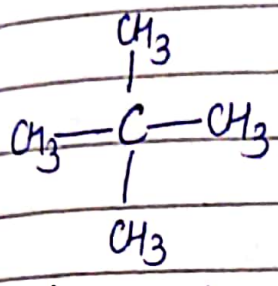
Mass Spectroscopy :-

→ M.S is used to determine mol. mass of the compounds.

→ It is the most accurate method amongst all other spectroscopic techniques.



C_5H_{12} ⇒ $(12\times5)+(12\times1)$

$= 60+12$

$= 72$

(neopentane)

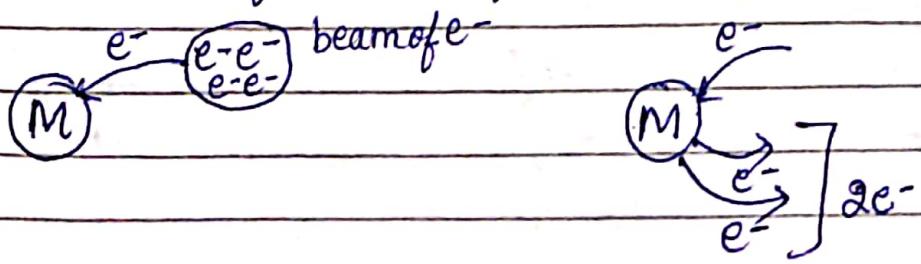
→ signal will appear in the form of mass to charge ratio (m/e or m/z)

→ Generally charge will be +1 in most of the cases, rarely it will be +2.

$\frac{72}{+1} = \frac{72}{} \rightarrow$ M.W.

⇒ Principle :-

→ A beam of electron is bombarded in the analyte compound and it will leads to removal of $1e^-$ from analyte.



C_2H_6
C_3H_8
C_4H_8

→ Due to removal of 1e⁻ ~~from analyte~~, molecule will be positively charge and known as molecular ion.

$$M + e^- \longrightarrow \overset{+\cdot}{M} + 2e^- \quad (e^-,\ e^-)$$

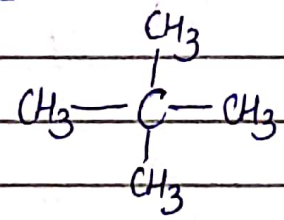
[from beam of e⁻]

$\overset{+\cdot}{M}$ (radical cation) → Molecular ion

$\overset{+}{m_1} + \dot{m}_2$, $\dot{m}_1 + \overset{+}{m}_2$] fragment ions

→ Molecular ions will be fragmented
→ Only Positive ions are detected in M.S. i.e, M^+, m_1^+, m_2^+ → stable ions

Eg:- Neopentane



⇒ C_5H_{12}

C_5H_{12} + e⁻ → $[C_5H_{12}]^{+\cdot}$ → Molecular ions

fragment ion

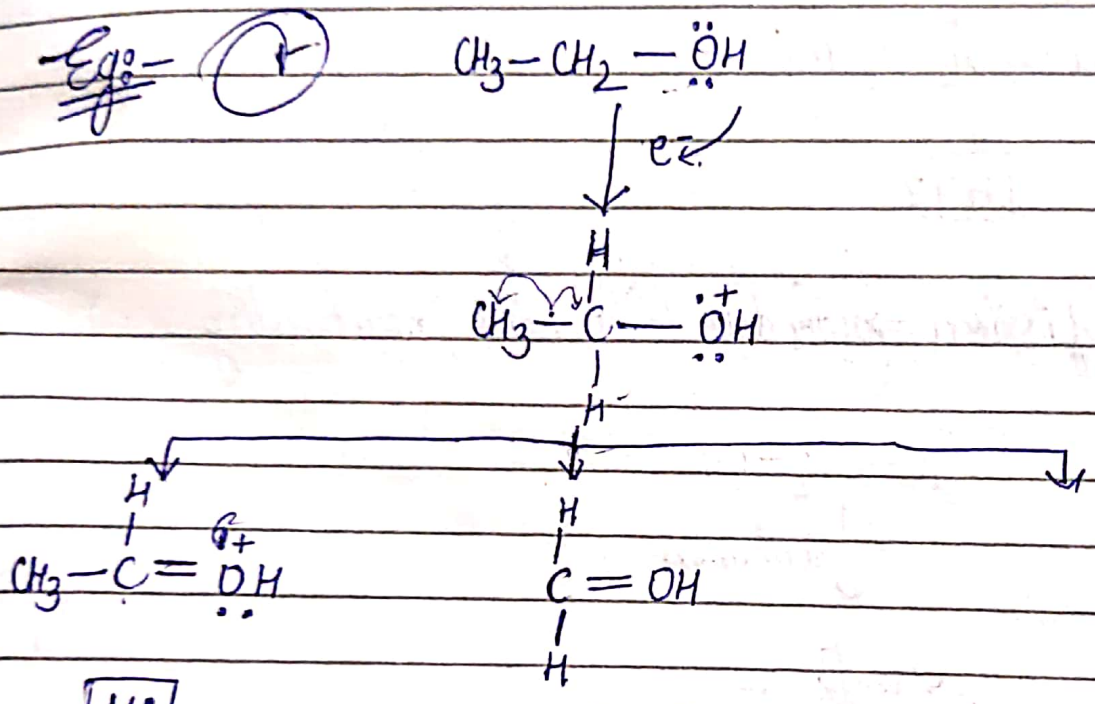
CH_3^+	$C_2H_5^+$	$C_3H_7^+$	$C_4H_9^+$
+	+	+	+
$C_4H_9^\cdot$	$C_3H_7^\cdot$	$C_2H_5^\cdot$	$CH_3^\cdot$
→ free radicals			

* Fragmentation

→ In fragmentation, ionization occur i.e, removal of e⁻.

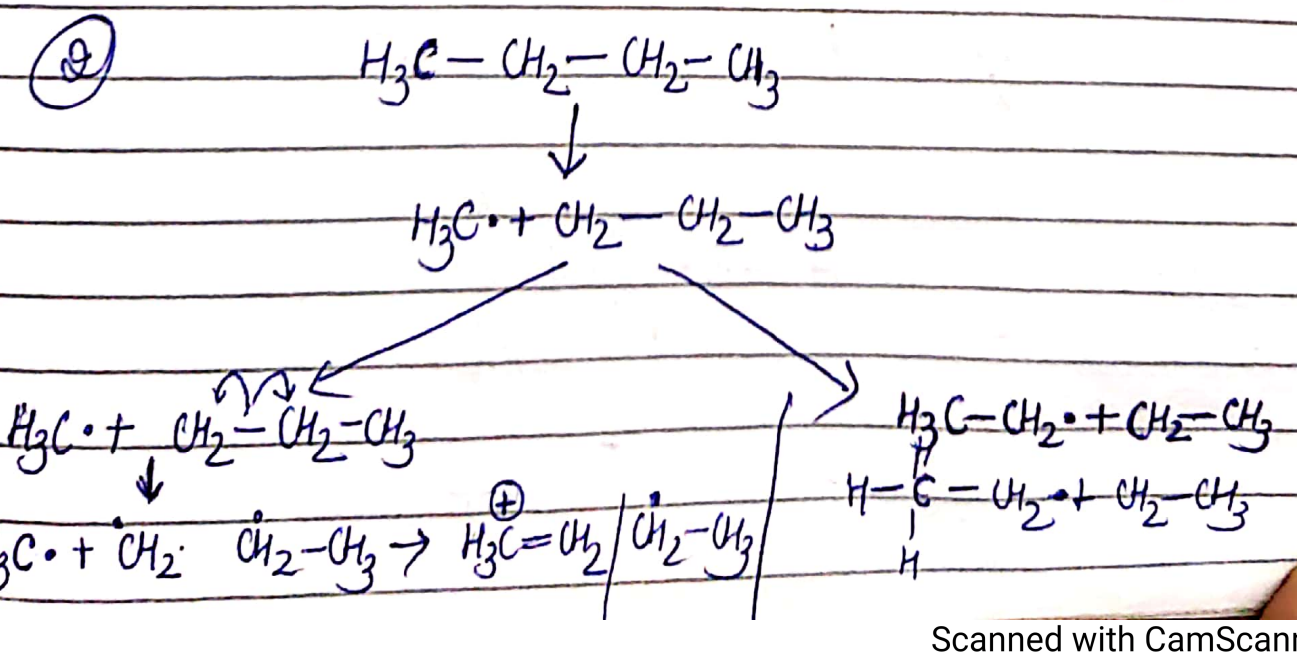
→ Firstly the loosely bound e⁻ comes out.
non-bonding e⁻ > π-bond > σ bond
(lone pairs) ⓔ ⓔ

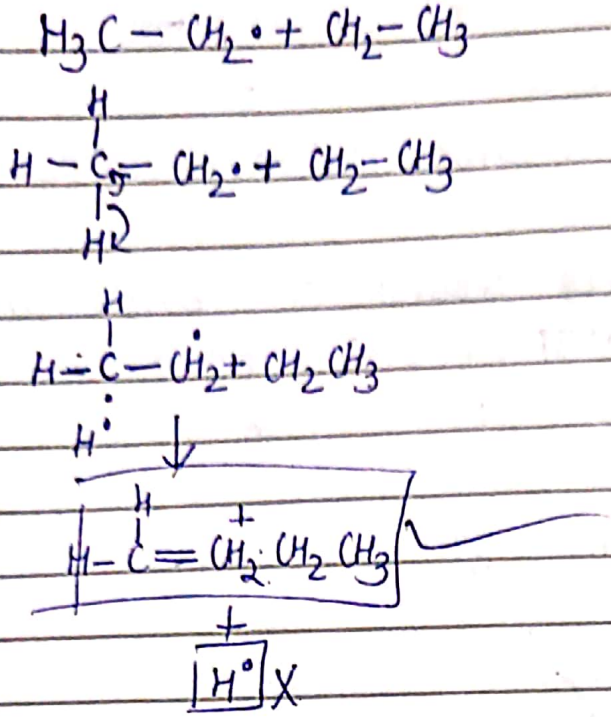
Eg:- ①



→ bulky group leaves as a fragment prefrenially.

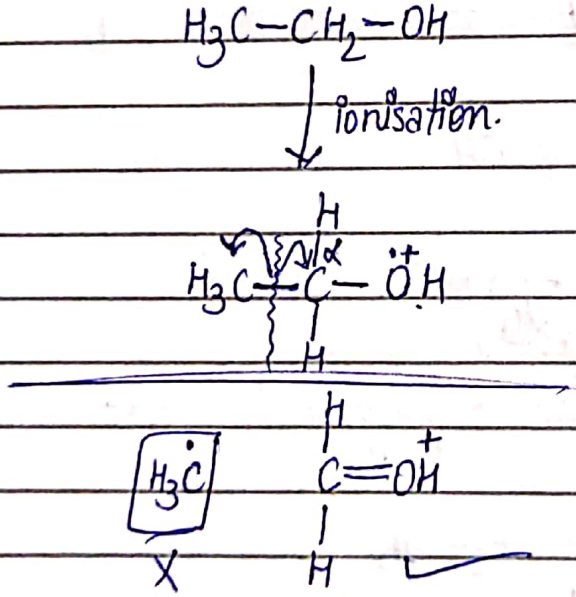
②





$\Rightarrow$ α- fission $\Rightarrow$ (occurs due to presence of π bond / nonbonding e⁻)

Eg:-



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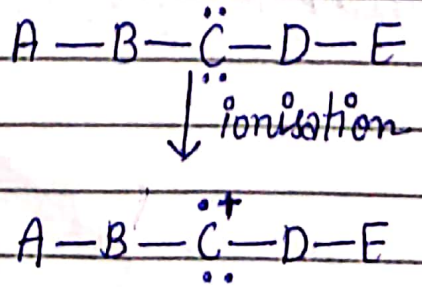
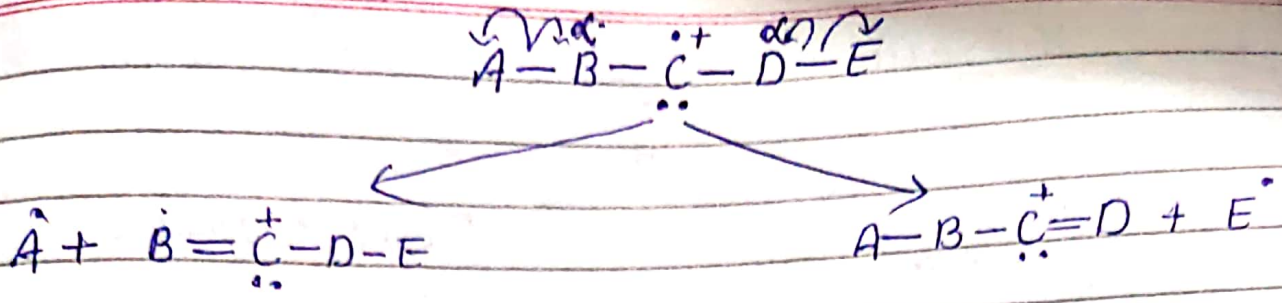
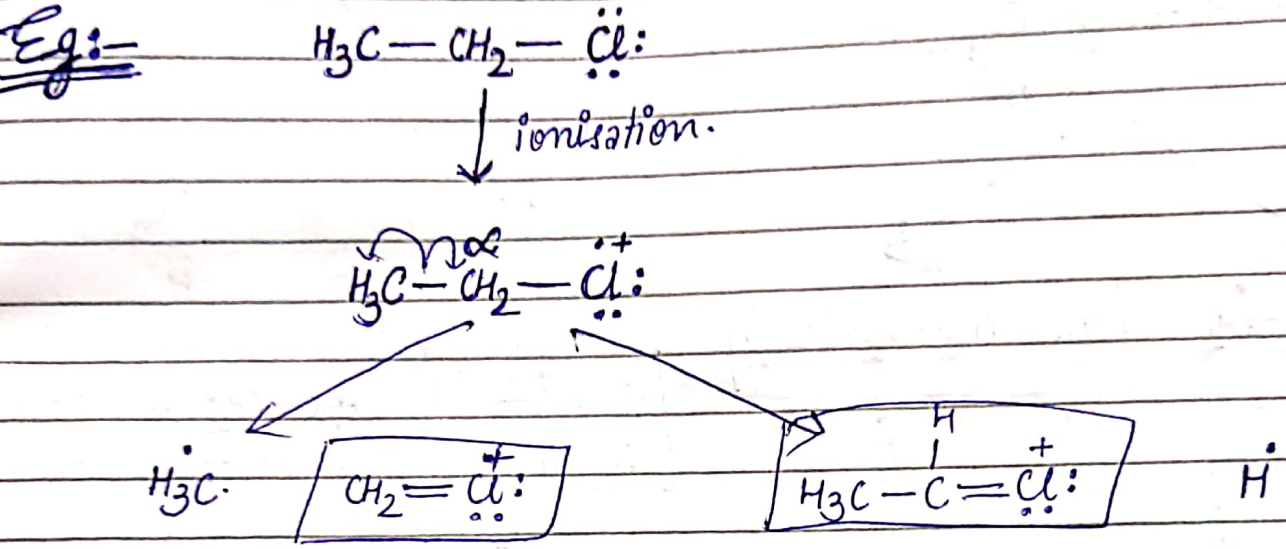
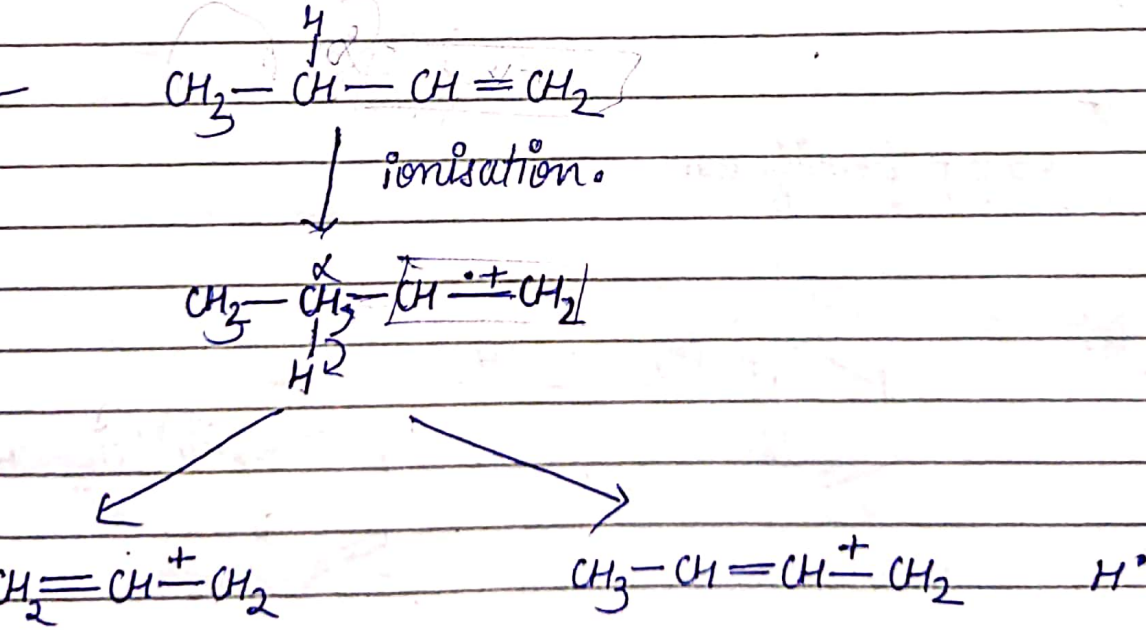






Eg:-



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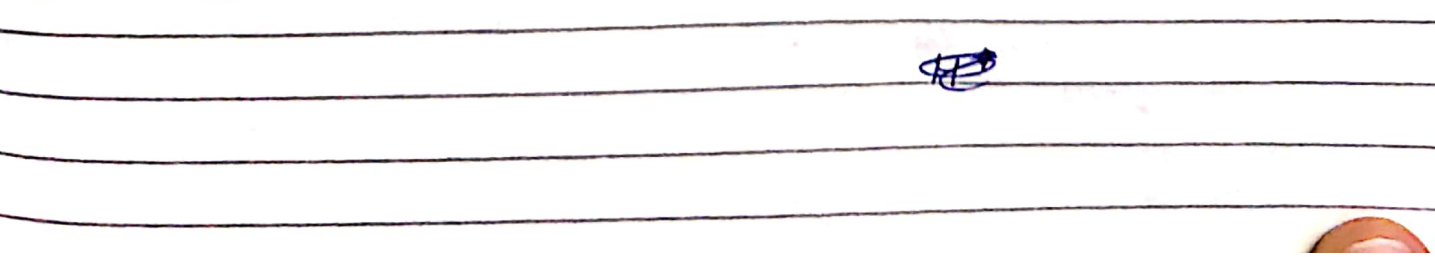

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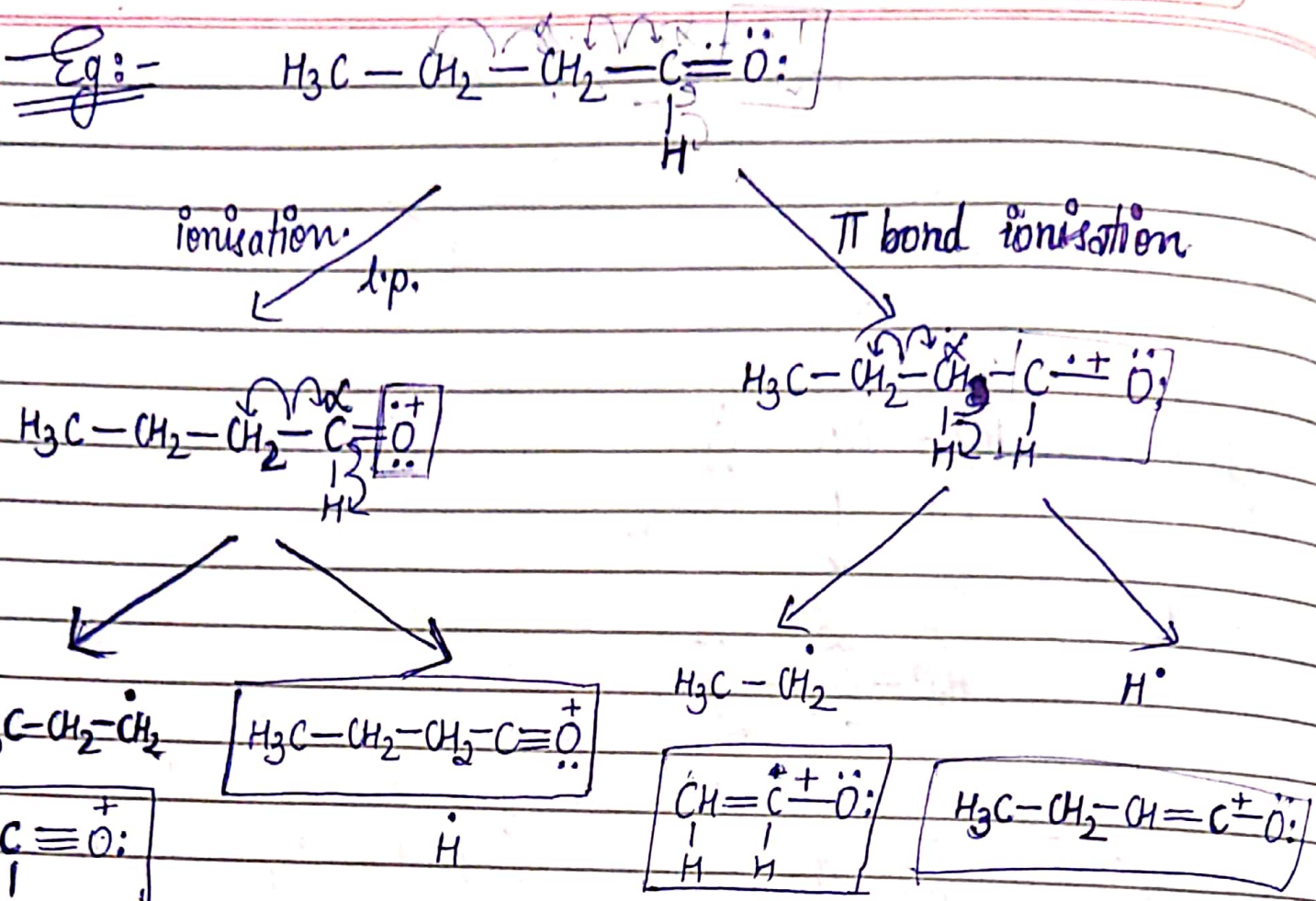
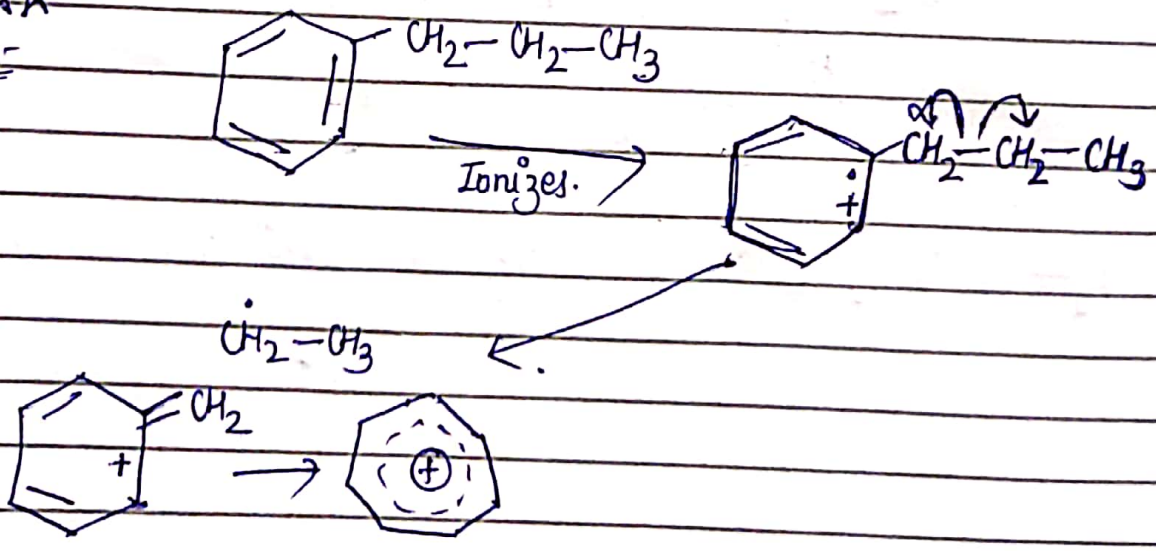


favarable product

bcoz bulky group preferably leave

Eg:-



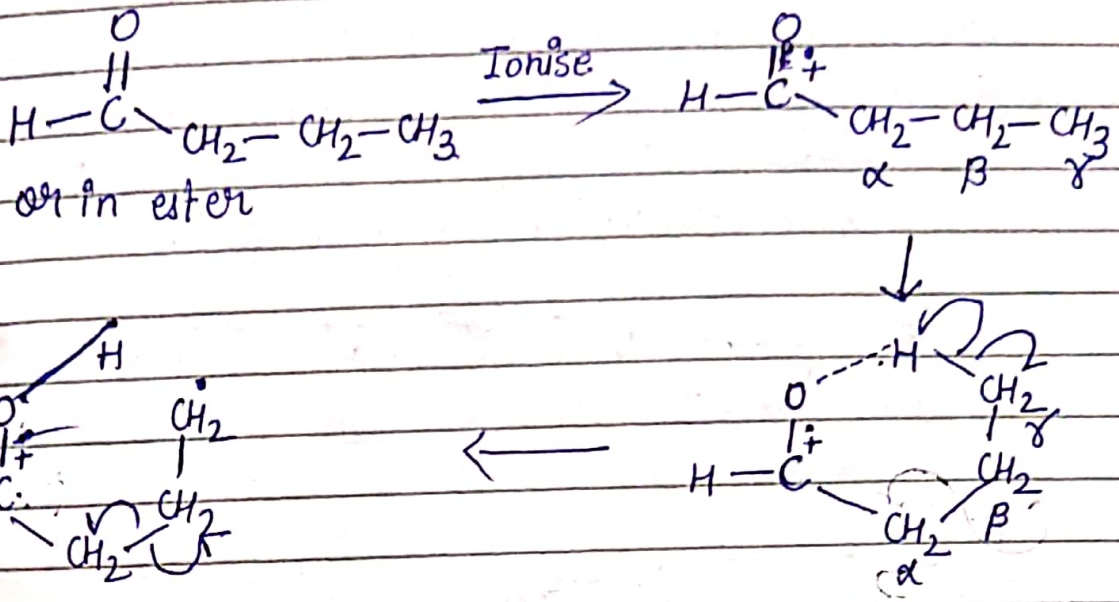
* Mc Lafferty Rearrangement

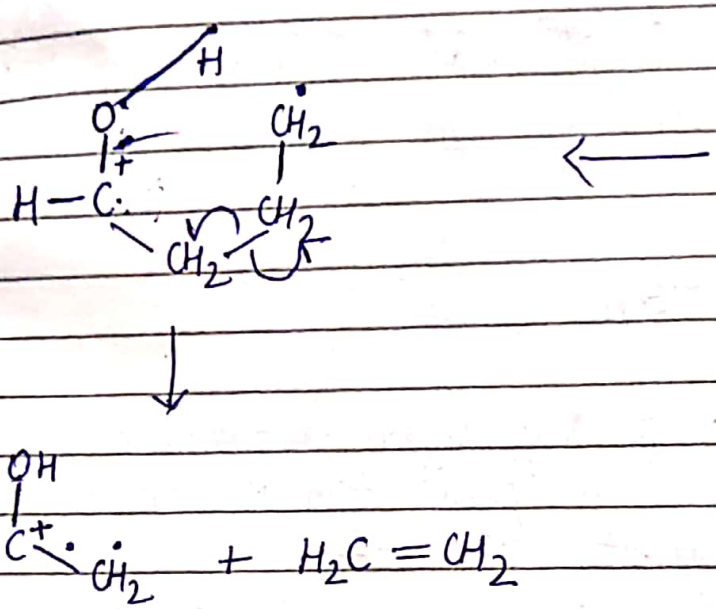
↓

[it requires γ-H]

6 membered T.S is formed.

Eg:-





→ aldehyde, ketone, ester, amide show this type.

→ When γ H containing aldehyde, ketone, ester acid anhydride, alkene, alkyne, CN undergo γ-H transfer followed by α and β bond cleavage rxn

→ In this rxn we get molecular ion peak as well as lapperty peak.

* Electron Impact ⇒

→ e^- are accelarated from the hot tungsten filament to an anode, usually through a pot. diff. of 70 V.

→ Since 1 eV = 23 Kcal mol^{-1} = 96.6 KJ mol^{-1}, a 70 eV e^- has sufficient E not only to ionise an organic molecule but also to cause extensive fragmentation.

$$e \underset{(70eV)}{\longrightarrow} M \xrightarrow[\text{EI}]{\text{ionisation}} \dot{M}^+ \xrightarrow{\text{frag}} \text{Base peak.}$$

* Chemical Ionisation

→ In this technique, a reagent gas [methane, isobutane or ammonia] is allowed to pass into the ion chamber at a pressure of about $10^2 Nm^{-2}$.

→ This gas is ionised by using e^- with energies upto 300 eV.

Eg:

$$CH_4 + e \longrightarrow \dot{C}H_4^+ + 2e$$

Fragmentation then occurs. $CH_4^+ \longrightarrow CH_3^+ + H^\cdot$

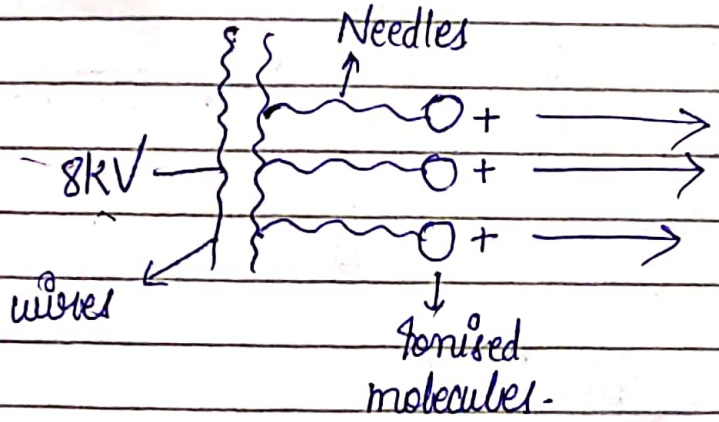
→ The ion so produced collide with its neutral component.

$$CH_4^+ + CH_4 \longrightarrow CH_5^+ + \dot{C}H_3$$

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2$$

* Field Desorption (FD)

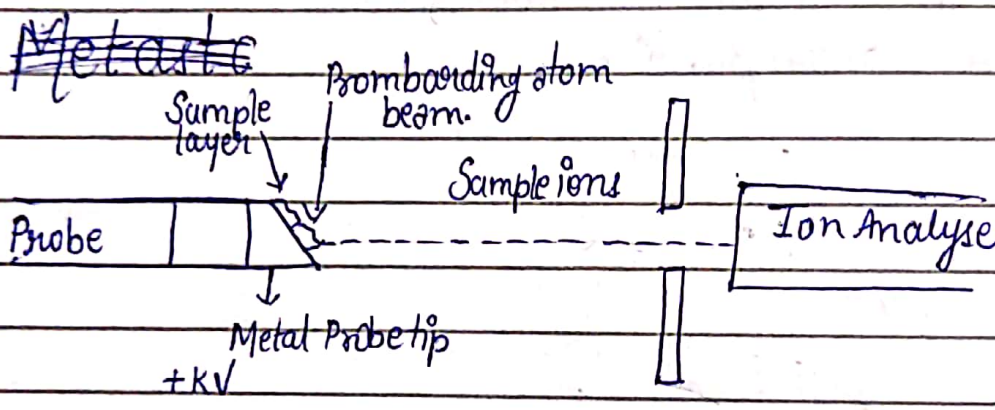
→ In this technique, a soln of about 1 uG sample is deposited on a wire.
→ The wire is maintained at +8 KV and can be heated.
→ Since the needles on the wire are very sharp, the field at their tips may be as high as 10^8 V cm^{-1}
→ This results into discharge of an e$^-$ from the sample into vacant orbitals of metal from which wire is made.
→ Thus, the M^+ ion are made at positive wire & M^+ is disorbed by columbic repulsion.
→ Hence M^+ may be thrown into gas phase without thermal decomposition.



* FAB [Fast Atom Bombardment]

→ Polar molecules, such as peptides with molecules weights upto 10000 Daltons can be analyzed by soft desorption Ionisation technique called FAB

→ A few micrograms of sample are dissolved in few microlitres of glycerol as matrix.
→ The soln is then bombarded by beam of Xenon atoms. These fast atoms ($\vec{Xe}$) are prepared by accelerating xenon ions ($\vec{Xe^+}$) to an energy of 6-9 KeV, and then neutralising these ions by e- transfer.
→ After the impact of fast xenon atoms into soln of sample in matrix, the sample is desorbed as an ion by momentum transfer.
→ The beam of sample ion is then analysed in mass spectrometer.



* Metastable Ion Peak:-

→ The ions resulting from decomposition b/w the source region & magnetic analyser are called metastable ion peaks.

Characteristics:-

m/e

→ These peaks are much broader, i.e, they spread over several mass unit.
→ These peaks appear in the mass spectrum usually at non-Integral m/e values.
→ These peaks are and relatively low abundance or low intensity.
→ The MIP can be detected by a double focusing mass spectrometer.

* → The broadning of metastable peak is due to the fact that some of excitation energy level to bend capture may be converted into additional K.E.
→ The Metastable peaks in mass spectrum greatly contribute to structure elucidation.
⇒ From the position of parent ion and daughter ion the position and metastable ion can be calculated.

$m_1 \times m_2$ / M_2 Position of Metastable I.P = $\frac{M_2 \times M_2}{M_1}$ → daughter ion / Parent ion

⇒ Molecular Ion Peak.

In Mass Spectra peak which has max. value of M/e or M/z & minimum intensity known as MIP . It represent mol. wt. of compounds.

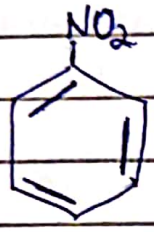
* Base peak :-

→ Peak in mass spectra by most stable fragment and has max. intensity known as base peak.

* Nitrogen Rule :-

→ It states that a molecule of even no. molecular mass must contain no or even no. of N_2 atoms.

→ An odd numbered molecular mass requires an odd no. of N_2 atoms.

→ 

$\frac{123}{1} \rightarrow 123\cdot\cdot$

→ The signal for molecular ion appears at m/e 123 i.e, at odd numbered molecular mass since the compound contains only one N_2 atom.

* Ion Abudances :-

→ All singly charged ions in mass spectrum which contain carbon also give rise to a peak at one mass

unit together. It is becoz of natural abudance of C^{13}. (1.1%).

→ For an ion containing n carbon atoms, the abudance of the isotope peak is n × 1.1% of C^{12} containing peak.

→ The probability of finding two C^{13} atoms in an ion is very low, and M+2 peaks are accordingly of low abudance.

→ The isotope patterns provide a useful test of ion composition in those cases where polyisotopic elements are involved.

* Factors Affecting Fragmentation :-

① Thermal Decomposition ⇒

Thermolabile compounds may undergo thermal decomposition in ion source before ionisation which may cause problem in interpretation of mass spectra. Hence, if thermal decomposition is suspected, the compound can be ionised in a cooled ion source, so that e^- bombardment of entire molecule takes place or compound may be converted to a more volatile derivative.

② Bombardment Energies :- In general, the compounds are bombarded with a beam of energetic electrons accelarated from filament to an energy of 70eV to form molecular ion which posses a max of 6eV in

excess of their ionisation potential. If this high energy of (70eV) of e⁻ is reduced to 20eV, there is a little change in fragmentation pattern but efficiency of ionisation is reduced and spectra are weaker in intensity.

→ Recording low energy spectra, is thus a valuable tool for study of bond energy.

③ Relative Rates of Competing Fragmentation Routes :-

→ Acc. to even e⁻ rule the radical ions, being odd-e⁻ species, undergo fragmentation resulting in the formation of radical ion & a neutral molecule or can be degraded to radical and ion.

$A^{+\cdot} \longrightarrow B^{+\cdot} + C$ or $A^{+\cdot} \longrightarrow B^{+} + C^{\cdot}$

Factors Governing Rxn Pathways :-

① Stability of ions, radicals or neutral molecules formed as a result of fragmentation of Molecular ion affect the mass spectral rxn pathways.

→ Stability of ion is affected by :- ① Resonance effects
② Inductive effect
③ Chain branching
④ Polarizability.

② H transfer rearrangement takes place at radical sites whereas skeletal rearrangement of even e⁻ fragment ions appear to take place at e⁻ deficient positive centres.

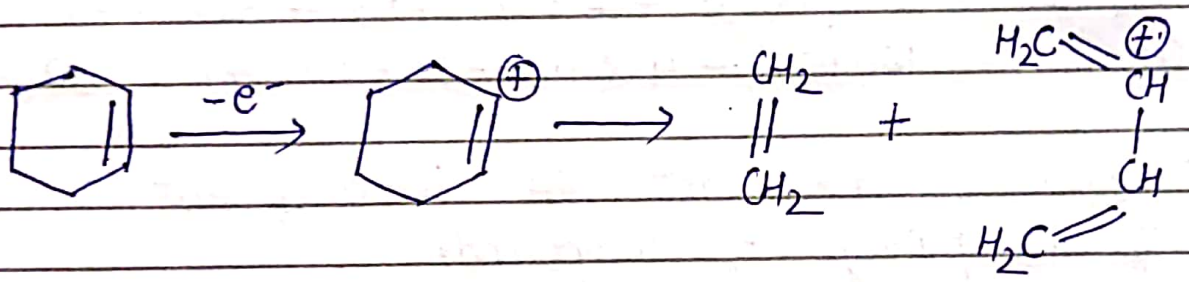
③ Steric factors also play significant role in altering the frequency factors & thereby directing fragmentation modes.

* Retro-Diel's Alder Reaction :-

→ This rxn is characteristics of cyclic olefins which involve multicentered fragmentation.

→ Here the cleavage of two bonds of a cyclic system occurs resulting in formation of two stable unsaturated fragments in which two new bonds are formed.

→ The highly substituted or more conjugated fragment which has a lower ionisation potential carries a charge. In simple system, the charge is carried by a diene.



* High Resolution Mass Spectrometry [HRMS]

⇒ Determination of MW & MF by HRMS :-

→ Low resolution mass spectrometer measures M/e values to the nearest whole number mass unit.

→ High resolution mass spectrometere measures m/e values to three or four decimal places & hence, provide an extremely accurate method for determining MF.

→ HRMS uses extra stages of electrostatic or magnetic focussing to form a very precise beam and to detect the exact masses to an accuracy of about 1 part in 40,000.

→ The determination of accurate molecular weight is possible by HRMS because the actual masses of atomic nuclides are not integers.

For Eg:- A molecule whose MW is 32 could be O_2, N_2H_4 or CH_3OH. However these molecules have the following precise masses:

$$O_2 = 2 \times 15.9949 = 31.9898,$$
$$N_2H_4 = 2 \times 14.0031 + 4 \times 1.00783 = 32.0375$$
$$CH_3OH = 12.0000 + 4 \times 1.00783 + 15.9949 = 32.0262.$$

→ HRMS provides the exact MF but does not give indication of the purity of compound.

⇒ Relative Abudance of Natural Isotopes:-

→ The relative abudance of natural isotopes is determined at masses 2 or more larger than the parent ion.

→ The heavy isotopic contribution is calcuted using formula.

$$\frac{Z+1}{Z} \times 100 = 0.015x + 1.11w + 0.37y + 0.037z$$

where $w \rightarrow C$, $x \rightarrow H$, $Z \rightarrow O$, $y \rightarrow N$ — atoms respectively

Z → mass of non-isotopic peak.
Z+1 or Z+2 → masses of non-isotopic peaks at 1 or 2 units more than parent ion.

⇒ Component Analysis :-

→ A large no. of compounds and high MW polymeric material can be analysed and characterised by mass spectrometry.
→ The sample is first pyrolysed and volatile products then led into the spectrometer.