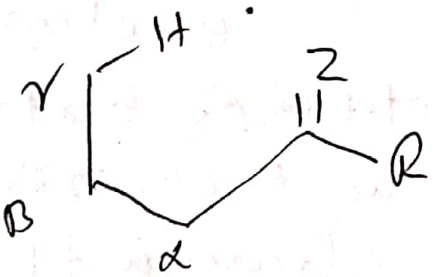
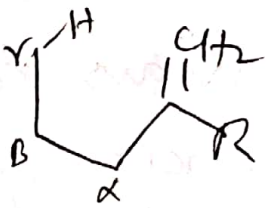
TDC-III
PG-III
ORGANIC

Mass Spectrometry

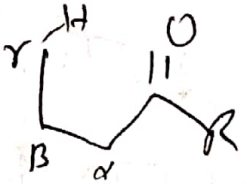
McLafferty Rearrangement

- It is a very common rearrangement involving fragmentation reaction. Observed in Mass Spectrometry.
- Such fragmentation is first described by Fred McLafferty in 1956.
- The neccessary condition of McLafferty rearrangement is that it must contain γ-H and involves the formation of radical cation.

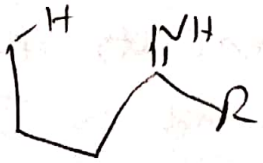




alkene

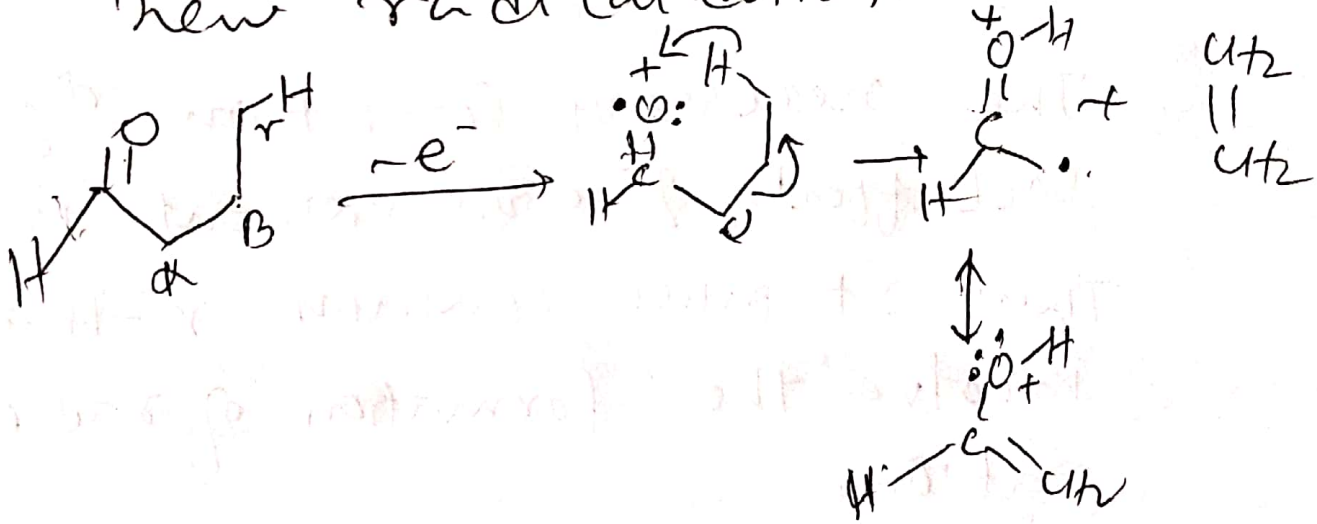


Z = C, N, O



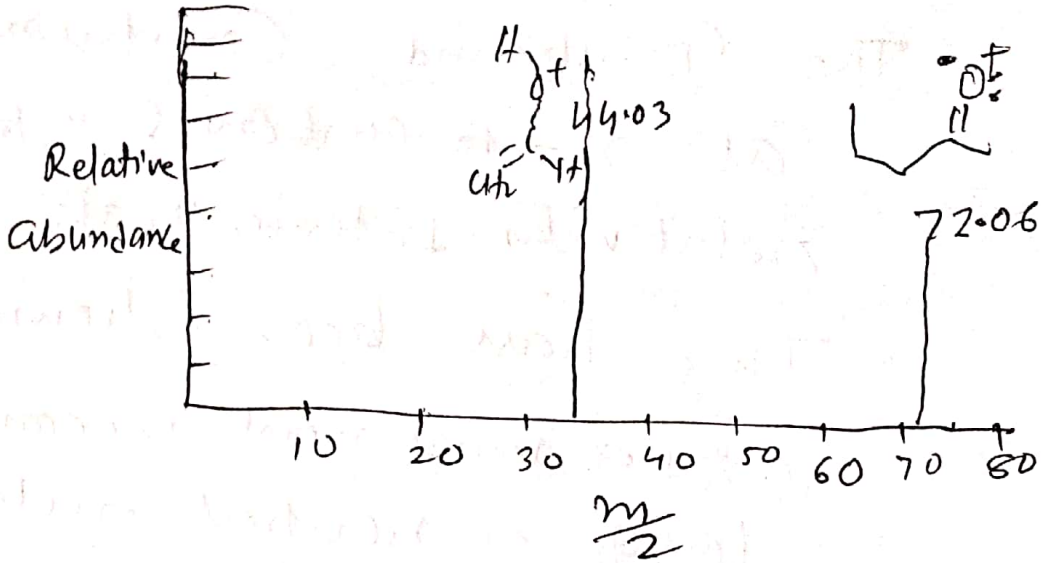
All such compound undergoes McLafferty rearrangement.

In McLafferty rearrangement reaction radical centre in molecular ion abstracts one H-atom from γ-position during which π-bond is formed between β & γ-position and σ-bond between α & β position is broken and produce alkene & new radical cation



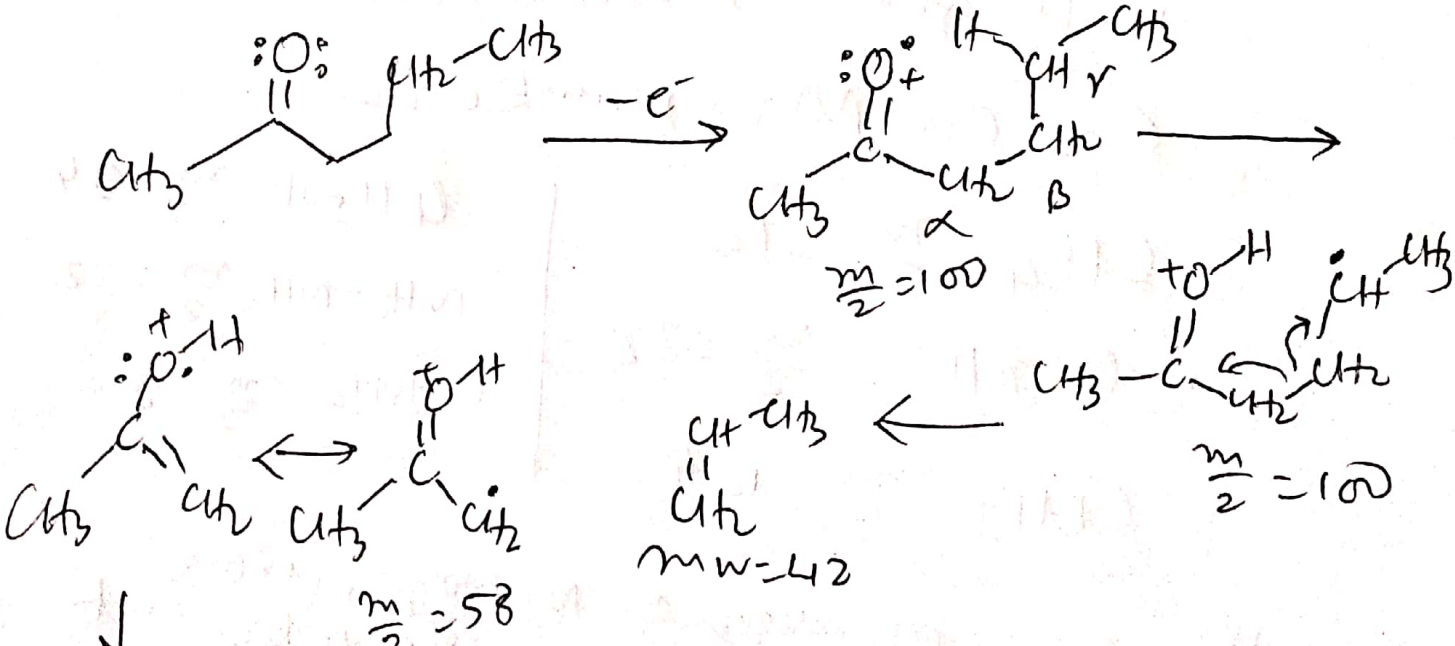
· enol radical cation

In The mass spectrum of butanal on the x-axis value represent $\frac{\text{mass}}{\text{charge}}$ ratio - In this case charge is +1 hence $\frac{m}{z}$ represents molecular weight of compound - The value on y-axis represents relative abundance



Mass peak at 72.06 is for molecular ion. 44.03 is for fragment and/ Cation. The Right most highest molecular weight is molecular ion peak. Tallest ion peak is base Peak

Similarly Rearrangement of 2-hexanone



Odd electron ion is identified by Nitrogen rule. most peaks found in the mass spectra of organic compound

The Compound Containing H-atom at γ- to carbonyl show a relatively intense peak with even $\frac{m}{2}$ value This has been shown due to a rearrangement accompanied by loss of a neutral molecule

— This McLafferty rearrangement is an intra molecular elimination.

Nitrogen Rule = It is stated That The Compounds containing an even number of Nitrogen (zero is even) will give Molecular ion with even Mass Number

CH_4 $\frac{m}{2}=16$

CH_3OH $\frac{m}{2}=32$

$CClF_3$ $\frac{m}{2}=104$

C_6H_5OH $\frac{m}{2}=94$

NH_2-NH_2 $\frac{m}{2}=32$

$C_6H_5N_2$ $\frac{m}{2}=94$

An odd number of Nitrogen atom at Causes the Molecular ion to be odd mass number

NH_3 $\frac{m}{2}=17$

$C_2H_5NH_2$ $\frac{m}{2}=45$

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Meta stable ion

If An ion (molecular or fragment) m_1^+ is accelerated before it breaks down and when it decomposes into m_2^+ and m_3, Then part of kinetic Energy m_1^+ is lost to the neutral m_3 and m_2^+ Continues to be accelerated and Then is Collected

$$m_1^+ \longrightarrow m_2^+ + m_3$$

Ion m_2^+ produced in This way is not recorded as mass m_2 but as mass m^*, where $m^* = \frac{m_2^2}{m_1}$

Then ion is known as meta stable ion. and such ion is Usually recorded a a weak broad peak and is not an integral value.

The presence of meta stable Peak is very useful for deducing fragmentation mechanism since Then indicate conversion of m_1^+ into m_2^+ in one step

Three ions $\frac{m}{e}$ 32, 31 & 30 are recorded

This Suggest loss of H atom one at a time The broad peak of metastable ion were also recorded at $28.1 = \frac{30^2}{32}$ This means That $\frac{m}{e}$ 32 was Converted into ion $\frac{m}{e}$ 30 in one Step.

In absence of metastable ion

ion $\frac{m}{e}$ 32 → ion $\frac{m}{e}$ 30 not occur

ion $\frac{m}{e}$ 31 → ion $\frac{m}{e}$ 30 is possible

Thus metastable ion Provide Useful information on the nature of the fragmentation process.