

UNIT – V ORD - CD and Mass Spectrometry

(15 Hours)

ORD-CD: Definition, deduction of absolute configuration, octant rule for ketones, Cotton effect-axial haloketone rule.

Mass spectra – Basic principle, molecular ion peak, base peak, meta stable ion peak, isotopic peaks, Nitrogen rule, ring rule, McLafferty rearrangement, rules for fragmentation pattern, Examples of mass spectral fragmentation of organic compounds (alkanes, aromatic hydro carbons, alkyl halides, aldehydes, ketones, alcohols, acids and esters).

Organic Spectra

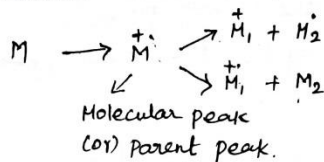
Mass Spectroscopy

uv. electron transfer. electron transfer.

Principle:

molecular formula

* It is the most accurate method for determining the molecular mass of the compound and its composition. Organic molecules are bombarded with a high energy electron and converted to highly energetic positively charged ion known as molecular ion (or) parent ion. These ion breakup into smaller fragments (or) ions. The molecular ion (M^+) commonly decomposes into pair of fragments which may be either a radical and a small neutral molecule and radical cation.



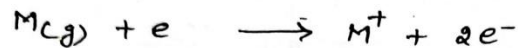
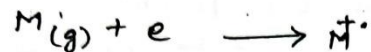
- * The molecular ion of the fragment ions and the fragment radical cation are separated by deflection in variable magnetic field according to their mass and charge (for most ion the charge is one). They generate a current known as ion current at the collector in proportion to their relative abundance.
- * A mass spectrum is a plot of relative abundance against m/e ratio for singly charged ion. The mass more easily the ion is deflected in the magnetic field. Neutral particle or radical produce in the fragmentation cannot be detected directly in the mass spectrometer.

* Mass Spectra used in two ways:

1) To establish the structure of compound (by giving exact molecular mass and by fragmentation pattern).

2) To prove the identity of the two compounds.

* A parent ion results when one electron is removed from the parent molecule of the substance.



* The m/e value of the parent ion is equal to the molecular mass of the compound. In a few cases the parent ion peak may be the base peak and can be easily recognised.

* In most of the cases, parent ion peak is not the base peak and is often of very small abundance. Many elements occur naturally as isotopes, out of these the lightest one greatly predominates. The mass spectrometer is designed to perform three basic functions. These are,

i) To vapourise compounds of varying volatility.

ii) To produce ions from the neutral compound in the vapour phase.

iii) To separate ions according to their mass over charge ratio (m/e) and to record them.

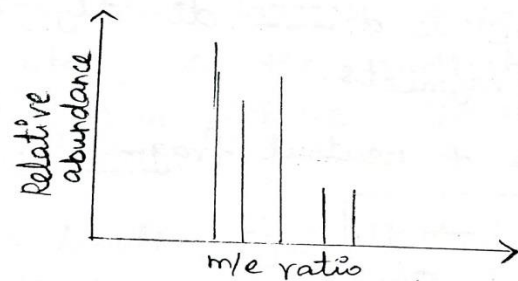
Differential Peak:

~~and mass spectrum~~ mass spectrum is a plot of relative abundance against m/e .

* The most stable ion will be present in large proportion (or) amount and the intensity corresponding to that peak is maximum (100%) it is known as the base peak.

* The intensity of all other ion (or) recorded as a percentage of base peak. The peak which is recorded at the extreme right is known as parent peak. (due to high m/e value).

Smaller peak (or) isotopic peak comes after the parent peak.



Types of peak:

1. Molecular ion (or) parent ion peak.
2. Base peak.
3. Fragment peak
4. Isotopic peak
5. Metastable peak.

Meta stable peak:

* If an ion fragments after ~~acceleration~~ ~~before~~ entering into the magnetic field. It will have been acceleration as mass M_1 , but dispersed in the magnetic field M_2 , the resulting ion current will be recorded as a low intensity broad peak at apparent mass M^* .

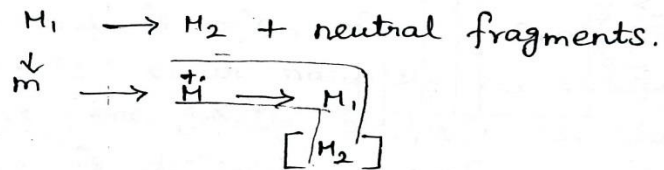
$$M^* = \frac{M_2^2}{M_1}$$

M_1 → Mass of ions before entering the magnetic field

M_2 → Mass of ions after " " "

M → Mass at which it will be recorded.

* Measurement of mass of metastable peak affords information that M_2 is derive directly from M_1 by a loss of neutral fragments.



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General rules for predicting predominant peak in mass spectra. (10M)

→ The relative abundance of the fragment ion depends on

i) The stability of the ion.

ii) The stability of radical lost.

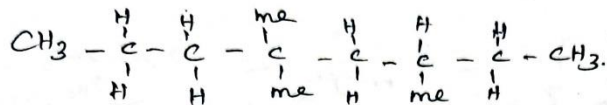
→ The stability of the ion can be decided by stabilisation of the charge which depends on

a) Resonance.

b) inductive effect

c) polarisability.

- i) The relative height of molecular ion is greatest for the straight chain cpd and decrease as the degree of branching increase.
- ii) The relative height of usually decrease with increase in molecular weight in straight chain cpd.
- iii) Cleavage is favoured at alkyl substituted carbon. More the substitution more will the cleavage.

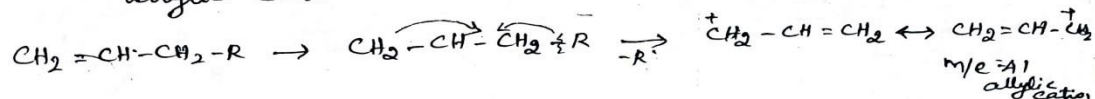


iii) cleavage takes place at position (a) due to high stability of 3° carbon.

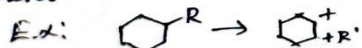
iv) Generally, the largest substituent at the branch eliminated as the radical. Because a long chain radical can achieve stability by delocalisation of odd electron.

v) Double bonds, cyclic structure, aromatic ring stabilised the molecular ion readily and thereby increase the appearance.

Ex: double bond favoured allylic cleavage and give allylic favour resonance stabilise allylic cation.



vi) Saturated rings tend to lose side chain at the α -position and the +ve charge tends to stay with the ring fragment.



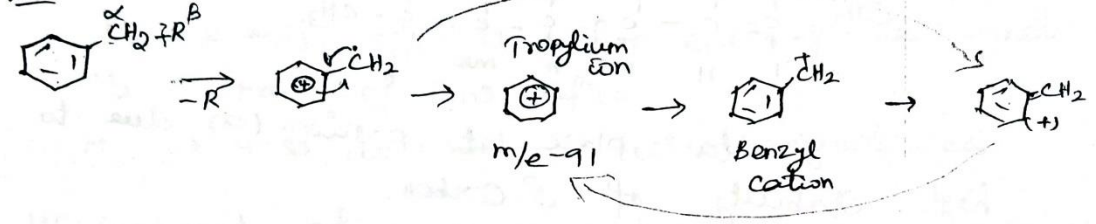
vii) unsaturated rings can undergo retro cleavage.

Ex:

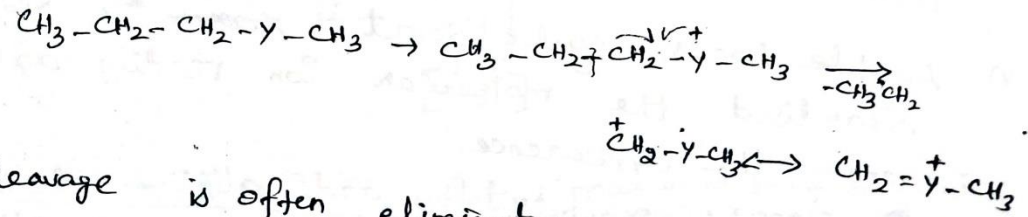


viii) In alkyl substituted aromatic cpd cleavage is very probable at the bond B. do the ring, giving the resonance stabilised benzyl ion (or) more likely tropylium ion.

Ex:



xi) C-C bond next to hetero atom cleave frequently leaving the charge on the fragment containing the hetero atom whose non bonding electron in the hetero atom provide resonance stabilisation.

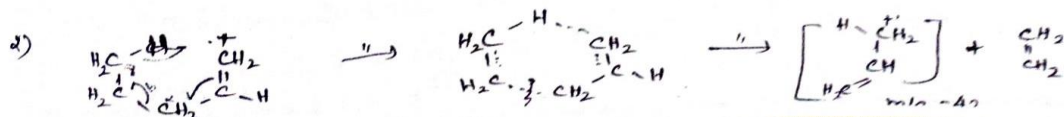
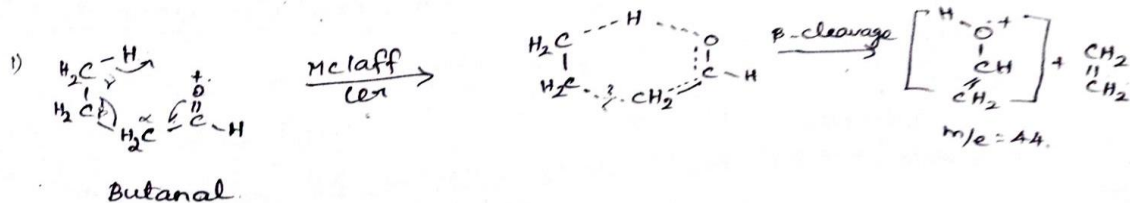


x) cleavage is often neutral molecule such as H₂O, CO, H₂S, NH₃, olefin etc is small, stable

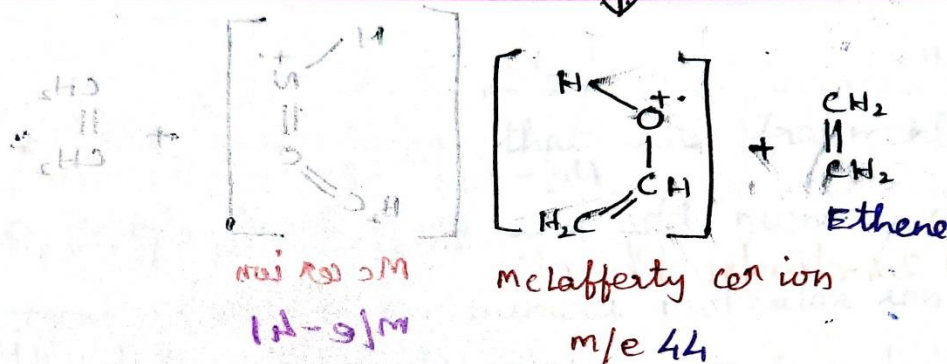
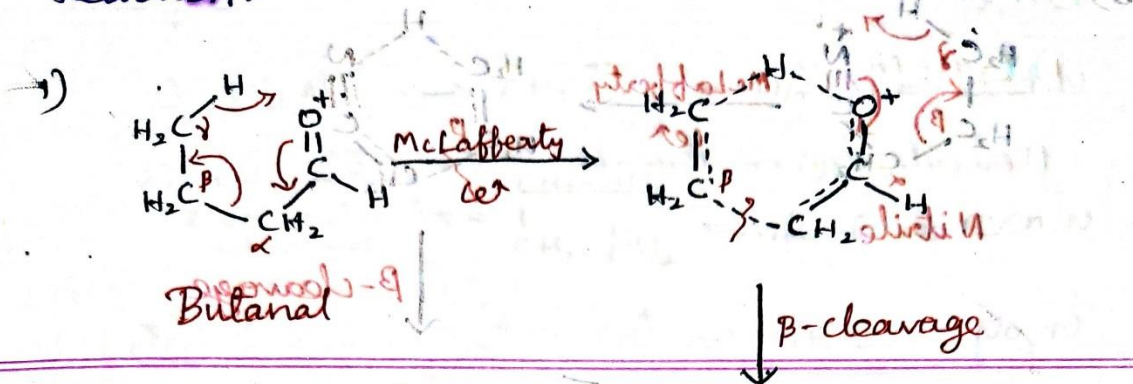
McLafferty $\text{C}\alpha^+$: (5 marks)

Condition:

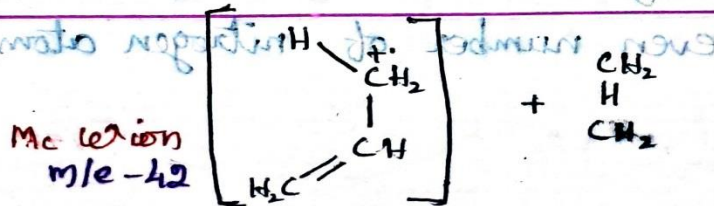
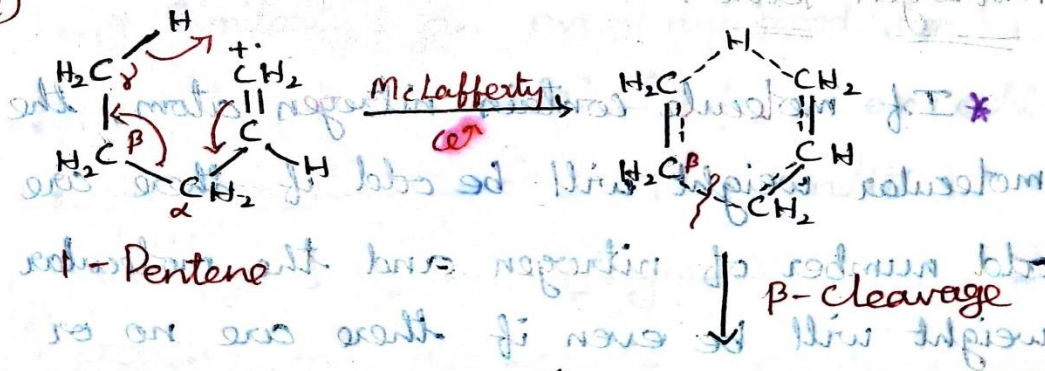
- 1) The molecule must possess side chain containing at least 3 carbon atom (α, β & γ). The γ carbon should have hydrogen atom.
 - i) There should be appropriately located hetero atom. (O or N) and a π system should be present.
- 2) This involves the migration of γ hydrogen atom followed by the cleavage of β -bond.
- 3) The $\text{C}\alpha^+$ proceeds through a sterically hindered 6-membered transition state.
- 4) Organic compounds like ketones, amines, alcohols, ester, acid which contain a γ -hydrogen as they form McLafferty $\text{C}\alpha^+$ ion whose m/e value is around 44.
- 5) This $\text{C}\alpha^+$ leads to elimination of simple neutral molecules and simple alkenes.
- 6) The molecular formula of unknown compound can be determined from the fragment ion and hence its parent ion.



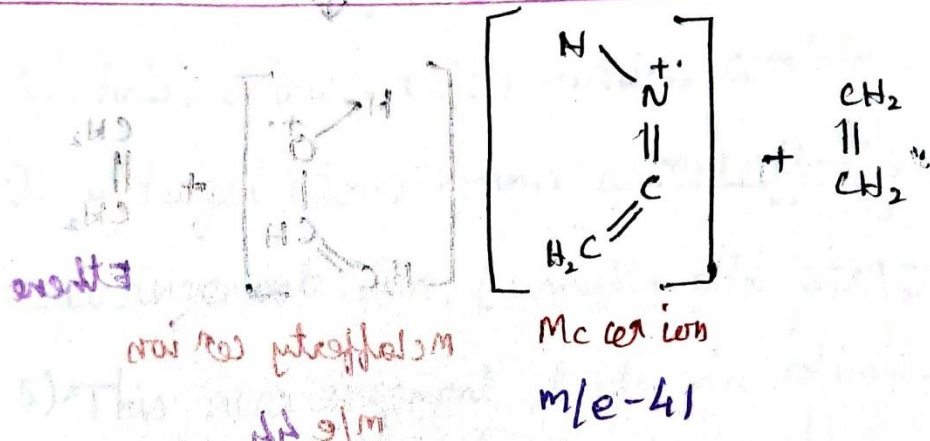
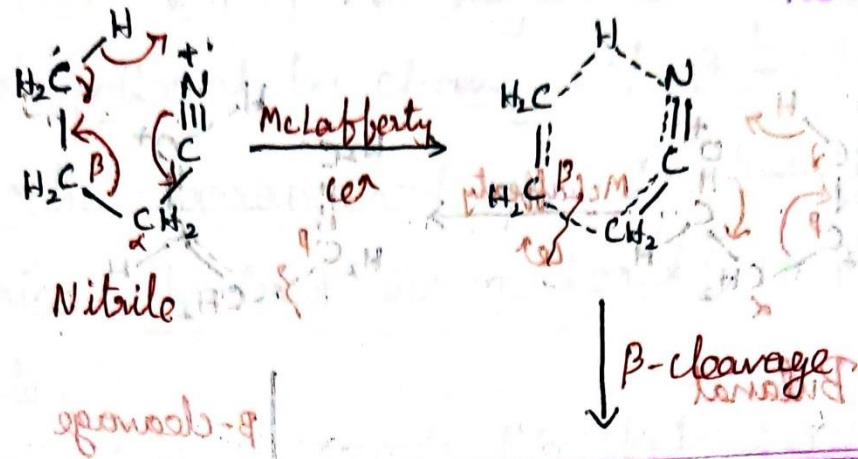
Reaction:-

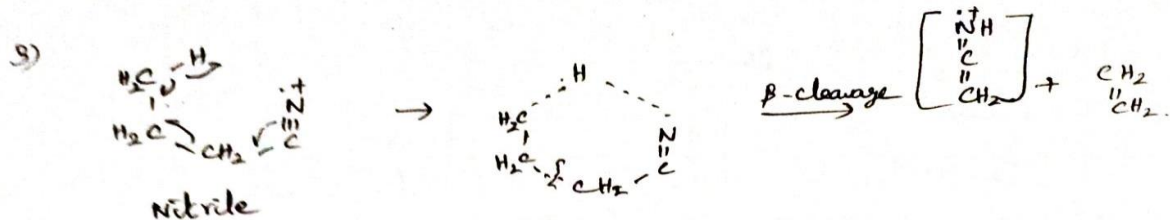


2)



3)

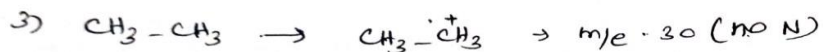
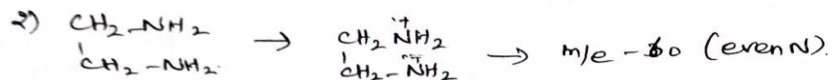
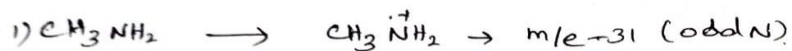




Nitrogen rule: (Cation).

If molecule contain nitrogen atom the molecular weight will be odd, if there are odd no. of nitrogen atoms. and the molecular weight will be even if there even no. of nitrogen atom. and molecular weight again even no number of nitrogen atom.

Ex:



This rule states that the fragmentation at a single bond gives an odd no. ion fragment from even no. molecular ion. similarly an even no. ion fragment should be obtained from an odd no. molecular ion. (This condition holds good for the fragment ion contain any type of nitrogen.)

ex: 1



molecular ion $m/e = 123 \rightarrow$ odd no. of molecular mass as cpd contain odd no. N-atom.

fragment ion formed are $\left. \begin{array}{l} \text{NO} \quad m/e = 30 \\ \text{NO}_2 \quad m/e = 46 \end{array} \right\}$ both appears at even mass no.

ex 2 2,4 dinitro phenol.

molecular ion $m/e = 184 \rightarrow$ even molecular mass as
cpd contain even no. of
N atom.

Fragment ions are $\overset{+}{M-H} m/e = 183$ } both appears at odd
 $\overset{+}{M-H-CO} m/e = 155$ } mass no. .