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Paper No and Title	**Paper 12: Organic spectroscopy**
Module No and Title	**28: α-, β-, allylic, benzylic cleavage and McLafferty rearrangement**
Module Tag	**CHE_P12_M28_e-Text**

Principal Investigator		**Co- Principal Investigator and Technical Coordinator**
Prof A.K.Bakhshi Sir Shankar Lal Professor, Department of Chemistry University of Delhi		**Dr Vimal Rarh** Deputy Director, Centre for e-Learning and Assistant Professor, Department of Chemistry, SGTB Khalsa College, University of Delhi *Specialised in : e-Learning and Educational Technologies*
Paper Coordinator	**Content Writer**	**Reviewer**
Prof Diwan S Rawat Professor Department of Chemistry University of Delhi	**Prof Diwan S Rawat** Professor Department of Chemistry University of Delhi **Dr. Beena Negi** Assistant Professor Bhim Rao Ambedkar College University of Delhi	**Prof MSM Rawat** Department of Chemistry Hemwati Nandan Bahuguna Garhwal University

Anchor Institute : SGTB Khalsa College, University of Delhi

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1. Learning Outcomes

After studying this module, you shall be able to

- Know what is alpha, beta cleavage
- Learn allylic cleavage and benzyllic rearrangement
- Identify Mc Lafferty rearrangement fragments
- Evaluate fragmentation pattern in mass spectrum

2. Introduction

Alkyl halides, ethers and alcohols show the following types of similar fragmentation behaviour:

1. Bond between C and more electronegative atom (O, halogen) breaks heterolytically.

2. α- bond between C and atom of similar electronegativity (C, H) breaks homolytically (α cleavage). Those bonds are most easily broken which that lead to resonance-stabilised cations

During fragmentation the following types of cleavage occur in ketones

1. α cleavage

2. β cleavage, involving McLafferty rearrangement and ethene extrusion

2. Alpha-cleavage in mass spectrometry

The fission of a bond originating at an atom which is adjacent to one assumed to bear the charge is known as α cleavage.

Alpha cleavage in alcohols

In alcohols α cleavage will occur with the fission of bond next to the functional group i.e, next to the hydroxyl group (figure 1).

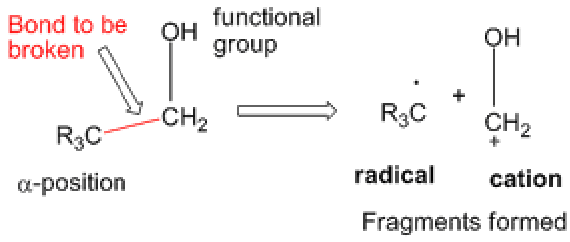


Figure 1: Alpha cleavage in alcohols

In decan-4-one-7-ol (mol wt 172.26), alpha cleavage can occur from either of the bond next to the hydroxyl group (figure 2).

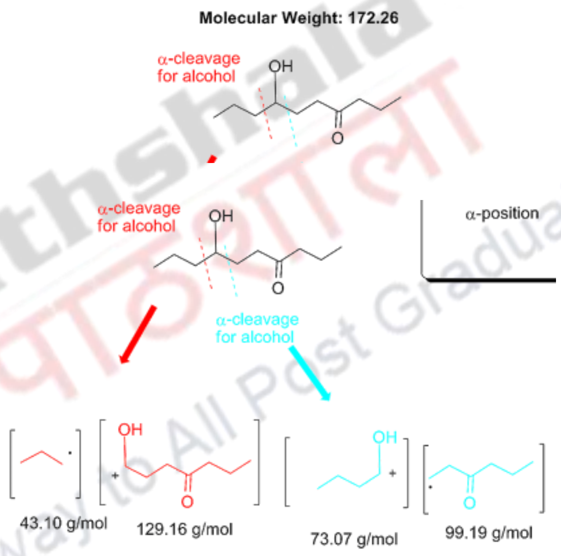


Figure 2: Alpha cleavage in decan-4-one-7-ol

Alpha cleavage in 3-methyl-3-hexanol, gives the most abundant peak for molecular ion formed by loss of largest alkyl group (propyl), then that formed by loss of ethyl group and least abundant is the molecular ion formed by loss of smallest alkyl group (methyl). The relative intensity of molecular ion at m/z 73, 87 and 101, decreases from being 100% to 50% then 10%, respectively (figure 3).

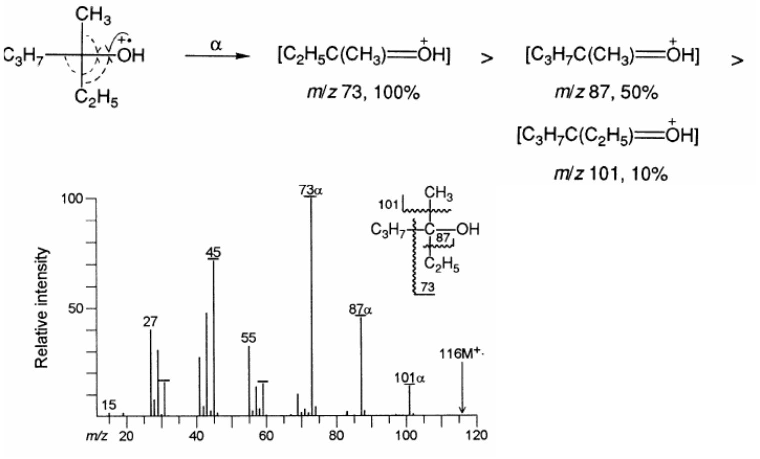
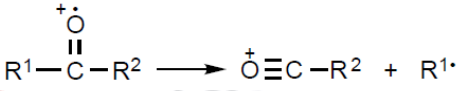


Figure 3: Mass spectrum of 3-methyl-3-hexanol showing alpha cleavage

Alpha cleavage in ketones

In ketones, R^1COR^2, the carbon atoms of the radical $R^{1\cdot}$ are called the α, β, γ- carbons, starting with the atom nearest the functional group. During α cleavage fission of the ketone with expulsion of a radical $R^{1\cdot}$ will take place.



$$R^1-\overset{\overset{+\cdot}{O}}{\overset{\|}{C}}-R^2 \longrightarrow \overset{+}{O}\equiv C-R^2 + R^{1\cdot}$$

Alpha cleavage in 2-methyl-3-pentanone gives fragment ions at m/z 71, 57 and 43 (figure 4).

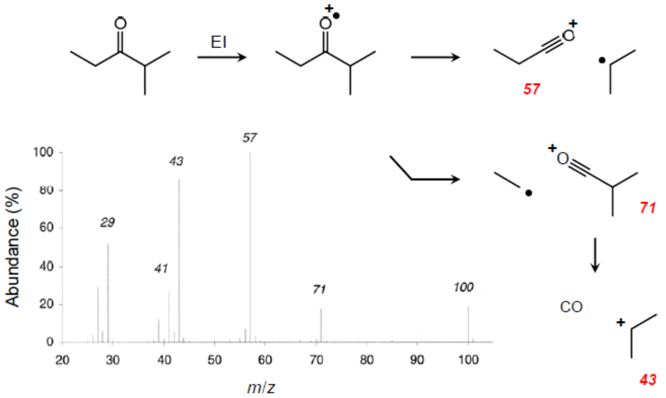


Figure 4: Mass spectrum showing alpha cleavage in 2-methyl-3-pentanone

Alpha cleavage in aliphatic amines

Tert-butyl amine undergoes alpha cleavage to give m/z peak at 58 (figure 5).

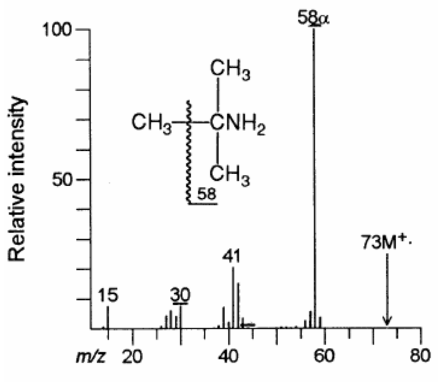


Figure 5: Mass spectrum showing alpha cleavage in tert-butyl amine

Alpha cleavage in N,N-diethyl amine gives m/z peaks at 58, 44 and 30 (figure6). The alpha cleavage in N,N-diethyl amine gives a very dominant peak at m/z 58, it is stabilised by the electron donating ability of nitrogen.

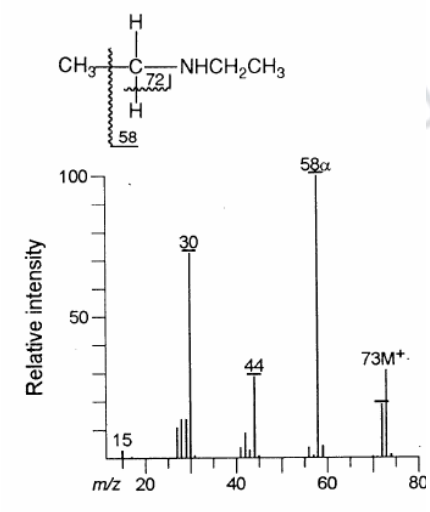


Figure 6: Mass spectrum showing alpha cleavage in N,N-diethyl amine

3. Beta-cleavage in mass spectrometry

Fission next, but one to a heteroatom or functional group producing a radical and an ion is called beta-cleavage in mass spectrometry.

β-Cleavage in ether

β-Cleavage in n-butyl ethyl ether occurs neither by simple bond fission with oxiranium ion formation nor by a mechanism analogous to the γ-cleavage reaction in carbonyl compounds, but instead it involves skeletal rearrangement within the butyl chain. This reaction is of some importance in n-butyl and n-pentyl but not in higher ethers and the sharply increased abundance of the product ion at low electron energies suggests that a rearrangement is involved.

n-Butyl ethyl ether (I) shows a β-cleavage product ion (*m/e* 73, $[C_4H_9O]^+$) of similar abundance to the molecular ion (4% abundance relative to the *m/e* 59 base peak). If β-cleavage in (I) is analogous to the process in ketones then path A of Scheme (figure 7) should be followed and the product ion should have structure (II). Moreover, the labeled ether (III) should lose $C_2H_4D^{\cdot}$, On the other hand were oxiranium ion formation to occur the labeled ether would lose $C_2H_5^{\cdot}$, Compound (III) was prepared by lithium aluminum deuteride reduction of 1-butyric acid followed by a Williamson synthesis employing ethyl bromide. The isotopic purity of the product as determined from the molecular ion region at a nominal 16 eV was d2 = 100%. The α-cleavage ions *m/e* 87 (89) and *m/e* 59 (61) indicate upper limits for the d1-ether of 1.8 and 2.4% respectively.

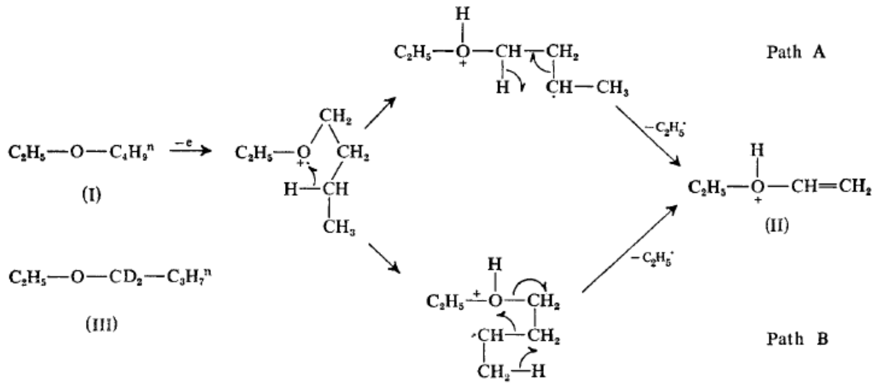
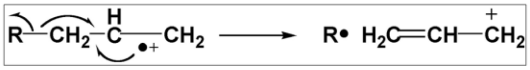


Figure 7: Mechanism of the β -cleavage reaction in ethers

4. Allylic cleavage

This is a major type of fragmentation for alkenes, leading to alkyl radical loss. Unfortunately, migration of the double bond occurs before fragmentation so that the observation of ions of this type is of little structural value. The mass spectra of many alkenes, especially polyenes, tend to be independent of the position of the double bond so that isomers cannot be distinguished.



The m/z 41 ion is the most common ion observed in the mass spectra of aliphatic compounds, together with homologoues of m/z 55, 69, 83,… (figure 8).

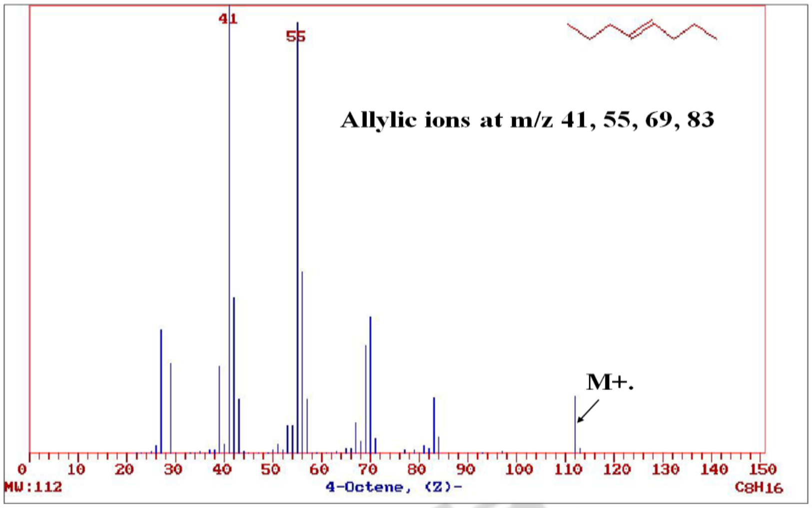
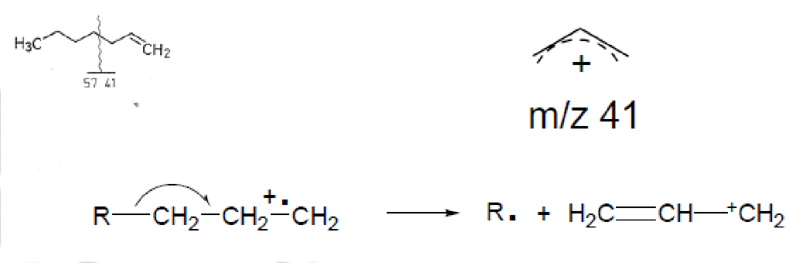


Figure 8: Mass spectrum of 4-octene

1-heptene undergoes cleavage to form stable allylic carbocation (figure given below).



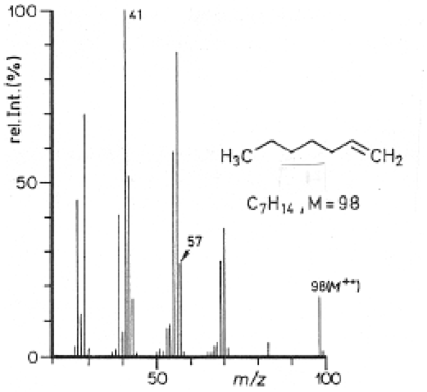


Figure 9: mass spectrum of 1-heptene

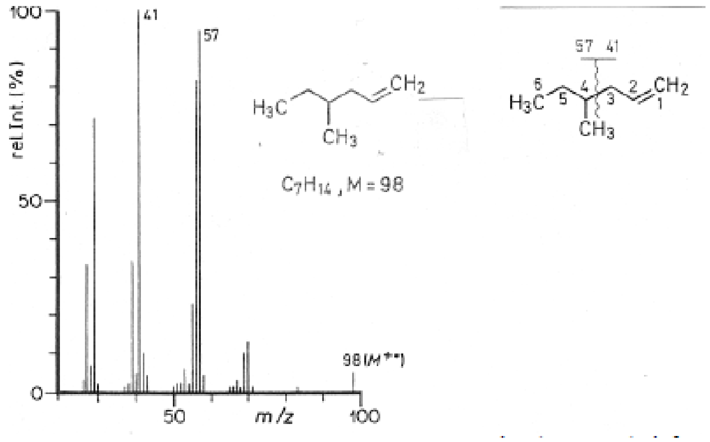


Figure 10: mass spectrum of 4-methyl-1-hexene

5. Formation of stable benzylic carbocation

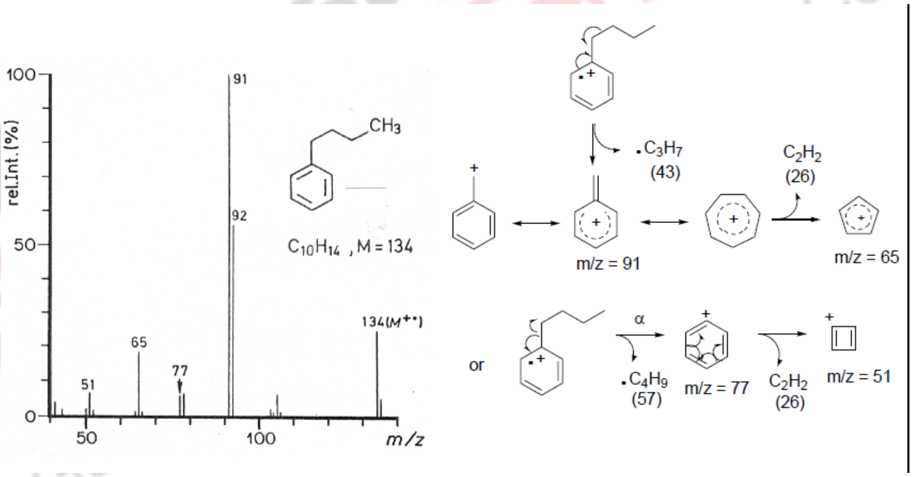
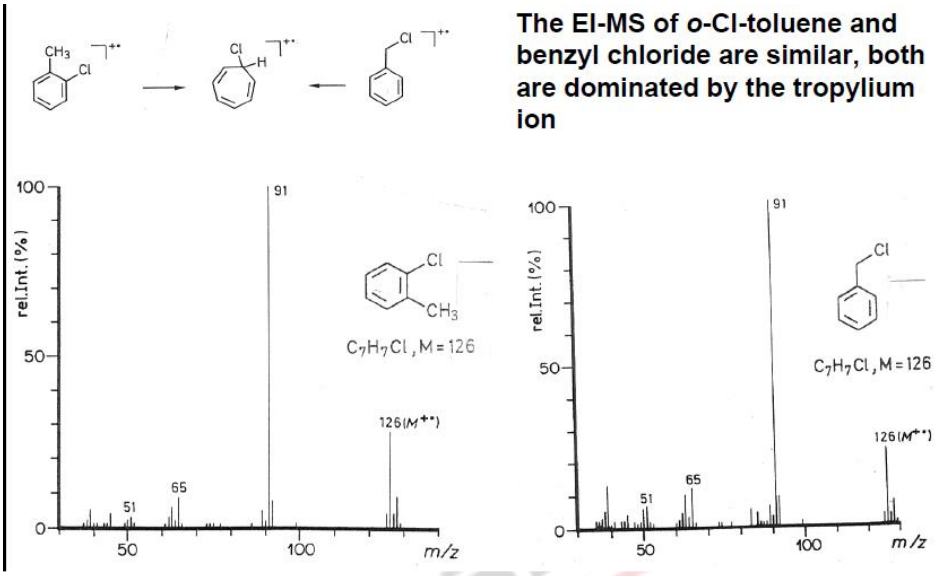


Figure 11: Mass spectrum of butyl benzene

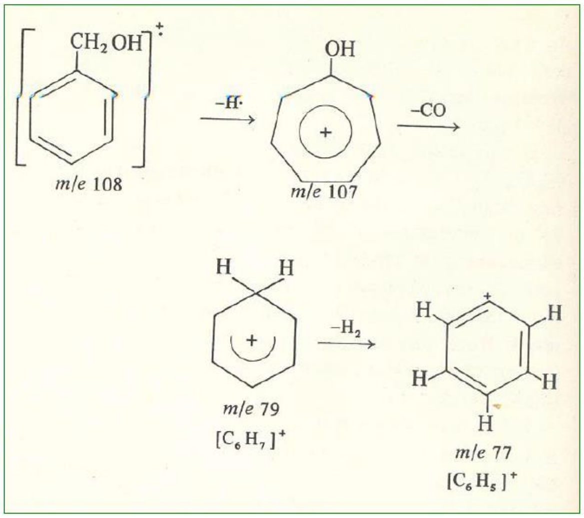
ortho-chloro-toluene and benzyl chloride undergo rearrangement to form tropylium ion and shows peak at m/z 91 (figure 12).



The EI-MS of *o*-Cl-toluene and benzyl chloride are similar, both are dominated by the tropylium ion

Figure 12: Mass spectrum of ortho-chloro-toluene and benzyl chloride

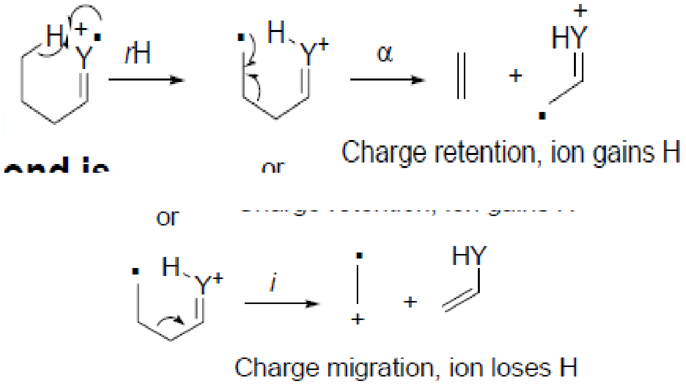
Benzyl alcohol also undergo rearrangement to fprm hydroxyl tropylium ion which is depicted as m/z 107.



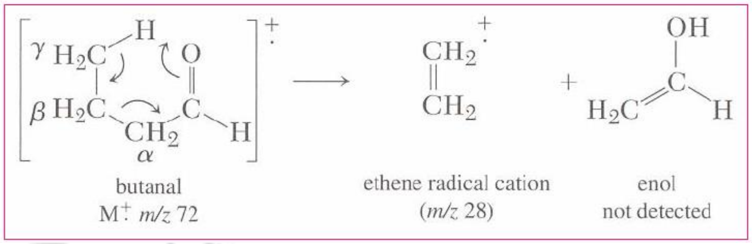
6. McLafferty rearrangement

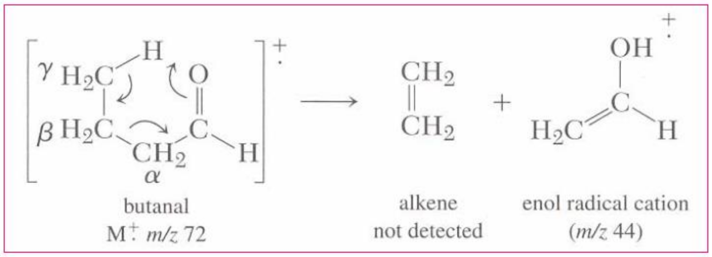
McLafferty rearrangement occurs in carbonyl compounds only if the gamma carbon contains hydrogen. The hydrogen from gamma carbon is transferred to an unsaturated receptor site.

It is accompanied by beta splitting. In the mass spectrum peaks from alkene and enol would occur.



McLafferty rearrangement of butanal produce two products ethylene radical cation (m/z 28) and enol radical cation (m/z 44) (figure 13).





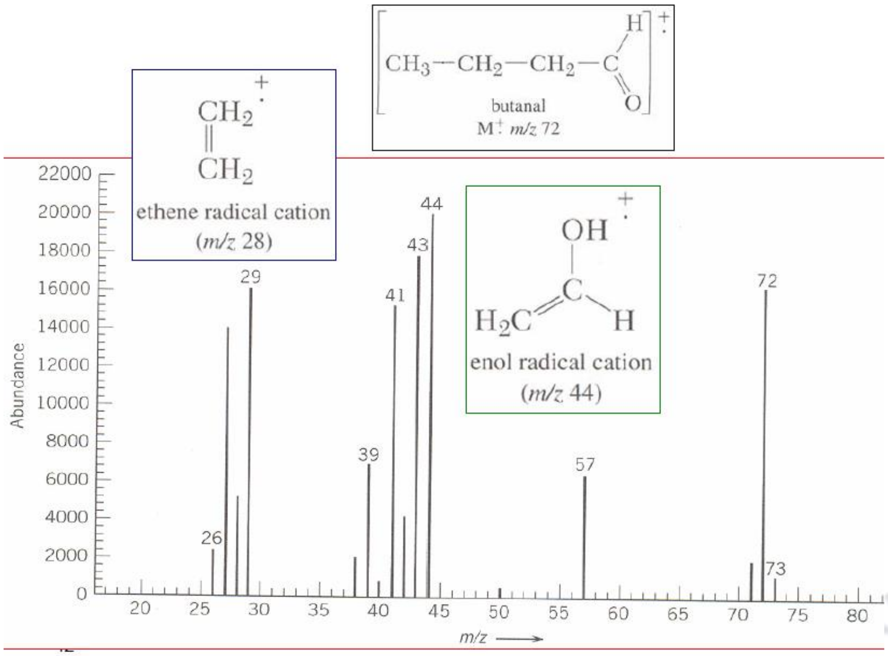
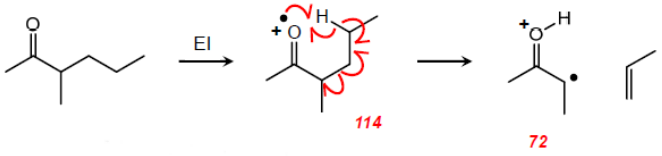


Figure 13: Mass spectrum showing Mc Lafferty rearrangement fragments in butanal

Single bond cleavage of an even mass ion will typically yield odd mass products (unless ion contains multiple nitrogens). So this fragmentation must involve two bond cleavage.

Mc Lafferty rearrangemen in 3-methyl-2-hexanone shows m/z peak at 72 (figure 14).



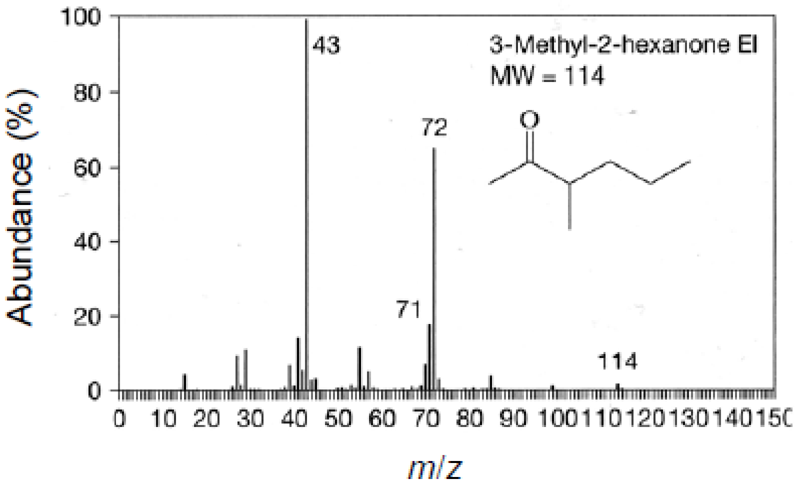


Figure 14: Mass spectrum showing Mc Lafferty rearrangement fragments in 3-methyl-2-hexanone

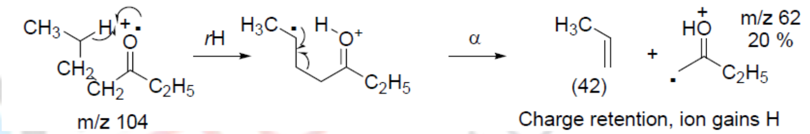


Figure 15: Mc Lafferty rearrangement in ketone

7. Summary

- Alkyl halides, ethers and alcohols show the following types of similar fragmentation behaviour.
- During fragmentation α cleavage and β cleavage, involving McLafferty rearrangement and ethene extrusion occurs in ketones.
- The fission of a bond originating at an atom which is adjacent to one assumed to bear the charge is known as α cleavage.
- In alcohols α cleavage will occur with the fission of bond next to the functional group i.e, next to the hydroxyl group.
- Fission next, but one to a heteroatom or functional group producing a radical and an ion is called beta-cleavage in mass spectrometry.
- McLafferty rearrangement occurs in carbonyl compounds only if the gamma carbon contains hydrogen. The hydrogen from gamma carbon is transferred to an unsaturated receptor site.