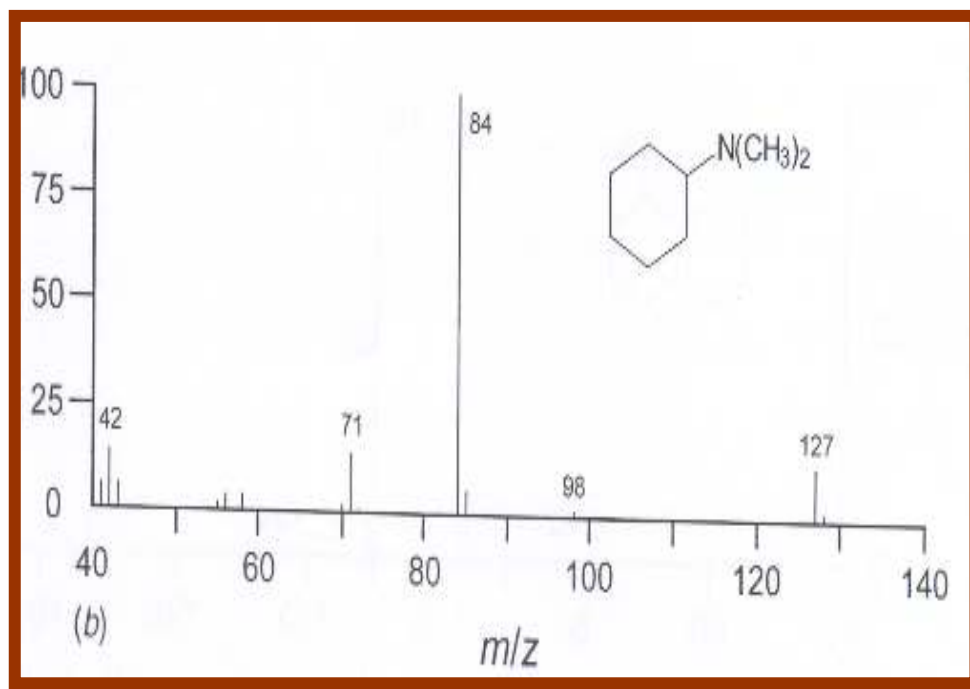
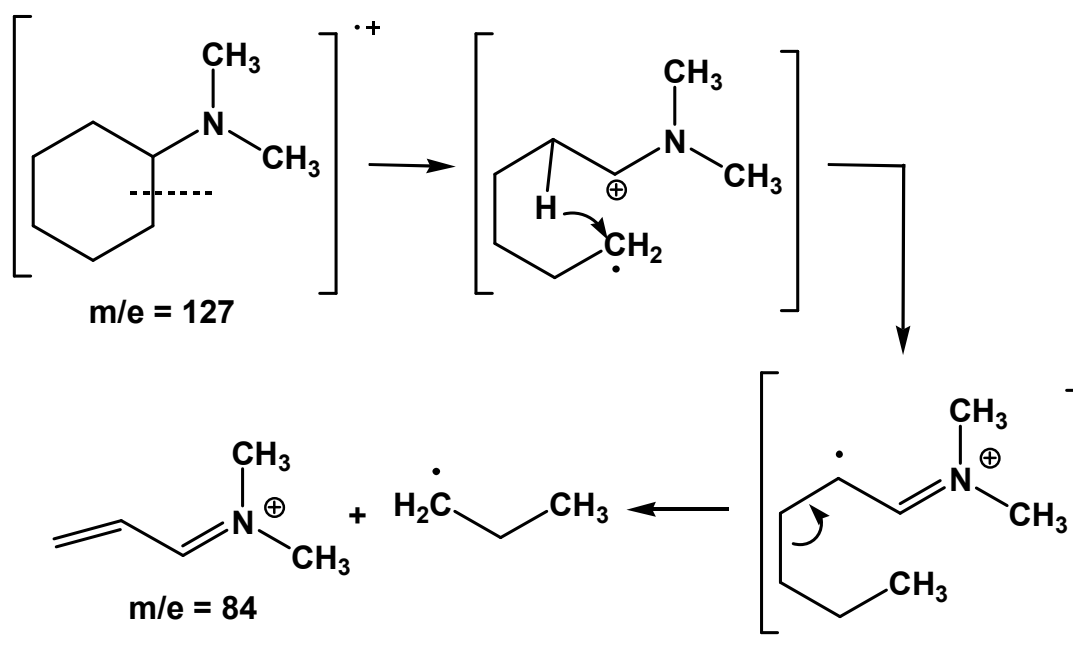




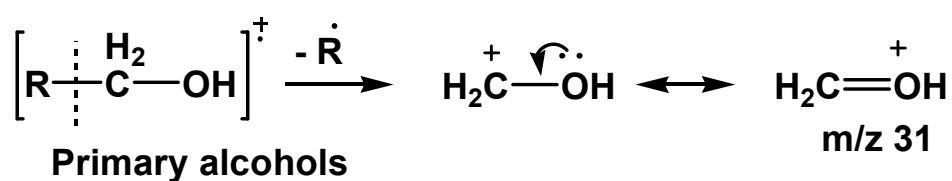
3-Aminopentane



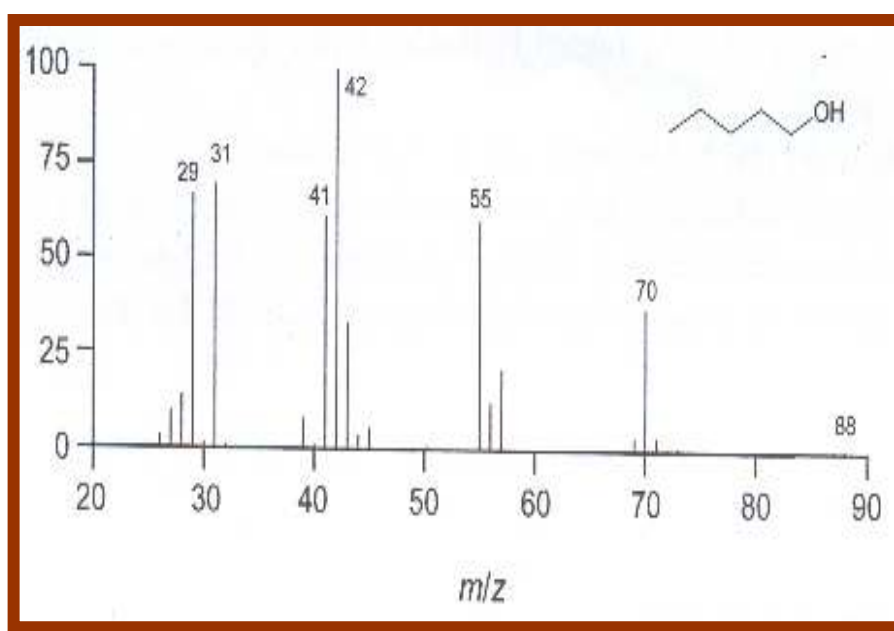
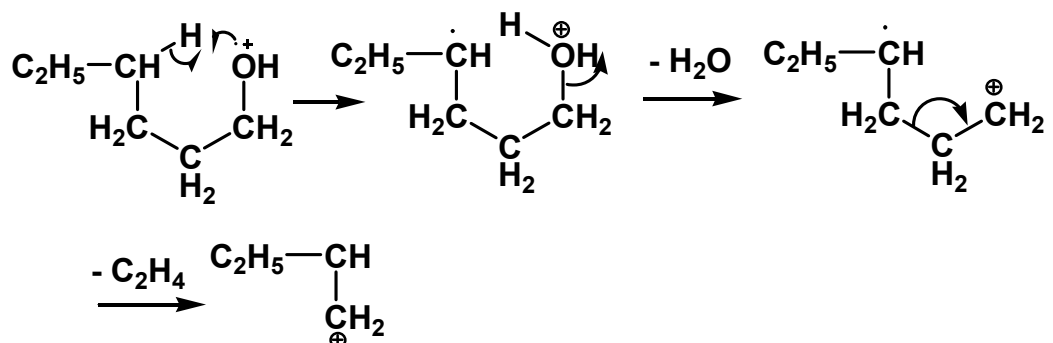
Cycloalkylamines (Cyclohexanone-type Rearrangement)



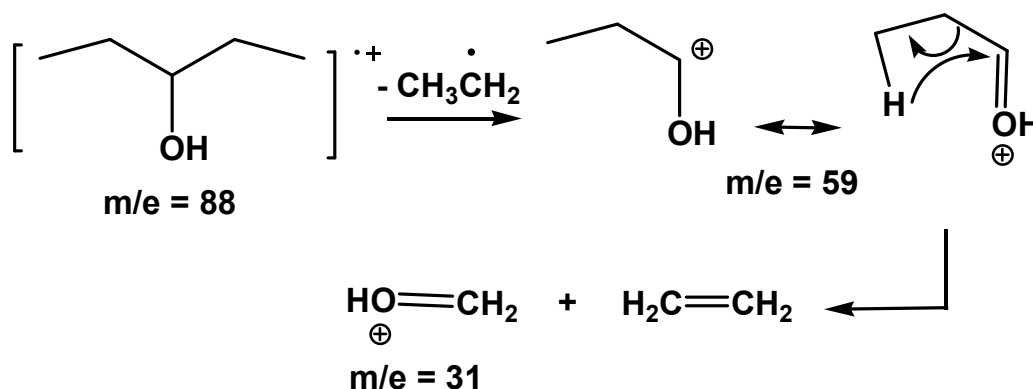
7. Alcohols: Cleavage of α -bond next to the OH group to give cation which stabilized by resonance

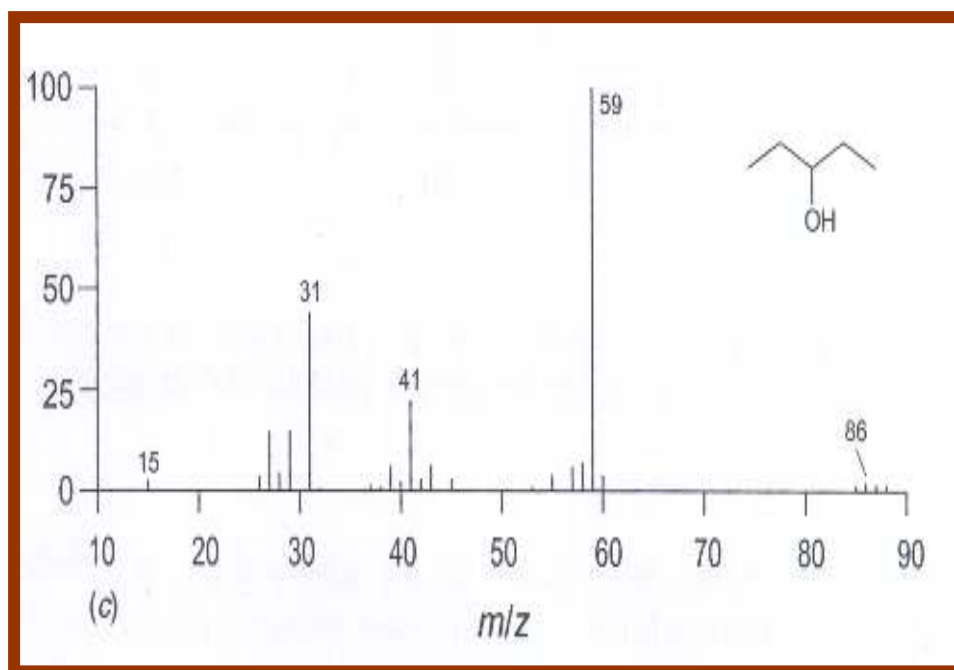


For alcohols containing four or more carbon atoms, they undergo simultaneous elimination of H_2O and ethylene molecules

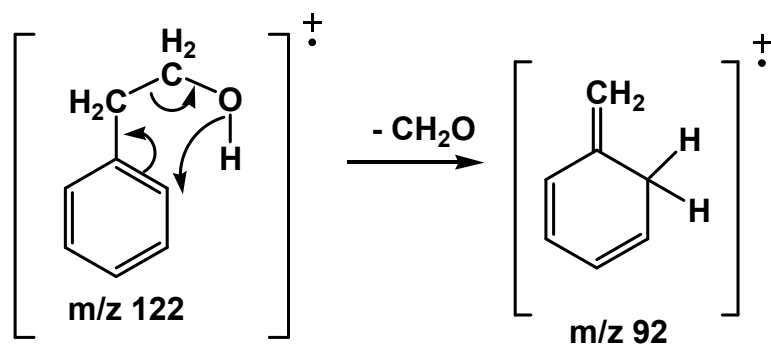


Many secondary and tertiary alcohols undergo α -cleavage followed by elimination of alkene molecule through hydride (H^-) shift. Same behavior was observed in case of primary alcohols in which the (OH) group is internal as shown in case of 3-pentanol.

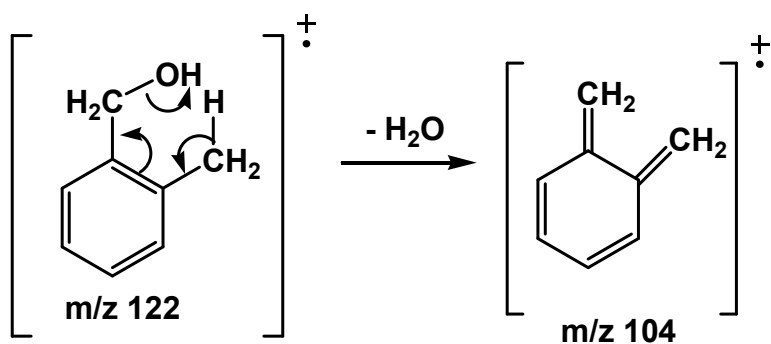




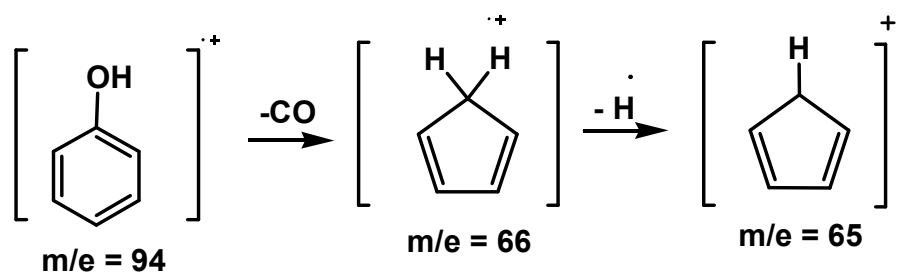
When the aromatic alcohols contains two or more carbon atoms on side chain (e.g. 2-phenylethanol) they loss CH_2O from the molecular ion peak



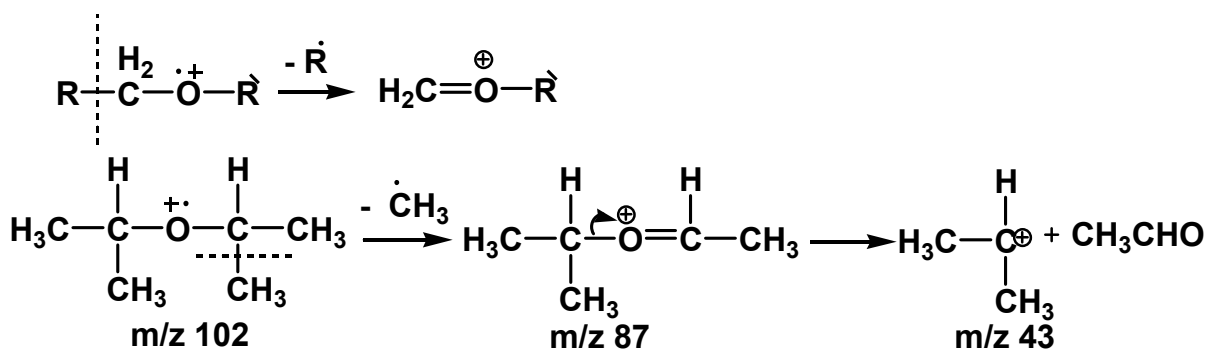
Ortho-Effect: in case of o-substituted aromatic alcohols they will loss water
e.g. 2-methyl benzyl alcohol



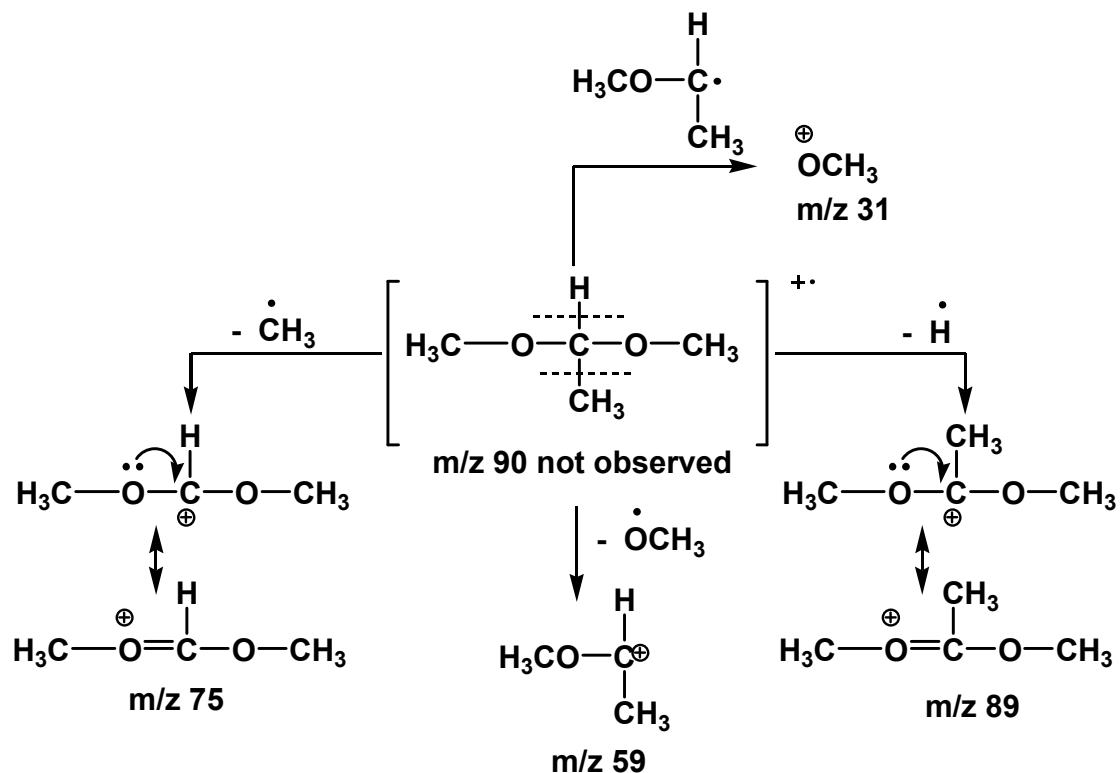
8. Phenols



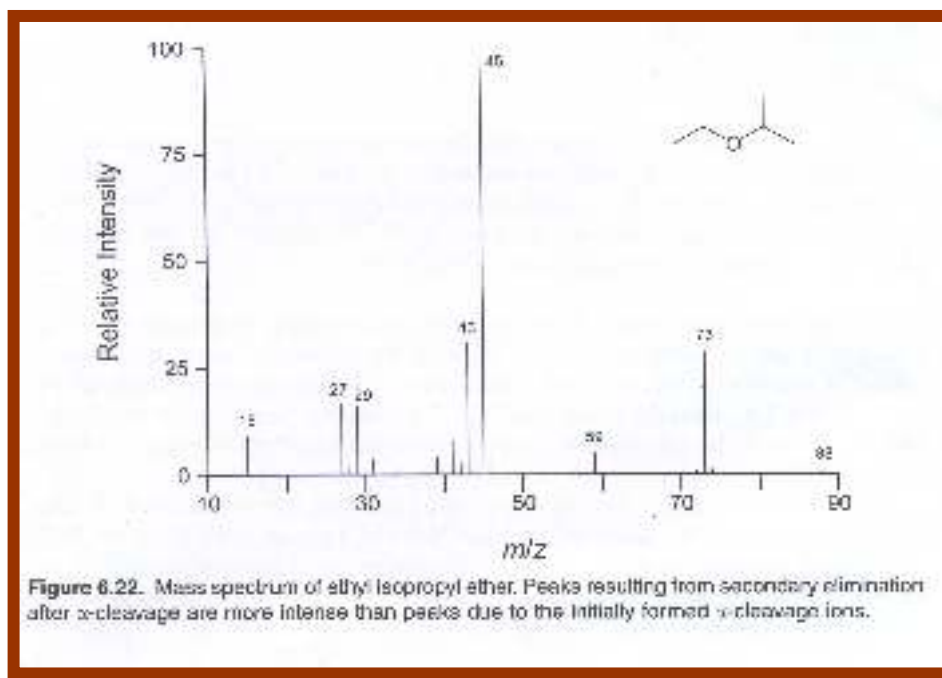
9. Ethers: Cleavage of α -bond to give stable carbocation as shown



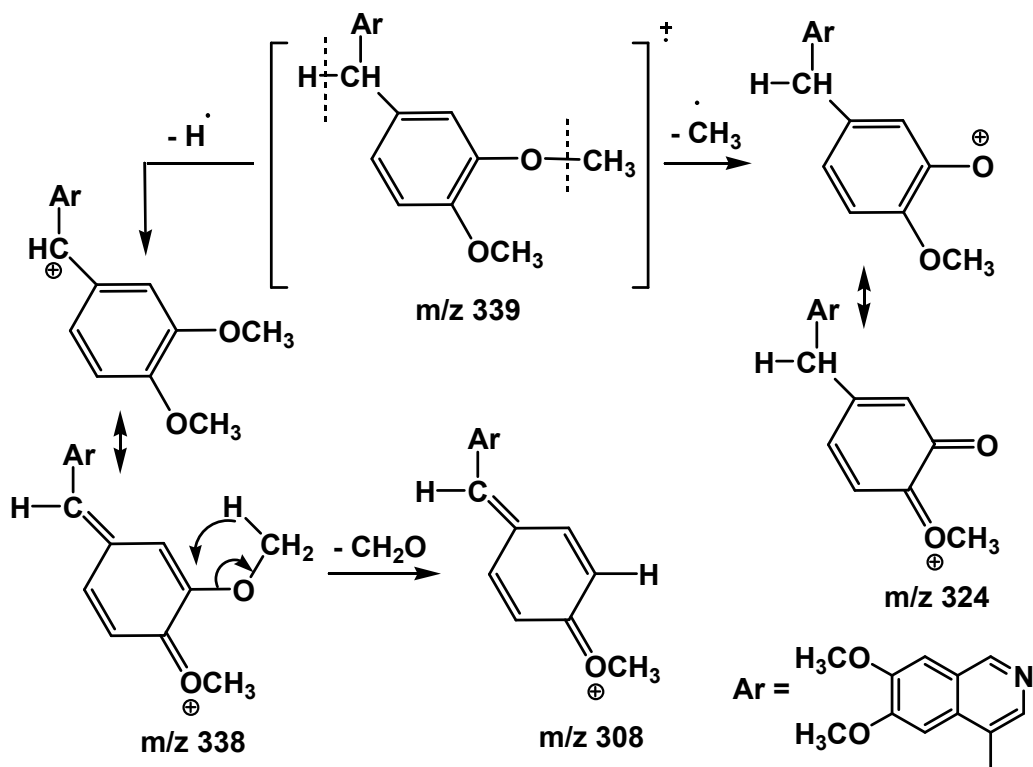
1,1-Dimethoxyethane

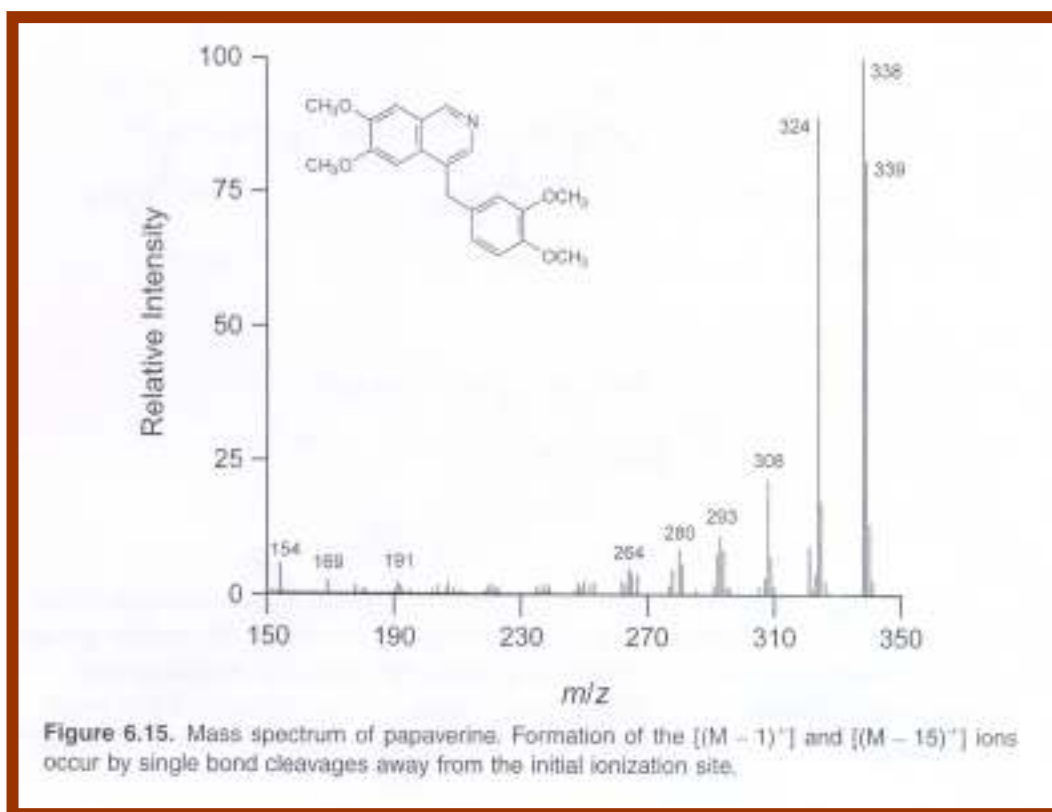


Much dialkyl ether undergoes α -cleavage followed by elimination of alkene molecule through hydride (H^-) shift. (Ethyl isopropyl ether)

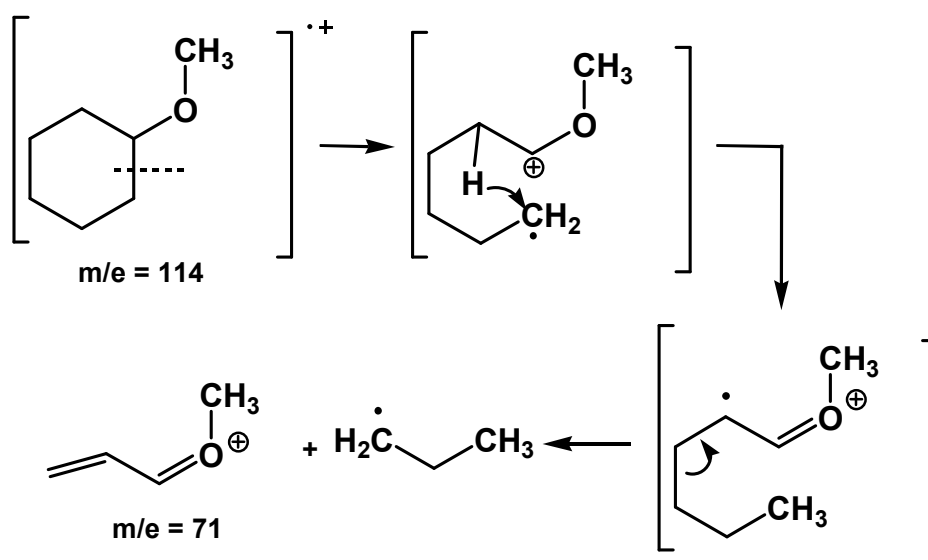


Aromatic ethers

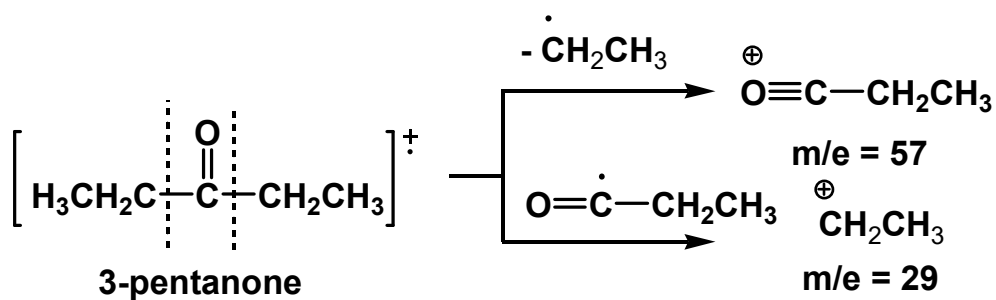
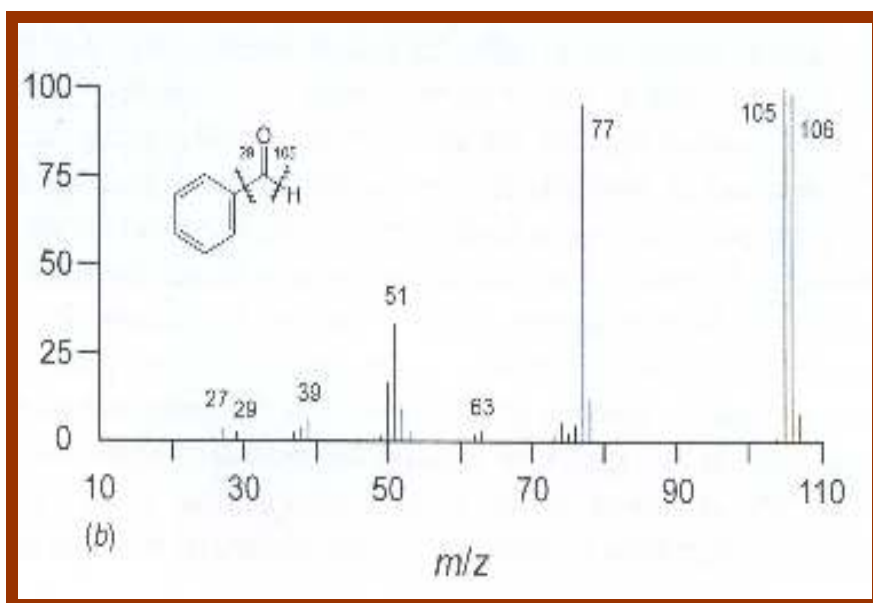
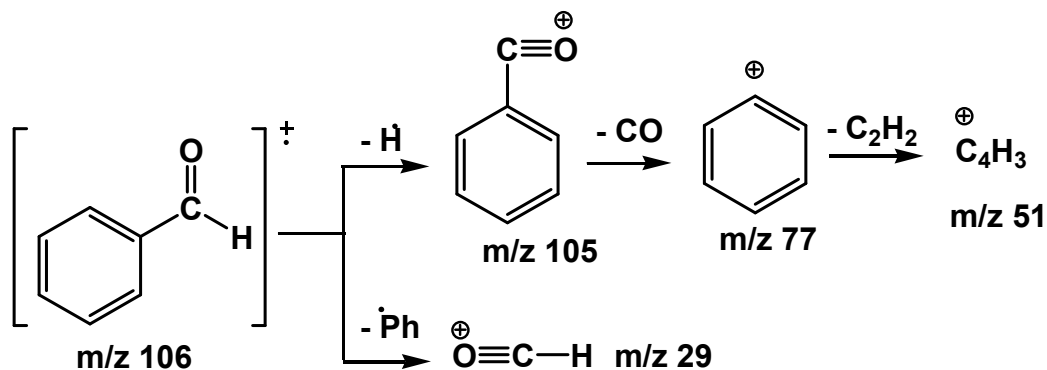
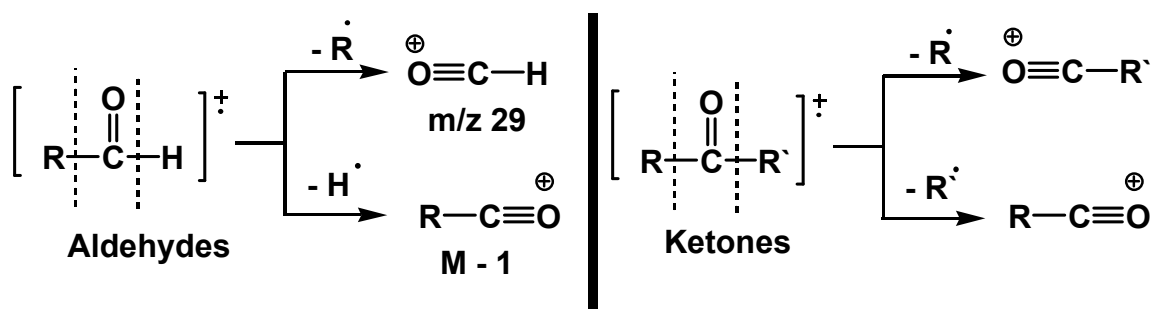


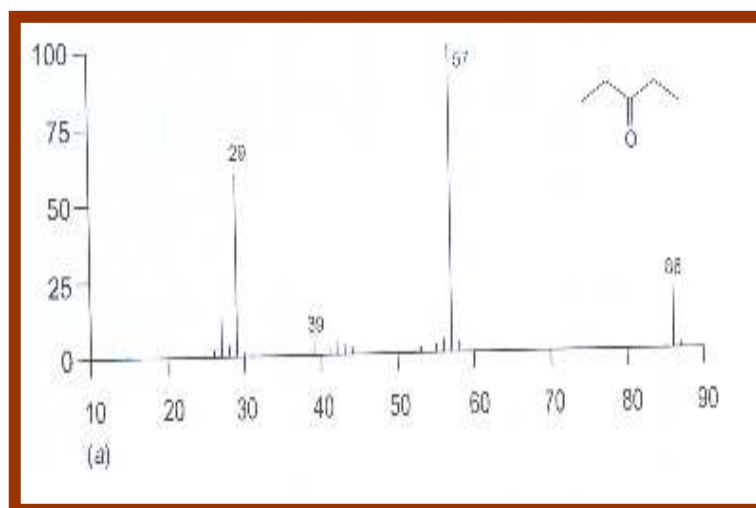


Cycloalkyl ether (Cyclohexanone-type Rearrangement)



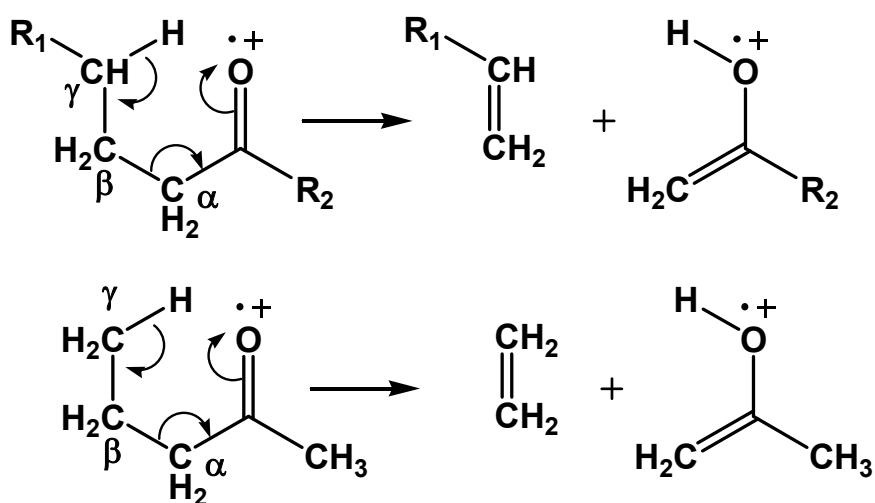
10. Aldehydes and Ketones : Cleavage at both side of carbonyl group

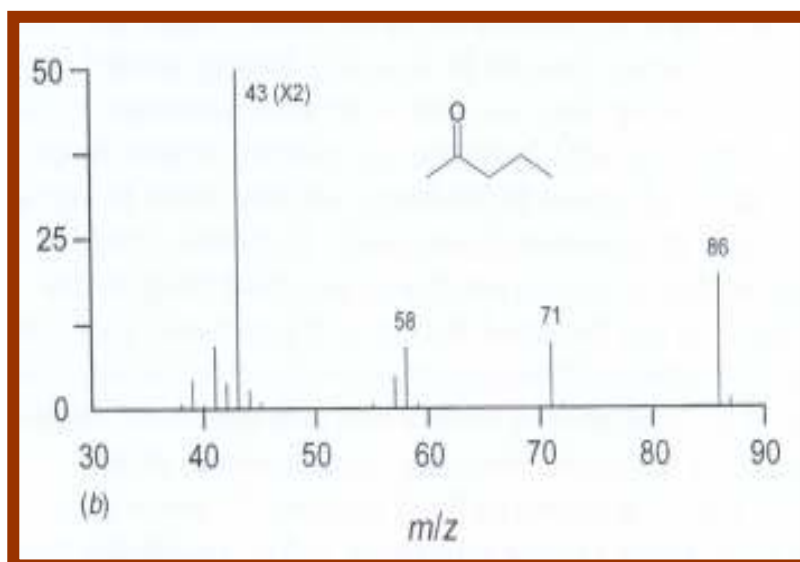




McLafferty type cleavage (γ -Hydrogen Rearrangement)

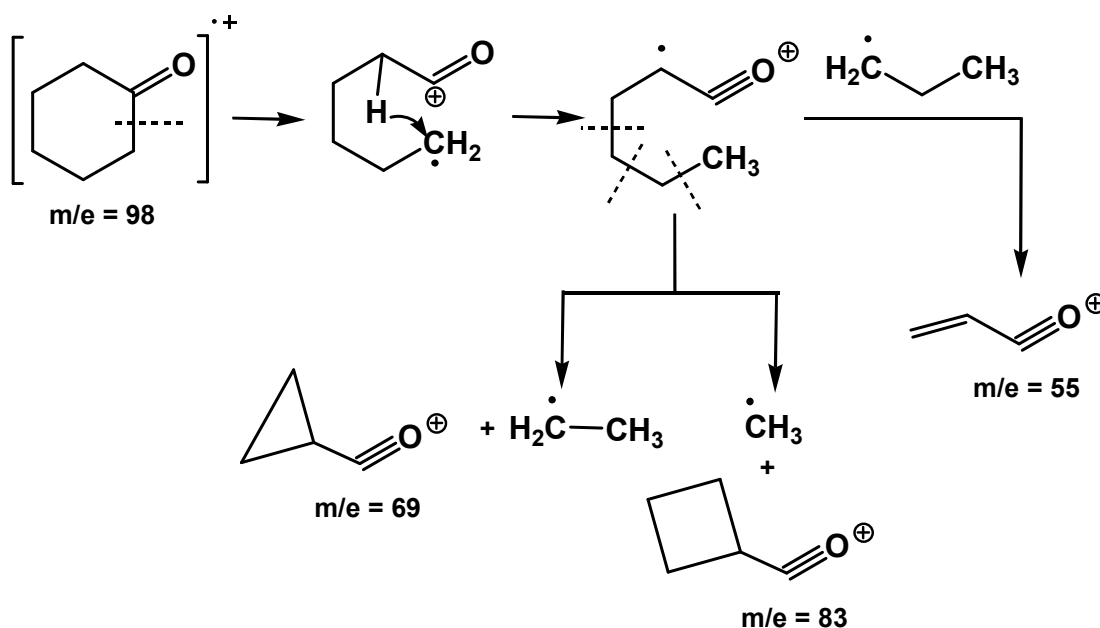
When the alkyl group attached to carbonyl group contain at least 3-carbon atoms (γ - carbon atom) it will carry out **McLafferty type cleavage** through γ -H migration followed by elimination of alkene at β -bond as shown in 2-pentanone

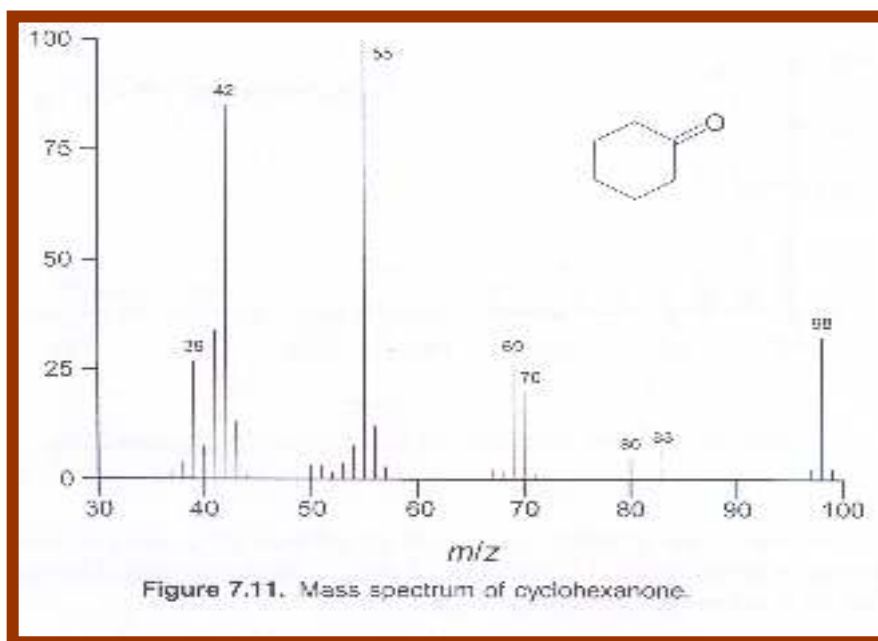
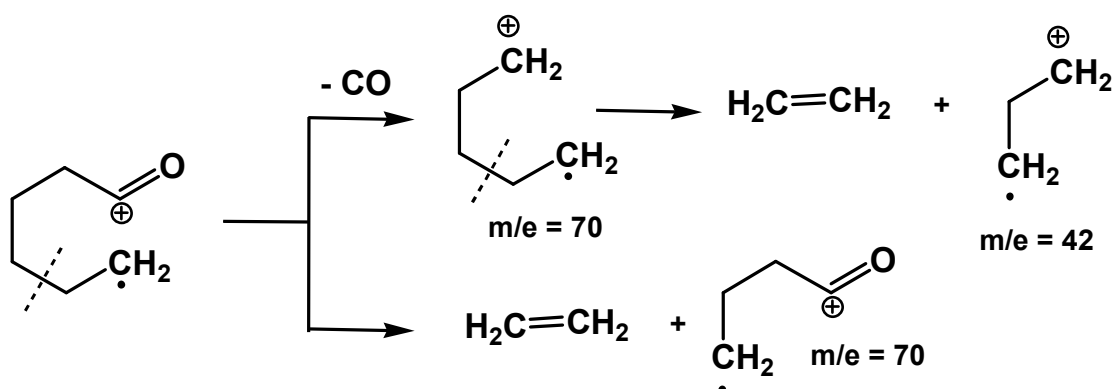




CYCLOHEXANONE-TYPE REARRANGEMENT

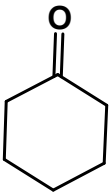
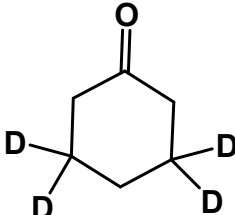
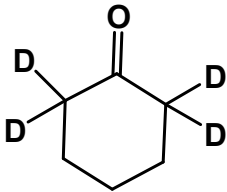
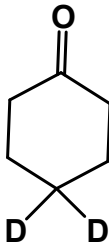
Cyclohexanone is a ketone, the most likely fragmentation to occur after initial ionization at the O atom is α -cleavage on either side of the carbonyl group. This cleavage involves no loss of mass. The spectrum of cyclohexanone shows the peak at m/z 83, representing the loss of $\cdot\text{CH}_3$, as well as those at m/z 69 (loss of $\cdot\text{CH}_2\text{CH}_3$), m/z 55 (base peak), m/z 70 (losses of $\text{CH}_2=\text{CH}_2$ or CO), and m/z 43 (losses of $\text{CH}_2=\text{CH}_2$ and CO).



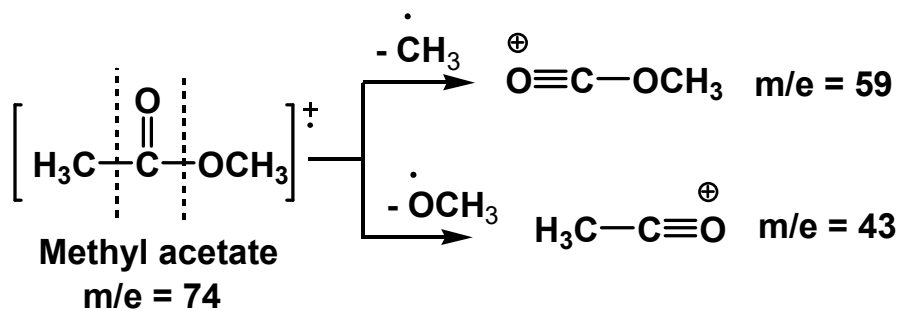
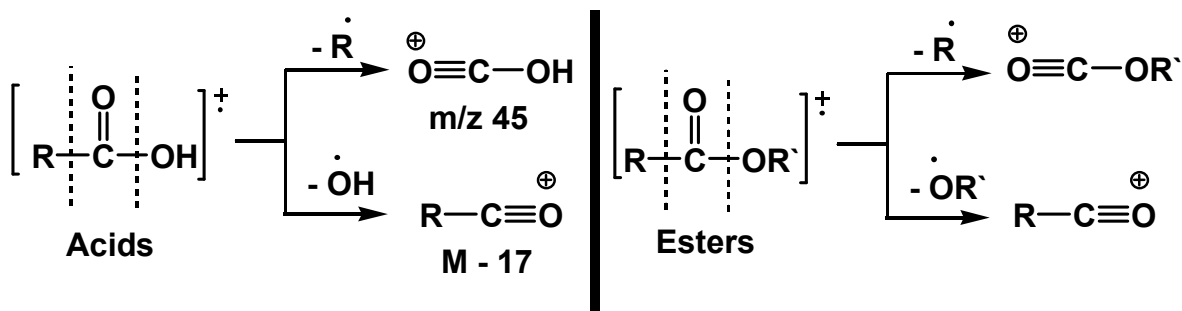


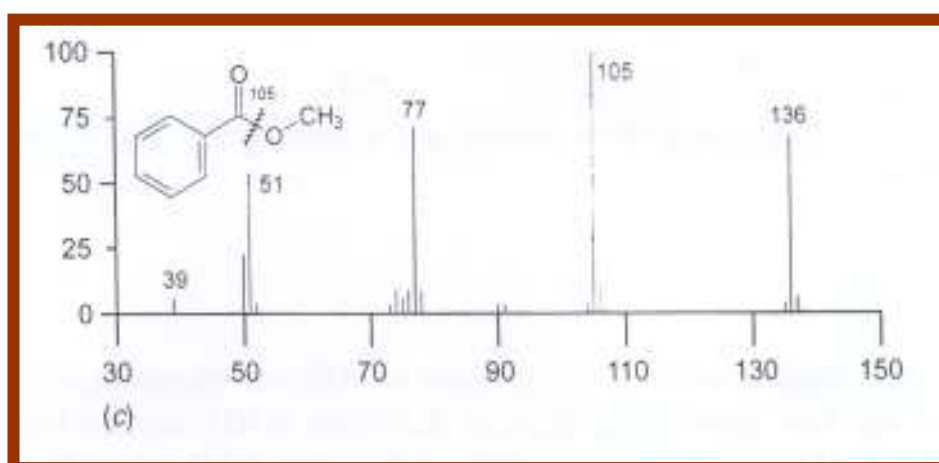
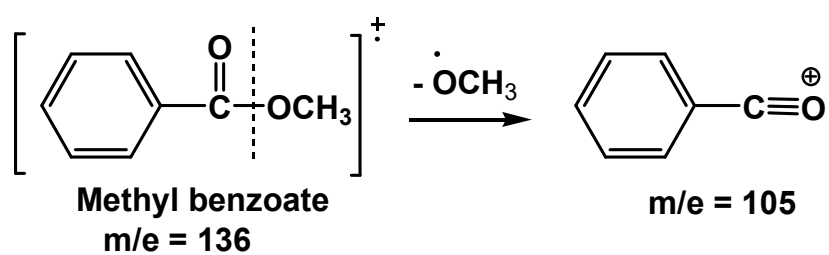
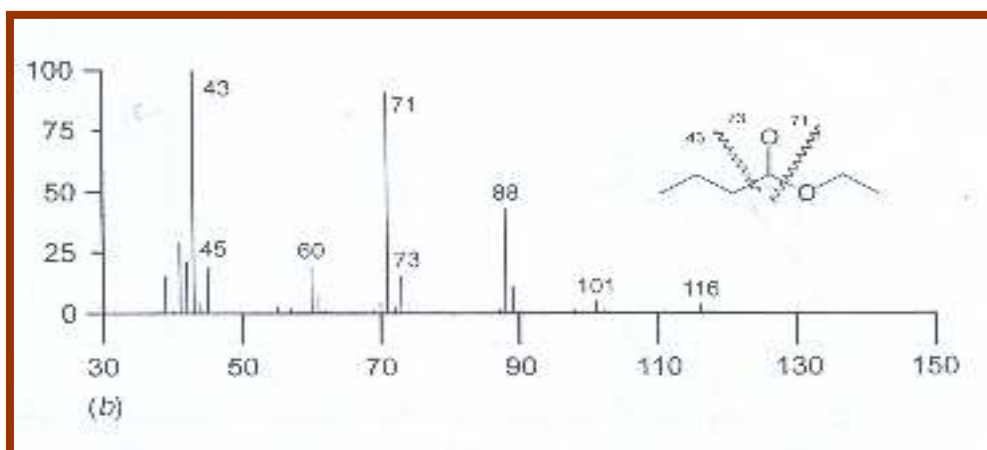
Determining a mechanism for formation of the base peak at m/z 55 involved studying the mass spectra of labeled derivatives in the spectrum of **2,2,6,6-tetradeuteriocyclohexanone**, the base peak was found at m/z 56 (three of the four D atoms were lost in the fragmentation). The spectrum of **3,3,5,5-tetradeuteriocyclohexanone** had a base peak at m/z 57, consistent with the loss of two of the four D atoms. Finally, the base peak in the spectrum of **4,4-dideuteriocyclohexanone** occurred at m/z 55, indicating the loss of C4 and its attached D atoms.

Cyclohexanone Rearrangement Deuterium Labeling Studies

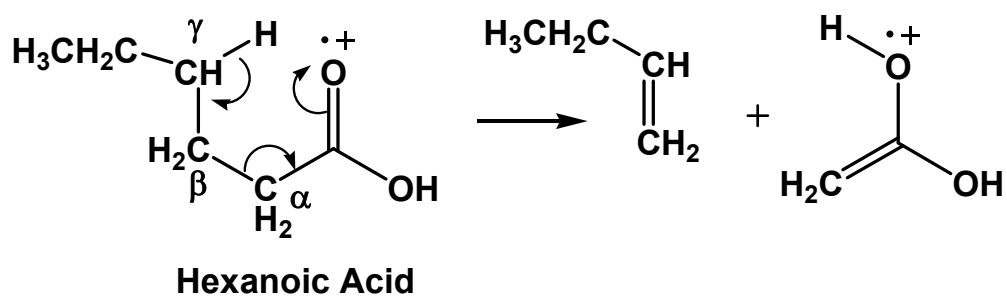
| Compound | Bese Peak | Compound | Bese Peak |
|---|--------------------------|--|-----------------------------|
|  Cyclohexanone | m/e = 55 |  3,3,5,5-Tetradeuterio cyclohexanone | m/e = 57 2D were lost |
|  2,2,6,6-Tetradeuterio cyclohexanone | m/e = 56 3D were lost |  4,4-Dideuterio cyclohexanone | m/e = 55 all D were lost |

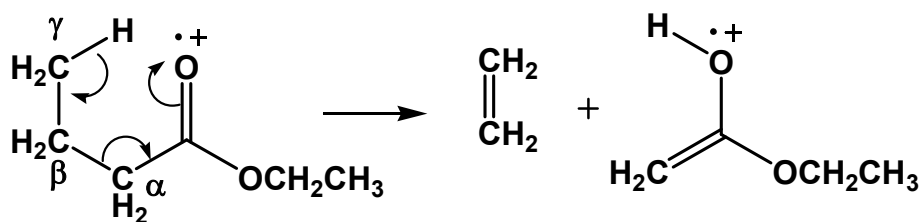
11. Acids and Esters



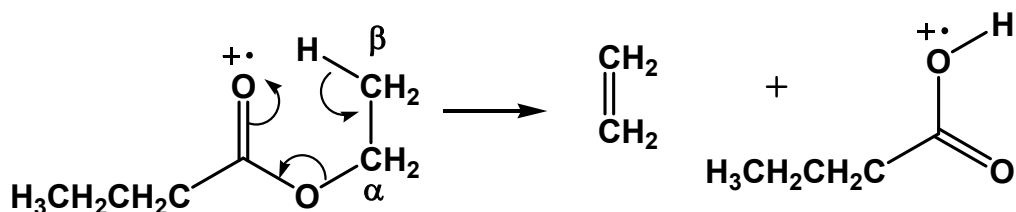


McLafferty type cleavage

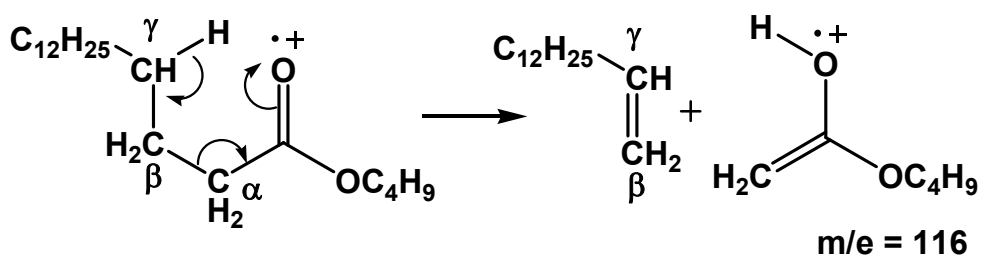




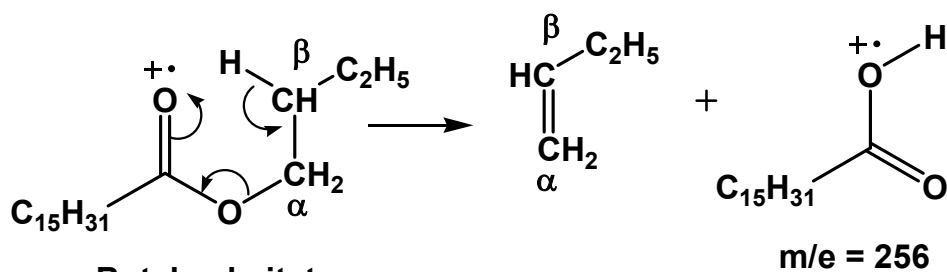
Ethyl butanoate



Ethyl butanoate



Butyl palmitate



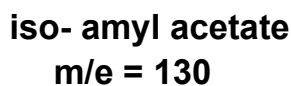
Butyl palmitate

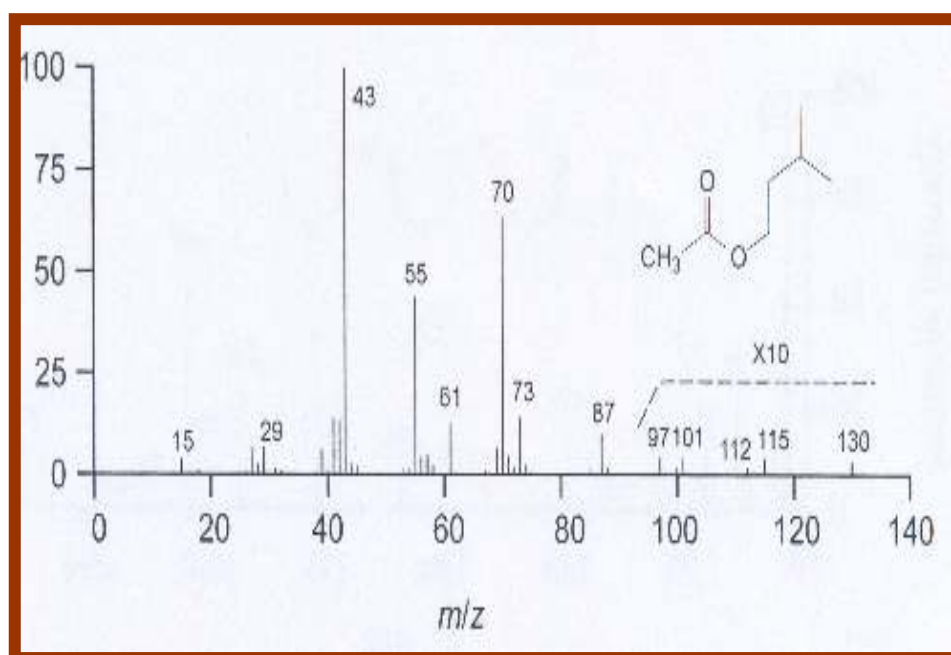
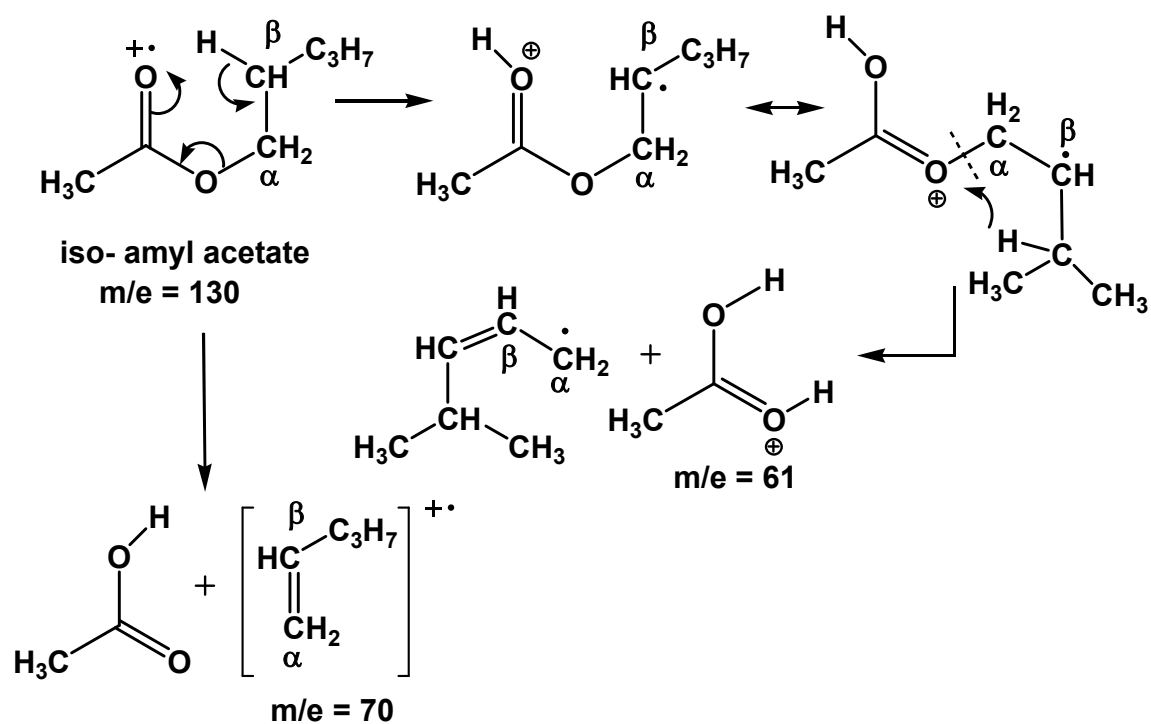
DOUBLE-HYDROGEN REARRANGEMENT (McLAFFERTY + 1)

In the spectrum of butyl palmitate, the ions resulting from the McLafferty rearrangement are (m/z 116 and 256). Another fragment ion at high mass has m/z 257, one m/z unit higher than that of the ion produced by the McLafferty rearrangement on the ester side of the carbonyl group due to the migration of **two H** atoms, it is known both as the **double-hydrogen rearrangement** or the **McLafferty +1** rearrangement.

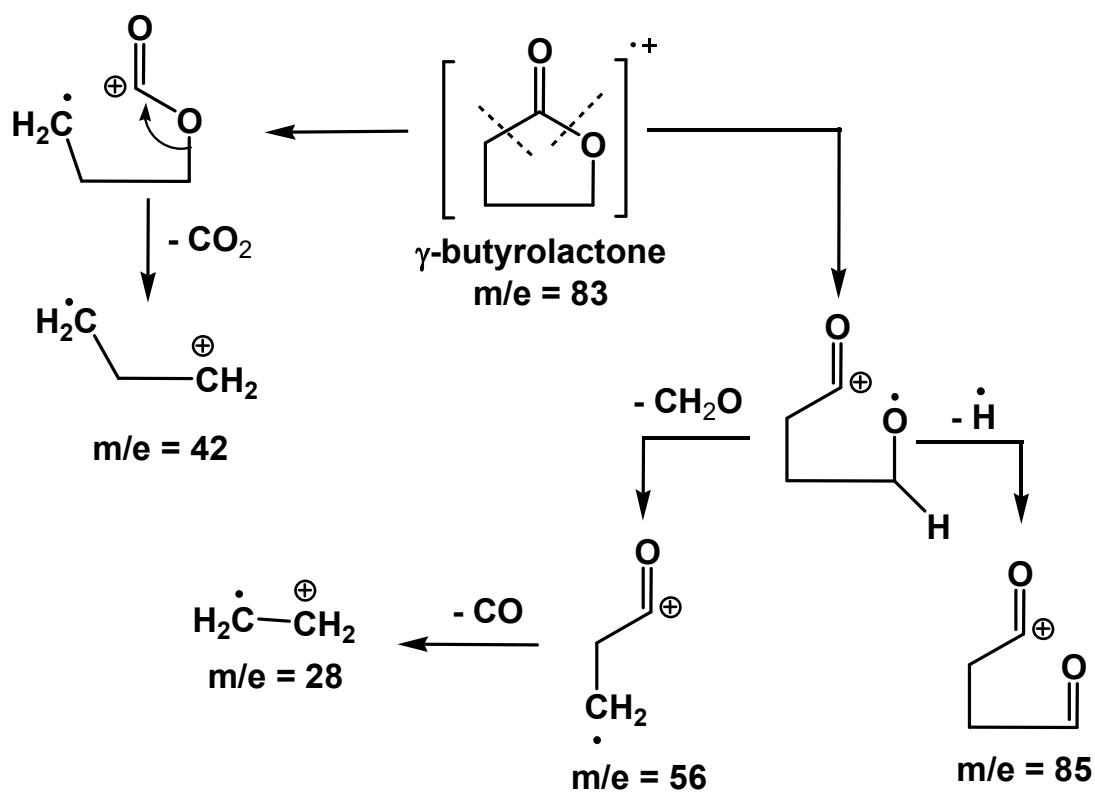


Isoamylacetate

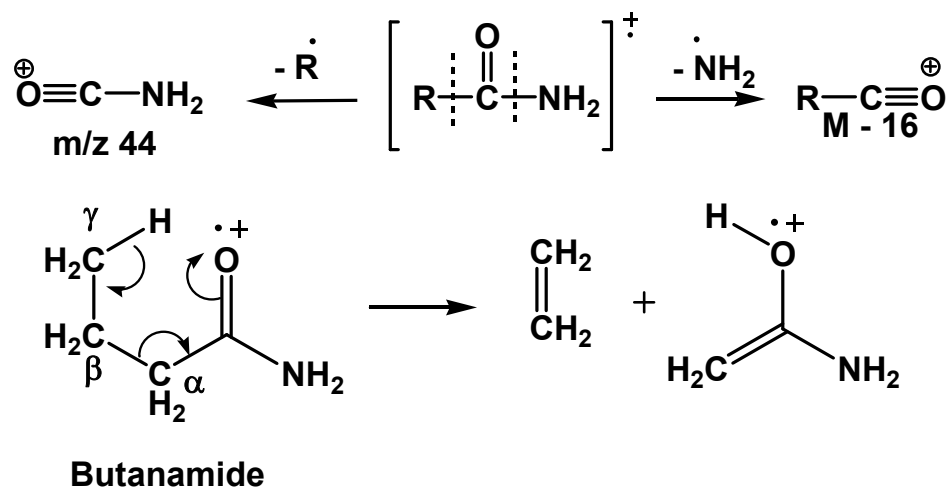


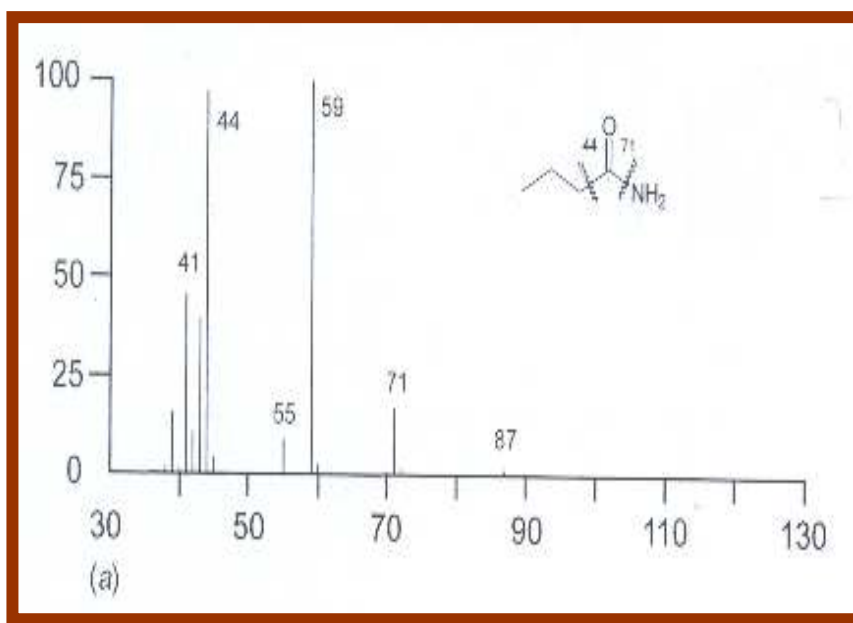


Cyclic Ester (γ -Butyrolactone) (GBL)

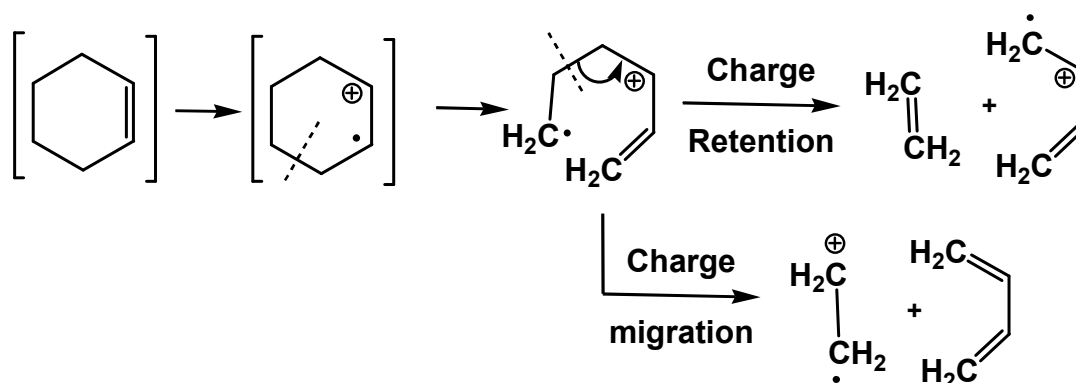


12. Acid amides

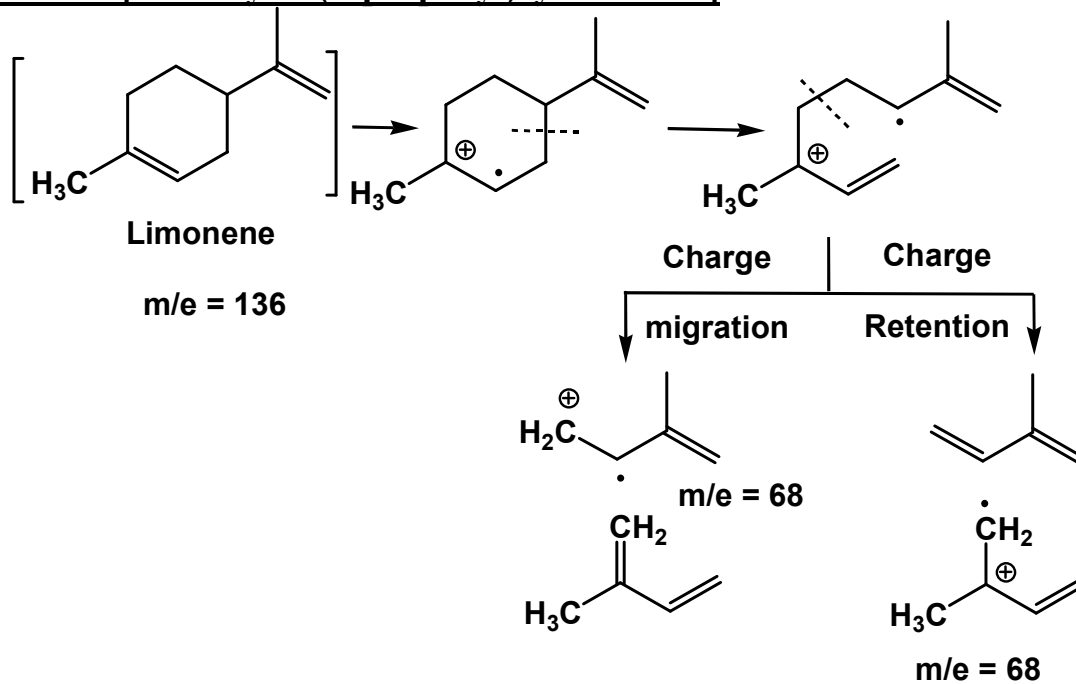


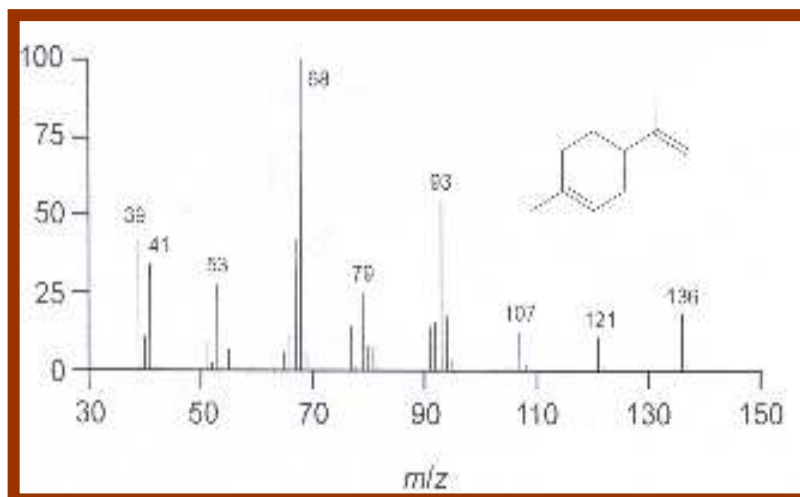


13. Cyclohexene Derivatives (Retro Diels-Alder Fragmentation)

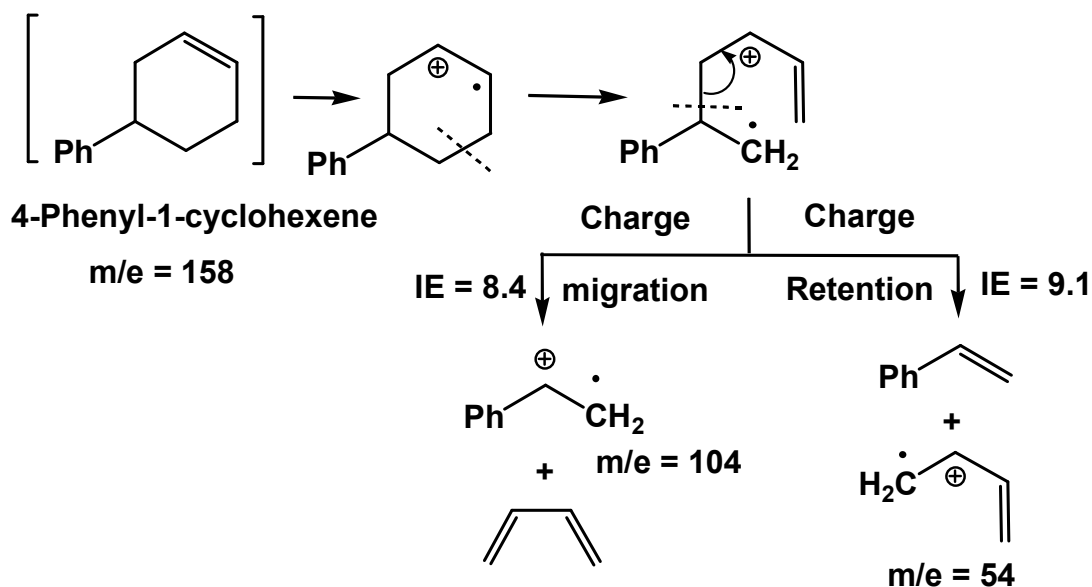


Limonene [1-methyl-4-(2-propenyl)cyclohexene]

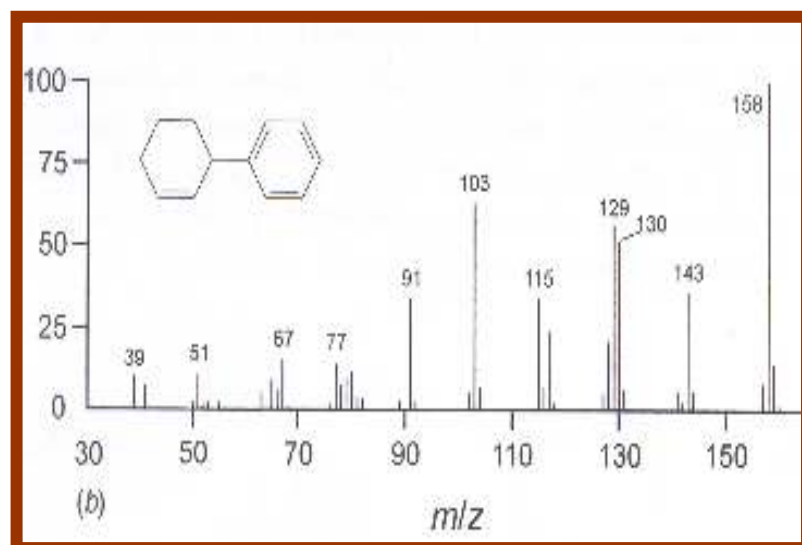
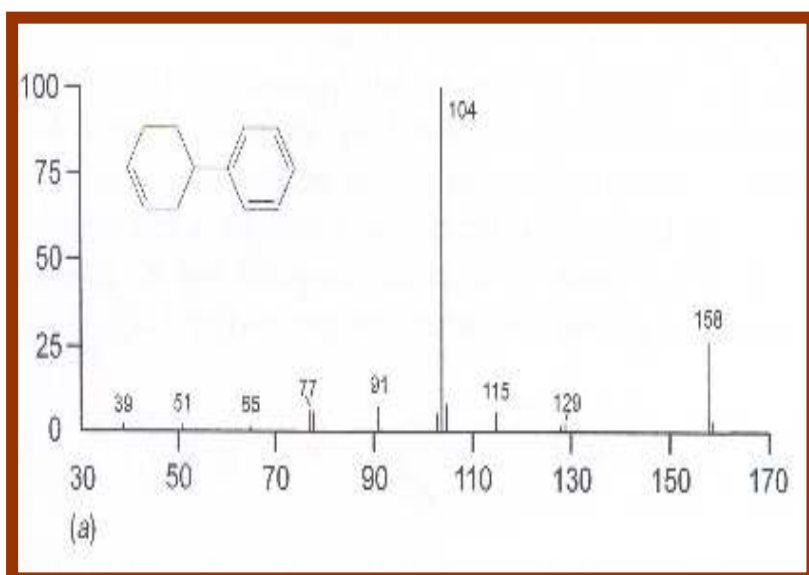
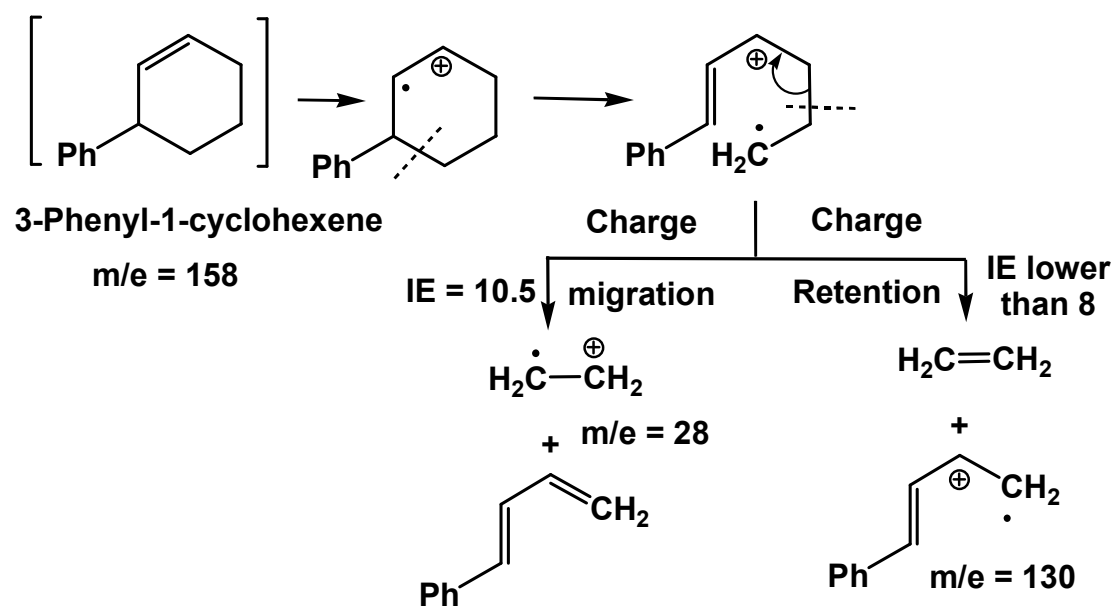




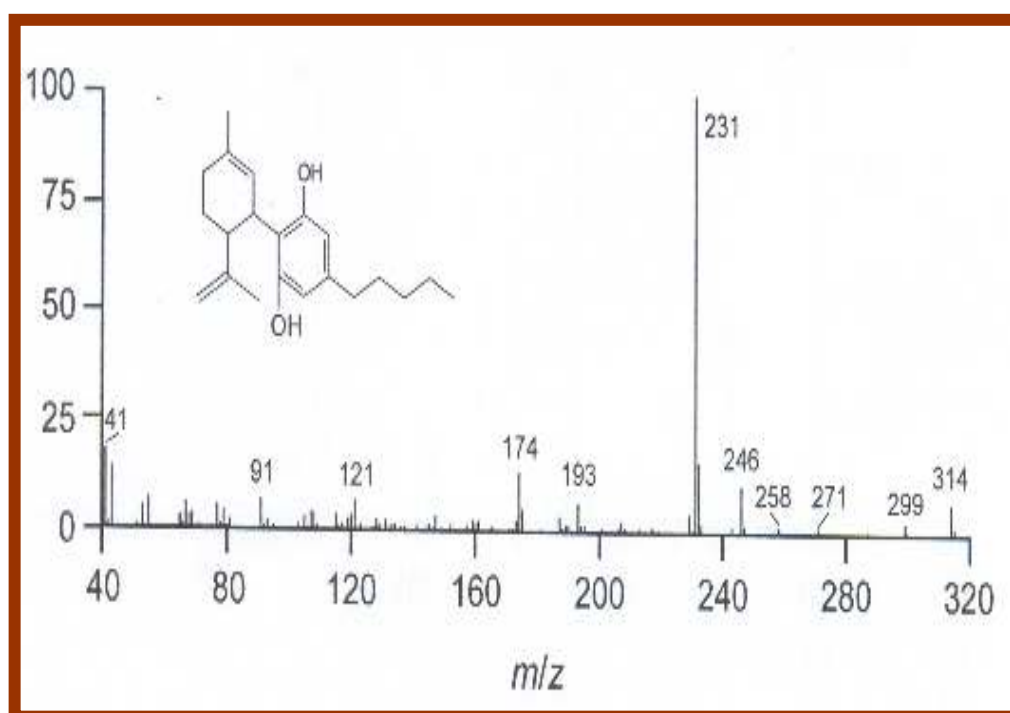
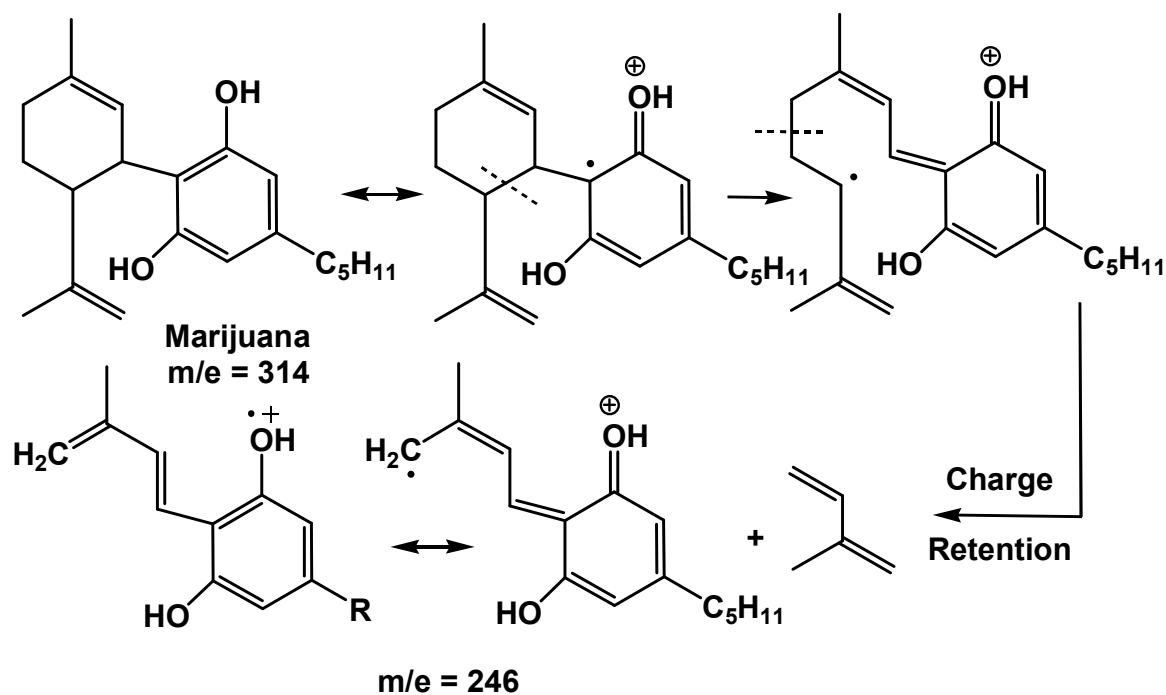
The mass spectra of 3-phenyl-1-cyclohexene and 4-phenyl-1-cyclohexene show quite different responses to the retro Diels-Alder reaction. The 4-phenyl isomer produces either butadiene (m/z 54) or styrene (m/z 104) fragments, with the latter preferred because of its lower IE. Fragmentation pathway prefers charge migration with lower ionization energy, so fragment 104 is more predominate.



On the other hand, 3-Phenyl-1-cyclohexene, produces either ethylene (m/z 28) or 1-phenylbutadiene (m/z 130) fragments. Fragmentation pathway prefers charge retention with lower ionization energy, so fragment 130 is more predominate.



Marijuana: the ionization took place from oxygen atom (with lower IE) instead of double bond inside cyclohexene ring.

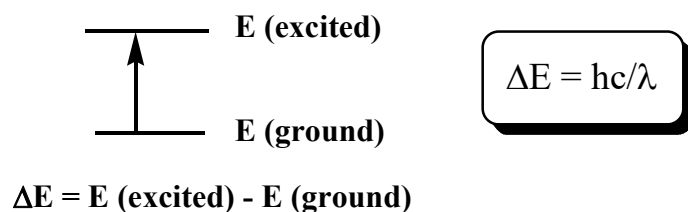


Pyridine: elimination of HCN from molecular ion peak produce cyclobutadiene as radical cation with m/e = 52.

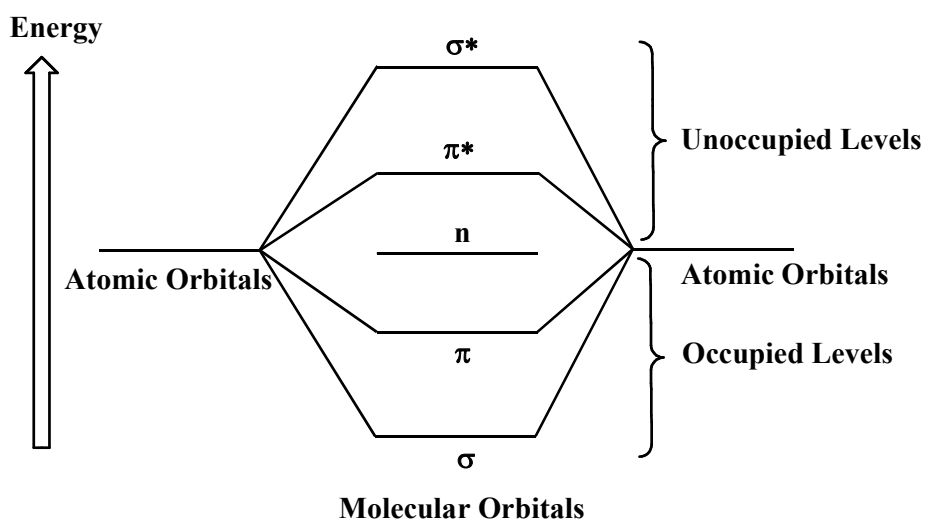
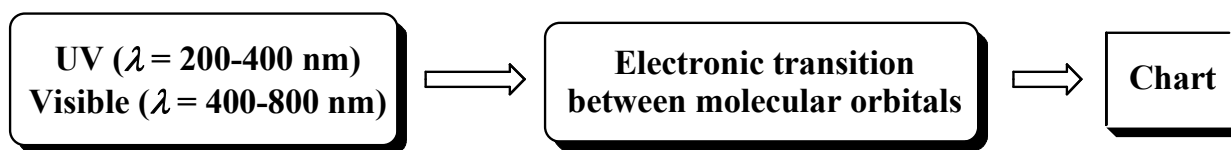
Ultraviolet Spectroscopy

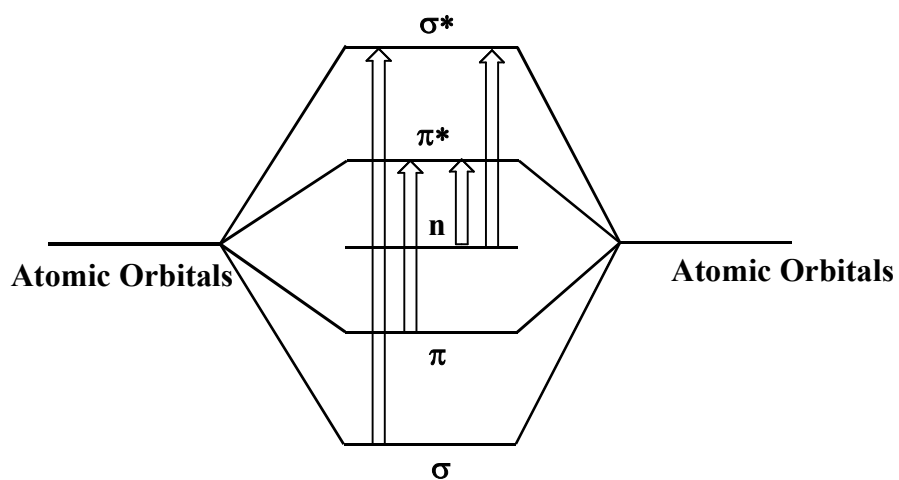
Nature of Electronic Transitions

Usually absorption of energy leads to transition of atoms or molecules from a **ground state** to the **excited state** as shown



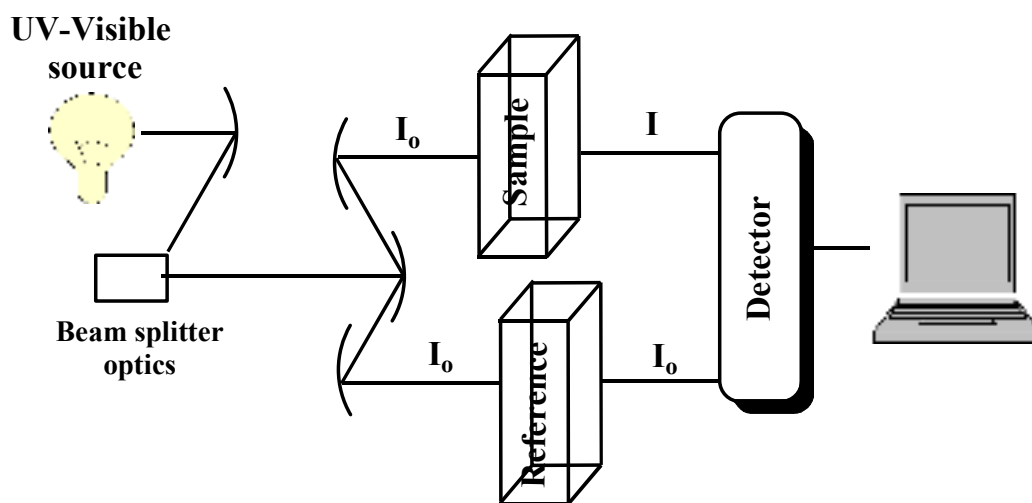
Absorption of **Ultraviolet** ($\lambda = 200\text{-}400\text{ nm}$) and **visible radiation** ($\lambda = 400\text{-}800\text{ nm}$) leads to electronic transition between molecular orbital levels





Electronic Transition between Molecular Orbitals

| Molecular Transition | Organic Compounds | λ (nm) |
|-----------------------------------|--|----------------|
| $\sigma \longrightarrow \sigma^*$ | Alkanes | 150 |
| $\pi \longrightarrow \pi^*$ | Alkenes, Carbonyl compounds Alkynes, Azo compounds, etc | 180 |
| $n \longrightarrow \sigma^*$ | Oxygen, Nitrogen, Sulfur and Halogen compounds | 190 |
| $n \longrightarrow \pi^*$ | Carbonyl compounds | 300 |



Principles of Absorption Spectra

Beer-Lambert Law

$$\text{Log } (I_0/I) = A = \epsilon cl$$

for a given wavelength

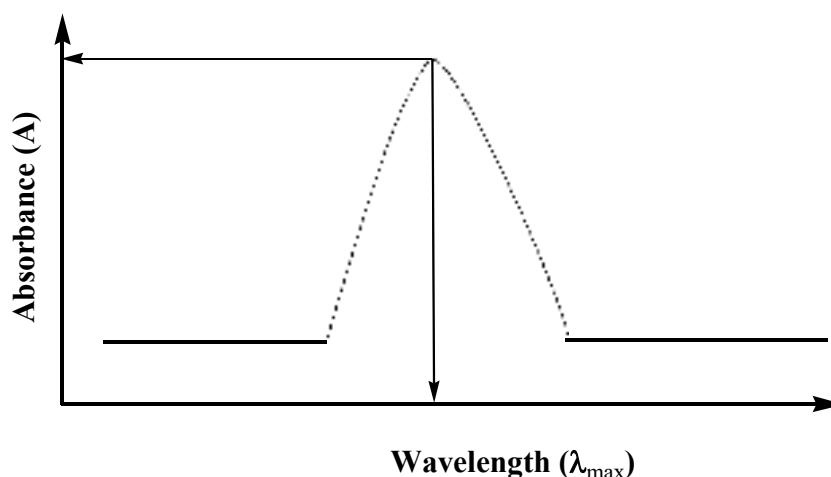
(I_0): the intensity of the incident light; (I): the intensity of the leaving light.

$\log (I_0/I)$ is known as **absorbance (A)**

(c): **molar concentration** of the sample; (l): **length of the cell** sample (cm)

(ϵ): **molar absorptivity** (more than 10^4 corresponding to high intensity absorption while less than 10^3 corresponding to low intensity absorption)

The spectrum in UV and Visible is a relation between wavelength (λ_{max}) and absorbance (A)



Solvents

Solvents, which used in the UV spectra, must have no absorption (transparent) band in the UV-Visible regions (200-800 nm).

Solvent cut-off points

| | | | |
|--------------|--------|----------|--------|
| Acetonitrile | 190 nm | n-Hexane | 201 nm |
| Chloroform | 240 nm | Methanol | 205 nm |
| Cyclohexane | 195 nm | Water | 190 nm |
| Ethanol | 205 nm | Dioxane | 215 nm |

Important Definitions

Chromophore: Unsaturated group responsible for electronic transition

(C=C, C=O, NO₂....etc)

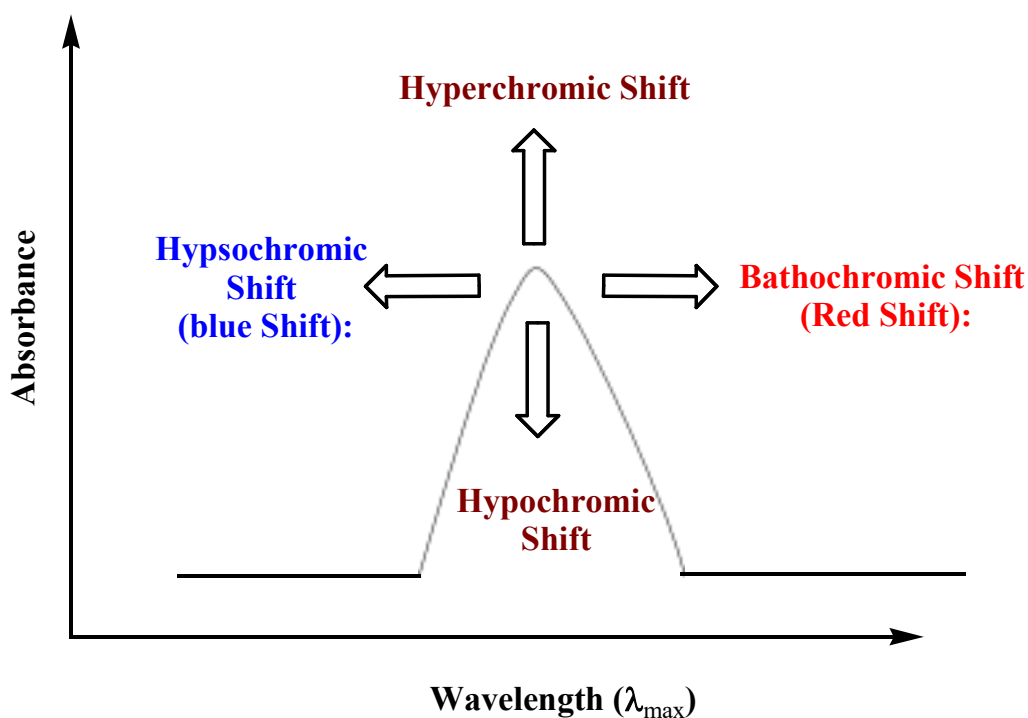
Auxochromophore: Saturated group which contains lone pair of electrons, when attached to the chromophore change the wavelength (λ_{\max}) and/or absorbance (A) e.g. NH₂, OH, SH, Cl

Bathochromic Shift (Red Shift): Shift to increase the wavelength (λ_{\max})

Hypsochromic Shift (blue Shift): Shift to decrease the wavelength (λ_{\max})

Hyperchromic Shift: shift to increase the absorbance (A)

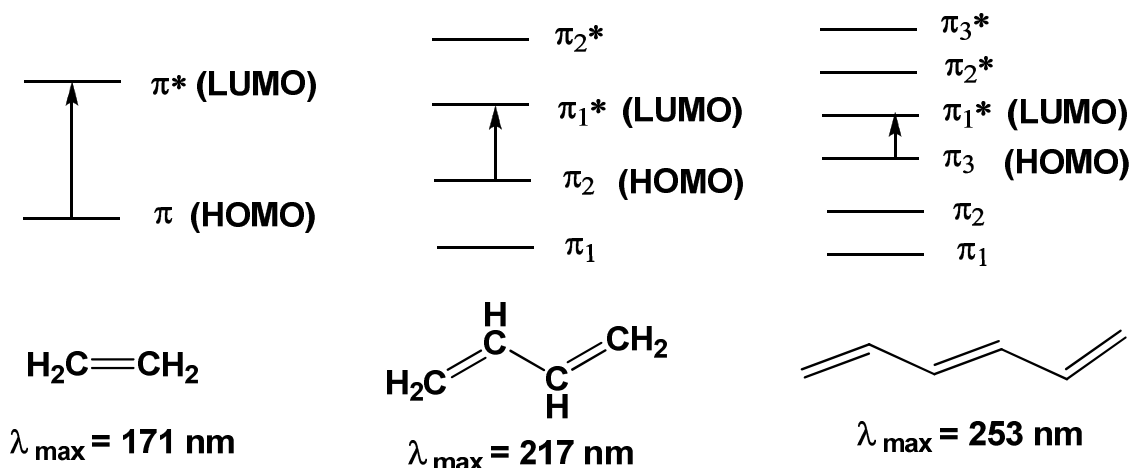
Hypochromic Shift: shift to decrease the absorbance (A)



Factors Affecting on the Wavelength (λ_{\max})

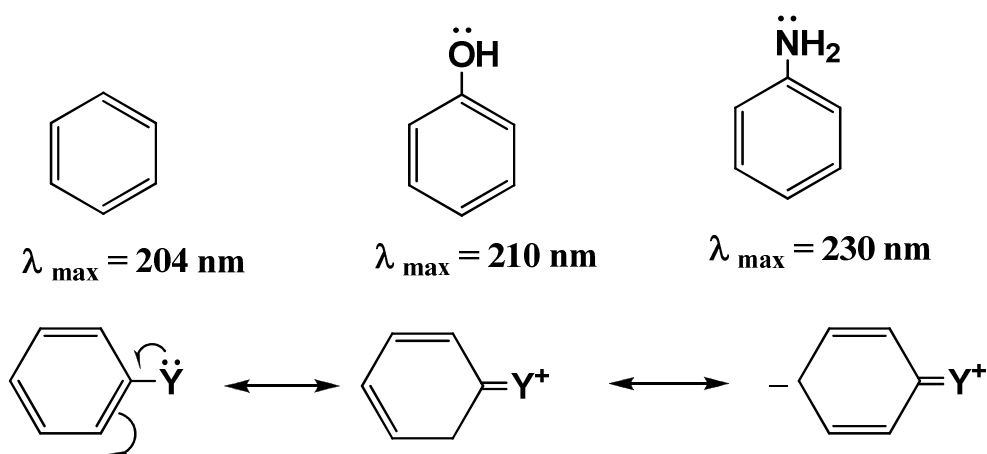
1. Effect of Conjugation

As the conjugation increase, the energy difference for electronic transition decrease and thus wavelength (λ_{\max}) increase



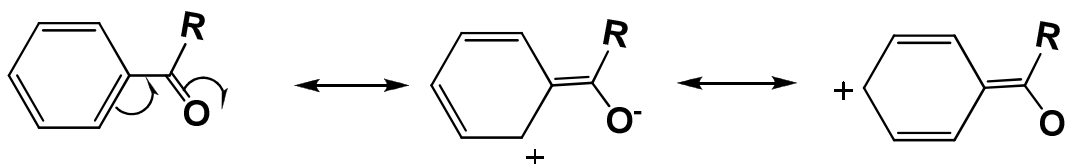
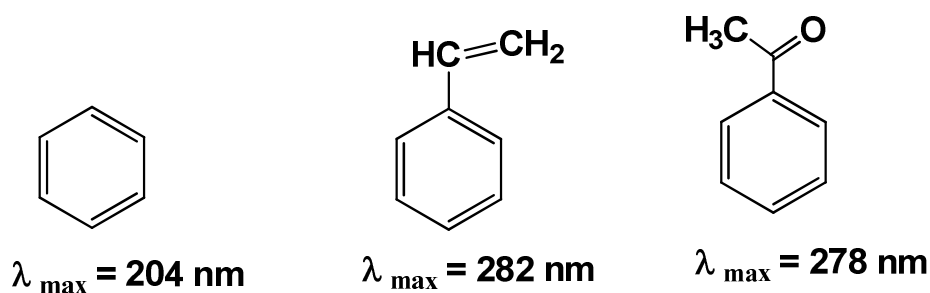
As the conjugation increase the difference in energy between HOMO and LUMO decrease, thus the wavelength (λ_{\max}) increase.

Substitution of a group with unshared electrons on benzene ring leads to increase of (λ_{\max}) due to the effect of conjugation

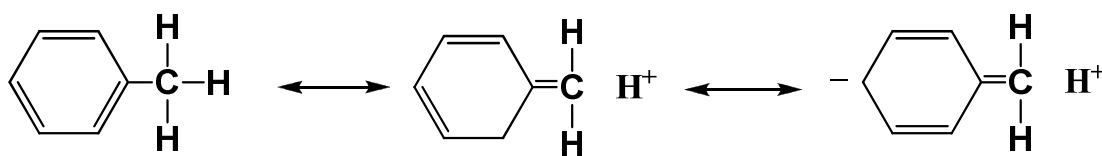
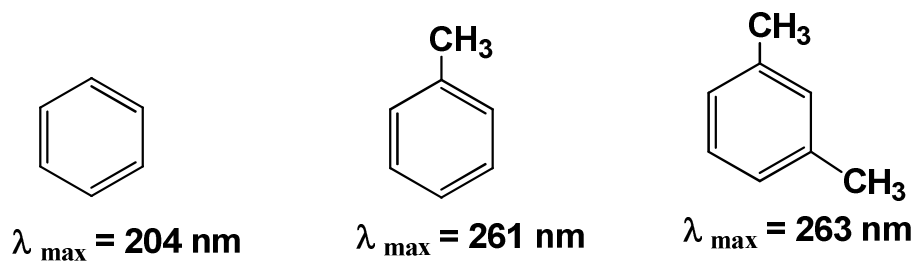


As the electronegativity of the atom attached to benzene ring increase, the effect of conjugation decrease and (λ_{\max}) decrease (Aniline and phenol).

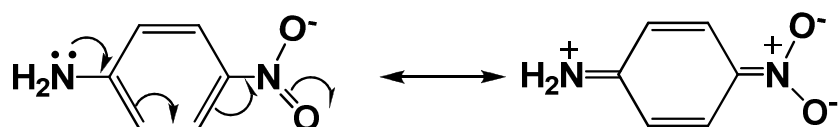
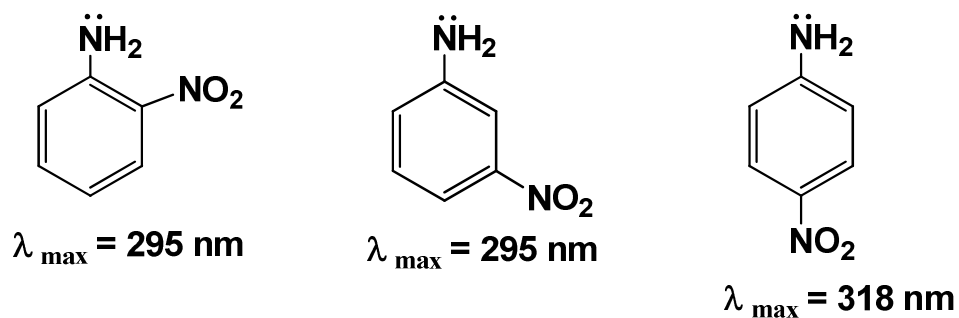
Substitution of a group which, contains π -bond on benzene ring leads to increase of (λ_{\max}) due to the effect of conjugation



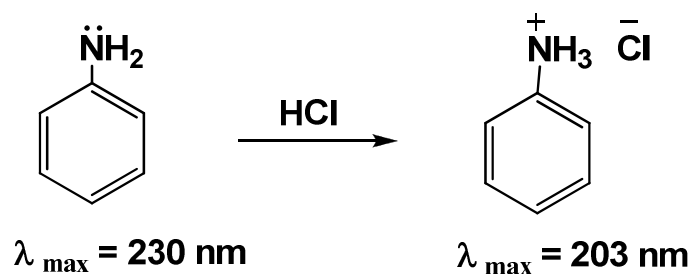
Substitution of an alkyl group on benzene ring leads to increase of (λ_{\max}) due to the effect of **hyperconjugation** (As the number of hydrogen atoms increase the effect of **hyperconjugation** increase, and (λ_{\max}) will increase).



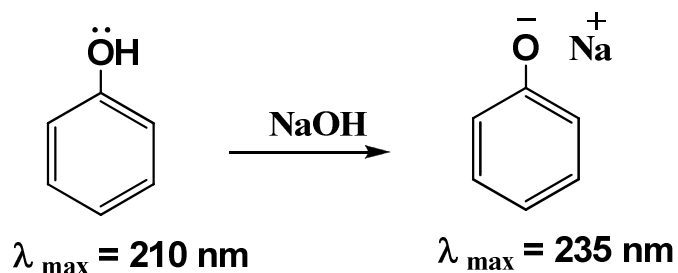
In case of disubstituted benzene ring when one group is **EDG** and other is **EWG** so (λ_{\max}) in case of *Ortho* = (λ_{\max}) in case of *meta* but less than in case of *para* due to direct interaction between two groups.



2. Effect of Medium

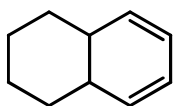


HCl make protonation for the lone pair of electron on nitrogen atom, decrease the conjugation so (λ_{\max}) will decrease

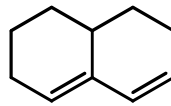


NaOH convert phenol into pheoxide ion, increase the conjugation so (λ_{\max}) will increase

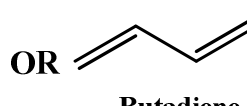
Woodward-Fieser Rules for Dienes



**Homoannular
(Cisoid)**

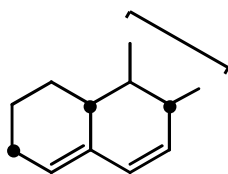


**Heteroannular
(Transoid)**



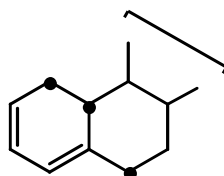
Butadiene

| Base Value | 253 | 214 |
|-----------------------------|-----|-----|
| Double bond extension | 30 | 30 |
| Exocyclic double bond | 5 | 5 |
| Alkyl group or ring residue | 5 | 5 |
| Polar groups | | |
| OAc | 0 | 0 |
| OR | 6 | 6 |
| SR | 30 | 30 |
| Cl, Br | 5 | 5 |
| N(R) ₂ | 60 | 60 |



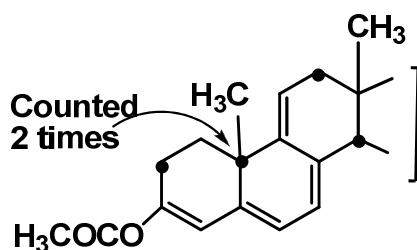
$$214 + 15 \text{ (3- ring residue)} + 5 \text{ (1-exocyclic C=C)} = 234 \text{ nm}$$

Observed = 235 nm



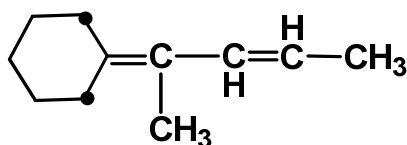
$$253 + 15 \text{ (3- ring residue)} + 5 \text{ (1-exocyclic C=C)} = 273 \text{ nm}$$

Observed = 275 nm



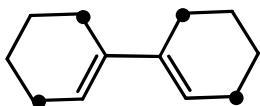
$$253 + 60 \text{ (2-extended C=C)} + 25 \text{ (5- ring residue)} + 15 \text{ (3-exocyclic C=C)} + 0 \text{ (one OCOCH}_3\text{)} = 353 \text{ nm}$$

Observed = 355 nm



$$214 + 10 \text{ (2- ring residue)} + 10 \text{ (2-alkyl groups)} + 5 \text{ (1-exocyclic C=C)} = 239 \text{ nm}$$

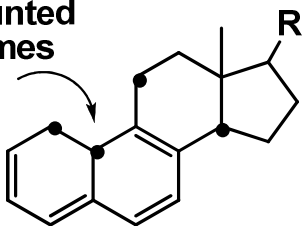
Observed = 238 nm



$$214 + 20 \text{ (4- ring residue)} = 234 \text{ nm}$$

$$\text{Observed} = 233 \text{ nm}$$

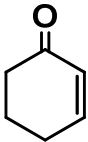
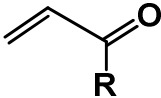
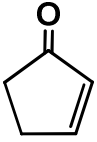
Counted
2 times

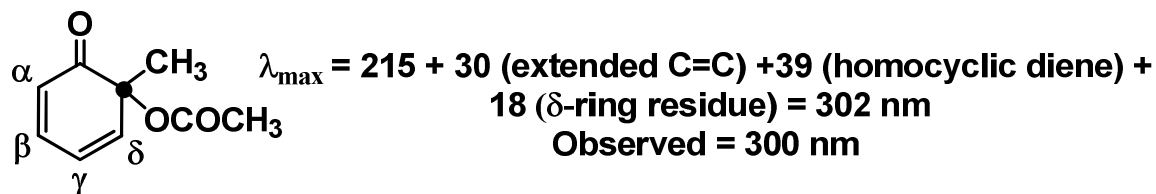
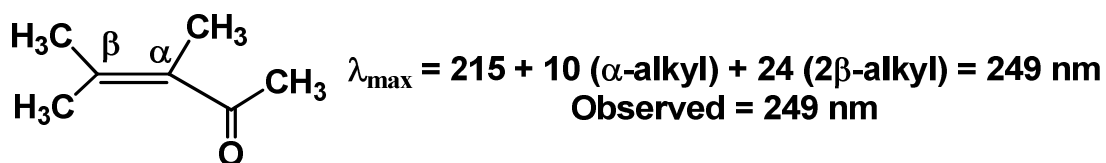


$$253 + 60 \text{ (2 extended C=C)} + 5 \text{ (one exocyclic C=C)} + 25 \text{ (5- ring residue)} = 343 \text{ nm}$$

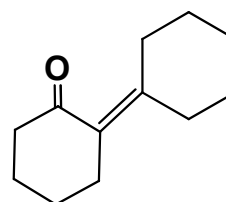
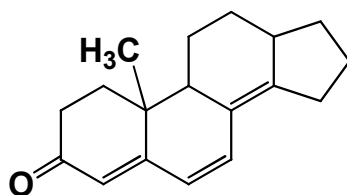
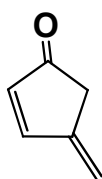
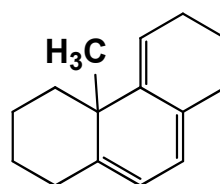
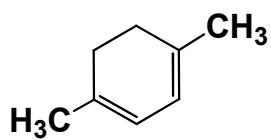
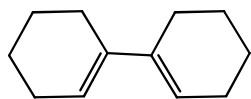
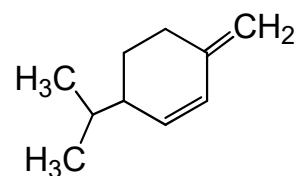
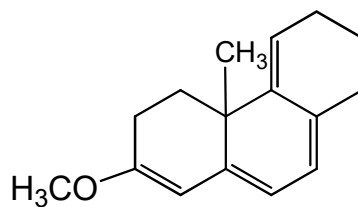
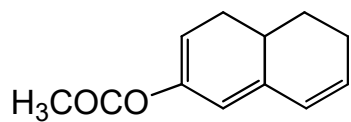
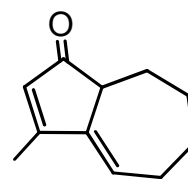
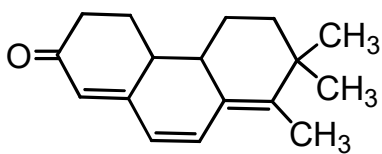
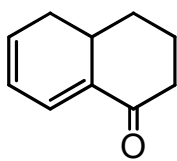
$$\text{Observed} = 343 \text{ nm}$$

Woodward Rules for Enones

| |  OR  |  |
|------------------------------------|---|---|
| Base Value | 215 | 202 |
| Double bond extension | 30 | 30 |
| Exocyclic double bond | 5 | 5 |
| Homocyclic diene | 39 | 39 |
| Alkyl group or ring residue | | |
| α- | 10 | 10 |
| β- | 12 | 12 |
| γ or higher | 18 | 18 |



Calculate (λ_{\max}) of the following compounds



Nuclear Magnetic Resonance

Technique used to detect the nucleus (atom) with **odd atomic number** and/or **odd mass number** (Nuclear spin quantum number higher than zero) but can not detect nucleus (atom) with both **even atomic number** and **even mass number** ((Nuclear spin quantum number equal to zero)

| Element | ^1_1H | ^3_1H | $^{12}_6\text{C}$ | $^{13}_6\text{C}$ | $^{14}_7\text{N}$ | $^{16}_8\text{O}$ | $^{19}_9\text{F}$ | $^{31}_{15}\text{P}$ |
|----------|----------------|----------------|-------------------|-------------------|-------------------|-------------------|-------------------|----------------------|
| N.S.Q.N. | 1/2 | 1 | 0 | 1/2 | 1 | 0 | 1/2 | 1/2 |

Proton Magnetic Resonance

For the hydrogen atom, it contains one electron and one proton inside the nucleus (N.S.Q.N. = $\frac{1}{2}$) and the number of spin state

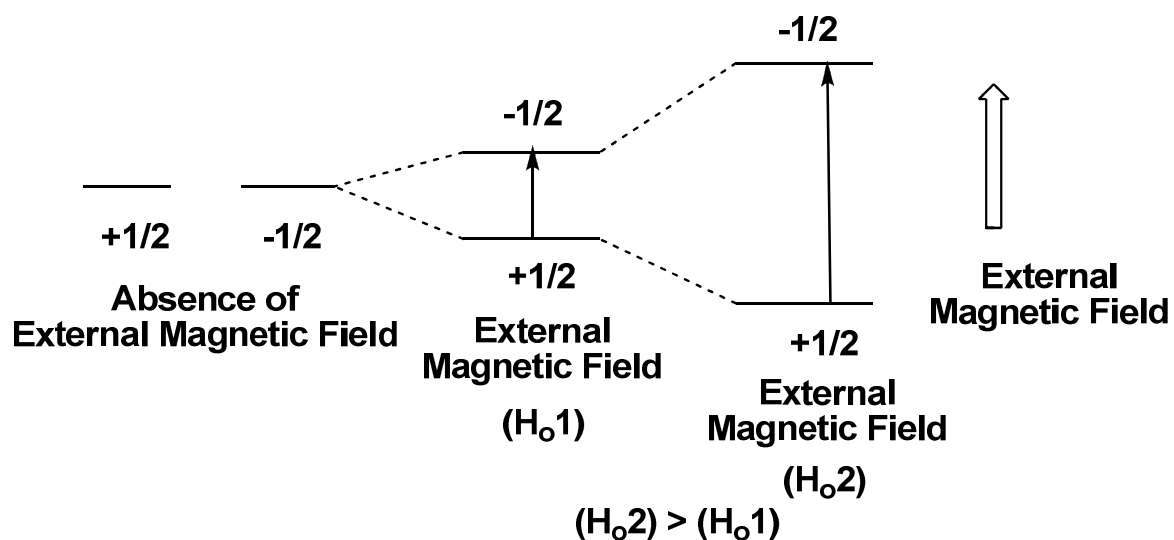
$$= 2I + 1 = 2 \times \frac{1}{2} + 1 = 2$$

For the spin state **+(1/2)** the direction of magnetic field **upward**. On the other hand, for the spin state **-(1/2)** the direction of magnetic field **downward**



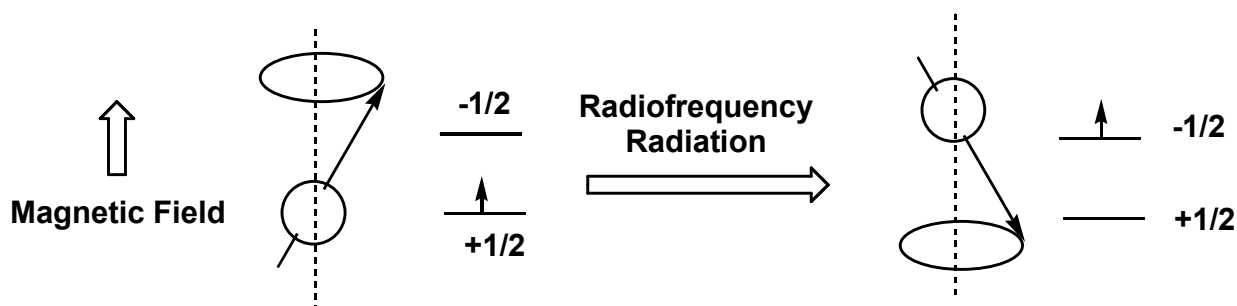
Spin state = +1/2 Spin state = -1/2

In the absence of external magnetic field, both states are equal in energy (Degenerate), while in the presence of external magnetic field (H_0) the two states will be different in energy levels and the difference in energy (ΔE) is directly proportional to the strength of the external magnetic field (H_0).

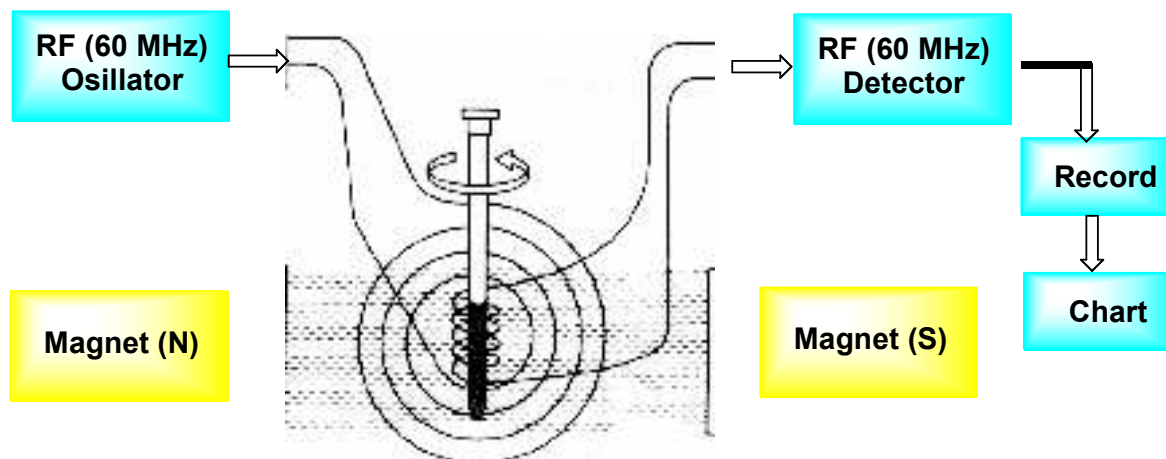


Mechanism of Resonance

If the proton in the ground state ($+1/2$) and absorb energy from the applied radio frequency source it will change its spin direction in the excited state ($-1/2$)

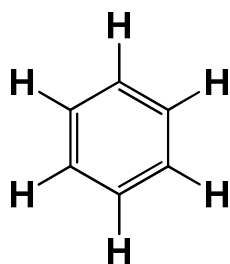


NMR Spectrometer

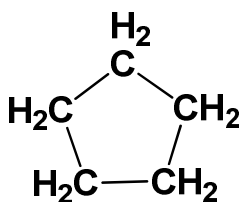


Types of Protons

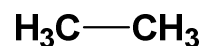
1. **Chemically equivalent protons**: magnetically equivalent protons, which have one signal e.g.



Benzene

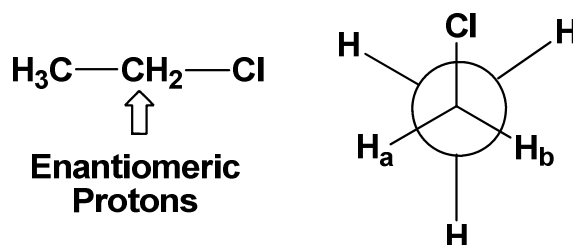


Cyclopentane



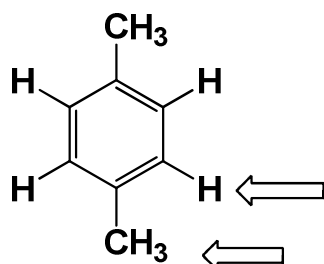
Ethane

2. **Enantiomeric Protons**: Chemically equivalent protons e.g ethyl chloride [CH_2 has Enantiomeric protons with the same signal]



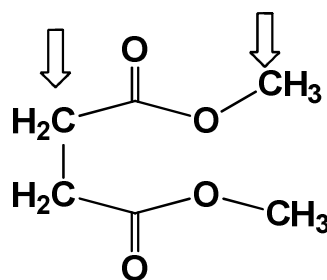
3. **Chemically Nonequivalent Protons**: magnetically nonequivalent protons, which have different signals e.g.

Chemically Nonequivalent Protons



p-Xylene

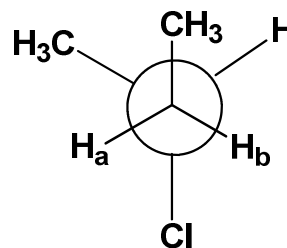
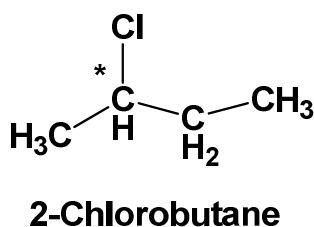
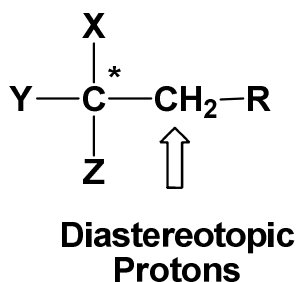
**Chemically
Nonequivalent
Protons**



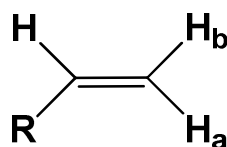
Dimethylsuccinate

4. **Diastereotopic protons**: Chemically nonequivalent protons have two different signals

a) Protons attached to carbon adjacent to chiral carbon atom. E.g. 2-chlorobutane [H_a , H_b are **diastereotopic protons**]

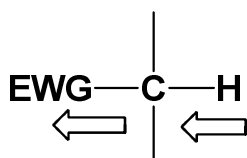


b) Protons on terminal double bonds: [H_a , H_b are **diastereotopic protons**]

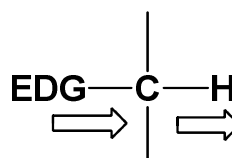


Shielding and Deshielding Protons

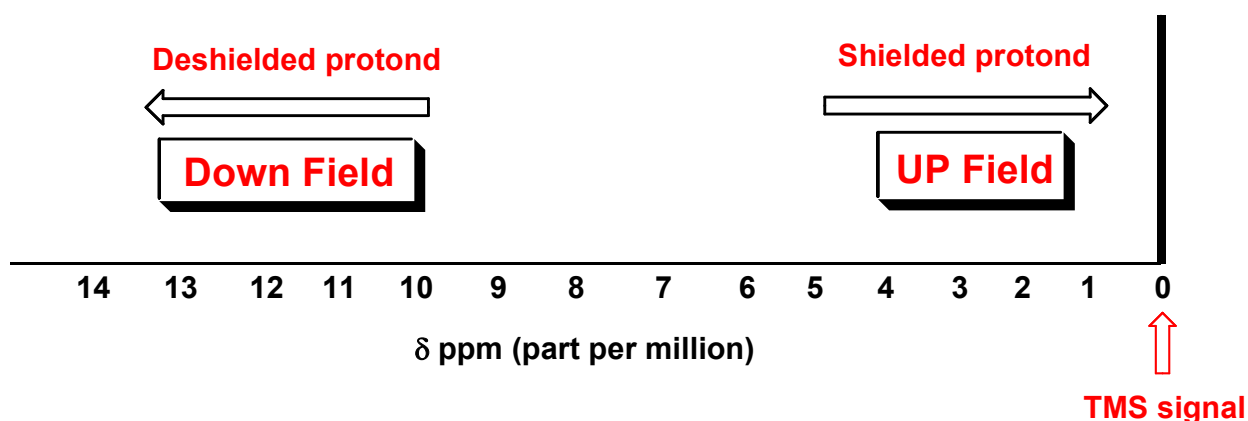
Not all the protons in the same molecule have the same resonance frequency but depend on the electronic environment around the proton



Decrease the electron cloud around the proton so decrease the applied field for resonance (Down field).
At the same time the energy difference between $+1/2$ and $-1/2$ will be large and δ value will increase (Deshielded proton)



Increase the electron cloud around the proton so increase the applied field for resonance (Up field).
At the same time the energy difference between $+1/2$ and $-1/2$ will be small and δ value will decrease (Shielded proton)



$$\text{Chemical Shift } (\delta) = [(\nu - \nu_{(r)}) / \nu_0] \times 10^6 \quad \text{ppm}$$

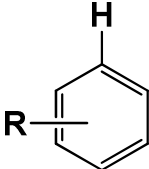
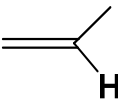
ν : The resonance frequency of the proton in the compound

$\nu(r)$: The resonance frequency of the proton in the reference compound
(**Tetramethyl silane** $(CH_3)_4Si$)

ν_0 : The oscillator frequency of the NMR spectrometer used.

Tetramethyl silane (TMS) is used as a reference compound because **a)** easy volatile **b)** chemically inert **c)** all the protons are chemically equivalent **d)** all the protons are highly shielded.

Position of Signals (δ)

| | | | | | | | |
|-------|------|---|---|--|---|--|---|
| RCOOH | RCHO |  |  | CH ₂ F CH ₂ Cl CH ₂ Br CH ₂ I CH ₂ O CH ₂ NO ₂ | CH ₂ Ar CH ₂ NR ₂ CH ₂ S CH ₂ -CO ≡C—H | CH ₃ -C CH ₂ -C CH-C | |
| 12 | 10 | 9 | 6.5 | 4.5 | 3 | 2 | 0 |

The solvent, which can be used for determination of (δ) value, is **Deutrated Chloroform** $[CDCl_3]$ or **Deutrated Dimethylsufoxide (DMSO)** CD_3SOCD_3 .

Factors Affecting on The Chemical Shift (δ)

- Electronegativity**: As the electronegativity increase the (δ) value increase

Dependence of the Chemical Shift of CH_3X on the Element X

| Compound CH_3X | CH ₃ F | CH ₃ OH | CH ₃ Cl | CH ₃ Br | CH ₃ I | CH ₄ | $(CH_3)_4Si$ |
|-----------------------------|-------------------|--------------------|--------------------|--------------------|-------------------|-----------------|--------------|
| Element X | F | O | Cl | Br | I | H | Si |
| Electronegativity | 4 | 3.5 | 3.1 | 2.8 | 2.5 | 2.1 | 1.8 |
| Chemical shift (δ) | 4.26 | 3.40 | 3.05 | 2.68 | 2.16 | 0.23 | 0 |

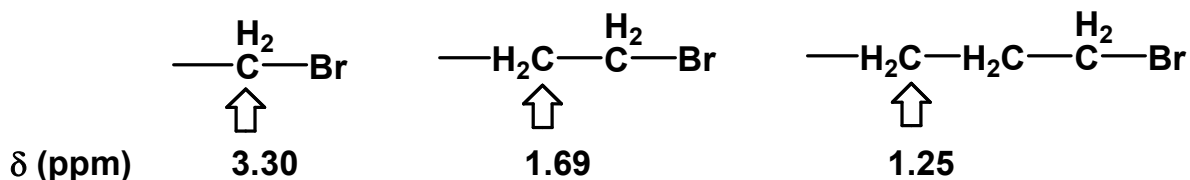
← TMS

deshielding increases with the electronegativity of atom X

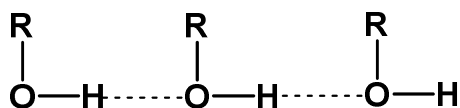
The effect increases with greater numbers of electronegative atoms.

| Compound | CH ₃ Cl | CH ₂ Cl ₂ | CHCl ₃ |
|------------------|--------------------|---------------------------------|-------------------|
| (δ) ppm | 3.05 | 5.30 | 7.27 |

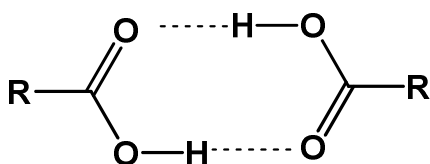
The effect decreases with increasing distance.



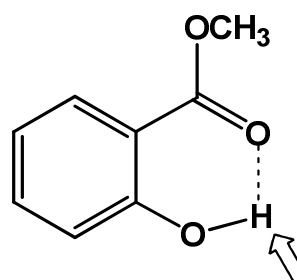
2. **Hydrogen bond:** Hydrogen bonding reduces the valence electron density around the proton (deshielded) and shifted downfield (δ will increase).



Alcohols vary in chemical shift (δ) from 0.5 ppm (free OH) to about 5.0 ppm (lots of H bonding).

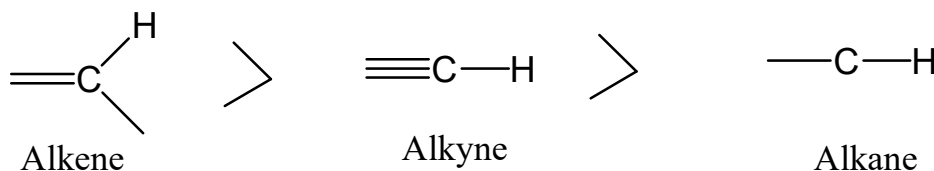


Carboxylic acid present in dimer form with chemical shift (δ) = 12 ppm (Intermolecular H-bond)



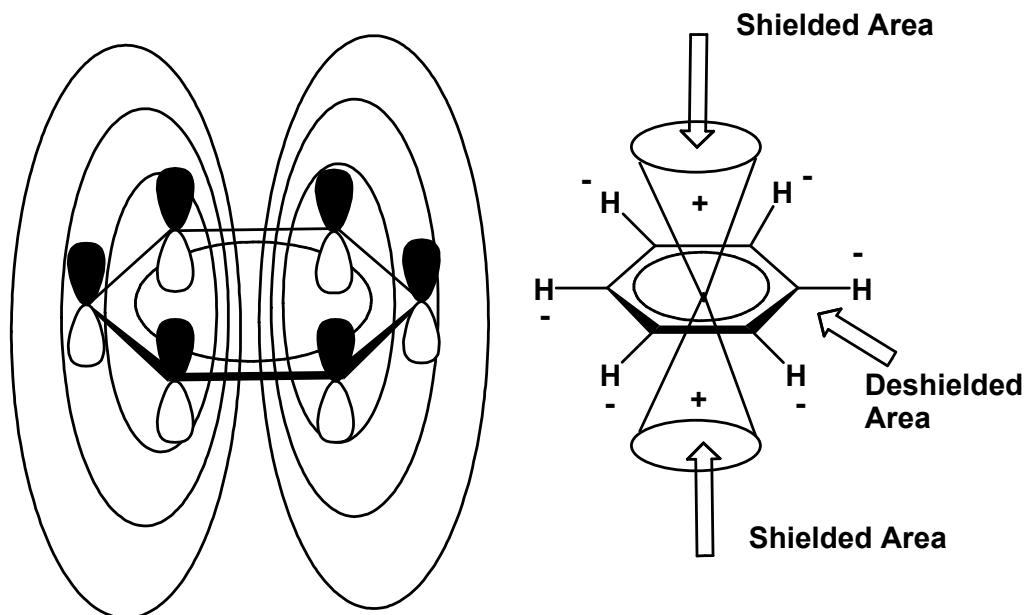
chemical shift (δ) of O-H in methyl salicylate = 13.5 ppm (Intramolecular H-bond)

3. **Hybridization** : $\text{SP}^2 > \text{SP} > \text{SP}^3$



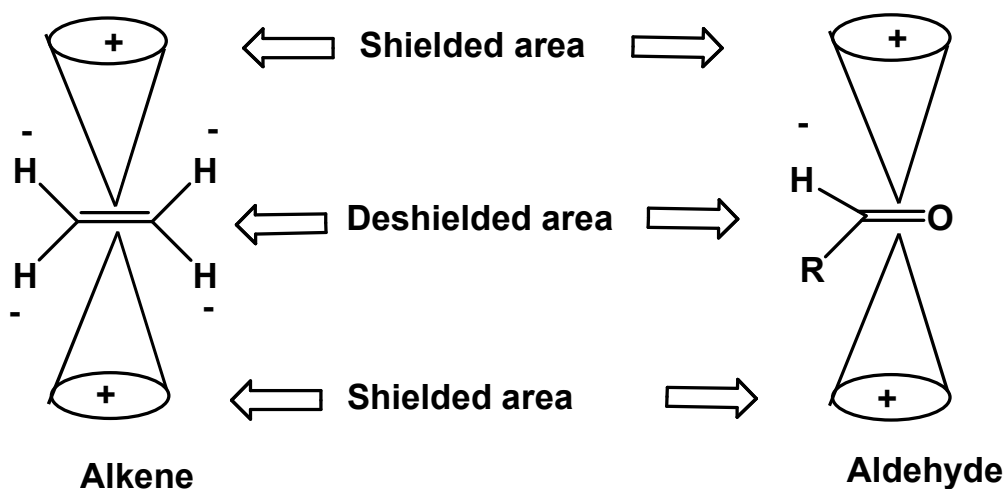
4. **Magnetic Anisotropic Effect (Ring Current Effect):** The effect resulted from circulation of π -electrons to give secondary magnetic field which increase or decrease (δ) value

- In case of Aromatic protons

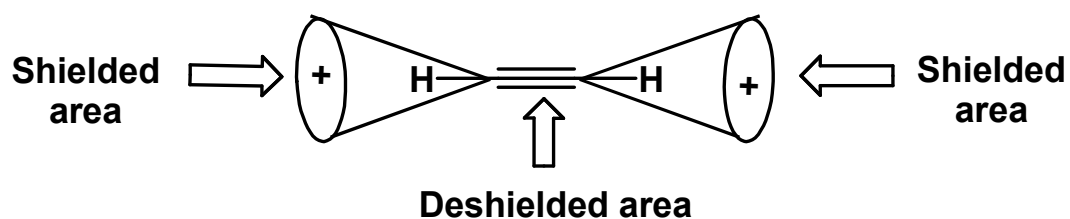


If the proton present in **shielded area** (δ) value will be small. On the other hand, if the proton present in the **deshielded area** (δ) value will be high

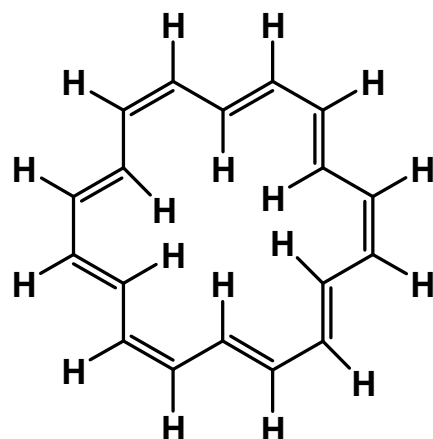
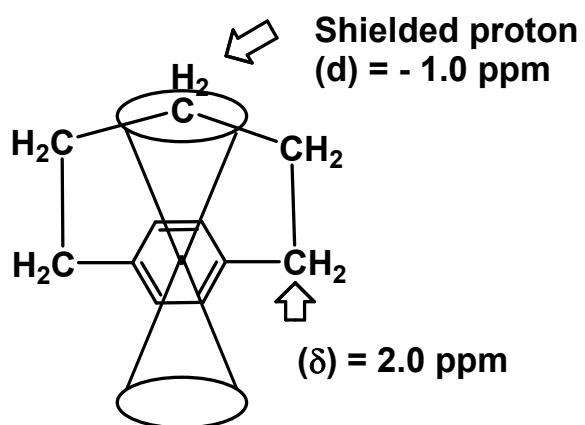
- In case of protons of alkene and aldehydes



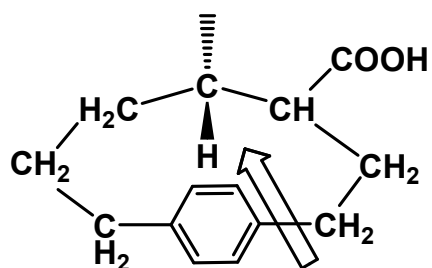
- In case of protons of Alkyne



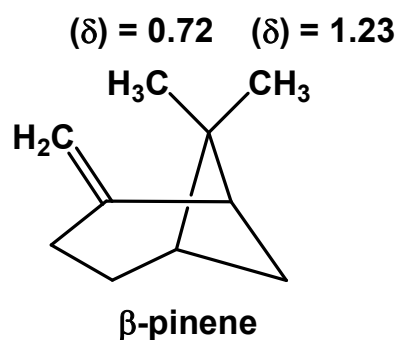
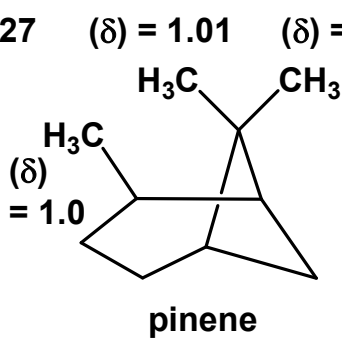
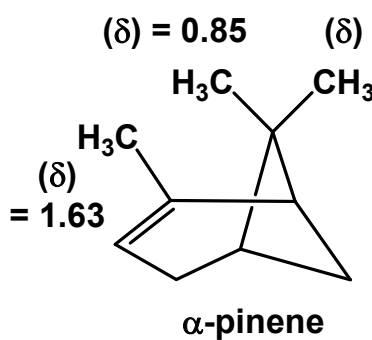
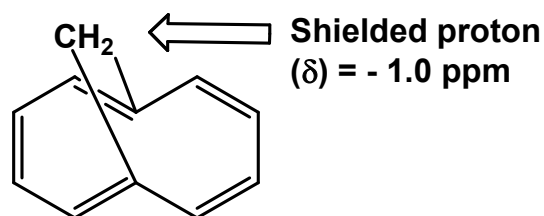
Examples illustrating the effect of Anisotropy



Inner Hydrogen (δ) = - 1.8 ppm
Outer Hydrogen (δ) = 8.9 ppm

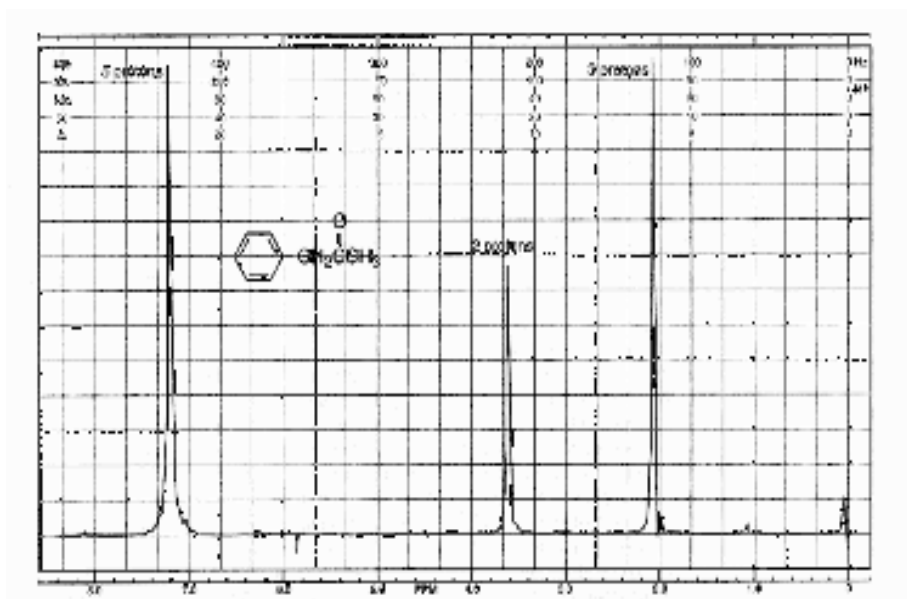


Shielded proton
(δ) = - 1.4 ppm

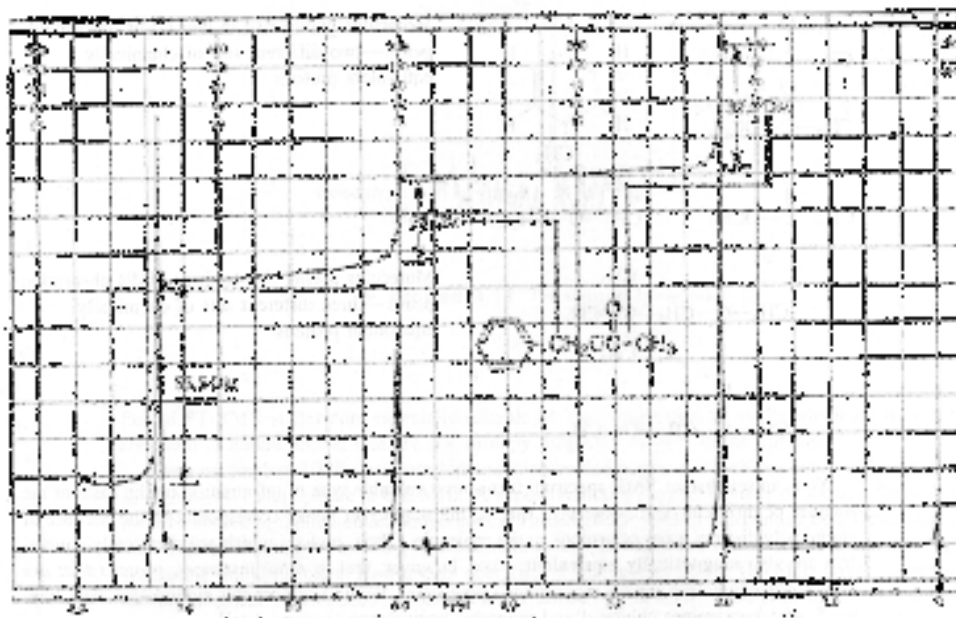


Information from NMR

1- The number of signals = types of protons in the given compounds



2- The number of protons in each signal can be calculated from the integration curve, where the ratio under area is related directly to the number of protons in each signal



No. of protons in signal (I) = $[32.5 / (32.5 + 22 + 55)] \times 10 = 3$ protons

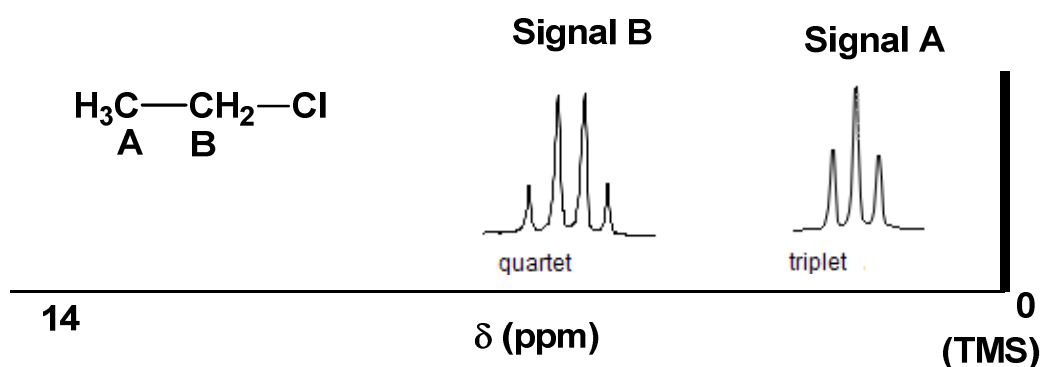
No. of protons in signal (II) = $[22 / (32.5 + 22 + 55)] \times 10 = 2$ protons

No. of protons in signal (III) = $[55 / (32.5 + 22 + 55)] \times 10 = 5$ protons

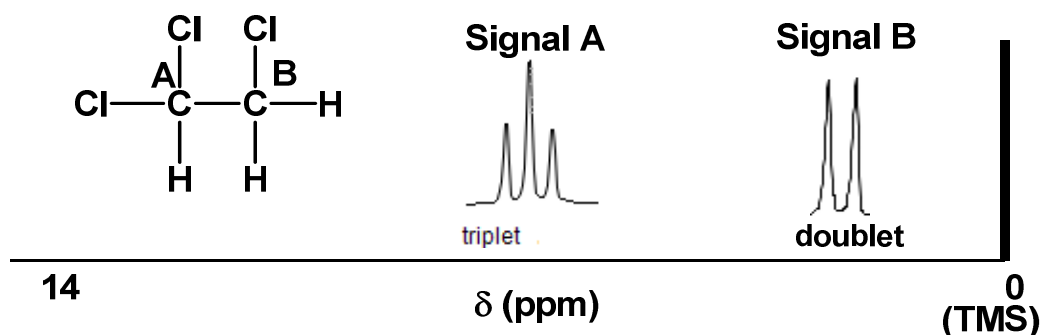
3. Multiplicity of NMR signals: Spin-Spin Coupling (Spin-Spin Splitting)

Each type of equivalent protons is **split into (n+1) signals** where **n:** is the **number of protons on the adjacent carbon**.

For example the splitted signals of **ethyl chloride**. The protons of signal (A) will splitted into $(2 + 1) = 3$ (triplet) and the protons of signal (B) will splitted into $(3 + 1) = 4$ (quartet) as shown



Another example 1,1,2-trichloroethane. The protons of signal (A) will splitted into $(2 + 1) = 3$ (triplet) and the protons of signal (b) will splitted into $(1 + 1) = 2$ (doublet) as shown

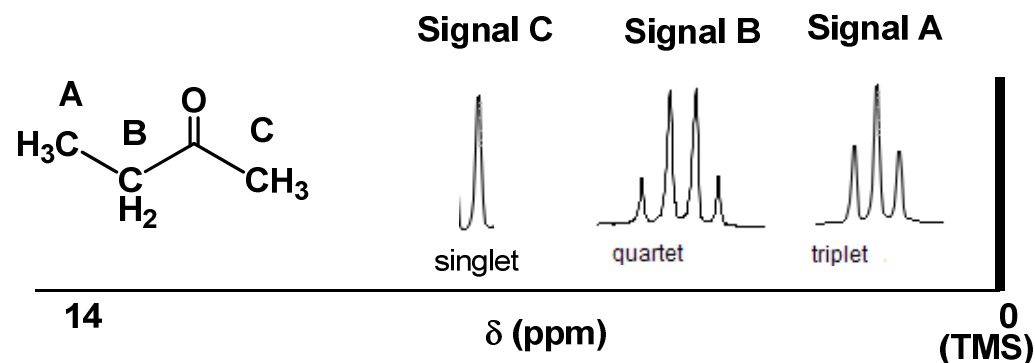


Third example butanone (methyl ethyl ketone)

The protons of signal (A) will splitted into $(2 + 1) = 3$ (triplet)

The protons of signal (B) will splitted into $(3 + 1) = 4$ (quartet)

The protons of signal (C) will splitted into $(0 + 1) = 1$ (singlet)



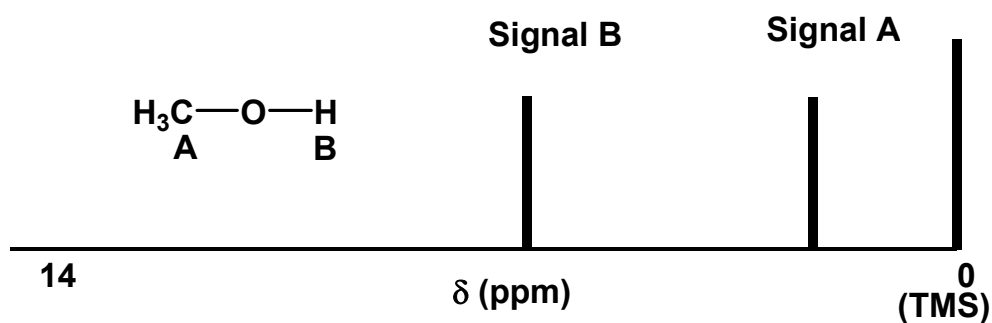
Pascal's Triangle

To determine the relative intensity of splitted signals derived from (n+1) rule

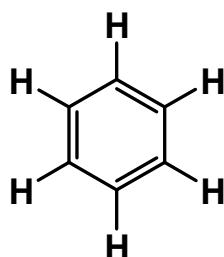
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Exception of (N+1) rule

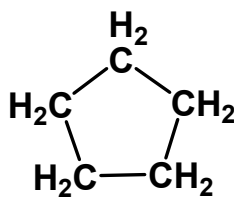
1. No coupling with acidic protons (exchangeable protons) such as COOH, SH, NH, OH, NH₂



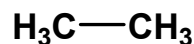
2. No coupling with equivalent protons such as



Benzene



Cyclopentane



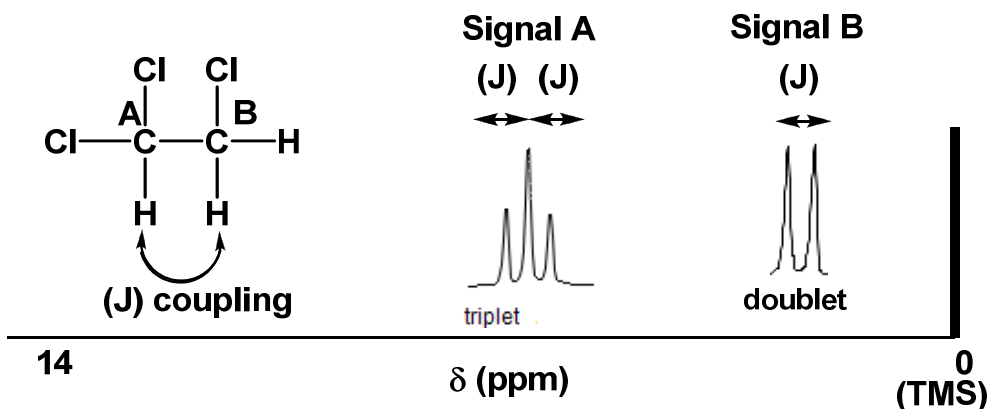
Ethane

The protons on benzene ring, cyclopentane and ethane will appear as one **singlet** signals respectively.

The coupling constant (J)

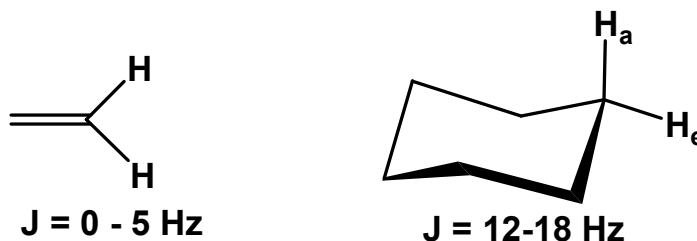
“The distance in Hz between the splitted signals within the same molecule”

The value is dependent on the interacting nuclei and is independent on the strength of applied magnetic field, for example the (J) value between (CH) and (CH₂) in trichloroethane was determined as shown

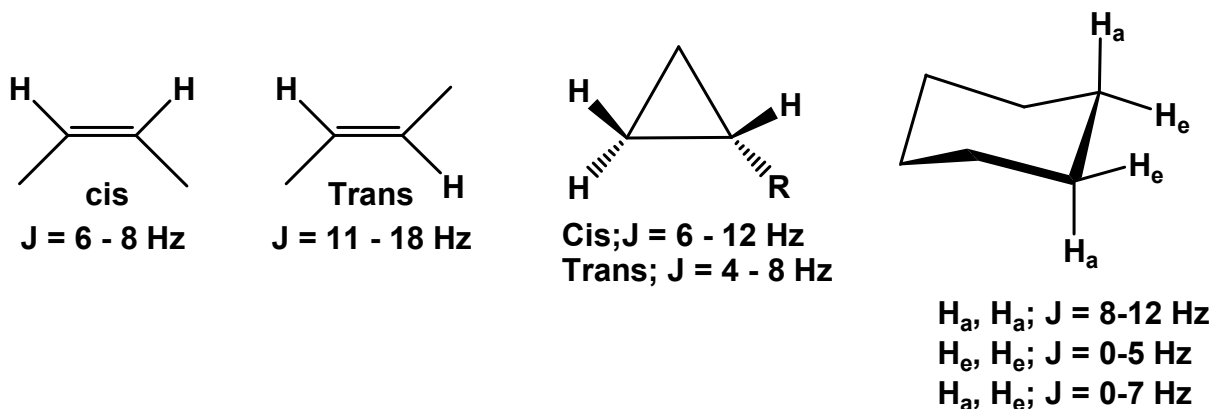


Types of Coupling

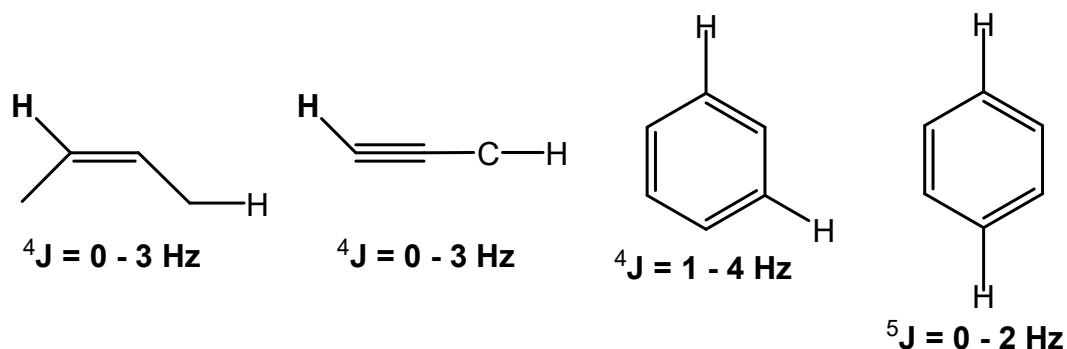
1. **Direct Coupling (¹J)** : Through one bond (¹³C-¹H), J = 125-250 Hz
2. **Geminal Coupling (²J)**: Through two bonds (H^a-C-H^b), the value of (²J) depend on the angle between two hydrogens.



3. **Vicinal Coupling (³J)**: Through three bonds (H^a-C-C-H^b), the value of (³J) depends on the dihedral angle between two hydrogens.



4. **Long Range Coupling (nJ):** Through many bonds ($n > 3$), e.g. 4J (meta hydrogens), 5J (para hydrogens) in benzene ring, 4J for allylic protons.

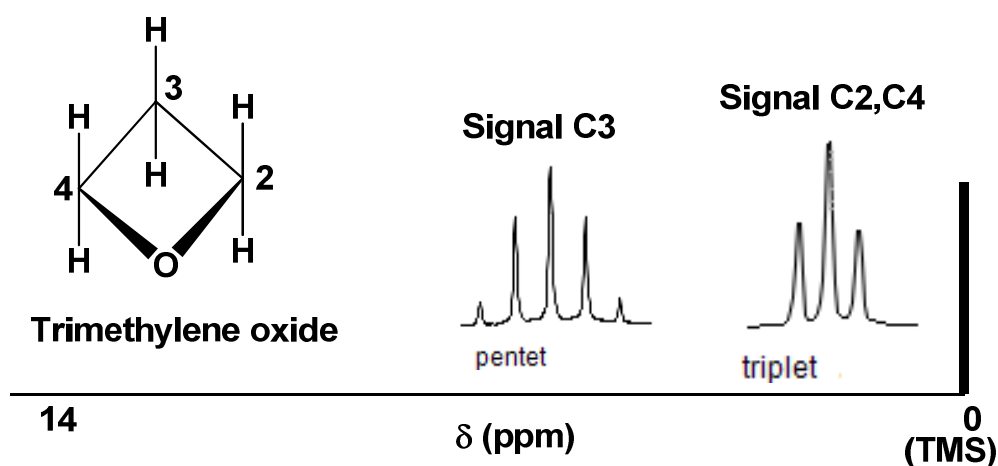


Failure of the ($n + 1$) rule to magnetic non-equivalence within a group

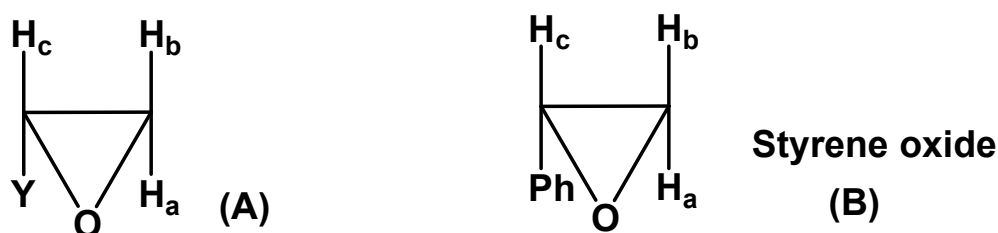
Spin-spin coupling ($n + 1$) rule can not applied for the magnetically equivalence protons in the following situations

A) In Case of Cyclic Rings

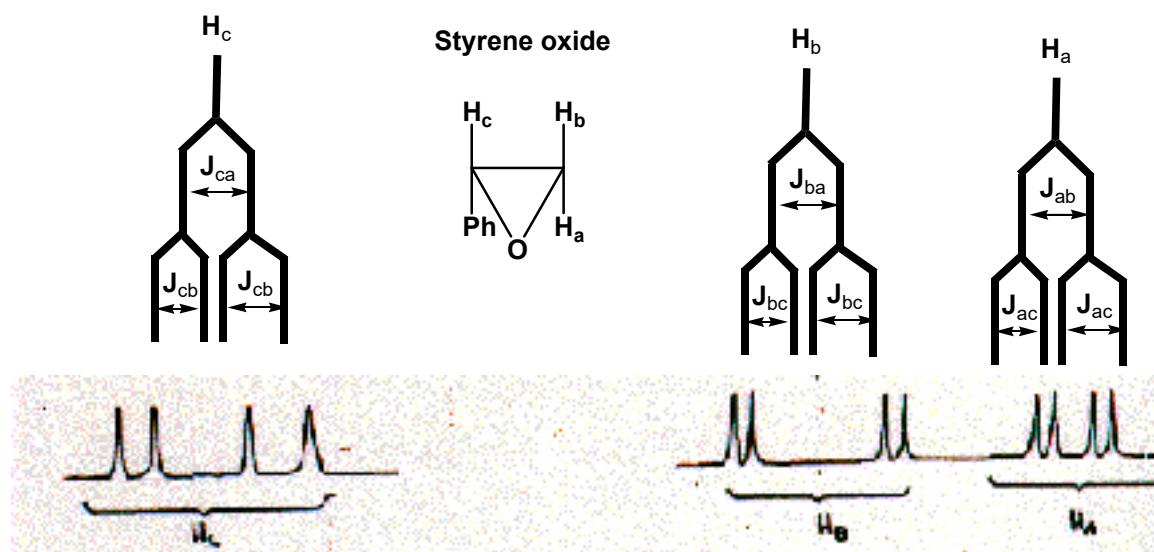
In the NMR spectra of trimethylene oxide, we can apply ($n + 1$) rule because on each carbon the two hydrogens are equivalent where the environment above the plane of the ring is similar to the environment below the plane of the ring so two hydrogens on C2 are equivalent with C4 and appear as triplet while the two hydrogens on C3 will be affected by four protons on C2 and C4 and appear as quintet ($4 + 1$).



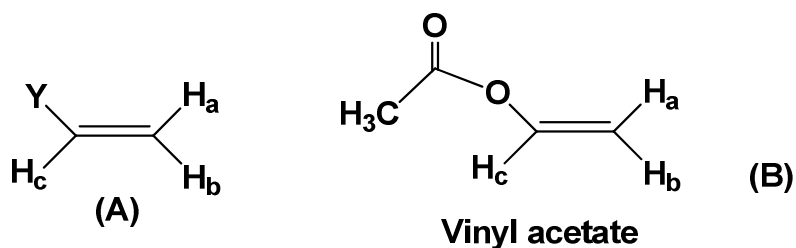
In case of three-membered ring with general formula (compound A)



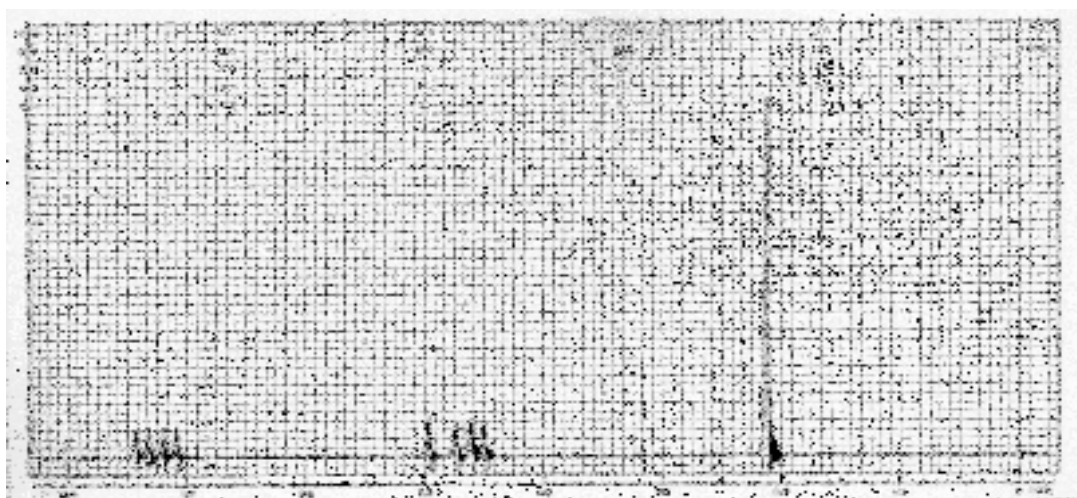
In this case H_a , H_b are **magnetically non equivalent** and will couple with each others by (2J), also H_c will be different and affected by H_a , H_b independently as shown in the following example of styrene oxide (**B**)



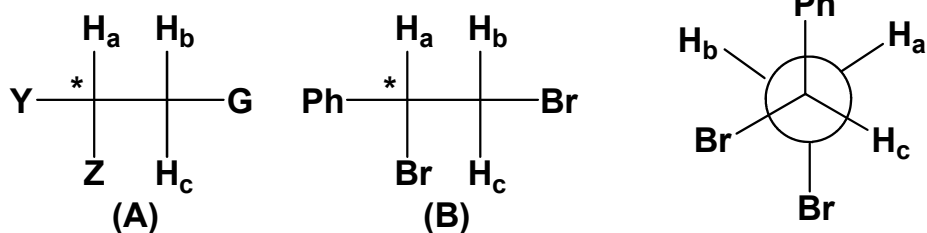
(B) In Case of Olefinic Hydrogens



In this case H_a , H_b are **magnetically non equivalent** and will couple with each others by (2J), also H_c will be different and affected by H_a , H_b independently as shown in the following example of vinyl acetate (**B**)

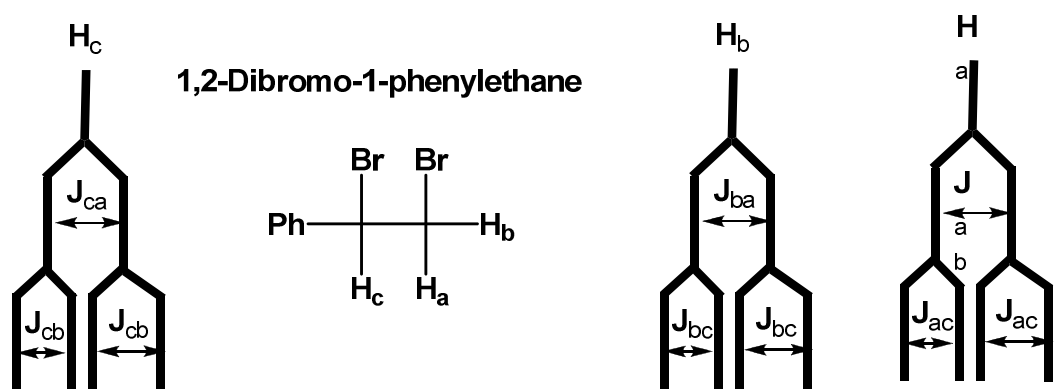


C) In Case of Diastereotopic Protons

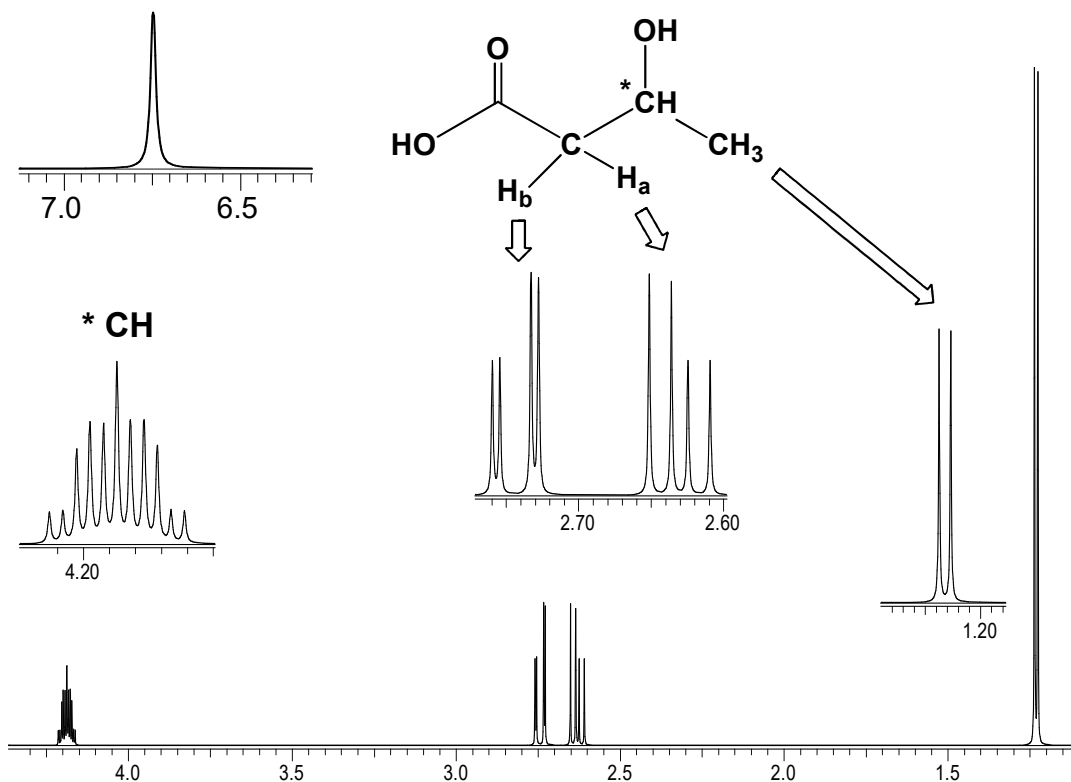


1,2-Dibromo-1-phenylethane

In this case H_c , H_b are **magnetically non equivalent** and will couple with each others by (2J), also H_a will be different and affected by H_c , H_b (3J) independently (H_a , H_b and H_c will appear as pair of doublets) as shown in the following example of 1,2-dibromo-1-phenylethane.

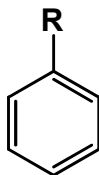


OH (exchangeable with D_2O)

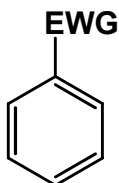


Aromatic Compounds

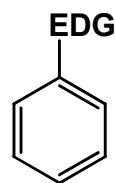
1. Monosubstituted benzene ring



R = CH₃, C₂H₅,
All H's have the same δ value

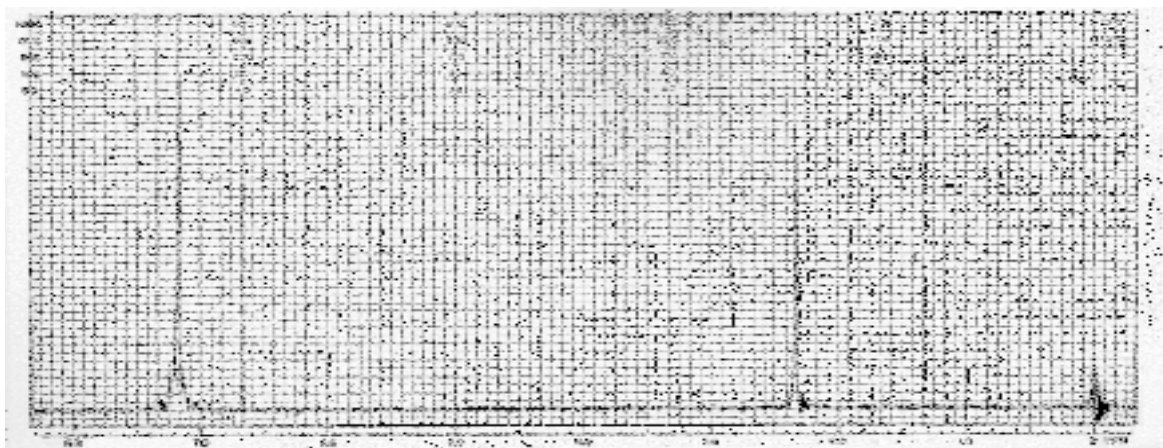


EWG = NO₂, CHO, CN,
Hydrogens on ortho and para
will be deshielded while, hydrogens
on meta will be shielded with the
ratio of 3:2

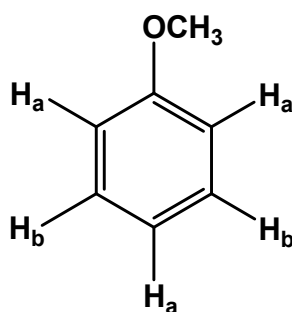


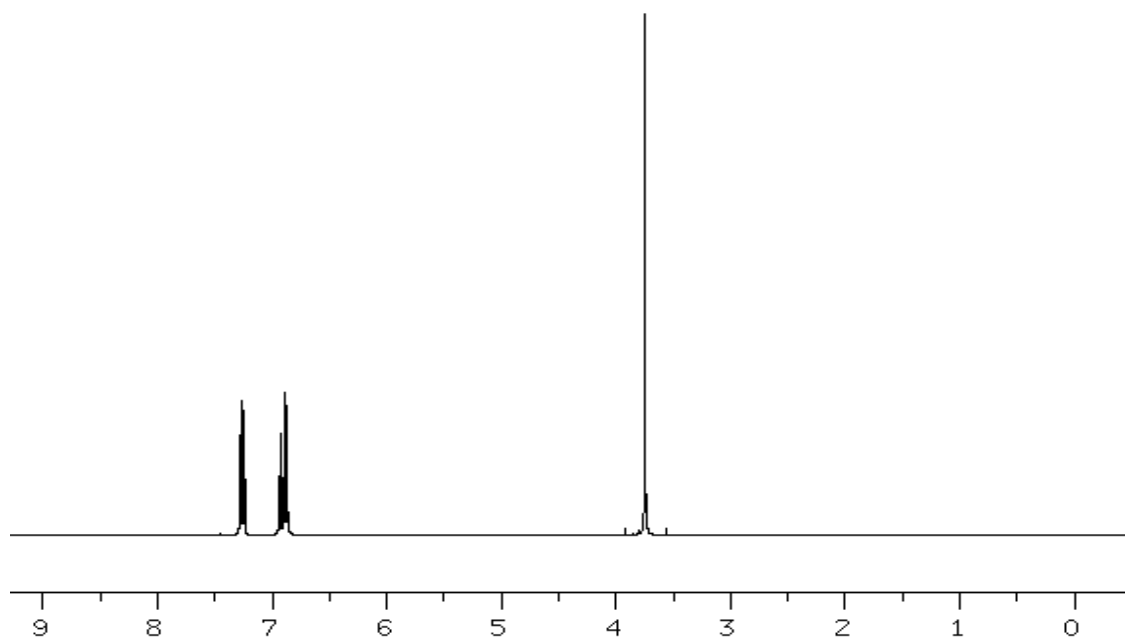
EDG = OCH₃, NH₂, OH,
Hydrogens on ortho and para
will be shielded while, hydrogens
on meta will be deshielded with the
ratio of 3:2

NMR Spectrum of Toluene

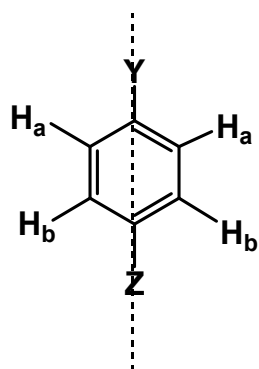


NMR Spectrum of Anisole





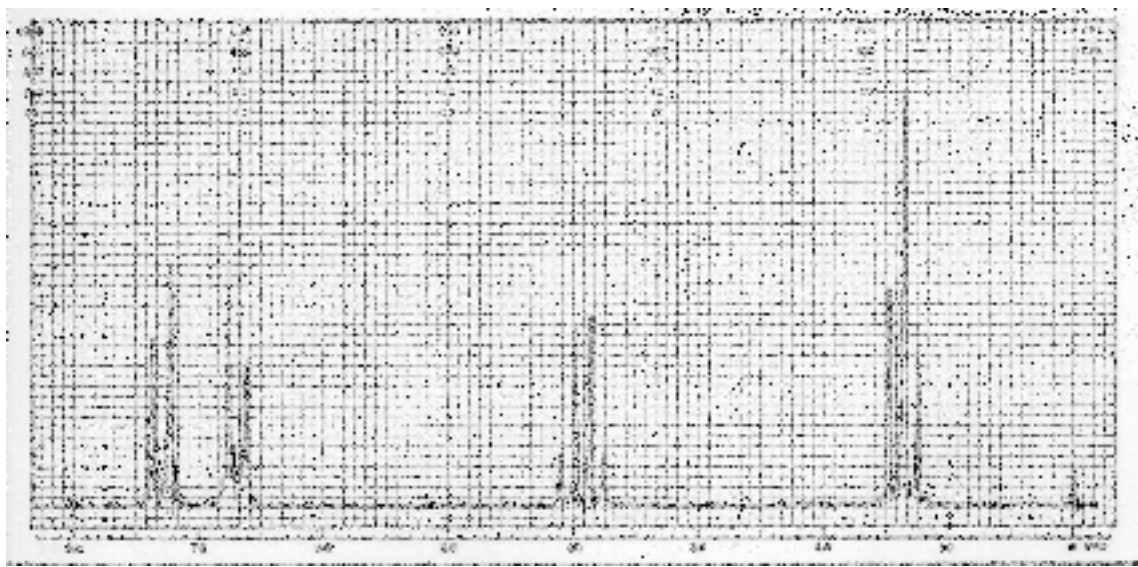
2. Para-disubstituted benzene ring



H_a will appear as doublet, and H_b will appear as doublet

Plane of symmetry

NMR Spectrum of 1-bromo-4-ethoxybenzene

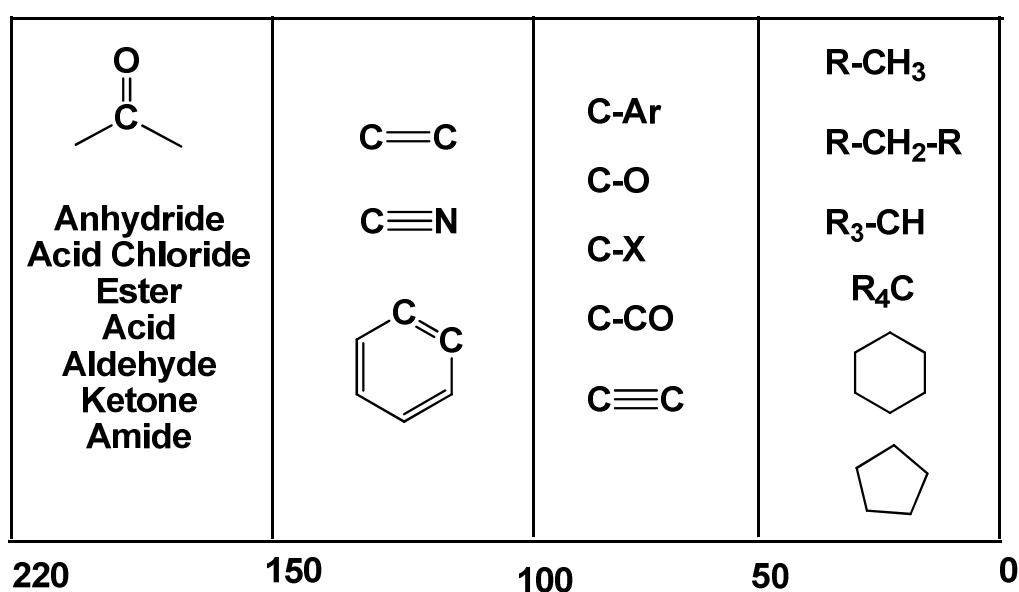


^{13}C NMR Spectroscopy

$^{12}_6\text{C}$ With even mass number and even atomic number has no NMR signal because (N. S. Q. N. = zero). On the other hand, $^{13}_6\text{C}$ ($I = \frac{1}{2}$) has signal.

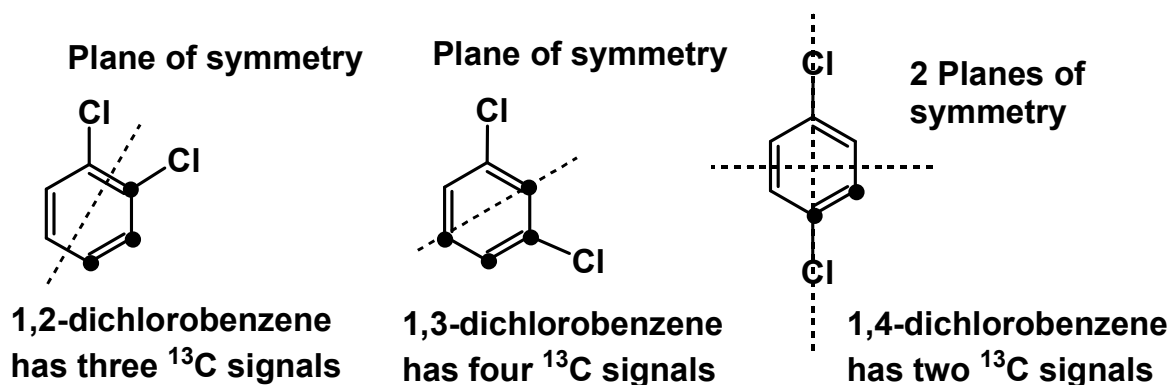
The ratio for relative abundance between $^{12}_6\text{C}$: $^{13}_6\text{C}$ is (98.9 : 1.1) which means that the intensity of $^{13}_6\text{C}$ signal will be very small. In order to increase the intensity of $^{13}_6\text{C}$ signal we use **Pulse Fourier Transform Technique** which depends on the accumulation of signals by hundreds (100, 200,)

The spectra of $^{13}_6\text{C}$ signal is measured by (δ) in the range 0-220 as shown

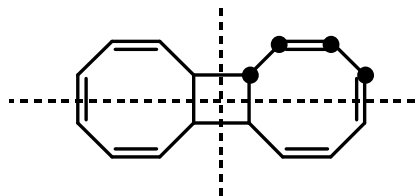


Symmetry of the ^{13}C signals in NMR

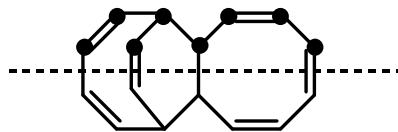
^{13}C -NMR can be used to differentiate between different isomers according to the number of signals (depends on symmetry).



Dimerization of cyclooctatetraene can be took place to give isomer **A** or **B**, by measuring ^{13}C -NMR we can deduce which isomer we could obtain



Isomer A has four ^{13}C signals

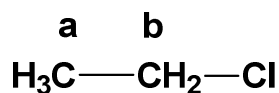


Isomer B has eight ^{13}C signals

Different Techniques of ^{13}C -NMR

1. Undecoupled ^{13}C -NMR

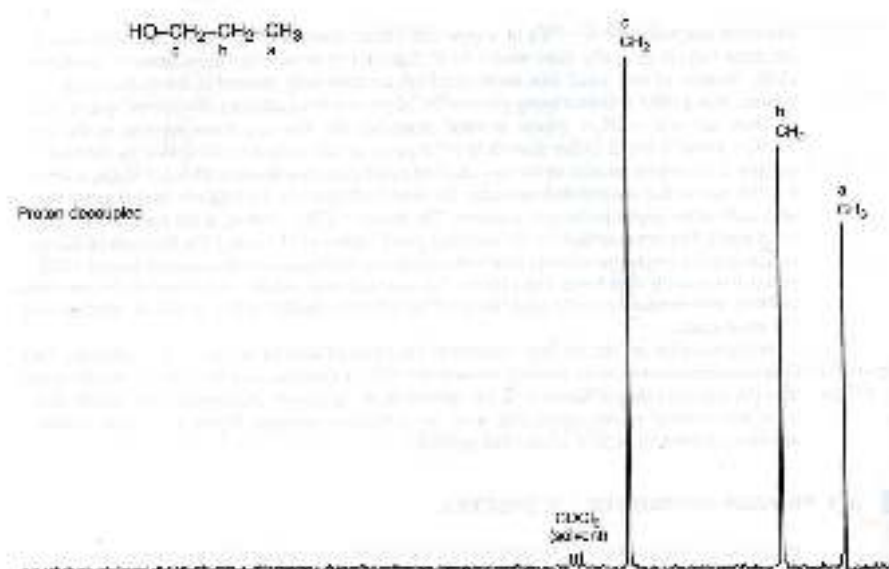
In this case, the carbon atom splitted according to the number of hydrogen on it into (n+1) then each signal will split according to the number of hydrogen on the adjacent carbon atom into (n+1) e.g.



The ^{13}C signal (a) will splitted into $(3 + 1) = 4$ (quartet) then each signal will split into $(2 + 1) = 3$ (triplet). The ^{13}C signal (b) will splitted into $(2 + 1) = 3$ (triplet) then each signal will split into $(3 + 1) = 4$ (quartet).

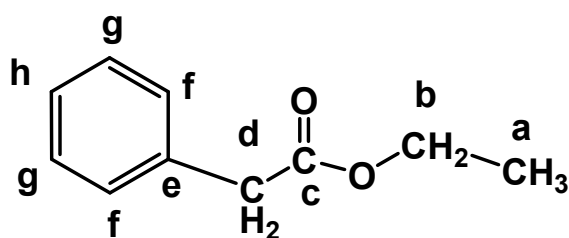
2. Proton Decoupled ^{13}C -NMR

The ^{13}C signal will not affected by the protons and appear as singlet signal. Therefore, the number of signals in this technique indicates different types of carbons in molecule

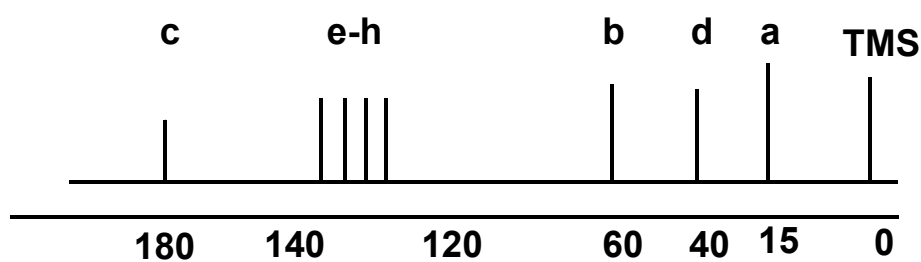


3. Off Resonance Proton Decoupled ¹³C-NMR

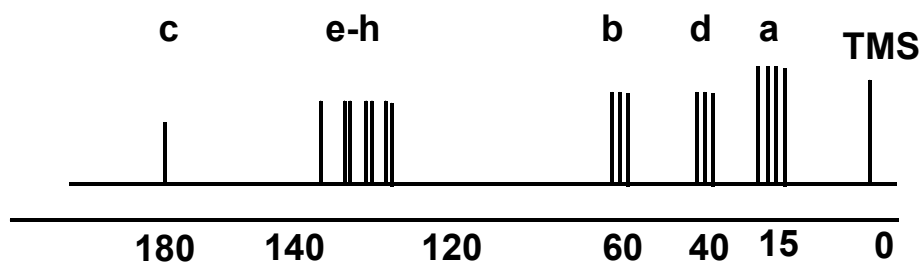
The ¹³C signal will split into (n+1) by the number of hydrogen bearing it e.g.



Ethyl phenylacetate



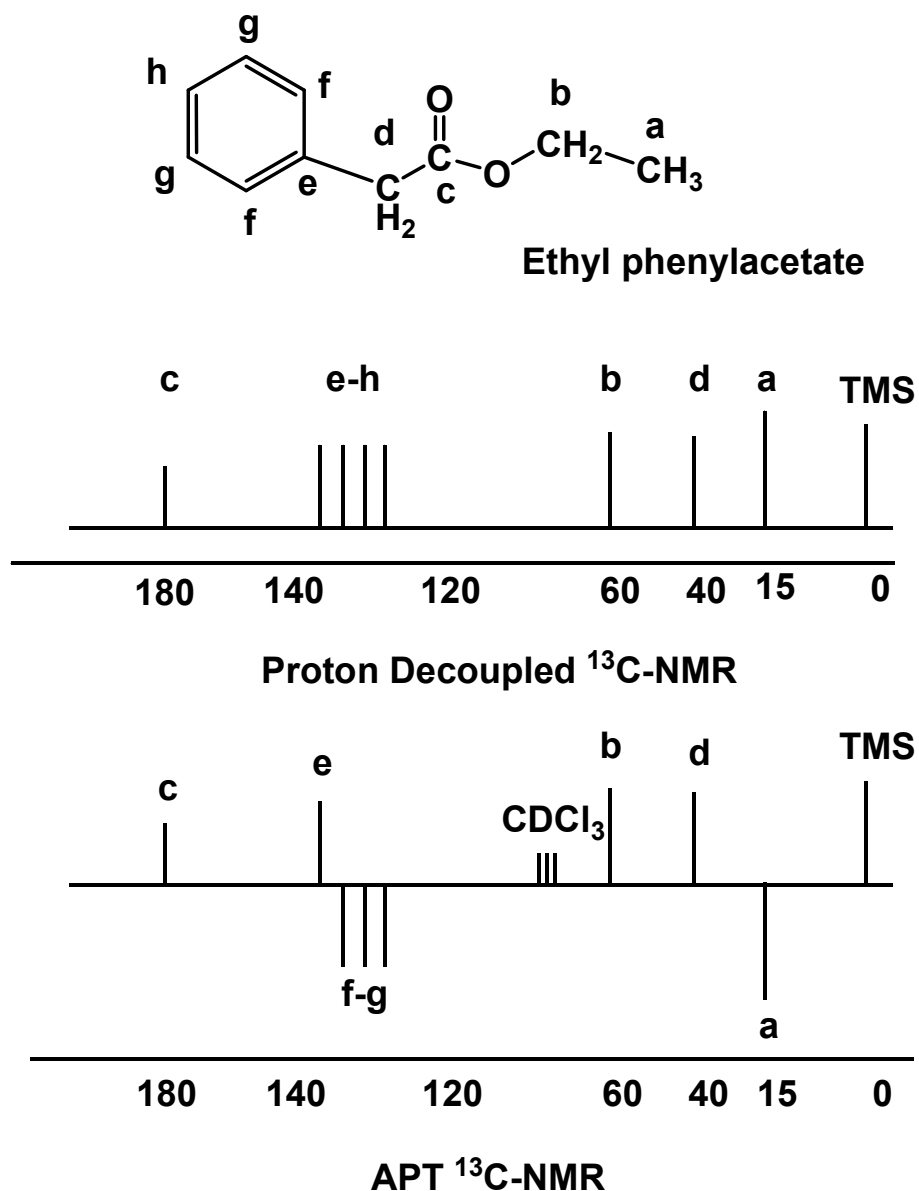
Proton Decoupled ¹³C-NMR



Off Resonance Proton Decoupled ¹³C-NMR

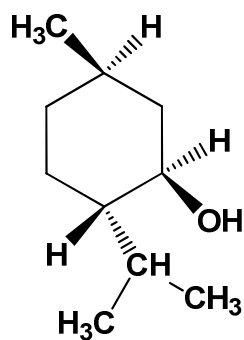
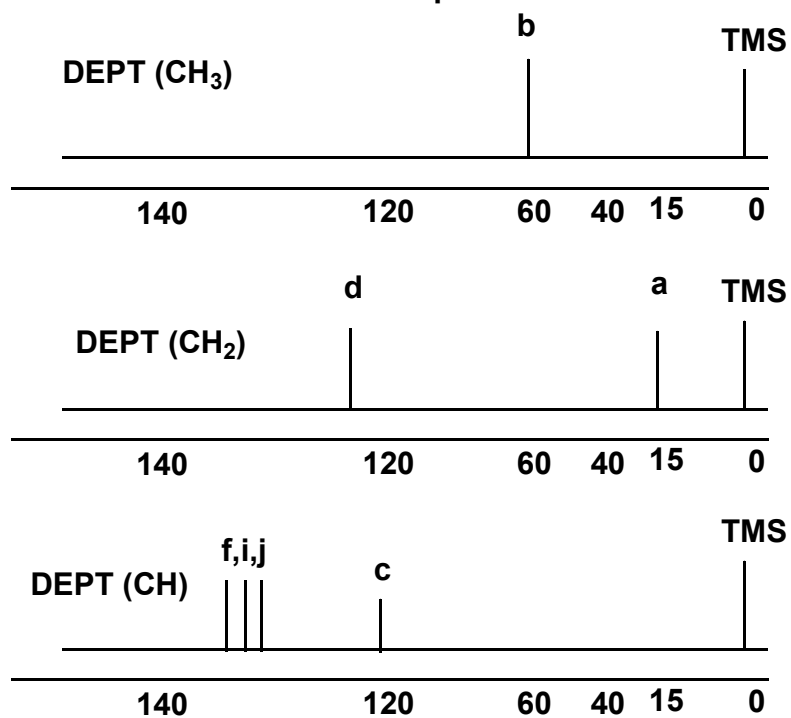
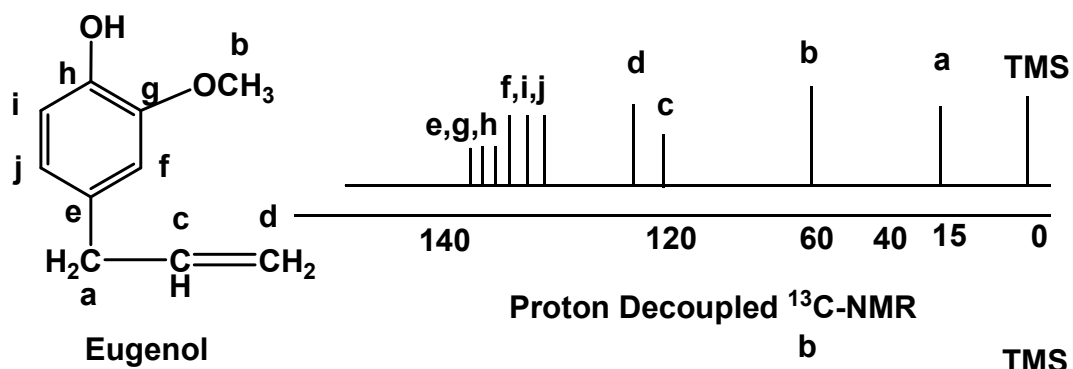
4. Attached Proton Test (APT)

The decoupled ^{13}C signals is plotted in two phases, where the carbon atoms with **even number of protons** (C , CH_2) will appear in one phase while, the carbon atoms with **odd number of protons** (CH , CH_3) will appear in another phase. The solvent CDCl_3 or $\text{CD}_3\text{-SO-CD}_3$ (DMSO) with the same phase of **even number of carbon atom**

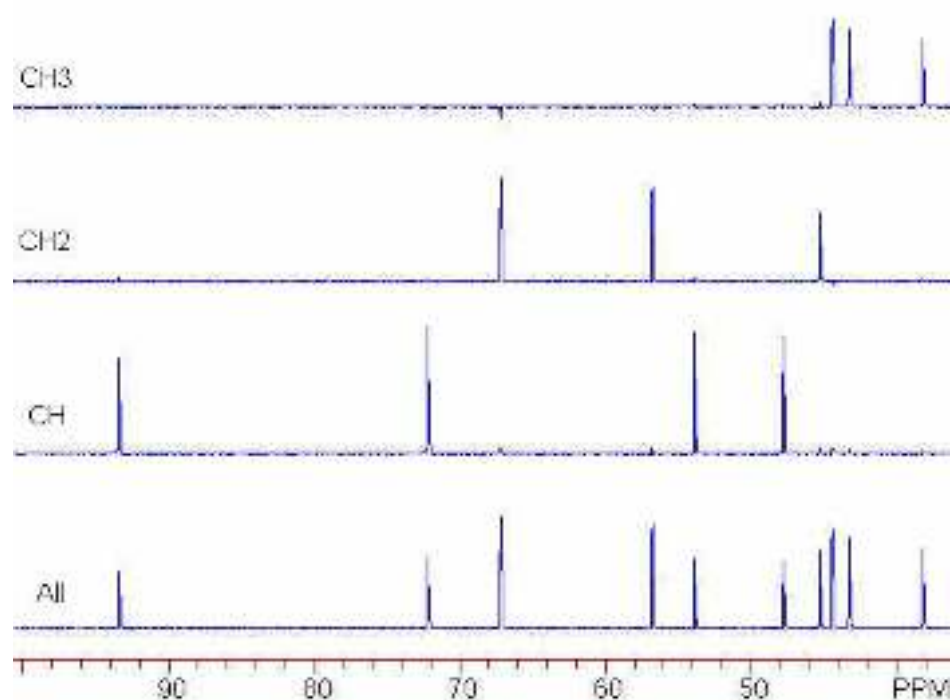


5. Distortionless Enhancement by Polarization Transfer (DEPT)

Decoupled ^{13}C signals of CH , CH_2 , CH_3 will appear while C or C=O will not appear
e.g. ^{13}C of Eugenol



DEPT spectrum of Menthol



Two Dimensional NMR (2-D NMR)

More advanced technique gives more information about the structure of organic compounds. This technique can be classified into two categories

H-H COSY (Hydrogen-Hydrogen Correlation Spectroscopy): Correlation which describes the coupling between protons and adjacent protons according to (N+1) Rule.

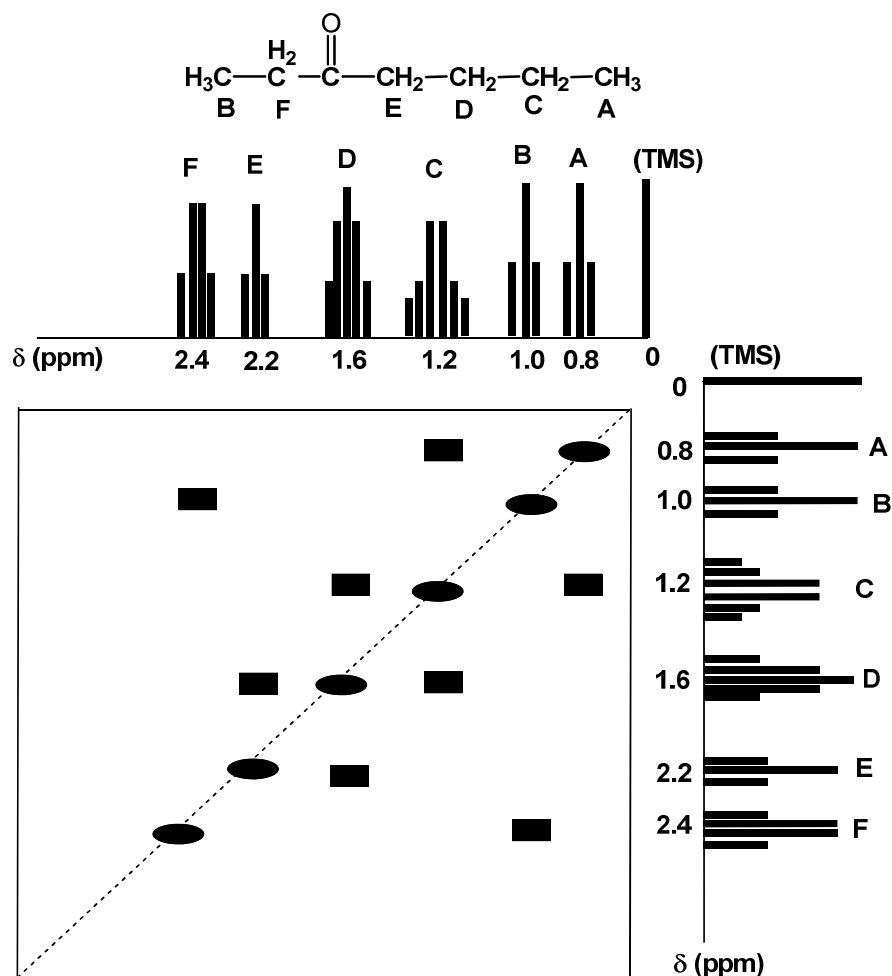
H-C Hetcor (Hydrogen-Carbon Heteronuclear Correlation): Correlation which describes the coupling between carbons and protons (on these carbons).

H-H COSY (Hydrogen-Hydrogen Correlation Spectroscopy):

In this technique we draw the ^1H -NMR signals two times in the horizontal and vertical directions then we correlate the coupled protons. In this chart we will find

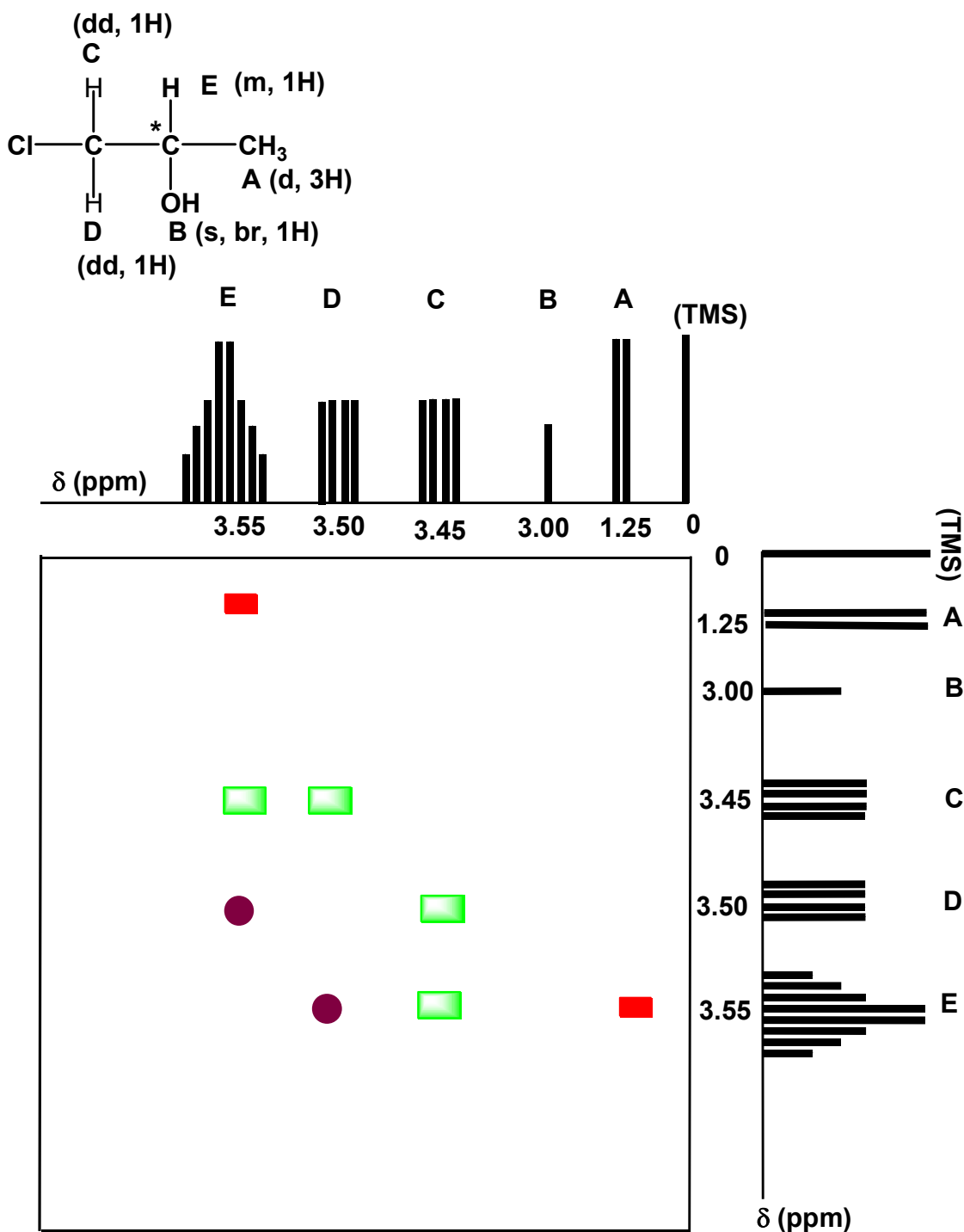
a) **Diagonal Peaks**: which correlate the coupling between proton and itself.

b) **Off Diagonal Peaks (Cross Peak)**: this correlate the coupling of protons and adjacent protons. As shown in chart of **3-heptanone**.



Problem : 1-Chloro-2-propanol has the following spectra

^1H NMR: $\delta = 1.25$ (d, 3H), 3.00 (s, br, 1H), 3.45 (dd, 1H), 3.50 (dd, 1H), 3.55 (m, 1H) ppm. **Draw and explain H-H COSY cross peak correlation.**



Note that the **carbon number 2** which carry (OH) group is **Chiral** so the adjacent carbon has **Diastereotopic protons** (nonequivalent protons **H_C**, **H_D**)

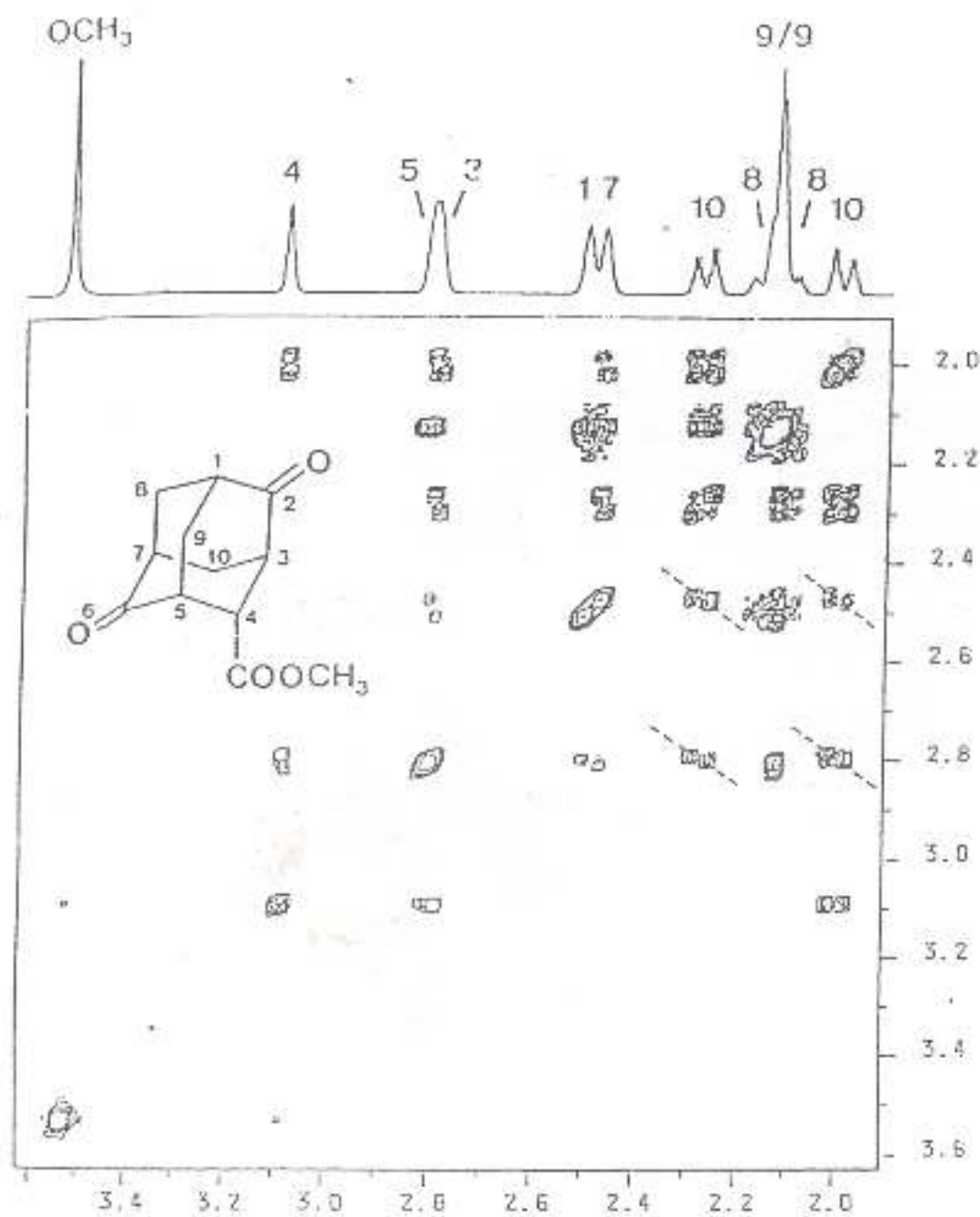
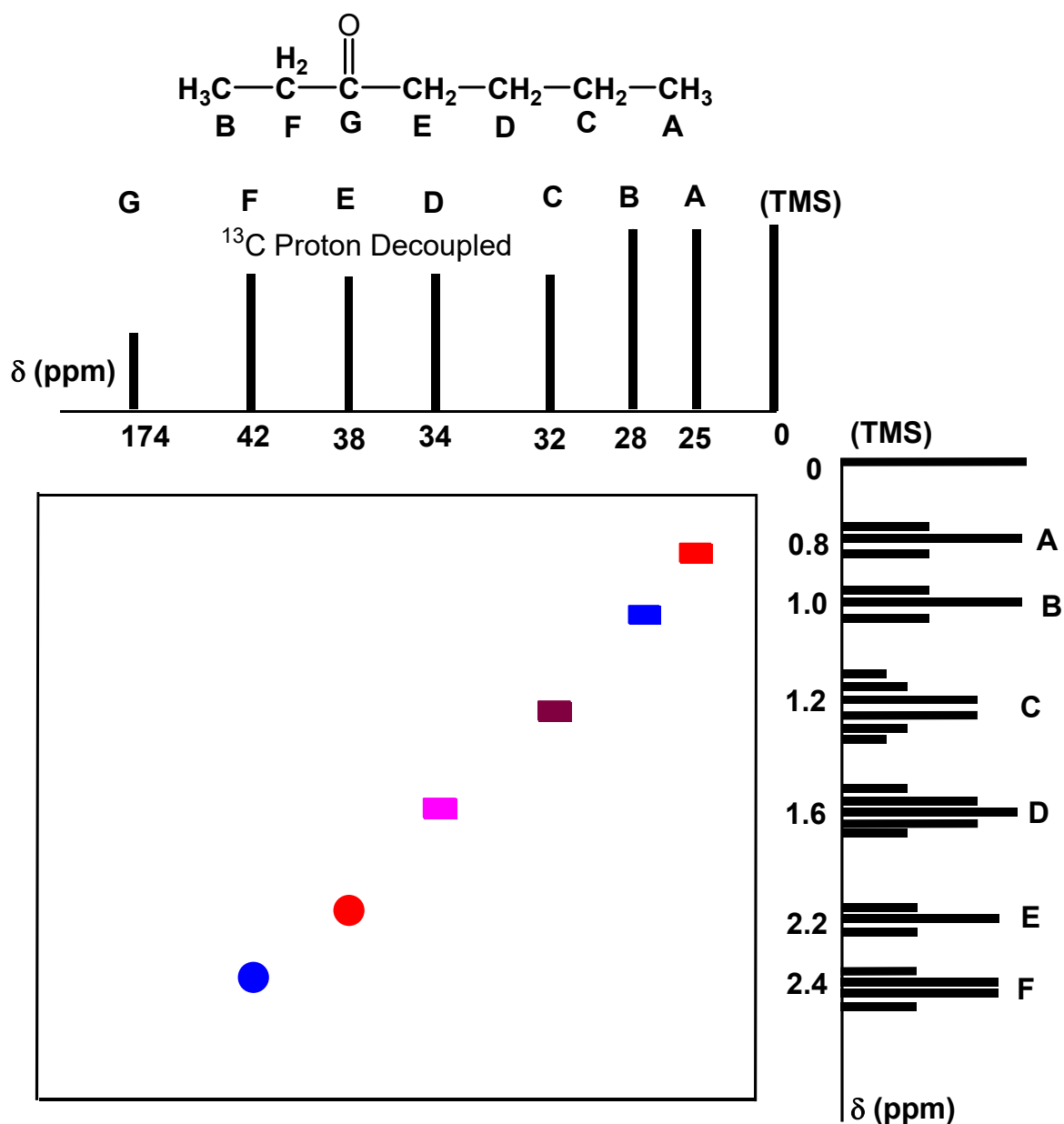


Fig. 2.4.4. ^1H , ^1H COSY spectrum (COSY 45) of 4-methoxycarbonyl-adamantane-2,6-dione.

H-C Hetcor (Hydrogen-Carbon Heteronuclear Correlation):

In this technique we draw the ^1H -NMR signals in the horizontal direction and ^{13}C -NMR signals in the vertical direction (or the opposite) In this chart we will find **Off Diagonal Peaks (Cross Peak)**: this correlates the coupling of carbons with protons on these carbons. If the ^{13}C -signal correlates to two proton signals mean that these protons are **diastereotopic protons** (adjacent to chiral carbon atom).



Problem: 1-Chloro-2-propanol has the following spectra

^1H NMR: $\delta = 1.25$ (d, 3H), 3.00 (s, br, 1H), 3.45 (dd, 1H), 3.50 (dd, 1H), 3.55 (m, 1H) ppm. ^{13}C NMR: $\delta = 20, 53, 68$ ppm.

Draw and explain H-C COSY Hetcor cross peak correlation

