

## CHAPTER 6

### GC EI and CI Fragmentation and Interpretation of Spectra

#### 6.1 Introduction

Before discussing fragmentation and interpretation, it is important to understand the many ways mass spectra are utilized. For the analytical chemist, a mass spectrum is useful for two applications. The first is the relatively simple case when the analyst is looking for a particular compound in a sample and has a reference material to compare spectra. The second occurs when an analyst observes the presence of an unknown and wishes to identify it. The mass spectrum allows an experienced analyst to identify the compound or at a minimum narrow the possibilities down to a few compounds from the millions of potential chemicals. Then, a reference standard can be more easily selected from this knowledge to confirm the identity of this unknown. A similar situation exists for the synthetic chemist except their analytical tool box is much larger. Sometimes synthetic chemists are attempting to synthesize a final product that is known (for example in an industrial process line). Here, the mass spectrum of the synthesized product is compared to a reference standard. Other times, a synthetic chemist is attempting to make a new compound where a reference standard is impossible to find.

All four problems center on the same difficult task, identifying the structure of a compound under various conditions. There are three main instruments that perform this task for organic compounds, infrared spectroscopy, mass spectroscopy and nuclear magnetic resonance (NMR). It is very important that both synthetic and analytical chemists are able to choose the best tool for their particular problem. The mass spectrometer has a few advantages over the other analytical methods. Mass spectroscopy, when coupled with either gas or liquid chromatography, can analyze a complex mixture that an NMR or IR could not. A

1 MS is also the only way to determine the molecular mass of a compound. The  
2 largest advantage for analytical chemists is that mass spectroscopy can  
3 elucidate structural information from a very small amount of a compound (part  
4 per million quantities).

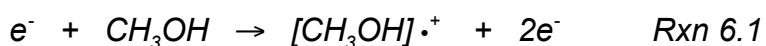
5  
6 The MS has a distinctive advantage over IR spectroscopy in that there is  
7 more structural information can be determined, though the information contained  
8 in a mass spectrum is more difficult to interpret. The MS has an advantage over  
9 NMR in that it can be performed more quickly. However, both IR spectroscopy  
10 and mass spectroscopy have a distinct disadvantage when analyzing  
11 compounds with multiple functional groups. For these types of compounds and  
12 when the analyst has mg quantities of a relatively pure compound, NMR is  
13 usually the best analytical tool.

14  
15 As a result of these advantages and disadvantages, mass spectroscopy is  
16 normally utilized to perform three tasks. The first is in analytical chemistry when  
17 there is a small concentration of analyte. The second is identifying compounds  
18 that contain few functional groups; a common procedure in industrial synthesis.  
19 The third is confirming steps in a complex synthesis of a new product to  
20 determine the molecular mass and possible some structural information. The  
21 products in the third example, however, are usually always checked by NMR.

22  
23 After choosing to use mass spectroscopy, the selection of gas  
24 chromatography or liquid chromatography is equally important. Gas  
25 chromatography is utilized for volatile and thermally stable compounds (up to 300  
26 °C). Liquid chromatography is usually utilized for all other compounds since it  
27 has poorer resolution than GC. As a result, this chapter will focus upon  
28 interpreting structural information from the types of compounds commonly  
29 analyzed with GC-MS. Once a chemist is able to determine the identity of a  
30 compound from a mass spectrum, their problem has been solved.

## 6.2 Creation of the Spectra

As sample molecules exit the GC column and enter into the mass spectrophotometer, they encounter an energy source. For the purposes of this chapter, the source is an electron impact tungsten filament at 70 eV (Section 5.2.1.2a). Energy emitted from the source removes a single electron from a sample molecule. This is the most basic reaction and is illustrated by methanol below (Figure 6.1).



After these products move through the mass spectrometer, the detector is only sensitive to the positively charged molecules and is not sensitive to any neutral or radical molecules. The detector transforms the number of molecules into an electrical signal, and a computer or integrator translates this individual signal peaks into a bar graph. The abundance is plotted as a function of a molecule's mass divided by its charge ( $m/z$ ) on a bar graph (Figure 6.1). Since almost all of the fragments detected by the GC-MS have only a single positive charge,  $m/z$  is also a measurement of the molecules' mass.

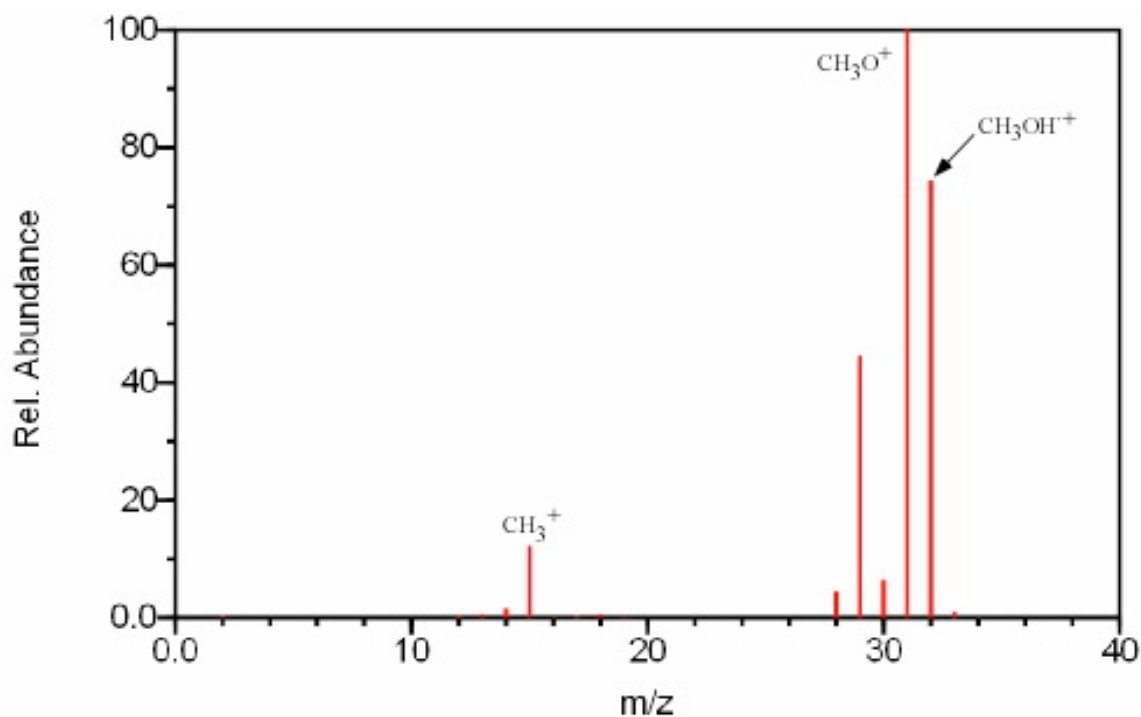
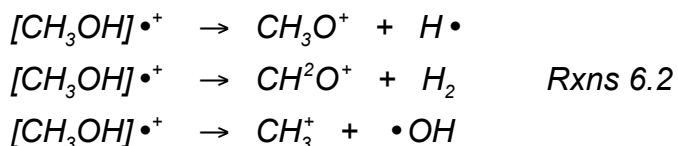


Figure 6.1 Mass Spectrum of Methanol

Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

There are more bars on the graph than just the mass of the sample molecule. These other peaks are attributed to the cleavage of bonds in the original sample molecule. These fragments allow for the original structure of the sample molecule to be determined by looking at its various components (Section 6.8). Since the energy of the source exceeds the ionization energy of the sample molecule, the excess energy that is not utilized in the removal of a single electron is distributed over various electronic, vibrational, and rotational degrees of freedom (Section 6.6). Fractionation occurs when this energy exceeds the activation energy of any bond cleavage (Section 6.6). This feature allows the instrument to distinguish between compounds with the same molecular mass and constitutional isomers. The major fragments for methanol (Figure 6.1) can be attributed to the following reactions.



The two most important peaks in any mass spectrum are the base peak and the molecular ion peak. *The base peak (also referred to as the parent peak) is the largest peak in the spectrum.* In the case of methane, the base peak is the peak at m/z 31 corresponding to the  $CH_3O^+$  fragment. Since the absolute height of any peak is dependent on the concentration of the sample, the other peaks in the spectrum are referenced as a percentage of the base peak and referred to as relative abundance. This normalization of peak heights greatly aids in identification of fragmentation pattern and therefore analyte identification.

The molecular ion peak corresponds to an analyte molecule that has not undergone fragmentation. In Figure 6.1, the molecular ion peak is caused by the  $[CH_3OH]^+$  ion and corresponds to m/z 32. The molecular ion peak is often referred to as the  $M^+$  ion. The molecular ion is used as a reference point in identifying the other fragments. For example, the peak corresponding to m/z 15 is referred to as both  $M - OH$  and  $M - 17$ .

### 6.3 Identifying the Molecular Ion Peak

The molecular ion peak is both an important reference point and is integral in identifying an unknown compound. While it may seem that the molecular ion peak should be the most abundant peak in the spectrum, this is not the case for the majority of compounds. Compounds like alcohols, nitrogen containing organics, carboxylic acids, esters, and highly branched compounds may completely lack a visible molecular ion. In these cases, it is critical that fragment peaks are not mistakenly identified as the molecular ion peak in order to avoid misidentification of an analyte. Obtaining a chemical ionization spectrum can assist in correctly identifying the molecular ion (Section 5.2.1.2b).

Even without a CI spectrum of the compound, other rules can assist in ruling out potential masses as the molecular ion. The “nitrogen rule” is one valuable tool for identifying the molecular ion. This rule indicates that if a molecular ion has an odd mass it must have an odd number of nitrogen and that a molecular ion with an even mass must lack nitrogen atoms or contain an even number of them. Since the majority of organic compounds analyzed with the GC-MS contain either zero or one nitrogen atom, the rule practically states an odd molecular ion is attributed to a single nitrogen and an even molecular ion indicates the sample lacks nitrogen (Figure 6.2). This rule only applies to compounds that contain carbon, hydrogen, nitrogen, oxygen, sulfur, halogens, and a few other less common elements. Since the majority of organic compounds that are analyzed using the GC-MS are made up of these elements, this stipulation is practically ignored.

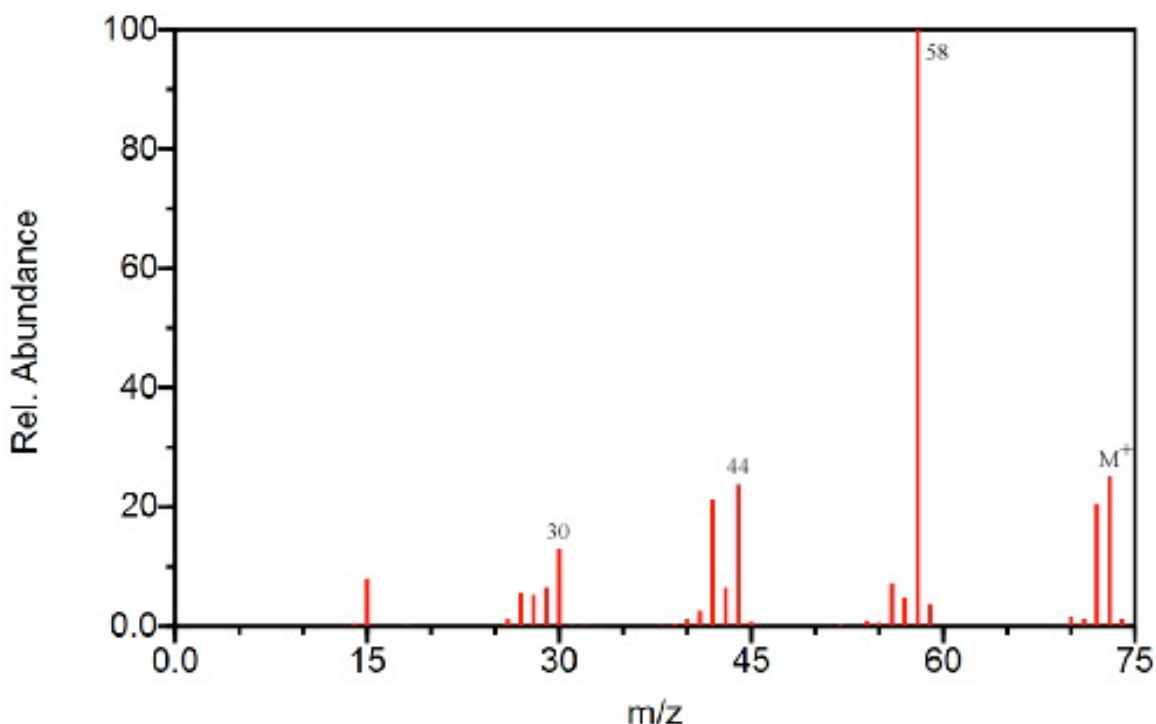


Figure 6.2 The Nitrogen Rule - The mass spectrum of N,N-dimethyl-ethanamine illustrates the presence of an odd molecular ion and even fragments.

1 Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with  
2 permission from NIST.

3  
4 This rule is a result of nitrogen's unique property. Nitrogen has an even  
5 atomic mass but bonds with three other atoms in its most stable form. Other  
6 atoms that have even molecular weights like carbon, oxygen, and sulfur bond  
7 with an even number of other atoms. Atoms that bond with an odd number of  
8 other atoms like hydrogen, chlorine, bromine, and iodine have odd molecular  
9 weights. This rule is invaluable when a chemist knows that a compound lacks  
10 nitrogen. This can occur if a sample is prepared from a synthesis whose  
11 products and solvents lack nitrogen atoms. In this case, any odd peak cannot be  
12 attributed to the molecular ion of the analyzed compound.

13  
14 Most fractionation excluding rearrangements (Section 6.6) occurs when a  
15 single bond is broken. The nitrogen rule indicates that when a molecule with an  
16 even mass produces a fragment by breaking a single bond, the fragment will  
17 have an odd mass. When the sample's mass is odd, fragmentation via a similar  
18 pathway will give an even fragment as long as the nitrogen is still contained in  
19 the observed fragment. Since this is generally the observed trend (See  
20 Stevenson's Rule Section 2.6), analyzing the major fragments can help  
21 determine if the molecular ion should be even or odd. Practically, if the major  
22 fragments are mostly odd, the molecular ion is likely even and contains no  
23 nitrogen. If the major fragments are even, the molecular ion is likely odd and  
24 contains one nitrogen atom as shown in Figure 6.3.

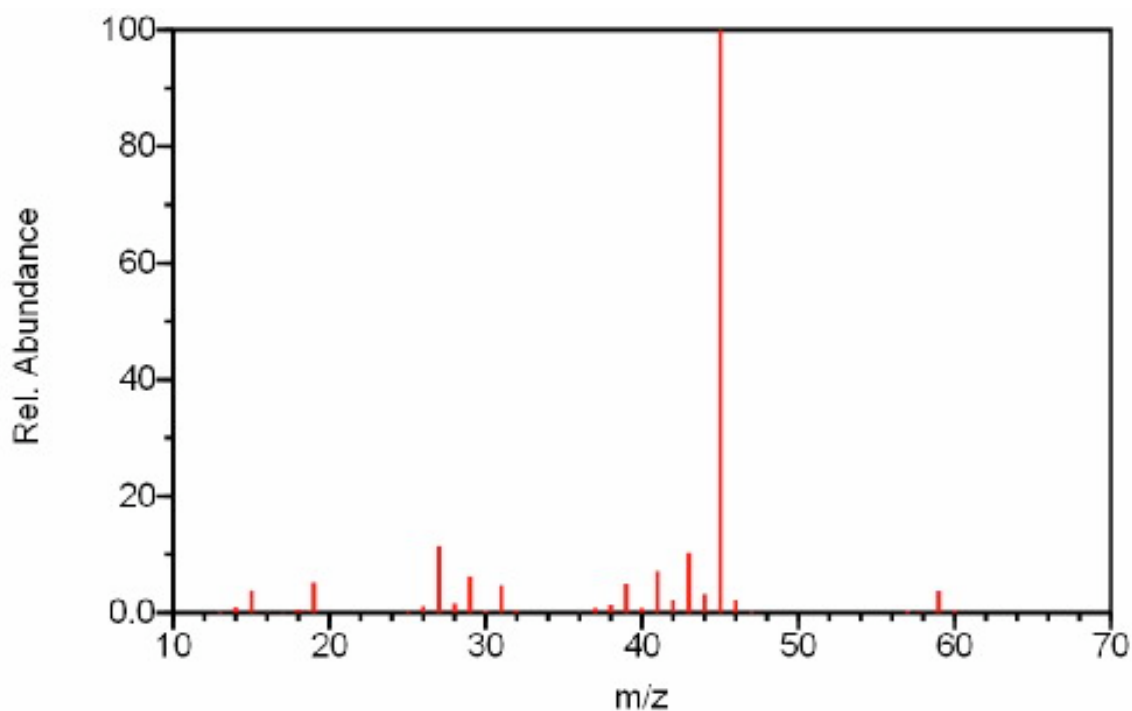


Figure 6.3. The Use of the Nitrogen Rule in Determining the Molecular Ion - Should the faint peak at  $m/z$  60 be attributed to the presence of  $C_{13}$  or is it the molecular ion? The presence of the base peak at 45 in combination with our knowledge about the nitrogen rule suggests that the peak at  $m/z$  60 is likely the molecular ion because even molecular ion usually produce odd molecular fragments by breaking single bonds. Given this spectrum is of Isopropyl alcohol, our deduction is correct although chemical ionization techniques could verify the molecular mass of the sample.

Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

Since molecular ions fragment in predictable ways, the presence of certain fragmentation peaks can suggest that a particular peak is the molecular ion. The observed fragments must be able to be attributed to logical losses. The existence of a  $M - 15$  peak from the loss of  $CH_3$ , a  $M - 18$  peak from the loss of  $H_2O$ , or a  $M - 31$  from the loss of  $OCH_3$  are a few examples of these logical fragments.



1           The opposite is true for fragments that are not logical. These peaks  
2 suggest that a particular peak is not the molecular ion. Some illogical  
3 fragmentation peaks include peaks that is 3 to 14 mass units away from the peak  
4 suggest that the identified peak is likely not the molecular ion peak. The loss of  
5 fragments of mass units 1-3 can result from the loss of up to three hydrogen  
6 atoms. From 14 to 18, multiple peaks can be explained from the loss of CH<sub>3</sub>,  
7 oxygen, a hydroxide ion, or water. The loss of fragments from the 19-25 range is  
8 also unlikely except in the case of fluorinated compounds which produce M - 19  
9 (loss of F) and M - 20 (loss of HF).

11           The molecular ion is difficult to identify with chemical ionization because  
12 there is no definitive test. While these patterns can greatly assist in identifying  
13 the molecular ion, they should not be trusted as confirmatory. Complex  
14 rearrangements can potentially result in the misidentification of the molecular ion.  
15 As a result, it is good practice to double check with a soft ionization technique  
16 such as chemical ionization when in doubt of the identity of the molecular ion.

## 18 **2.4 Use of the Molecular Ion**

20           Once the identity of the molecular ion has been determined much can be  
21 learned about the compound. One extremely valuable piece of information that  
22 can be determined from a high resolution mass spectrometer is the molecular  
23 formula of an unknown analyte. If a molecular ion was identified to be at m/z 80  
24 on an instrument with unit resolution little could be determined about the  
25 molecular formula. For example, some of the many possible molecular formulas  
26 include C<sub>4</sub>H<sub>4</sub>N<sub>2</sub> (80.0375), C<sub>5</sub>H<sub>4</sub>O (80.0262), and C<sub>6</sub>H<sub>8</sub> (80.0626). A high  
27 resolution instrument measurement of this peak at 80.0372 ± .0005 would  
28 indicate that the empirical formula is C<sub>4</sub>H<sub>4</sub>N<sub>2</sub>. Extensive tables and computer  
29 programs are used to perform this technique of a routine basis.

Once the molecular formula is known, it becomes possible to determine the degree of unsaturation. This allows the analyst to know the number of pi bonds and rings that are in their structure. The elements of unsaturation can be computed by using the following equation.

$$\text{Degree of Unsaturation} = \#C - \frac{\#H}{2} - \frac{\#X}{2} + \frac{\#N}{2} + 1$$

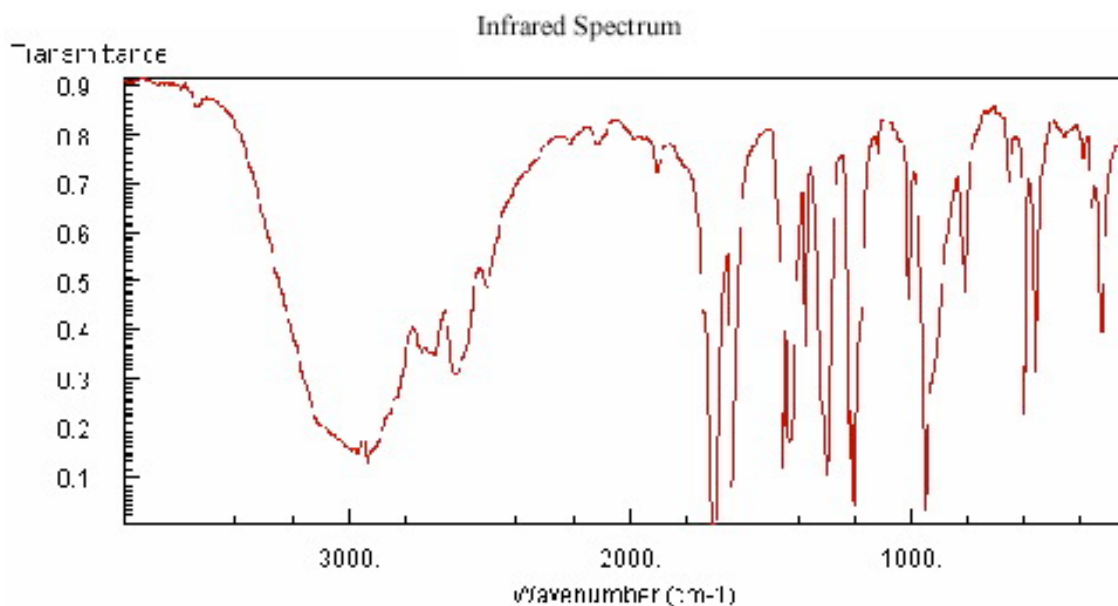
where H is the number of H atoms, X is the number of halogen atoms (F, Cl, Br, and I), and N is the number of nitrogen atoms in the chemical formula. As the equation indicates, the number of oxygen atoms does not affect the degree of unsaturation. By using this equation the molecular formula  $C_4H_4N_2$  has four degrees of unsaturation. The combination of the molecular formula with the degrees of unsaturation is important tools in identifying a particular compound.

The molecular ion along with other information from IR and NMR spectra can allow the identity of an unknown to be determined. If all three techniques can be utilized on a sample, the strengths of each allow for the easiest identification. Since IR identifies the unknown's functional groups, the mass of these groups are first subtracted from the mass of the molecular ion. This mass frequently represents the mass of the carbon and hydrogen contained in a sample. Taking this number and dividing by twelve will the number of carbon atoms and a fraction representing the number of hydrogen atoms. It is important to not blindly trust this method. If the molecular ion minus the mass of the functional groups gives 85, dividing by 12 would give a molecular formula of  $C_7H$ . Attempting to create this molecule will quickly indicate that a more logical molecular formula would be  $C_6H_{13}$ .

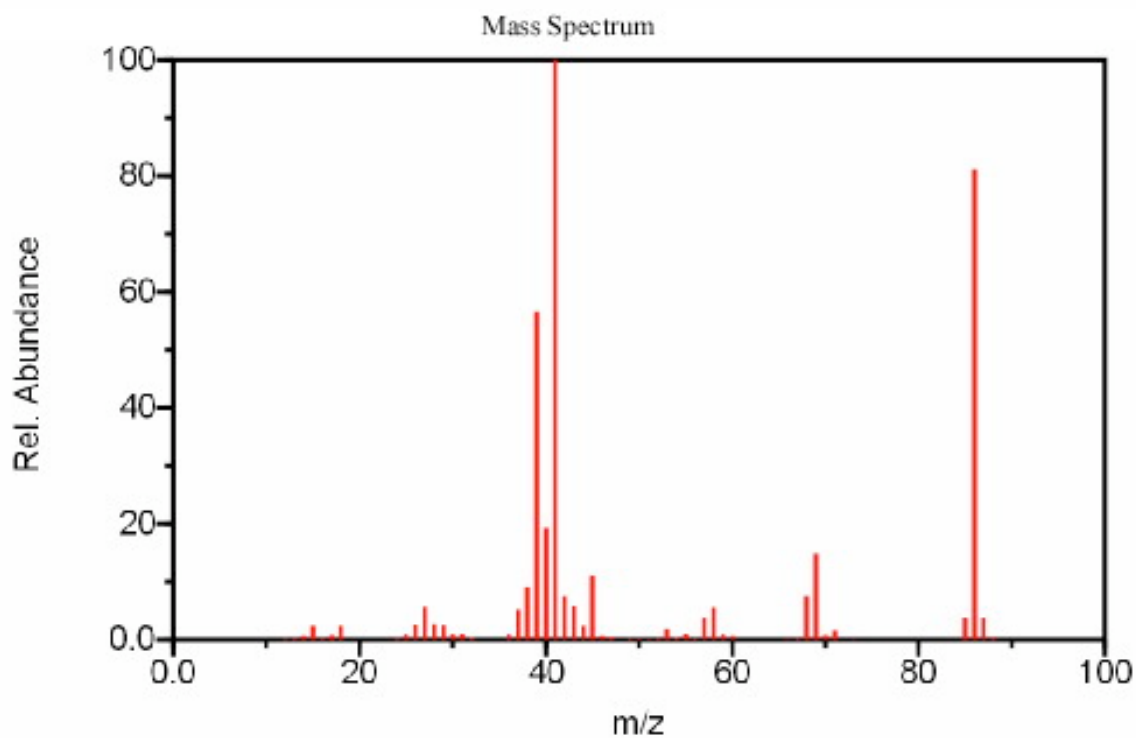
For the example unknown analyte illustrated in Figure 2.4, the IR spectrum indicates the compounds functional groups. The sharp peak observed at around  $1710\text{ cm}^{-1}$  indicates the presence of a carbonyl group. The large round

- 1 peak centered around  $3000\text{ cm}^{-1}$  suggests that the compound is a carboxylic  
2 acid. The large peak slightly above  $1600\text{ cm}^{-1}$  could indicate that the unknown  
3 contains an alkene or even possibly an imine.

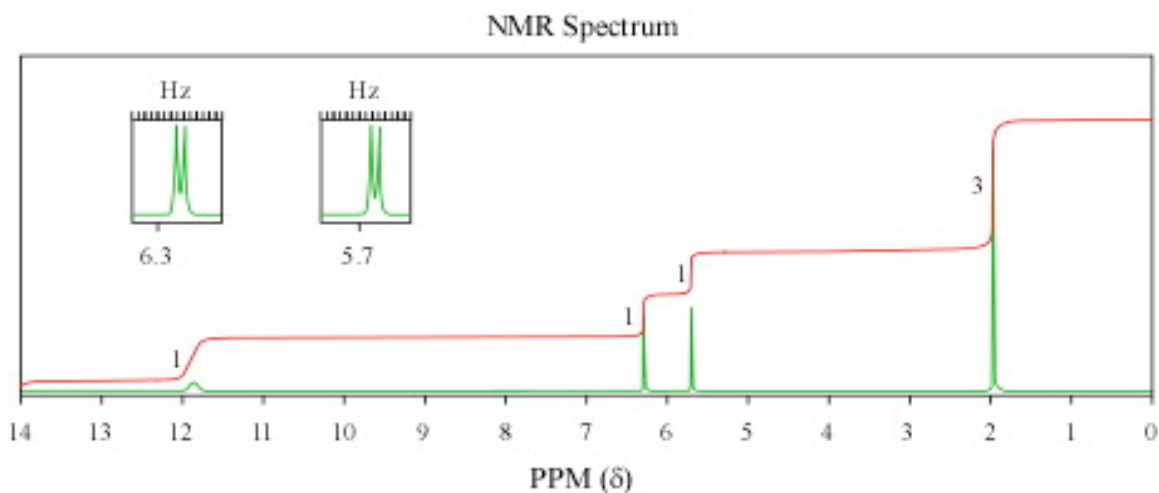
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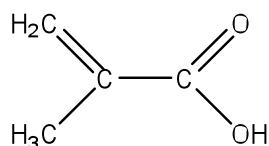
Figure 2.4 IR, Mass Spectrum, and NMR of an Unknown Analyte  
Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with  
permission from NIST.

After talking a mass spectrum of the compound, it is necessary to identify the molecular ion. We can identify the peak at 86 to be the molecular ion using the nitrogen rule (discussed above). Because its major fragments are both odd, 69 and 41, it is reasonable that its molecular ion should be even. The peaks at 85 (loss of H) and 71 (loss of  $\text{CH}_3$ ) can be explained in a logical fashion further confirming the  $m/z$  86 peak as the molecular ion.

From above, the compound's known mass is 86, thus, we can confirm that the compound is not an imine because it has an even molecular weight indicating that it does not contain an odd number of nitrogen atoms. Now it becomes possible to identify something about the carbon backbone of the atom. By subtracting the mass of the carboxylic acid functional group ( $\text{COOH}$ ) a mass of 41 is obtained. The IR spectrum indicates that the remainder of the molecule is likely only made up of carbon and hydrogen. This allows the analyst to deduce that the rest of the molecule is made up of 3 more carbon atoms and 5 hydrogen atoms. From taking these two easy measurements, one is able to determine that this compound's molecular formula is  $\text{C}_3\text{H}_5\text{COOH}$ . From this molecular formula

1 we can determine that the degree of unsaturation is two. One degree of  
2 unsaturation is attributed to the acid functional group while the other is a double  
3 bond since a three carbon ring is extremely unlikely.

4  
5 While both the IR and MS are able to determine a great deal about a  
6 compound's identity, NMR is necessary to identify this compound. The peak  
7 below 12 ppm is a result of the hydrogen on the carboxylic acid group. The  
8 doublet peaks 6.3 and 5.7 ppm are split by approximately 1.4 Hz which indicates  
9 that they are geminal protons. The fact that the peaks are doublets indicates that  
10 there are only two hydrogen atoms connected to the vinyl group. The presence  
11 of a methyl group is indicated by the peak at 2 ppm. As a result the unknown  
12 compound is methacrylic acid whose structure is shown below.



14  
15  
16 While utilizing IR and NMR, in combination with the mass spectra, made  
17 the identification of this compound relatively simple, these tools are not always  
18 available. If the analyte of interest is in a complex mixture or there is only a small  
19 concentration or quantity (parts per million), both IR and NMR are not effective  
20 tools. As a result, it is necessary to be able to identify as much information is  
21 possible from the mass spectrum alone. The rest of this chapter will be devoted  
22 to such a task by observing common fractionation trends in various types of  
23 compounds.

## 24 25 **2.5 Identification of Analytes using Isotopic Ratios**

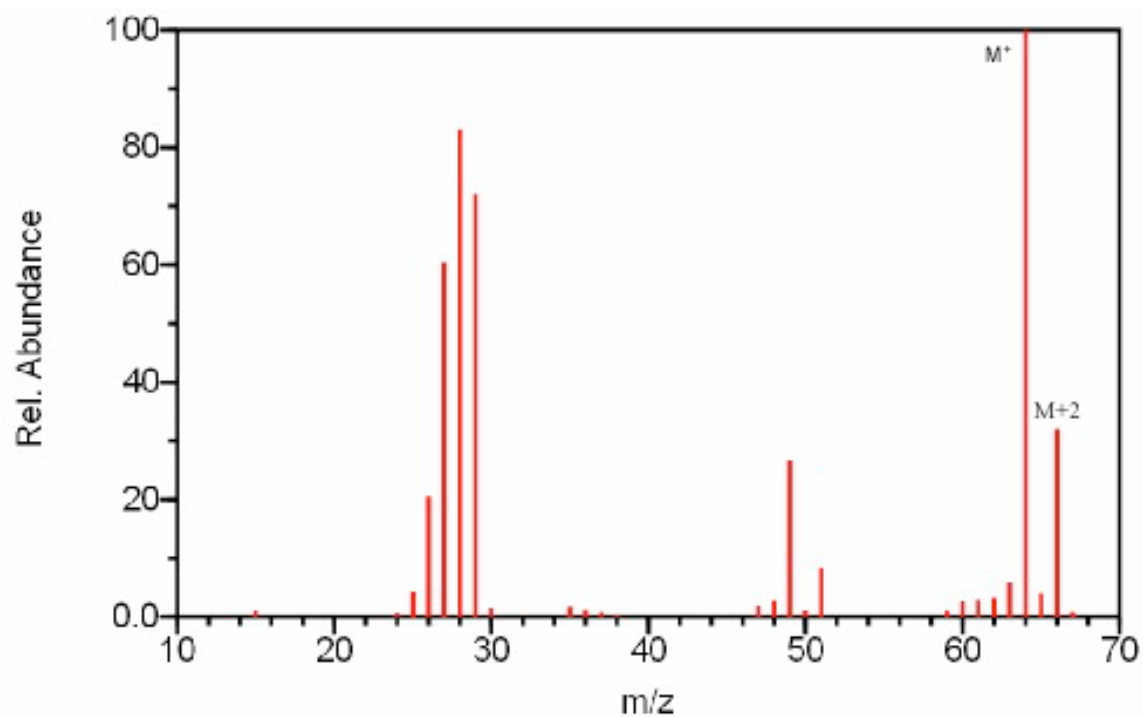
26  
27 Since the majority of elements have two or more isotopes, the ratio of  
28 these isotopes can be a powerful tool in deriving the composition of unknown  
29 samples. Prominent peaks will have a smaller peak one mass unit higher than

the prominent peak due to the presence of one  $^{13}\text{C}$  in some of the sample molecules. Background noise and a lack of resolution in the majority of mass spectrometers prevent the ratio of various isotopes from being an identification technique for all compounds.

However, some isotopes are so prominent that they can easily be observed with a quadrupole mass spectrophotometer with unit resolution. Chlorine, bromine, and sulfur can all be identified by their isotopic ratios. Their exact isotopic ratios are summarized in Table 2.1. Compounds containing chlorine have a  $M+2$  peak that is 25% of the molecular ion (Figure 2.5a). Compounds containing bromine have a  $M+2$  peak that is approximately the same height as a  $M^+$  peak (Figure 2.5b). Compounds containing sulfur have an unusually large  $M+2$  (Figure 2.5c).

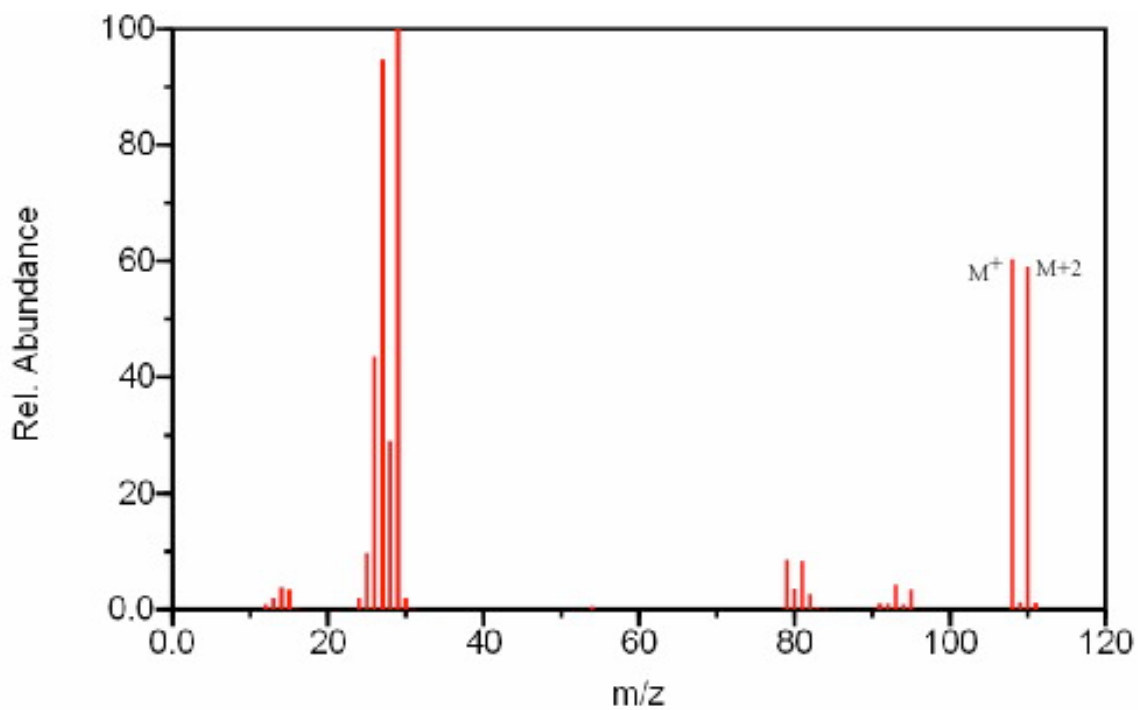
Table 2.1 Isotopic Abundances of Common Elements

| Element  | $M^+$            |        | $M + 1$         |      | $M + 2$          |        |
|----------|------------------|--------|-----------------|------|------------------|--------|
| hydrogen | $^1\text{H}$     | 100.0% |                 |      |                  |        |
| carbon   | $^{12}\text{C}$  | 98.9%  | $^{13}\text{C}$ | 1.1% |                  |        |
| nitrogen | $^{14}\text{N}$  | 99.6%  | $^{15}\text{N}$ | 0.4% |                  |        |
| oxygen   | $^{16}\text{O}$  | 99.8%  |                 |      | $^{18}\text{O}$  | 0.2%   |
| sulfur   | $^{32}\text{S}$  | 95.0%  | $^{33}\text{S}$ | 0.8% | $^{34}\text{S}$  | 4.2%   |
| chlorine | $^{35}\text{Cl}$ | 75.5%  |                 |      | $^{37}\text{Cl}$ | 24.5 % |
| bromine  | $^{79}\text{Br}$ | 50.5%  |                 |      | $^{81}\text{Br}$ | 49.5%  |
| iodine   | $^{127}\text{I}$ | 100.0% |                 |      |                  |        |
|          |                  |        |                 |      |                  |        |



- 1
- 2 Figure 2.5A of Ethyl Chloride illustrates the presence of a  $M+2$  peak that is
- 3 about 25% of the  $M^+$  peak.

4



- 5
- 6 Figure 2.5B of bromoethane has a characteristic  $M+2$  peak that has a similar
- 7 intensity as the  $M^+$  peak.

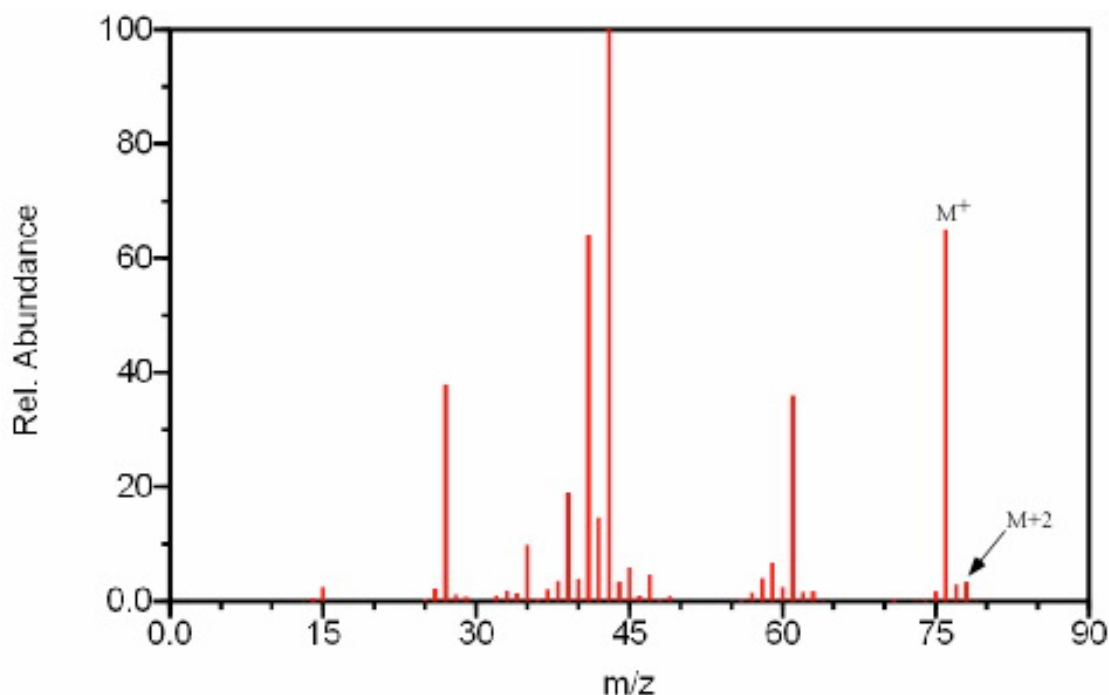


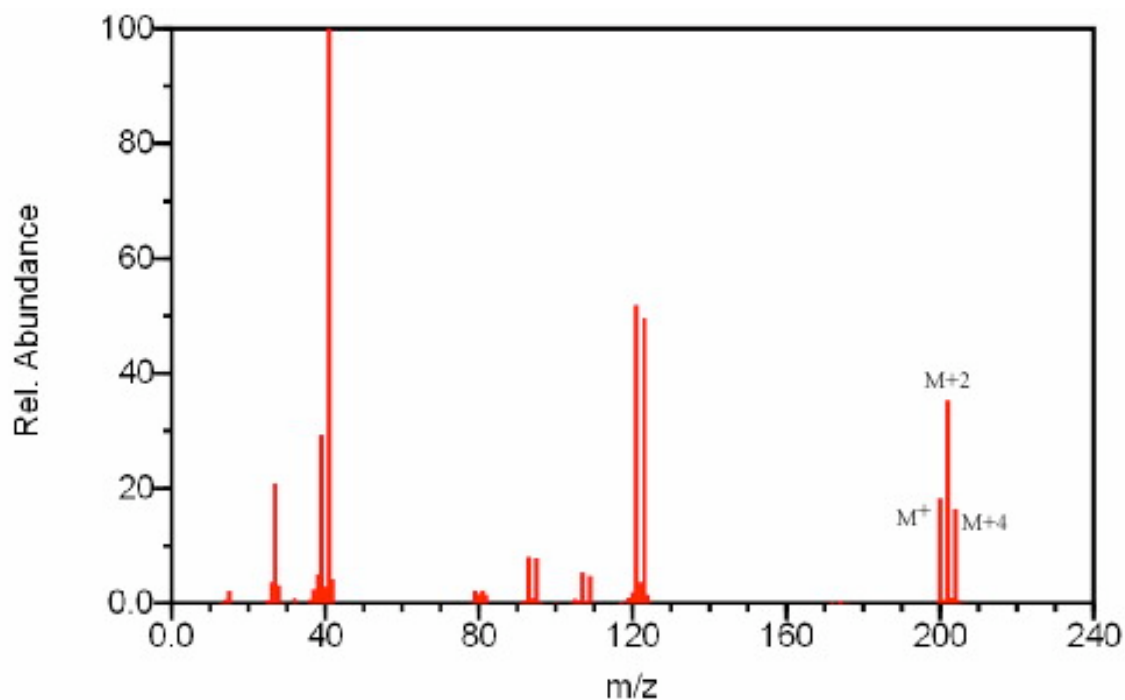
Figure 2.5C of 2-Propanethiol contains a larger than usual M+2 peak, a pattern observable in sulfur containing compounds.

#### Figure 2.5 Isotopic Identification

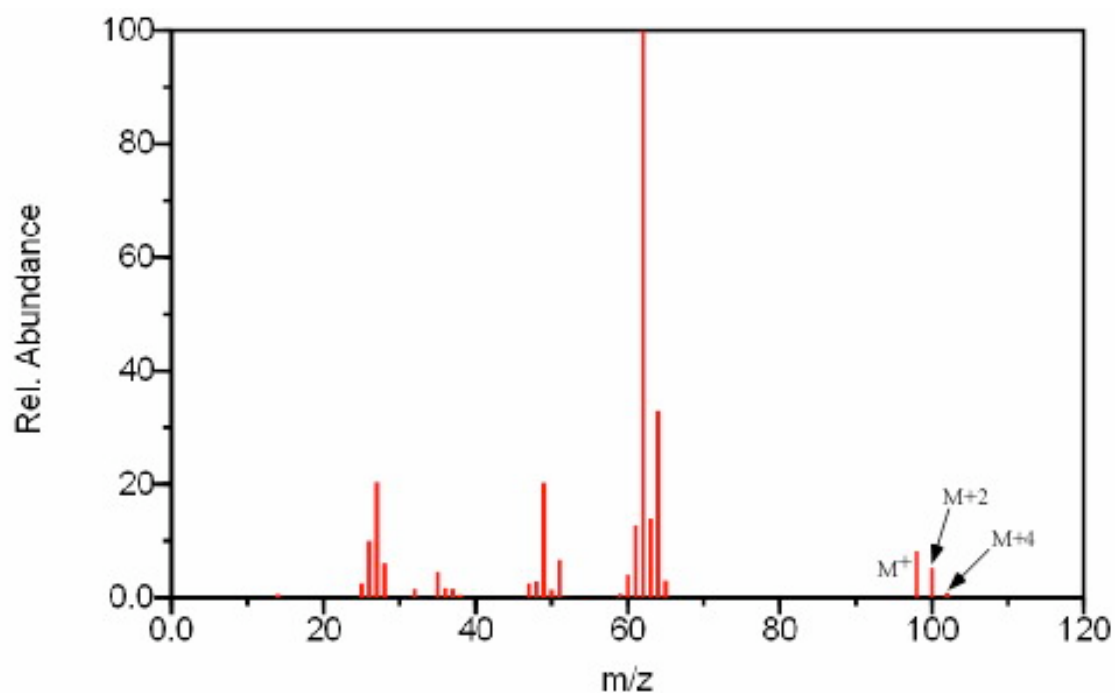
Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

Compounds can also contain any combination of multiple chlorine and bromine atoms. These samples will produce distinct peaks due to the various combinations of the isotopes. A compound containing two bromines will have a M+2 peak twice the size of the M+ peak and a M+4 peak the same size as the M+ peak (Figure 2.6a). A compound containing two chlorines will have a M+2 peak that is two thirds the size of the M<sup>+</sup> peak and a M+4 peak that is ten percent of the molecular ion (Figure 2.6b).





- 1
- 2 Figure 2.6A shows the mass spectrum the dibrominated compound 1,3-
- 3 dibromopropane.



- 4
- 5 Figure 2.6B shows the mass spectrum of the dichlorinated compound 1,2-
- 6 dichloroethane.

7

Figure 2.6 Polybrominated and Polychlorinated Compounds  
Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with  
permission from NIST.

Iodine is more difficult to detect because it is one of the few compounds  
that is monoisotopic. Despite this fact, the large atomic mass of iodine allows for  
its identification. The combination of a peak at  $m/z$  127 ( $I^+$ ) and a large gap of  
127 mass units between fragments containing iodine and fragments lacking in  
iodine allows for the compounds identification (Figure 2.7).

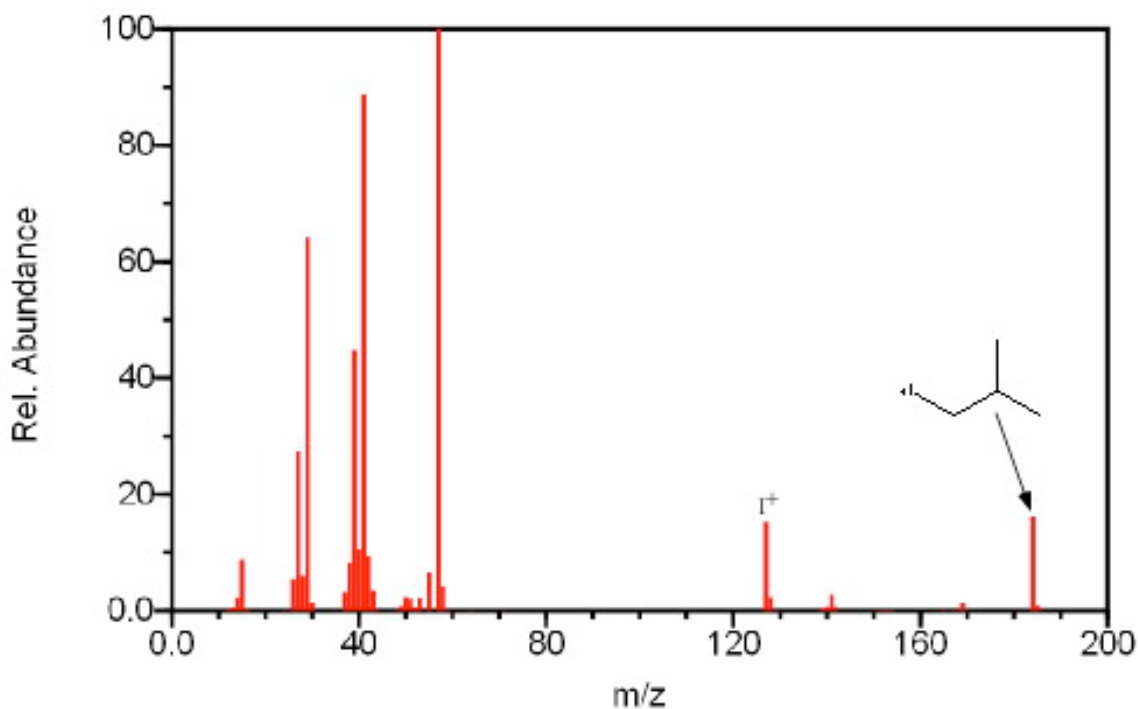
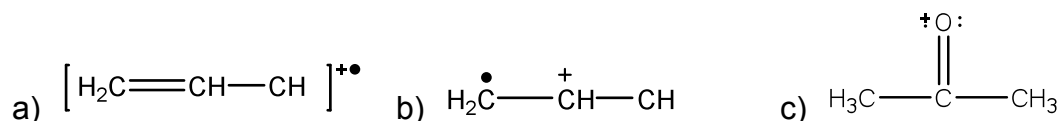


Figure 2.7 Mass Spectrum Containing Iodine  
Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with  
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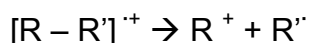
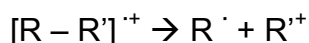
## 2.6 Fragmentation

While the molecular ion is one of the most important peaks in the spectra, it is also important to gain information from the peaks that are a result of fragmentation. The goal of interpreting mass spectra is identifying the structure of the molecular ion by examining pieces (fragments) of the original molecule. The frequency and size of the fragments is dependent on the structure and bond energy of the sample molecule. This property has resulted in the creation of unique and reproducible spectrum for a wide variety of compounds.

Before fragmentation can be discussed, it is necessary to develop a new notation because the cation fragments that will be encountered are not present in other branches of chemistry due to their high reactivity. The presence of the vacuum in the instrument prevents collisions with other molecules allowing these reactive cations to exist. The academic convention for notation is to either represent the charge as a delocalized one (Example A below) or localized it on either a  $\pi$  bond (Example B) or on a heteroatom (Example C).



The process that creates these observed fragments is the result with their interaction with the energy released from the source. This energy both removes a single electron, while the excess energy is distributed over various degrees of freedom. This distribution converts electronic energy into electronic, rotational, and vibration energy. The molecular ion is created when the sample molecule returns to its ground state via a relaxation. Other times this energy exceeds the activation energy of fragmentation and this energy is released via the breaking of bonds.



The fragmentation of a single bond can produce two peaks, one from  $R^+$  and the other from  $R'^+$ , since the instrument can only detect the positive ion. According to Stevenson's rule, if two fragments are in competition to produce a cation, the fragment with the lowest ionization energy will be formed more frequently (Figure 2.8).

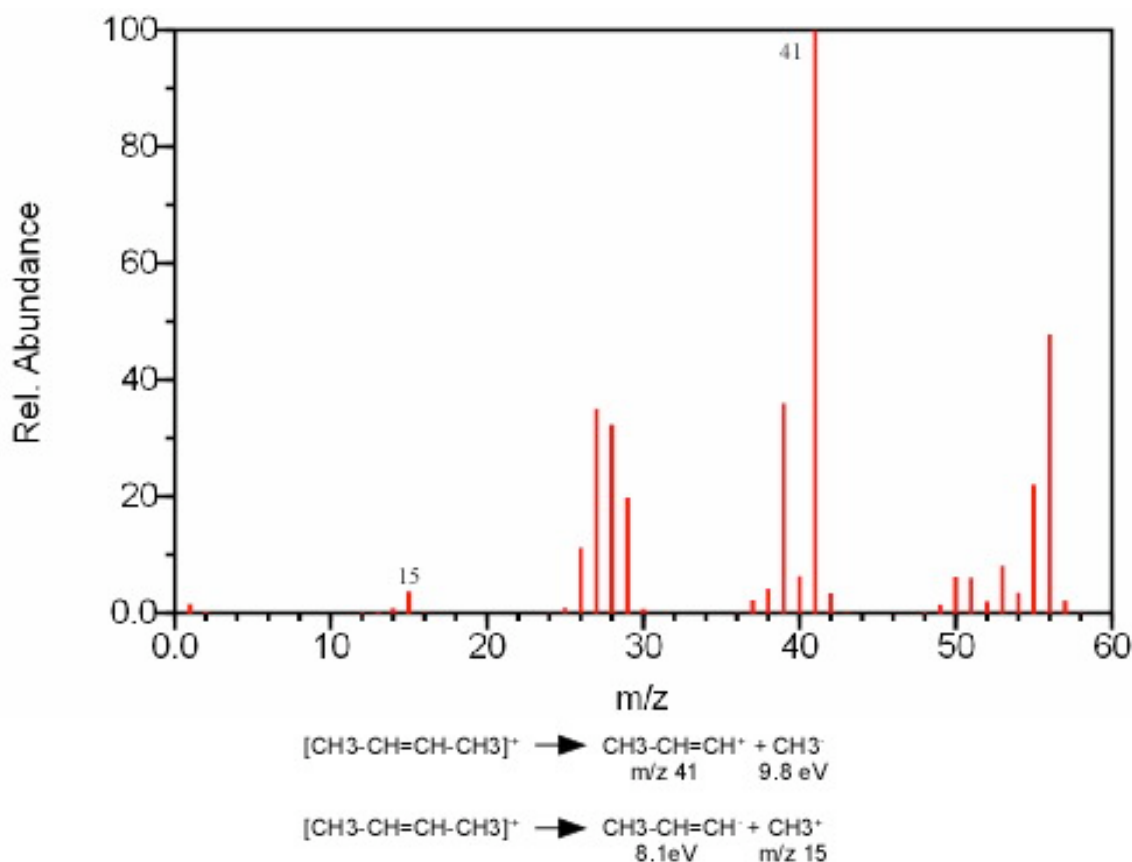


Figure 2.8 An Illustration of Stevenson's Rule

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The fragmentation of a bond can proceed through two pathways, either homolytic or heterolytic cleavage. In the heterolytic cleavage, a pair of electrons move towards the charged site as illustrated by the double headed arrow producing a cation and a radical.

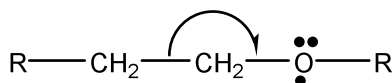


Where Y is a heteroatom

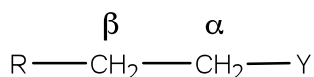
The fragmentation produced by a homolytic cleavage results from the movement of single electrons.



For simplicity, usually only one set of arrows is drawn to illustrate the movement of electrons.



These fragmentation patterns are usually the result of a functional group contained in the compound. As a result, the bonds that typically break are either located one, or two carbon atoms away from the functional group. These carbon atoms are referred to as the  $\alpha$  and  $\beta$  atoms.

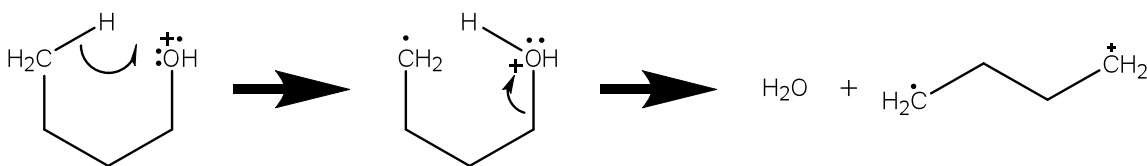


The bond between the functional group Y and the  $\alpha$  carbon is called the  $\alpha$  bond and the bond between the  $\alpha$  and  $\beta$  carbons is the  $\beta$  bond.

## 2.7 Rearrangements

Some fragments are the result of the cleavage of multiple bonds. The removal of water from an alcohol is only one example. The nitrogen rule (Figure 2.3) is helpful in identifying peaks that are produced via a rearrangement. If a molecular ion has an even molecular weight then generally peaks of even molecular weight were created from a rearrangement. If a molecule has an odd molecular weight, then its rearrangements peaks will also be odd.

One rearrangement is the loss of water from a primary alcohol. The mechanism is illustrated with butanol.



These rearrangements are favored because the low energy transitions help stabilize the products. Other rearrangements such as the McLafferty rearrangement will be explored in greater detail in the following sections.

## 2.8 Identification of Compounds

The ability to identify unknown samples is one of the most powerful uses of a mass spectrometer. This, however, requires an understanding of fractionation patterns for commonly encountered compounds. The following trends are only applicable to electron impact with a source at 70 eV. These trends are not comprehensive but are rather a selection of common fragments that are most useful in properly identifying common types of organic chemicals.

The actual likelihood of fragmentation is related to the activation energy of the reaction, the ability for rearrangements to occur, and the stability of the products. Trends that were observed in organic chemistry are helpful in predicting fragmentation patterns. Thinking about the stability of the products as

1 more or less stable cations and radicals is not entirely theoretically accurate but  
2 is usually a good, practical way to predict the spectrum of a molecule.

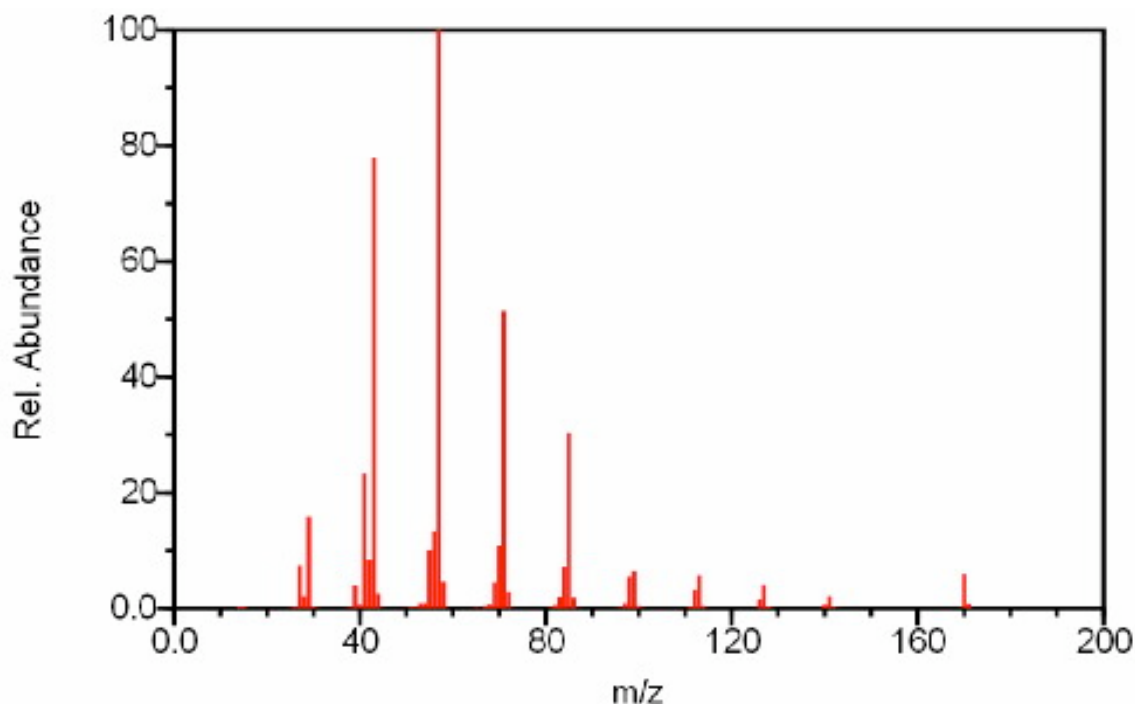
## 3 4 **2.9 Fragmentation of Hydrocarbons**

5  
6 There are two types of hydrocarbons that are analyzed with the GC-MS.  
7 One is long chain hydrocarbons and the other is the hydrocarbon portion of  
8 molecules containing other functional groups. Identifying the structure of these  
9 hydrocarbons can be difficult since rearrangements that are not easily explained  
10 are frequently observed. It is especially important to utilize reference compounds  
11 and GC retention times whenever possible to confirm the identity of the  
12 compound.

### 13 14 **2.9.1 Fragmentation of Straight Chain Alkanes**

15  
16 Straight chain alkanes always produce a molecular ion even in long chain  
17 compounds where the molecular ion is usually faint. The base peak in the  
18 spectra is usually the peak at  $m/z$  57 corresponding to the  $C_4H_9$  carbocation  
19 surrounded by other smaller peaks due to the rearrangement of hydrogen atoms.  
20 These groups are separated by 14 mass units resulting from the loss of another  
21  $CH_2$  group. The largest peak in each cluster is caused by the loss of  $(CH_2)_nCH_3$   
22 resulting in a fragment of molecular formula  $C_mH_{2m+1}$ . The subsequent fragments  
23 after the  $C_4$  peak decrease in an exponential fashion to a minimum at  $M-C_2H_5$ .  
24 The  $M - CH_3$  peak is weak in smaller compounds and absent in long chain  
25 compounds due to the relative instability of the methyl radical. The molecular ion  
26 is the unique identifiable peak in straight chain alkanes longer than eight carbon  
27 atoms.

1



2

3 Figure 2.9 Fragmentation of a straight Chain Alkane

4 Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with  
5 permission from NIST.

6

7 The example illustrated in Figure 2.9 illustrates these common trends  
8 discussed above. The prominent peaks at  $C_mH_{2m+1}$  combined with the decaying  
9 intensity of these peaks indicates this compound is an alkane. The base peak at  
10 m/z 57 caused by  $C_4H_9$  is further confirmation that there is a lack of other  
11 functional groups causing other prominent fragments. The molecular ion at m/z  
12 170 indicates that this compound is dodecane.

13

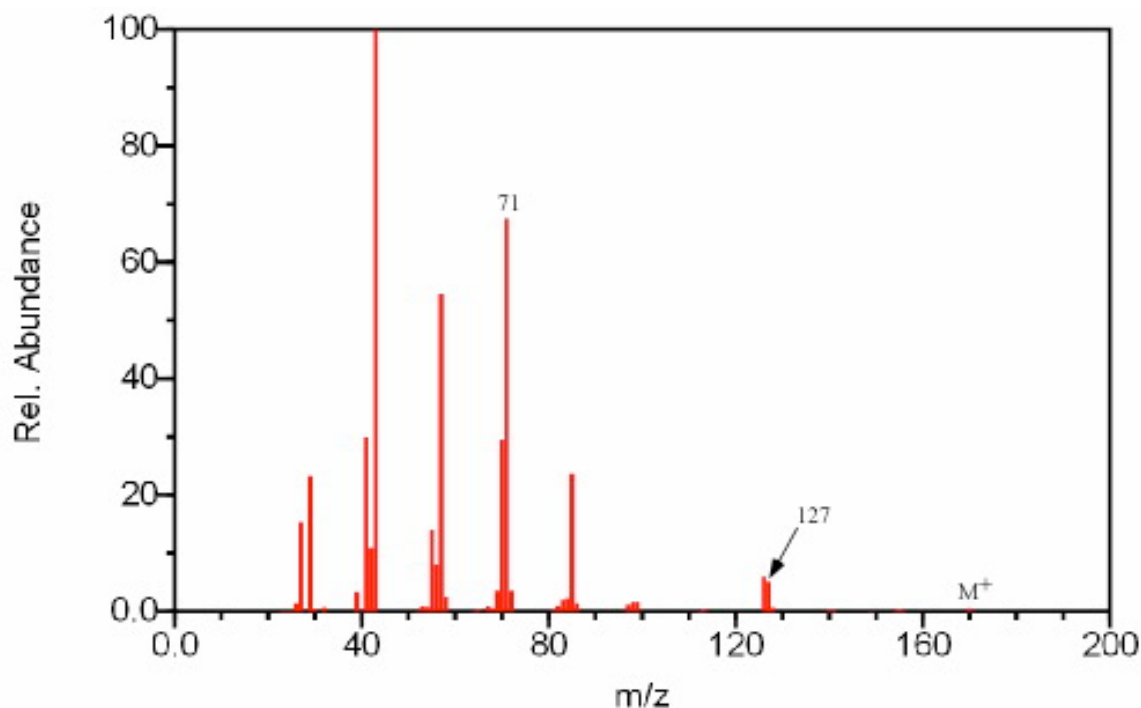
14 **2.9.2 Fragmentation of Branched Alkanes**

15

16 Branched alkanes have a smaller molecular ion that at times may be  
17 absent in highly branched compounds. In larger compounds branched alkanes  
18 contain peaks at  $C_mH_{2m+1}$ , similar to straight chain alkanes. They are  
19 distinguished by the lack of the smooth exponential decay beginning at the  $C_3$  or



1 C<sub>4</sub> carbon (Figure 2.9). This is caused by the increased frequency of  
2 fractionation at the branch since it results in a secondary rather than a primary  
3 carbocation and is hence favored. The loss of the largest alkyl fragment at the  
4 branching cite is favored because it helps to stabilize the radical.



5  
6 This mass spectrum of a C<sub>12</sub> alkane (determined from the molecular ion by CI at  
7 m/z 170) lacks the exponential decay seen in Figure 2.9 indicating the chain is  
8 branched. The intensity of the peak at m/z 71 indicates a favored C<sub>5</sub> fragment  
9 and the fragment at m/z 127 indicates a favored C<sub>9</sub> fragment suggesting that a  
10 methyl group on fourth carbon.

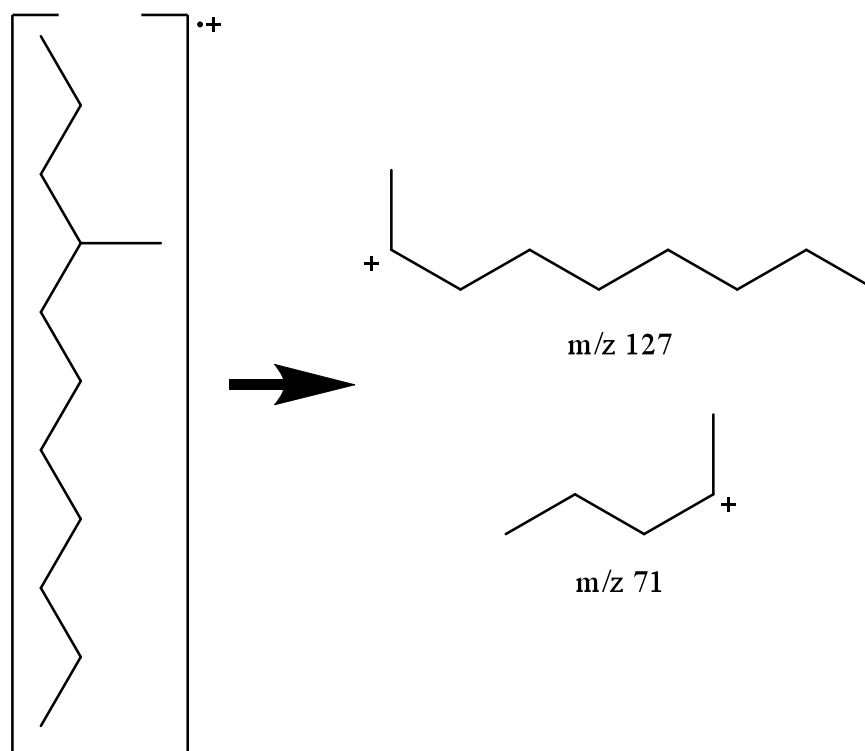


Figure 2.10 Fragmentation of a Branched Alkane

Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

The fragmentation at the branching point is often accompanied by hydrogen rearrangement causing the  $C_nH_{2n}$  peak to be more prominent and sometimes larger than  $C_nH_{2n+1}$  peak.

Identifying branched alkanes in organic compounds that contain another functional group is also an important task. The alkane portion of these molecules is usually smaller and is more governed by the stability of the produced radical and cation. Since an ethyl radical is more unstable than a methyl radical, the methyl radical will occur less frequently. Similarly, tertiary carbocations are more stable than secondary, which are more stable than primary. As the alkane portion of any molecule becomes larger, the presence of the  $C_nH_{2n+1}$  peaks become more prominent.

### 2.9.3 Fragmentation of Cyclic Alkanes

The ring structure of cyclic alkanes increases the intensity of the molecular ion. Its stability also increases the likelihood that side chains will fragment at the  $\alpha$  bond to the ring. The fragmentation of the cyclic structure is usually most often caused by the loss of more than two carbon atoms. The loss of a methyl radical occurs less frequently because of the instability of the methyl radical in comparison to the neutral ethylene molecule at M-28 or an ethyl radical at M-29.

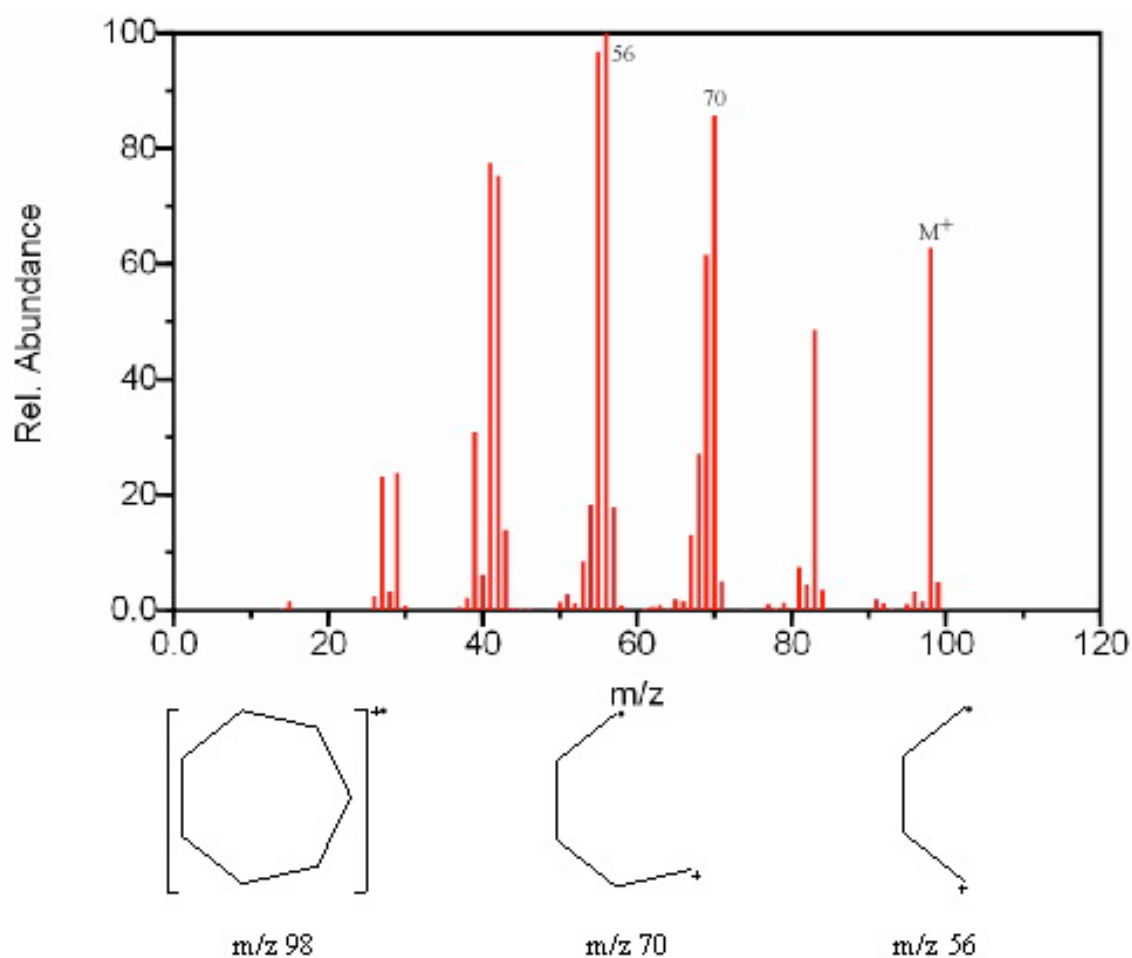


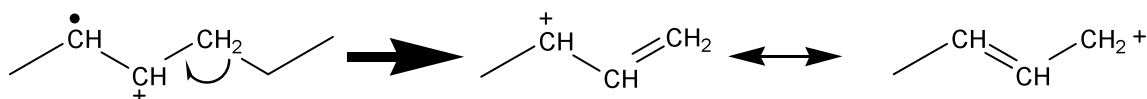
Figure 2.11 Fragmentation of a Cyclic Alkane

Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

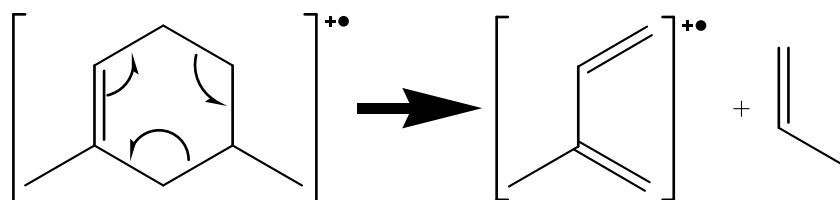
#### 2.9.4 Fragmentation of Alkenes

The molecular ion of alkenes, is usually distinct especially in compounds containing multiple double bonds. Alkene fragments, like alkane fragments are situated in clusters 14 units apart. In alkenes, the  $C_nH_{2n-1}$  and  $C_nH_{2n}$  peaks are more intense than the  $C_nH_{2n+1}$  peak of alkanes.

The presence of double bonds also allows for the production of resonance-stabilized cations. Allylic cleavage results in an allylic cation.

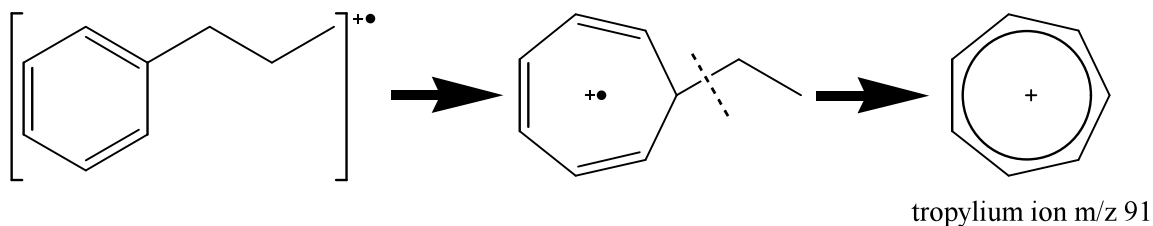


Determining the position of the double bonds in the sample molecule is especially difficult and usually requires reference spectra because of double bonds migration. Cyclic alkenes also undergo a retro-Diels-Alder fragmentation by the following mechanism.

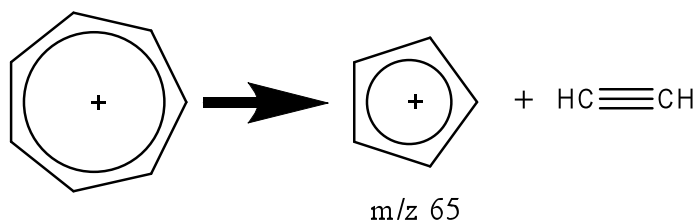


#### 2.9.5 Fragmentation of Aromatics

The presence of an aromatic ring in a compound results in a prominent molecular ion. A common peak at  $M - 1$  results from the cleavage of a hydrogen molecule from the benzene ring. Alkyl substituted benzene rings result in a prominent peak at  $m/z$  91 (Figure 2.12). In most cases, the peak at  $m/z$  91 is the result of a tropylium ion caused by the following rearrangement.



The peak observed in most aromatic compounds at m/z 65 results from the elimination of an acetylene molecule from the tropylium ion.



Benzene rings with highly branched substituted groups produce fragments larger than m/z 91 by intervals of 14 units. The largest of these peaks will result in a highly substituted cations and a large radical, like a simpler branched alkanes. The fragment at m/z 105 in Figure 2.12 is relatively small since it produces a primary carbocation and an unstable methyl radical. Substituted benzene rings also first undergo  $\alpha$  cleavage followed by hydrogen rearrangement producing a grouping of peaks at m/z 77 from  $\text{C}_6\text{H}_5^+$ , m/z 78 from  $\text{C}_6\text{H}_6^+$ , and m/z 79 from  $\text{C}_6\text{H}_7^+$ .

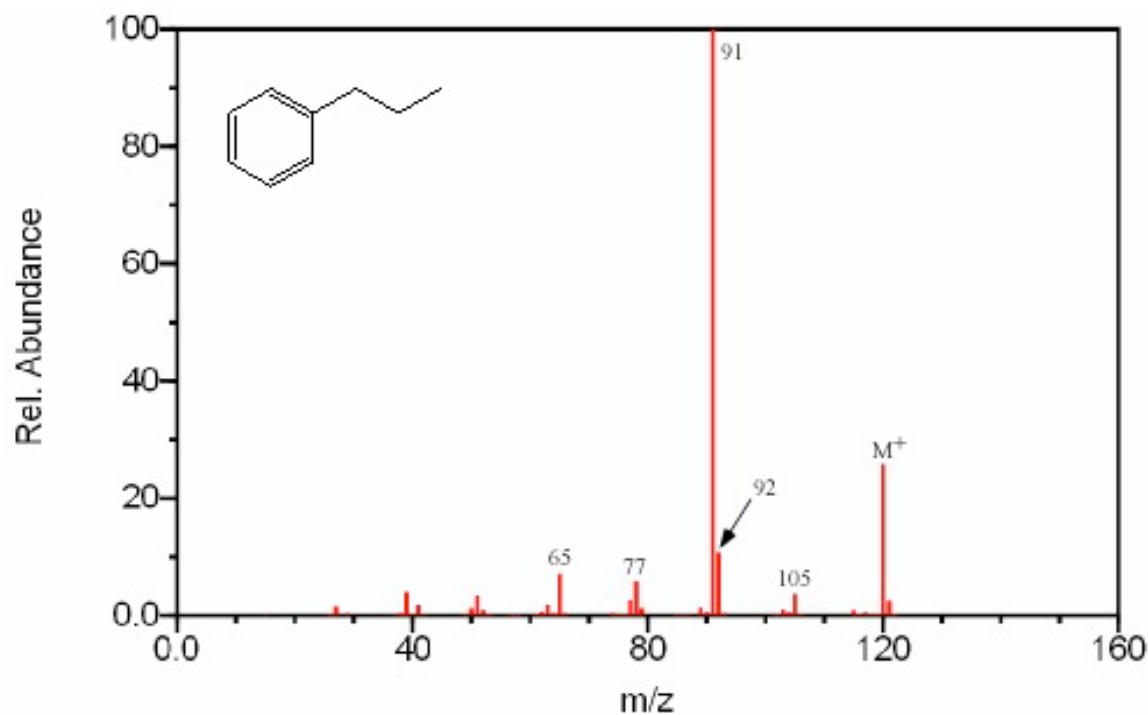
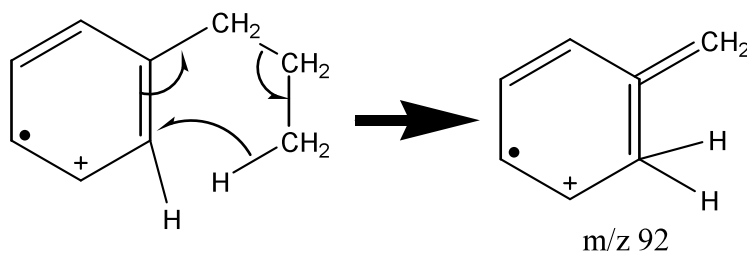


Figure 2.12 Fragmentation of an Aromatic  
Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with  
permission from NIST.

Side chains with a more than two carbon atoms create a peak at  $m/z$  92 (Figure 2.12). Unbranched groups result in a more prevalent peak than do branched groups.

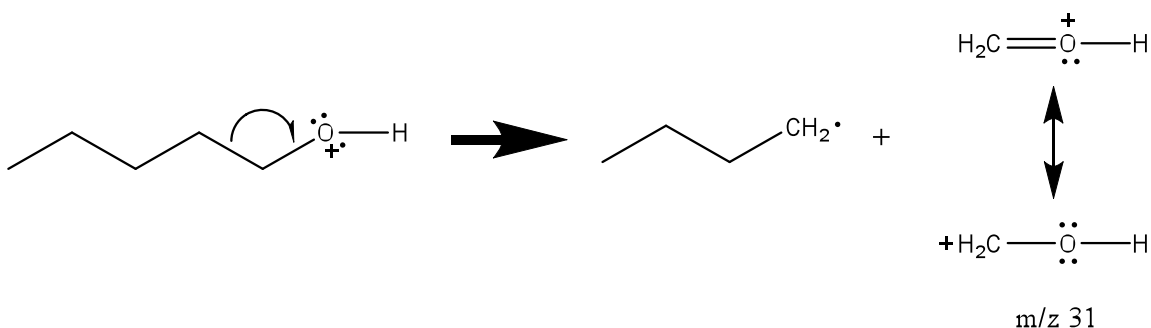


## 2.10 Fragmentation of Alcohols

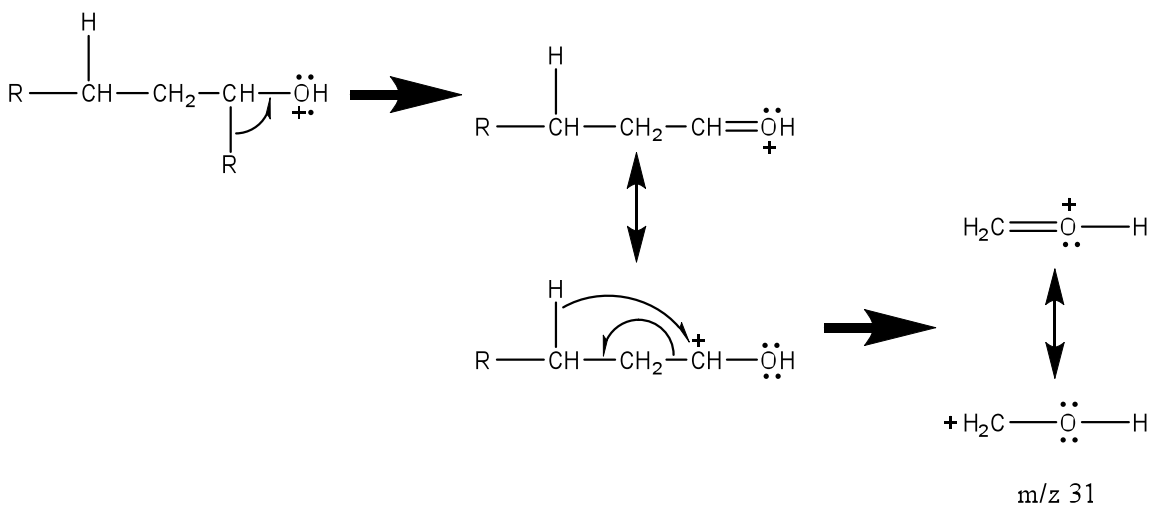
The molecular ion of alcohols is usually small and sometimes undetectable especially in tertiary alcohols. The identification of the molecular

ion is complicated by the prevalence of a M-1 peak caused by the loss of a single hydrogen from the  $\alpha$  carbon in primary and secondary alcohols.

Alcohols also frequently cleave to give resonance stabilized cations due to the breaking of the  $\beta$  bond. As a result of this cleavage, primary alcohols show a prominent peak at m/z 31 (Figure 2.13).

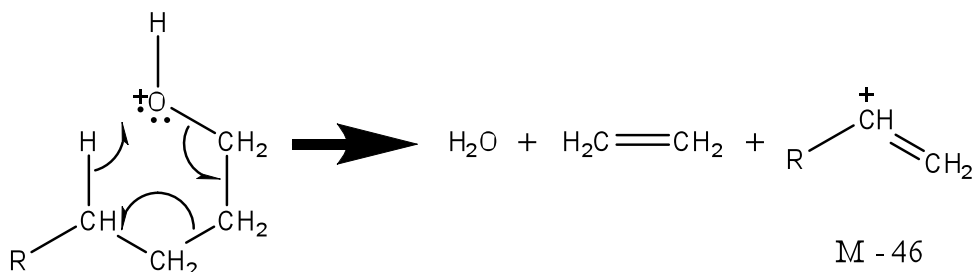


The presence of a m/z 31 peak is not confirmation of a primary alcohol. It is necessary for the peak to be relatively large in comparison to other peaks in the spectrum. This is because secondary alcohols and sometimes even tertiary alcohols can undergo a rearrangement resulting in a peak at m/z 31.



H

Alcohols also frequently undergo the rearrangement described in Section 2.7 resulting in a M-18 peak from the loss of water. This peak is most easily visible in primary alcohols but can be found in secondary and tertiary alcohols as well. Primary alcohols also can lose both water and an alkene.



Primary alcohols also produce a M-2 peak caused by  $\text{R}-\text{CH}=\text{O}^+$  and M-3 attributed to  $\text{R}-\text{C}\equiv\text{O}^+$ . Alcohols with carbon chains containing methyl groups frequently lose both the methyl group and water at M-33.

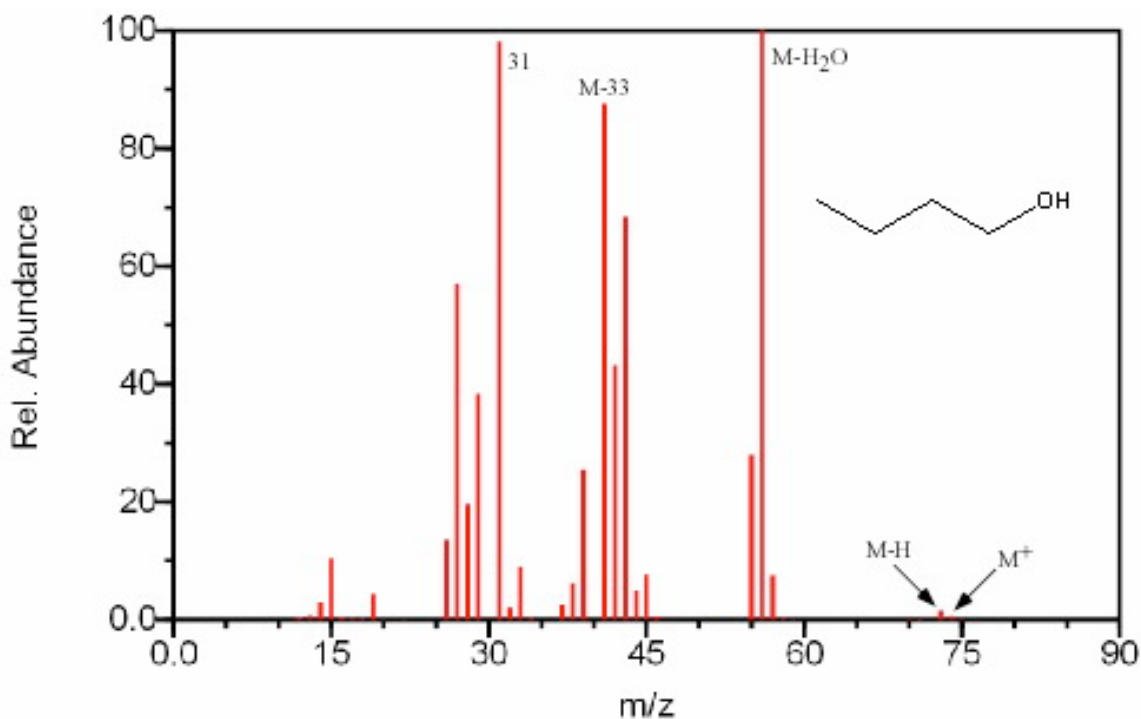
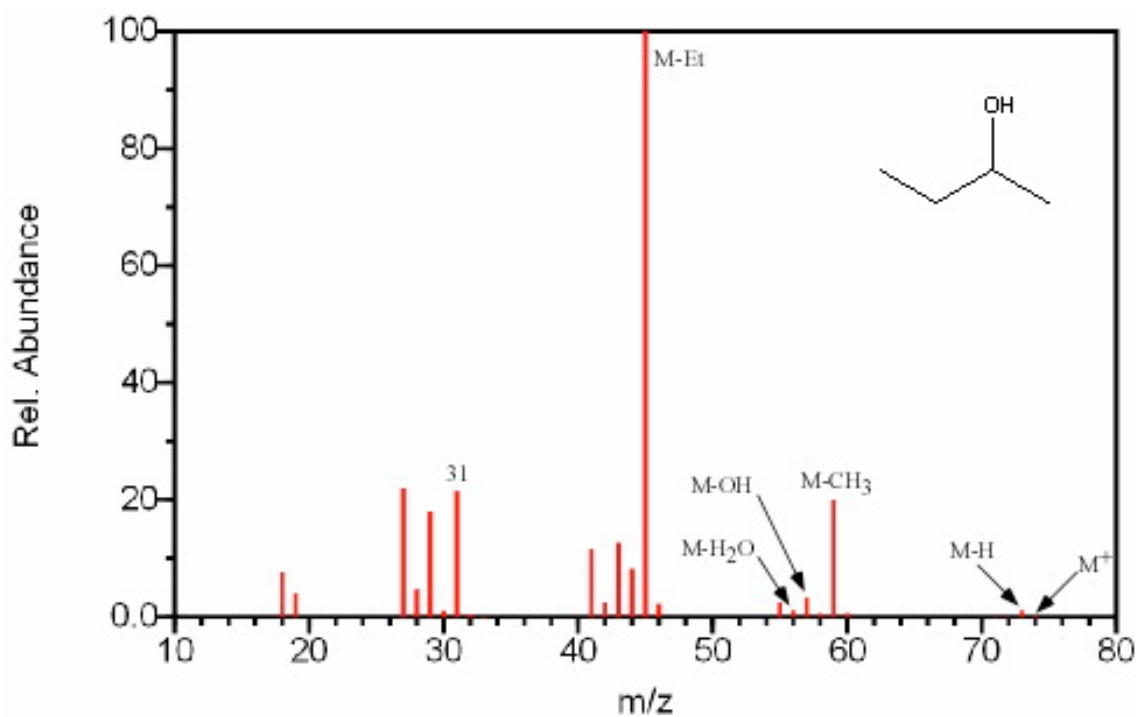
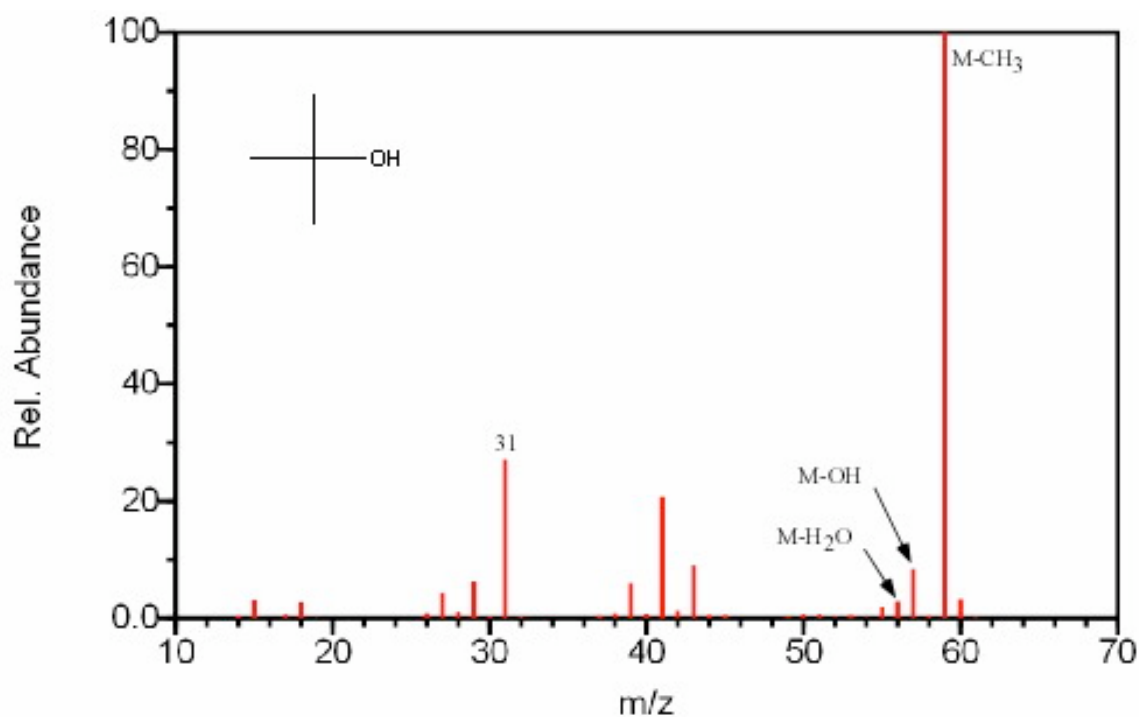


Figure 2.13A can be identified as an alcohol because of the characteristic peak at M-H<sub>2</sub>O, M - 33, and m/z 31. The peak at m/z 31 can attributed to a primary alcohol because it is one of the larger peaks in the spectrum.





- 1
- 2 Figure 2.13B has a small peak at m/z 31 but the base peak in the spectrum
- 3 indicates that this alcohol is not a primary alcohol. The presence of a M - Et and
- 4 M - CH<sub>3</sub> peak indicates that this four carbon alcohol (determined from its
- 5 molecular mass) is the secondary alcohol 2-butanol.



6

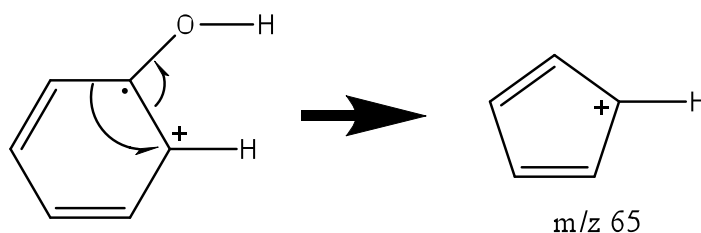
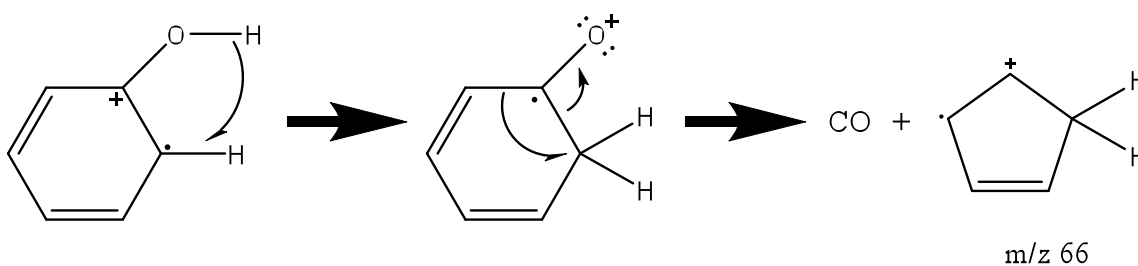
Figure 2.13C illustrates trends common to tertiary alcohols. The spectrum is easily discernable since the single prevalent peak is characterized by  $M - CH_3$ . The lack of a molecular ion helps to confirm the spectrum of a tertiary alcohol.

### Figure 2.13 Fragmentation of Three Alcohols

Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

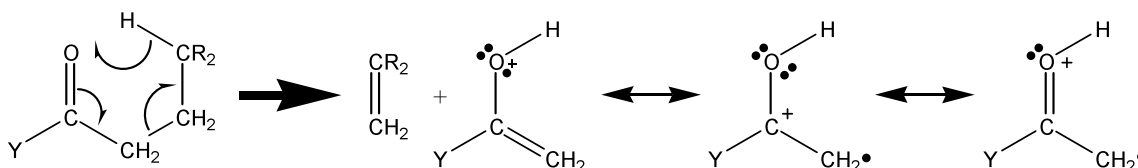
Cyclic alcohols fragment similar to straight chain alcohols in that they give a  $M-1$  peak from the loss of hydrogen and an  $M-18$  peak from the loss of water. They also create a peak at  $m/z$  57 via a complex ring cleavage.

Aromatic alcohols, unlike other alcohols, have a prominent molecular ion peak due to the stability of the aromatic group. Phenols usually give a weaker peak at  $m/z$  77 attributed to a rearrangement and can be identified by two peaks at  $M - CO$  and  $M - COH$ .



## 2.11 Fragmentation of Ketones and Aldehydes

Both ketones and aldehydes give prominent molecular ion peaks though the  $M^+$  peak is more prominent in ketones. The majority of compounds in these categories undergo an important rearrangement, the McLafferty rearrangement.

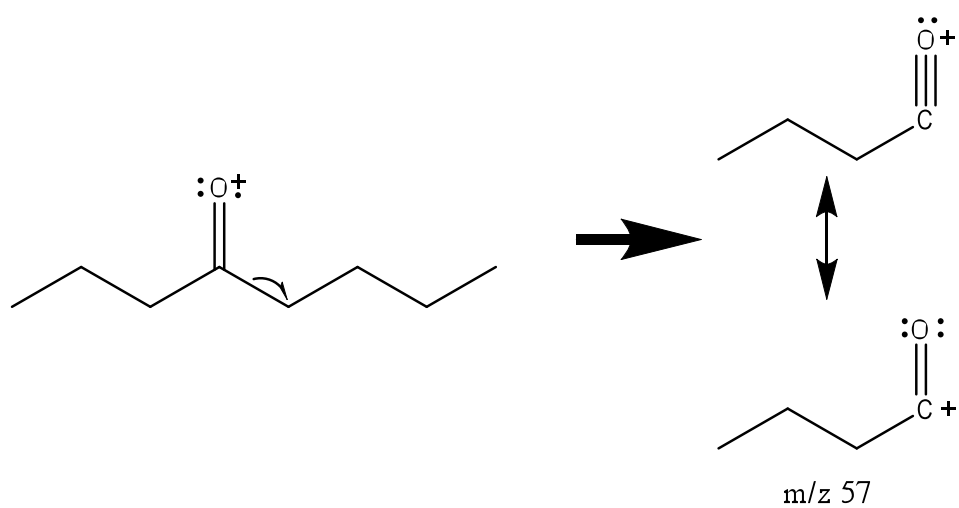
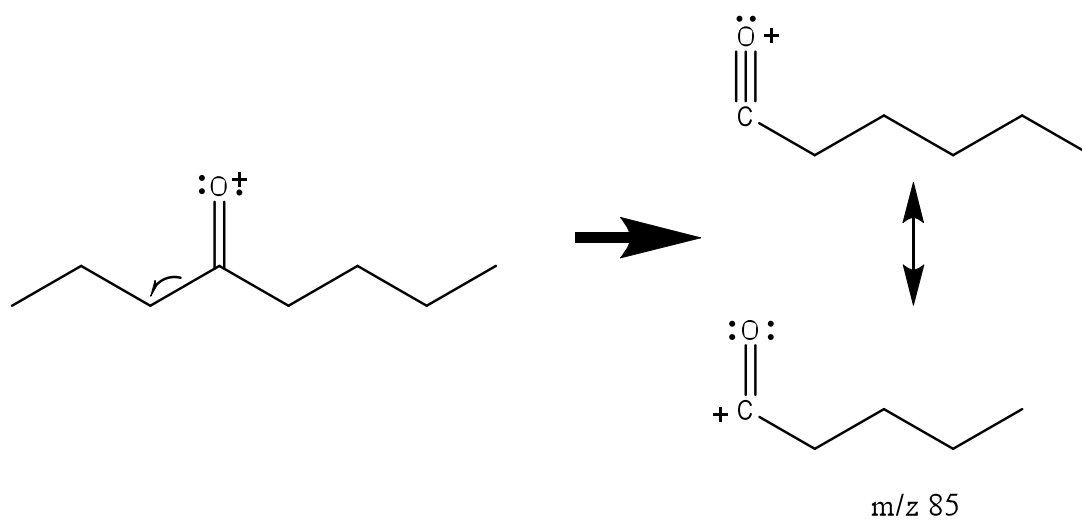


Y can be H, R, OH, OR,  $\text{NR}_2$

This rearrangement is mediated by the p systems of the carbonyl group but can occur in other p systems such as in nitriles (Section 2.17). The only ketones and aldehydes that do not undergo this rearrangement lack a three-carbon side chain allowing for the necessary hydrogen donation.

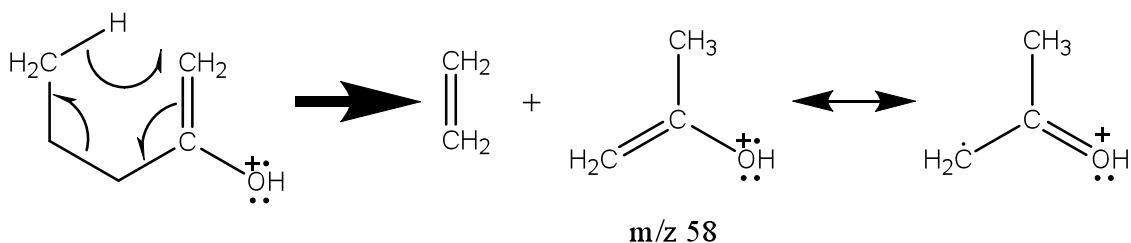
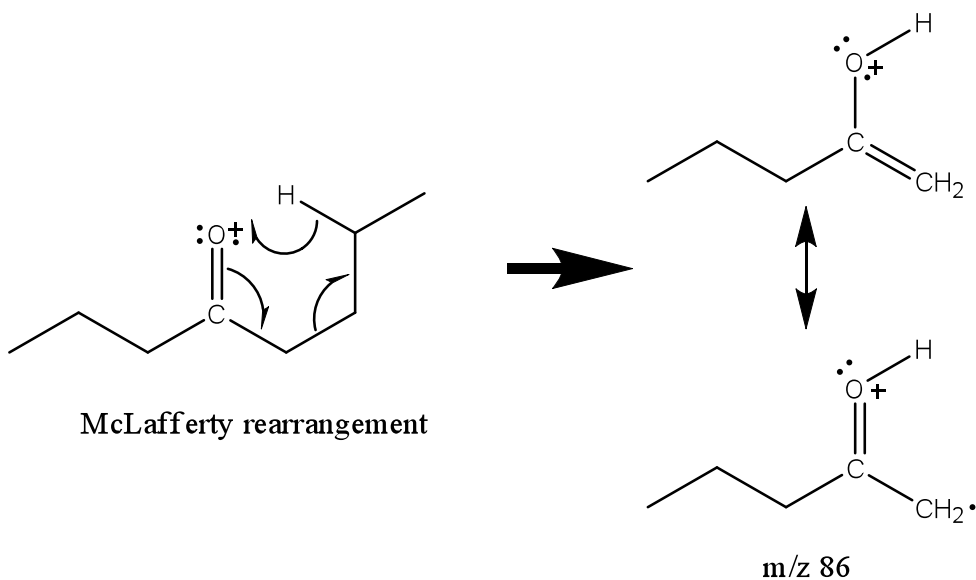
### 2.11.1 Ketones

One major fragment of ketones is the creation of the resonance stabilized acylium ion resulting from the cleavage of the  $\alpha$  bond. The base peak in the spectrum is usually caused by the removal of the larger alkyl group since it forms a more stable radical illustrated by 4-Octanone (Figure 2.14).



1  
2  
3  
4  
5

While ketones undergo a single McLafferty rearrangement described above, they also undergo a subsequent McLafferty rearrangement.



The second rearrangement is mediated by the p system of the alkene group. The ketone functional group is often easily discernable due to the prevalent fragments and rearrangements described above. The configuration of the carbon structure can be difficult to discern. Reduction of the carbonyl group to a methylene group is commonly performed to determine the complete structure of the molecule.

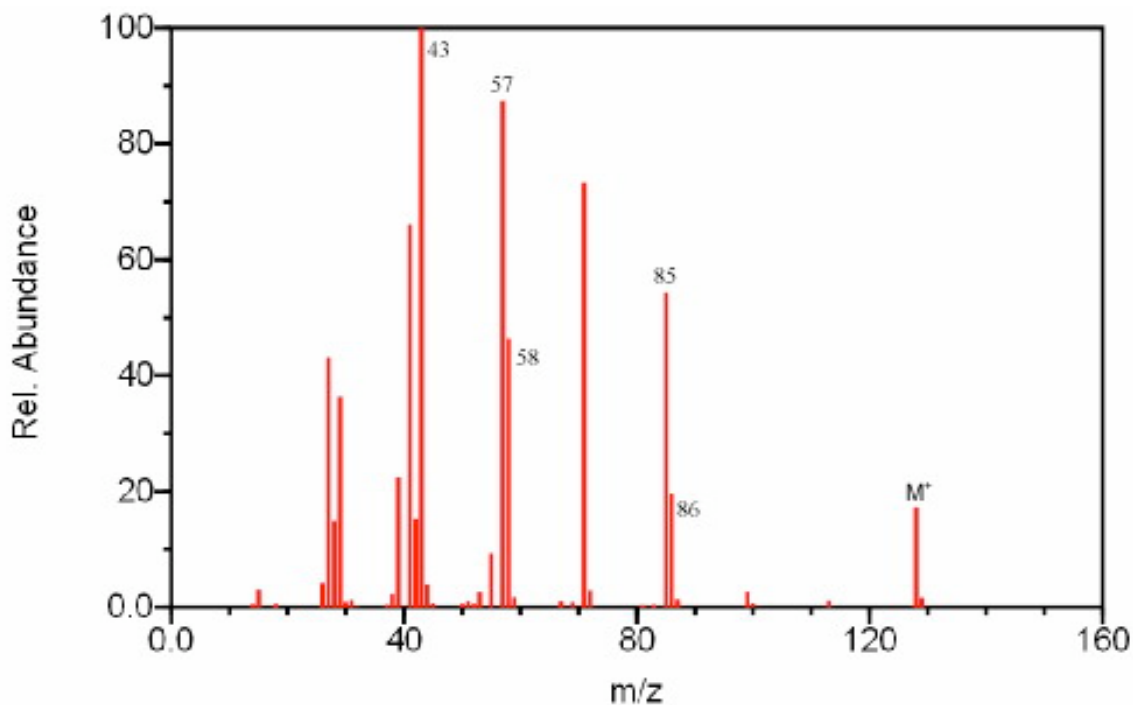
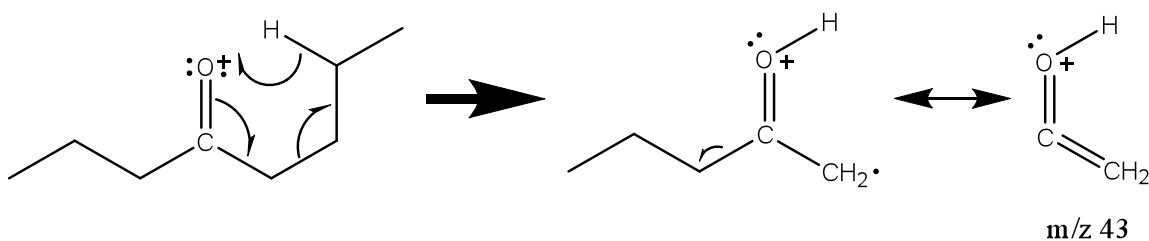


Figure 2.14 Fragmentation of a Ketone

Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

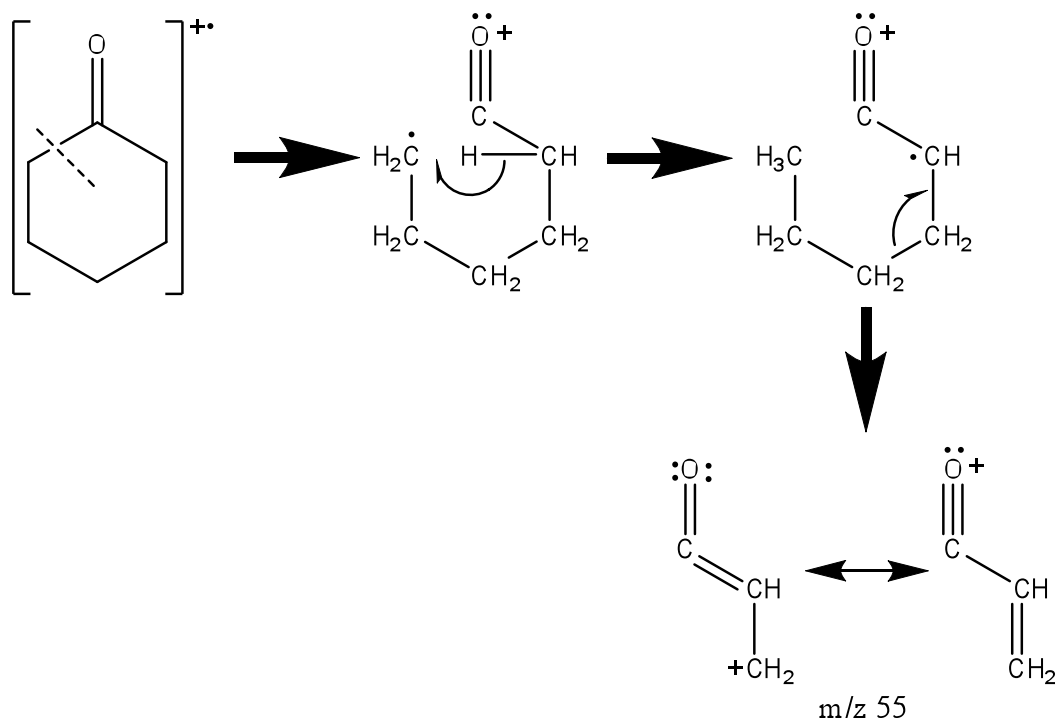
The base peak in Figure 2.14 is the result of a McLafferty rearrangement and an  $\alpha$  cleavage.



### 2.11.2 Fragmentation of Cyclic Ketones

Cyclic ketones major cleavage is also at the  $\alpha$  bond. Due to the ring structure, this cleavage will be detected as the molecular ion unless another

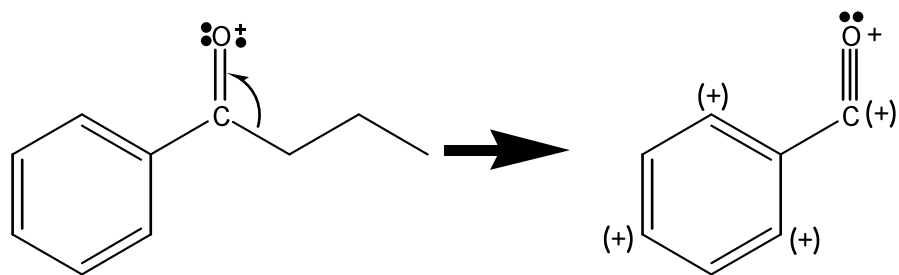
bond is broken. Saturated cyclic ketones produce a fragment at  $m/z$  55 illustrated by cyclohexanone.



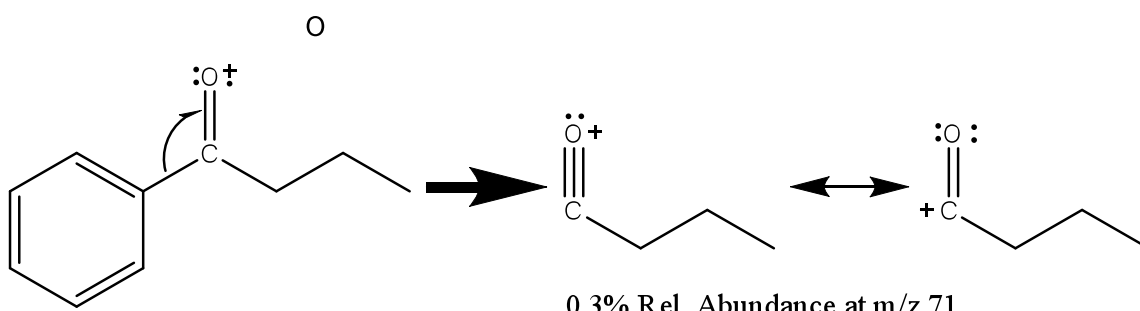
In cyclohexanone, this peak is the base peak. In absence of a reference standard, cyclic ketones are difficult to identify given the difficulty explained earlier in determining the composition of the alkyl portion of the ketone.

### 2.11.3 Fragmentation of Aromatic Ketones

Aromatic ketones create fragments via almost identical pathways as aliphatic ketones. One prominent peak, and usually the base peak, is the result of the cleavage of the less stable alkyl fragment resulting in the  $\text{ArC}\equiv\text{O}$  fragment located at  $m/z$  105. The alpha cleavage resulting in a benzyl radical is infrequent given the stability of the competing reaction (Figure 2.15).

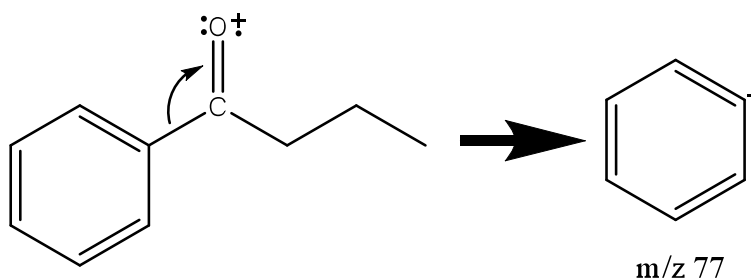


100% Rel. Abundance at  $m/z$  105



0.3% Rel. Abundance at  $m/z$  71

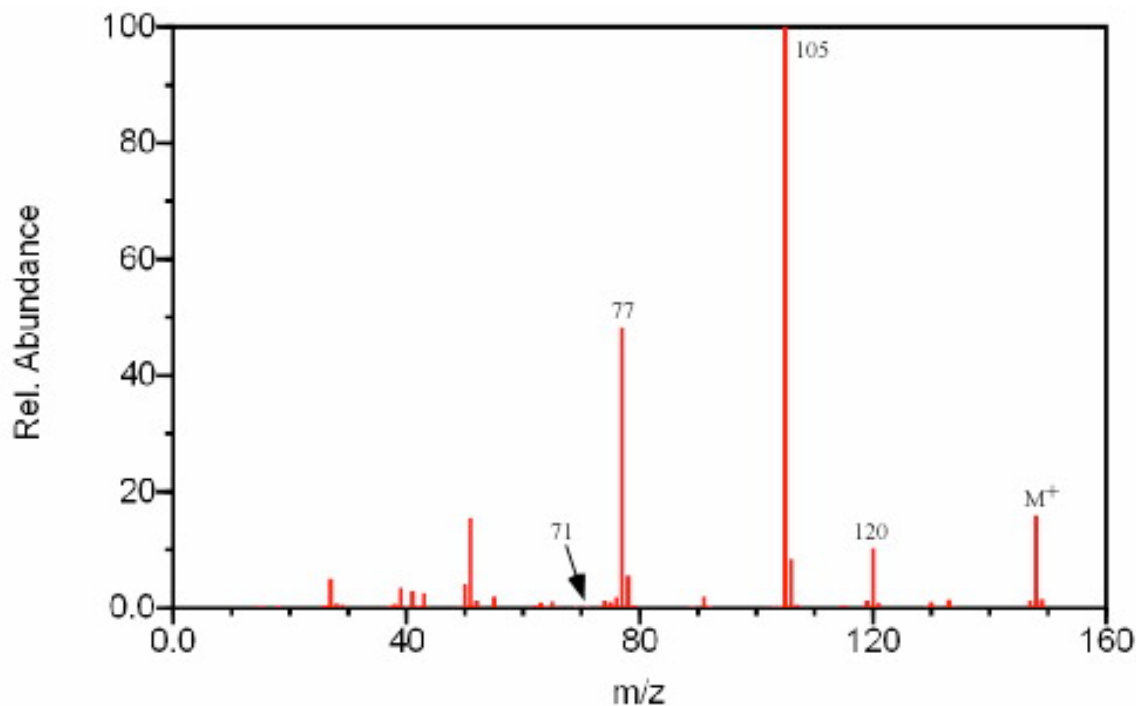
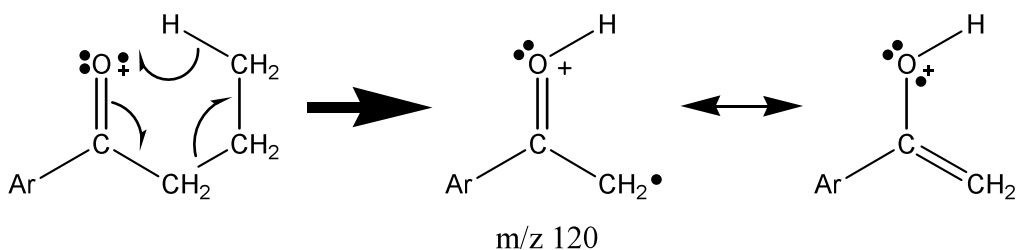
The cleavage of the bond  $\alpha$  to the aromatic group results in a peak at  $m/z$  77.



$m/z$  77

Further fragmentation results in a peak at  $m/z$  55 after the loss of  $\text{HC}\equiv\text{CH}$ . Some aromatic ketones undergo the typical McLafferty rearrangement if the other alkyl component contains an abstractable hydrogen atom.





5 Figure 2.15 Fragmentation of a Cyclic Ketone

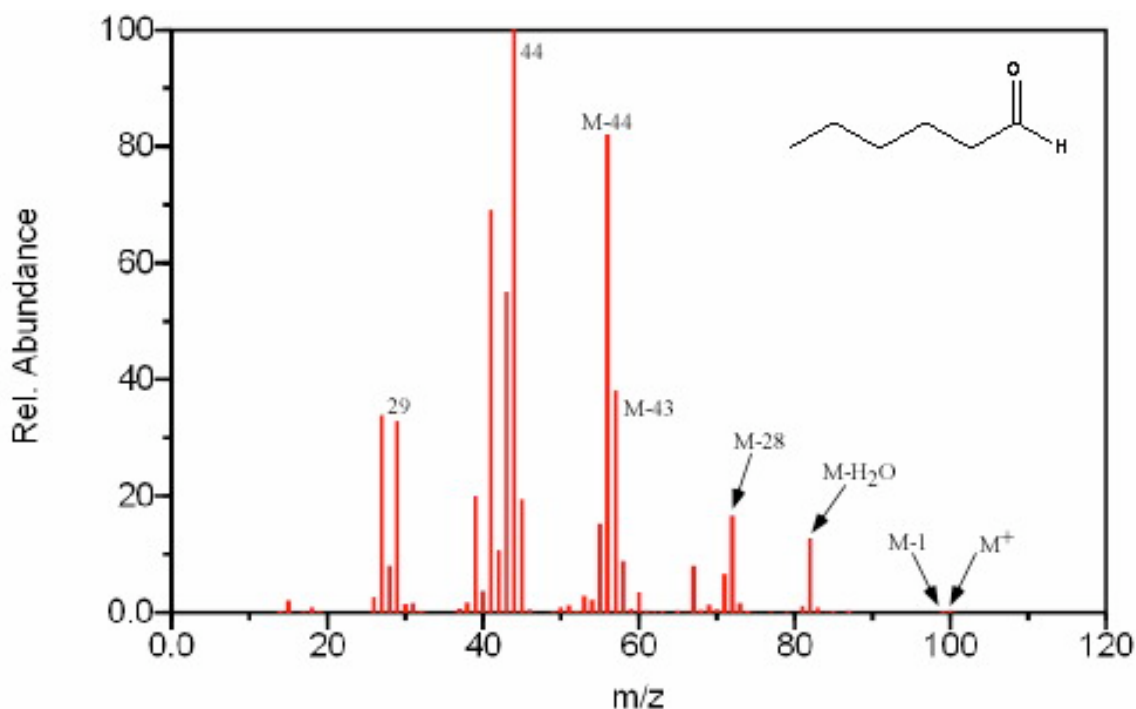
6 Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with  
7 permission from NIST.

#### 8 9 2.11.4 Fragmentation of Aldehydes

10  
11 The major peaks observed in spectrums of aldehyde are the result of the  
12 same  $\alpha$  cleavage as in ketones. This fragmentation results in an M-1 peak and a  
13 peak at M-R from the  $\text{COH}^+$  ion. The presence of an M-1 peak helps to identify  
14 the aldehyde but the hydrocarbon rearrangement at  $\text{C}_2\text{H}_5$  prevents the M-R ( $m/z$   
15 29) peak from being truly useful. Another prominent peak is the McLafferty

1 rearrangement located at  $m/z$  44. The only aldehydes that do not contain this  
2 peak are ones that lack an the necessary hydrogen atom for this rearrangement.

3  
4 Straight chain aldehydes have unique features that help in identification.  
5 These compounds will have a  $M - 18$  fragment from the loose of water,  $M - 28$   
6 from the loss of ethylene,  $M - 43$  loss of  $\text{CH}_2=\text{CH}-\text{O}$  and  $M - 44$  from the loss of  
7  $\text{CH}_2=\text{CH}-\text{OH}$  (Figure 2.16).



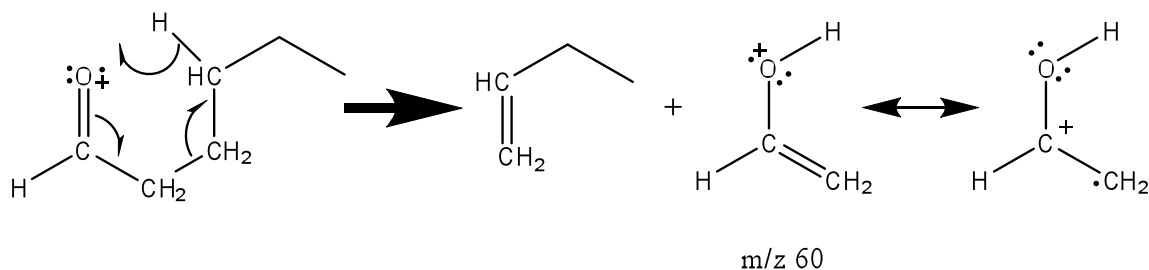
9  
10 Figure 2.16 Fragmentation of an Aldehyde

11 Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with  
12 permission from NIST.

13  
14 The patterns resulting from aromatic ketones are almost identical to those  
15 governing aromatic aldehydes. The characteristic molecular ion is accompanied  
16 by a  $M-1$  peak from the loss of hydrogen. The  $\text{ArC}\equiv\text{O}$  fragment loses  $\text{CO}$  to  
17 form the phenyl ion at  $m/z$  77 that further degrades to give a peak at  $m/z$  51.

## 18 19 2.12 Fragmentation of Carboxylic Acids

The molecular ion of straight chain carboxylic acids is weak but usually present. The prominent and often times the base peak results from the McLafferty rearrangement.



Short chain carboxylic acids give prevalent peaks at  $M - OH$  and  $M - CO_2H$ . In larger carboxylic acids these peaks are less prevalent. Long chain carboxylic acids are better identified by the fragments at  $C_nH_{2n-1}O_2$  (Figure 2.17). There is also the presence of the hydrocarbon fragment at  $C_mH_{2m+1}$  illustrated in Section 2.9.

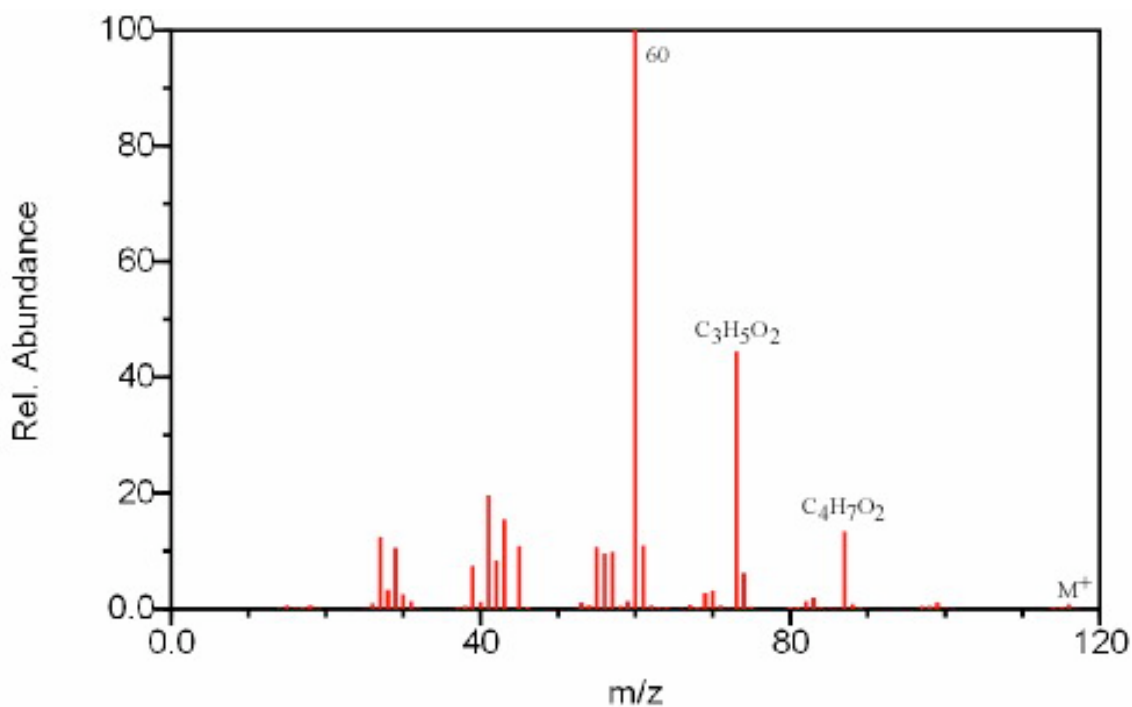
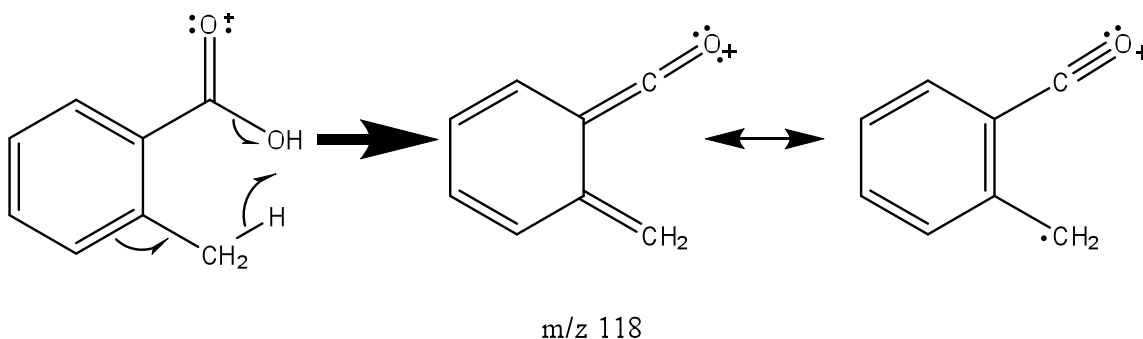


Figure 2.17 Fragmentation of a Carboxylic Acid

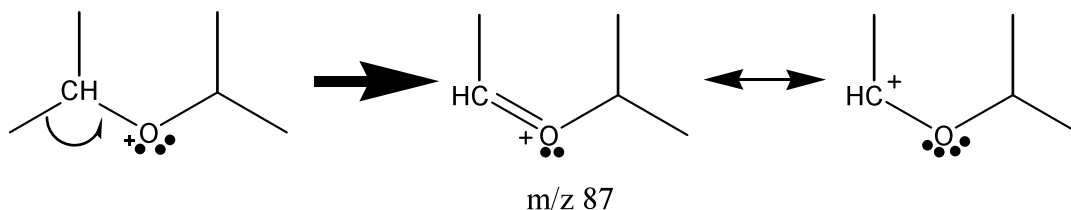
Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

Aromatic acids have a more prominent molecular ion peak but undergo similar fragmentation to short chain hydrocarbons. They produce large peaks at  $M - OH$  and  $M - CO_2H$ . Aromatic acids can also lose water if an ortho group contains an abstractable hydrogen atom.

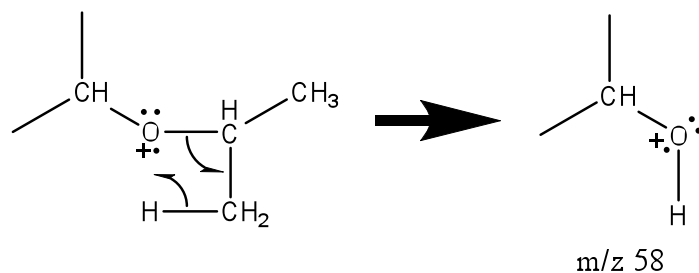


### 2.13 Fragmentation of Ethers

The molecular ion peak is usually weak in ethers. The oxygen atom mediates the major fragment and creates a  $\beta$  cleavage that results in a resonance stabilized cation. This peak is prominent and sometimes is the base peak.



The fragment can also undergo a subsequent rearrangement which typically creates the base peak when the  $\alpha$  carbon is substituted.



Ethers also produce prominent alkyl fragments when the C–O bond ( $\alpha$  bond) is broken and the fragment containing oxygen is a radical.

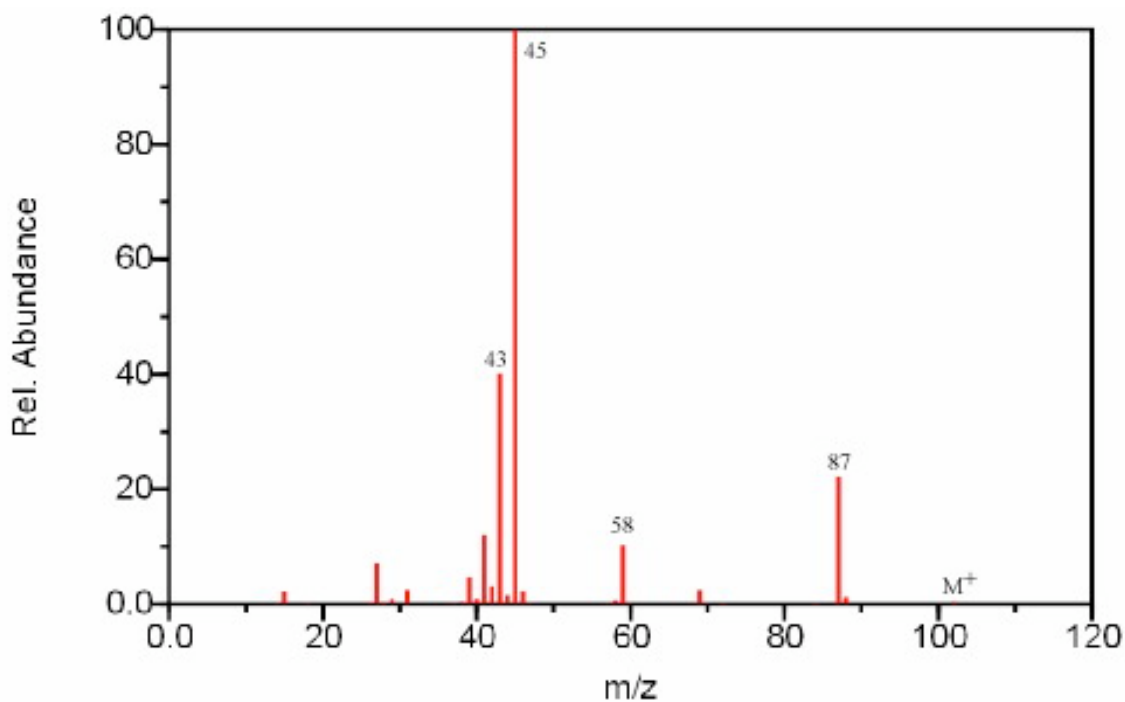
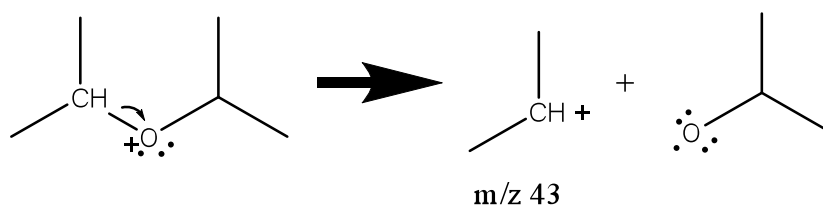
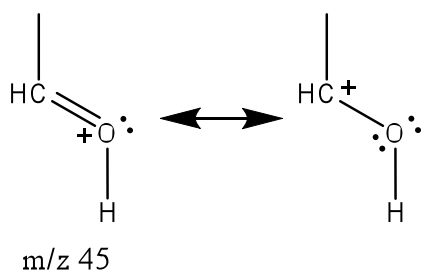


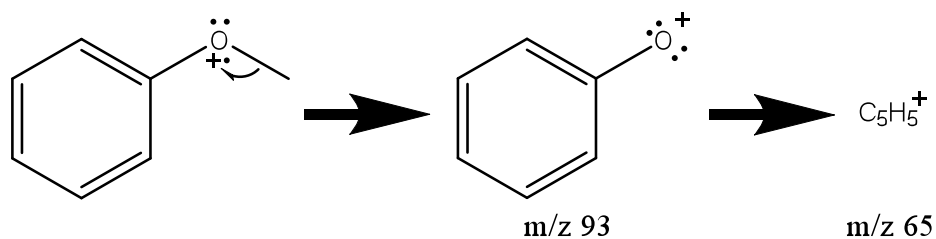
Figure 2.18 Fragmentation of an Ether

Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

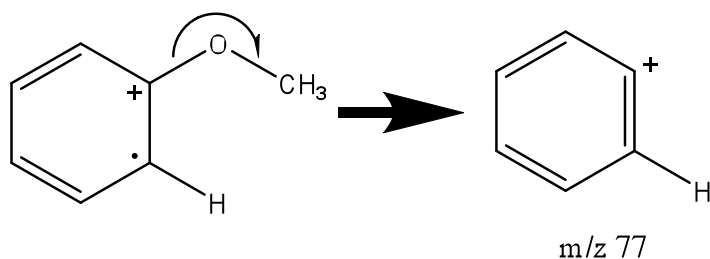
1 The base peak in Figure 2.18 is the result of both a  $\beta$  cleavage and the  
2 above rearrangement.



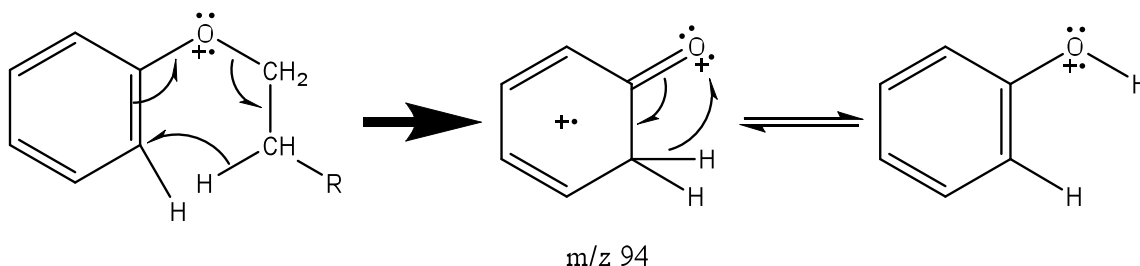
6 Aromatic ethers have a slightly different pattern of fragmentation. They  
7 produce prominent molecular ions due to the stability of the benzene ring. The  
8 major fragmentation occurs at the  $\beta$  bond to the aromatic ring. This fragment can  
9 decompose further with the loss of  $\text{CO}$ .



13 Aromatic ethers also cleave at the bond  $\alpha$  to the ring to create a peak at  
14  $m/z$  78 and 77 due to hydrogen migration.

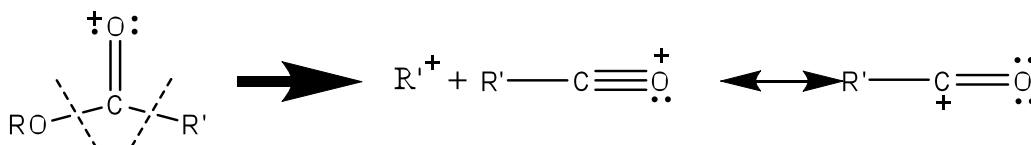


When the alkyl portion of the sample is larger than two carbons, the  $\beta$  is accompanied by hydrogen migration caused by the presence of the aromatic group. This cleavage results in a peak located at  $m/z$  94.

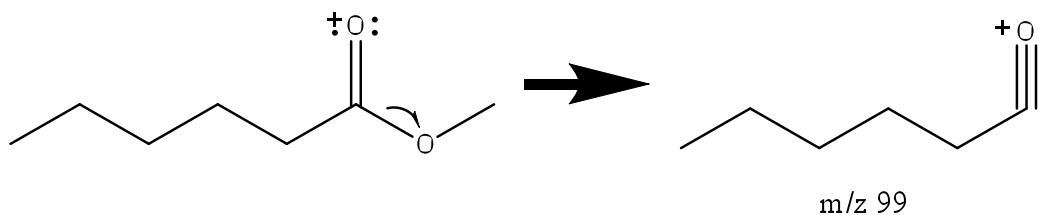


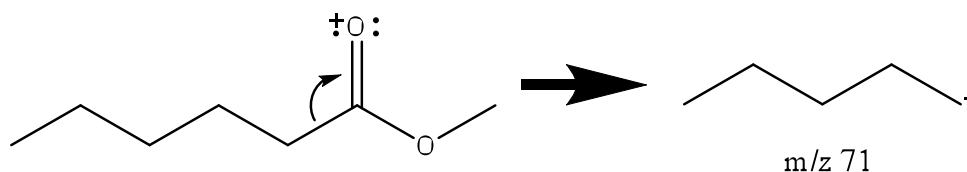
## 2.14 Fragmentation of Esters

The molecular ion peak of straight chain esters is sometimes discernable. A prevalent peak and often the base peak results from the familiar McLafferty rearrangement. The size of the alcohol that formed the ester and the presence of  $\alpha$  substituents can normally be discerned by the mass of these two peaks.



The cleavage of the above bonds results in other fragments, however these peaks are too small to be of great significance. For example, hexanoic acid methyl ester produces the following fragments.





The resonance stabilized  $R'-C\equiv\overset{+}{O}:$  ion gives a discernable peak for almost all esters. The  $R'^+$  ion is prominent in short chain esters but is barely visible in esters with more than six carbon atoms. For hexanoic acid methyl ester, the  $R'^+$  ion is only 9.5% of the base peak.

Until this point, this chapter has covered individual functional groups in isolation. Since esters have both an alcohol and an acid component, fractionation patterns can be observed from both of these types of compounds. The prevalence of the fragments described earlier is dependent on the size of each part of the ester. The increased size of each portion results in a unique rearrangement.

When the acid portion is the major component like in hexanoic acid methyl ester, the fractionation pattern is partially characterized by typical acid peaks. For these straight chain esters, cleavage of successive carbon atoms gives an alkyl fragment and a fragment containing oxygen. This pattern results in the familiar grouping of fragments spaced 14 units apart with the largest fragment in the cluster resulting from the  $C_nH_{2n-1}O_2$  ion (Figure 2.19).



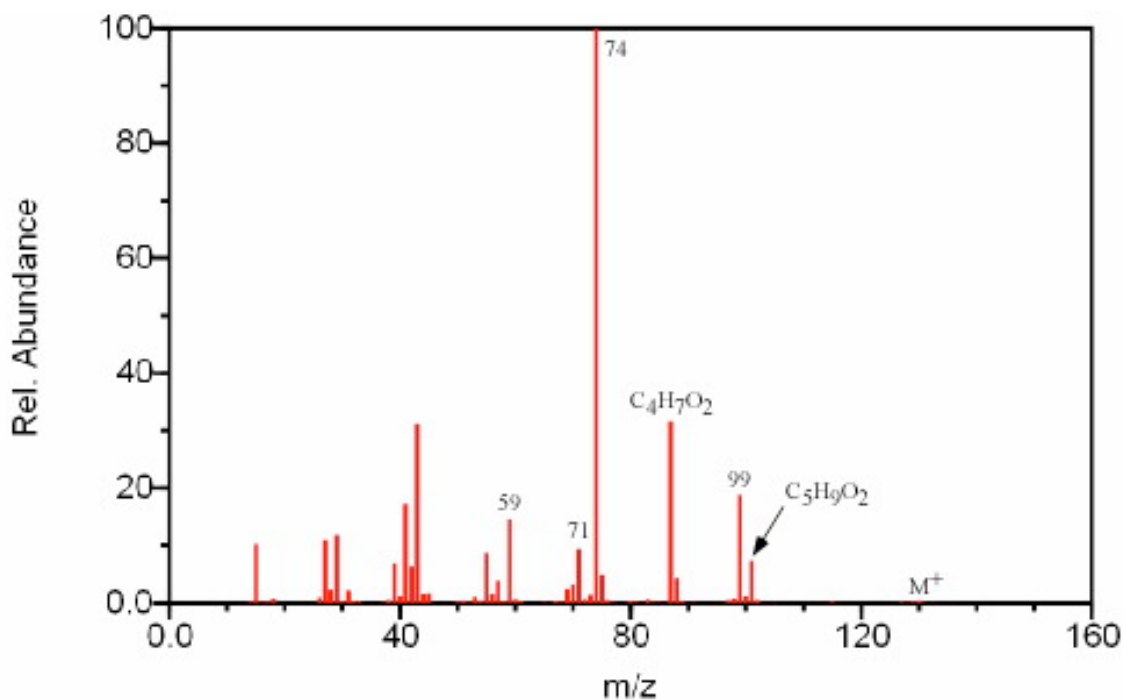
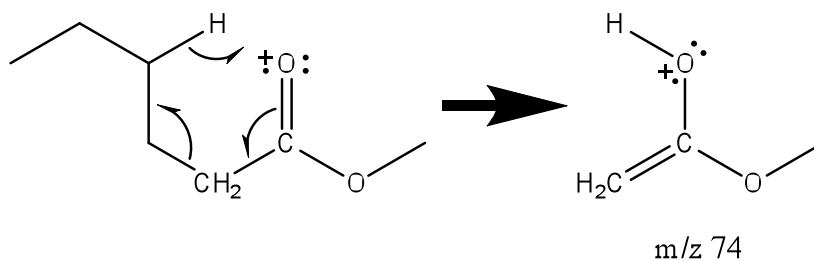


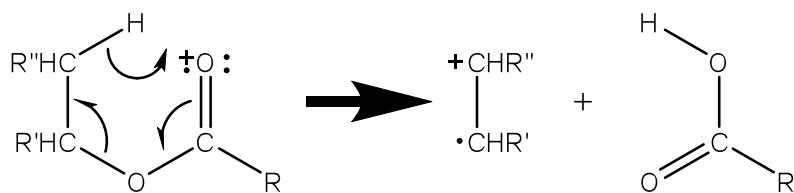
Figure 2.19 Fragmentation of an Ester

Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

The base peak in Figure 2.19 is a result of the McLafferty rearrangement.

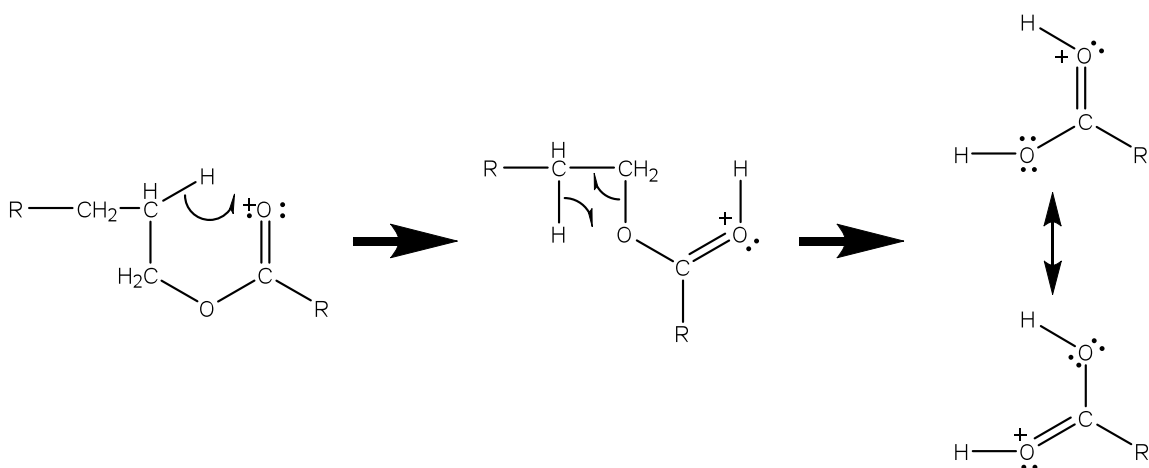


When the alcohol portion of the ester is the prominent portion of the ester, fragments similar to that of an alcohol is observed. These esters will lose a molecule of acid like alcohols lose a molecule of water.

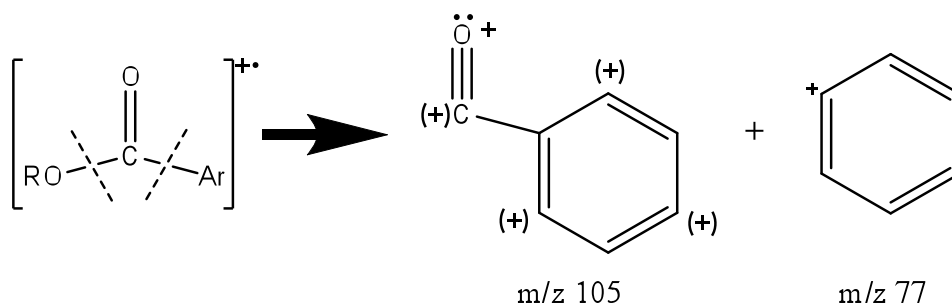


Where  $R \ll R' \text{ or } R''$

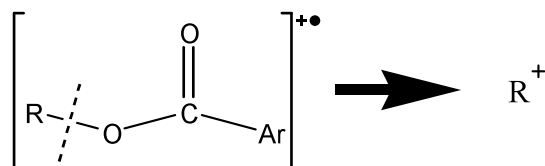
Like alcohols, the prevalence of this rearrangement is so frequent that the molecular ion is normally absent from the spectra. These long chain alcohols will also lose the alkyl fragment from the alcohol accompanied by two hydrogen migration.



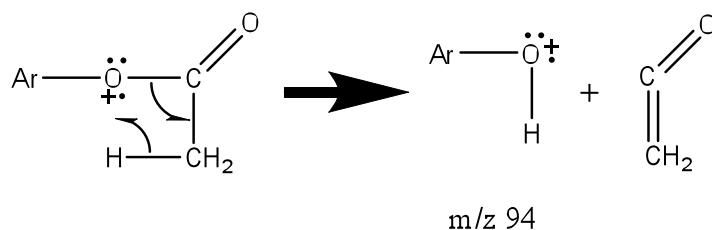
In aromatic esters, the molecular ion is prominent due to the aromatic group. There are two distinctive types of aromatic esters that have their own unique fragmentation patterns. Esters synthesized from aromatic acids mostly undergo  $\alpha$  cleavages.



The loss of  $\cdot\text{OR}$  results in the base peak because of the multiple resonance forms stabilizing the cation. When the alkyl portion of the alcohol becomes longer, the McLafferty rearrangement and the loss of R with two hydrogen migrations explained above is more favorable. Increasing the size of the R chain will cause the alkyl portion to retain the charge.



The presence of an aromatic group in the alcohol that formed the ester results in the creation of the  $\text{CH}_3\text{C}\equiv\text{O}^+$  ion. These esters also undergo a rearrangement that results in the loss of a ketene molecule.

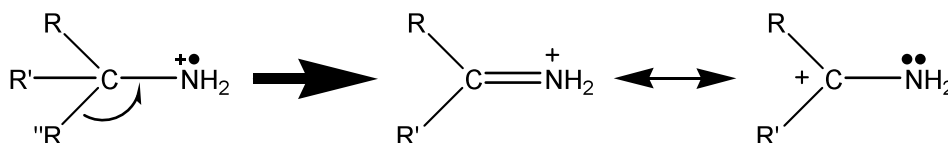


## 2.15 Fragmentation of Amines

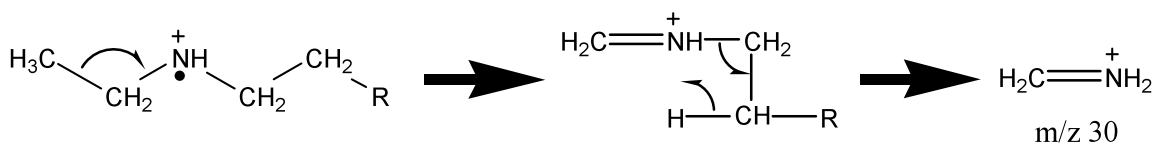
The presence of nitrogen in an amine can be detected by its odd molecular weight and the even fragments that it produces (Section 2.3). Often

times the presence of the molecular ion in longer straight chain amines is not detectable. In these cases, chemical ionization techniques are often used in determining the molecular mass in order to determine the presence of nitrogen.

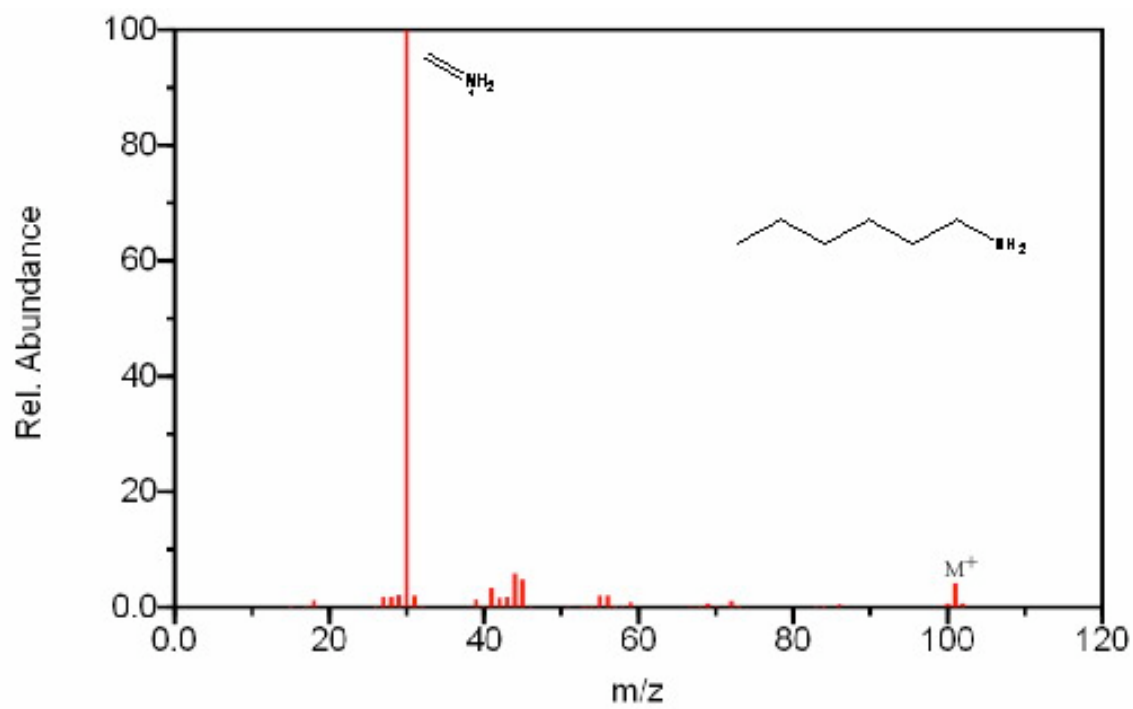
The base peak in most amines results from the cleavage of the  $\beta$  bond. The loss of the largest branch ( $R''$ ) is preferred because the larger alkyl fragment stabilizes the produced radical.



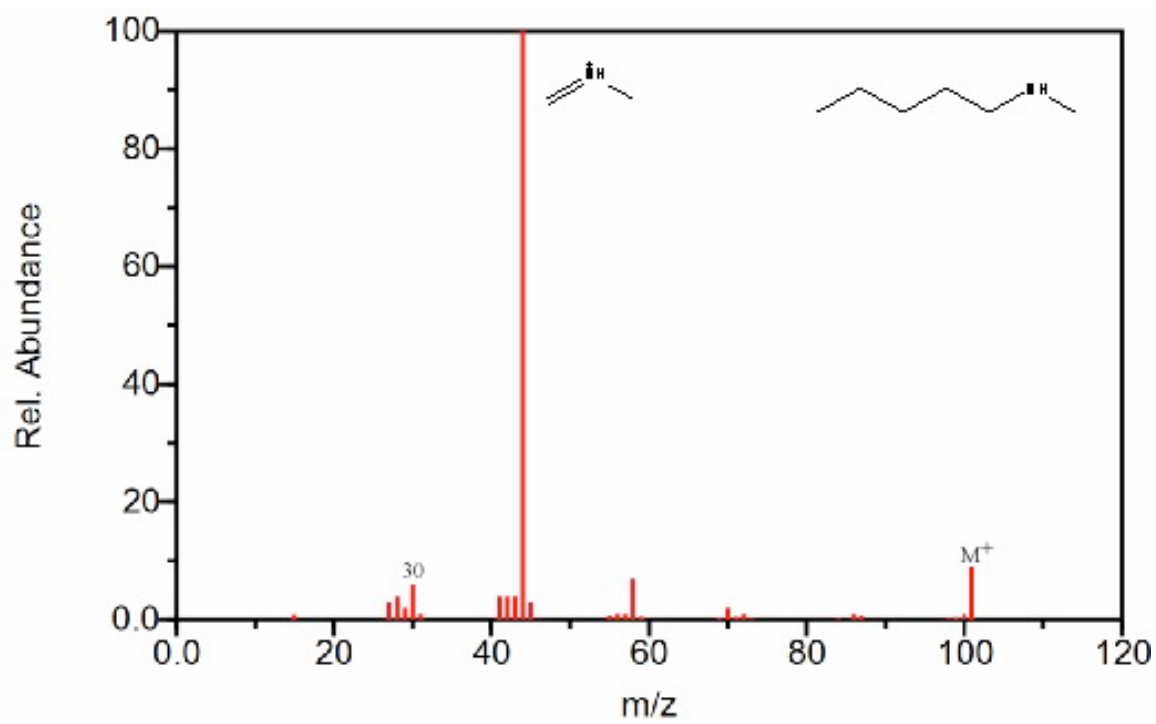
Like alcohols, if the  $\alpha$  carbon is bonded to a hydrogen atom, a  $M - H$  peak is usually visible. In primary amines with an unbranched  $\alpha$  carbon, cleavage of the  $\beta$  bond produces a peak at  $m/z$  30. This peak is not conclusive proof of a primary amine because secondary and tertiary amines undergo a rearrangement similar to that of alcohols.



Amines also produce even fragments caused the cleavage of  $C - C$  bonds farther away from the functional group. The fragment containing the nitrogen group usually retains the charge resulting at peaks characterized by  $C_nH_{2n+2}N$  spaced at 14 units. There is also the less prevalent hydrocarbon pattern of  $C_nH_{2n+1}$ ,  $C_nH_{2n}$ , and  $C_nH_{2n-1}$ .



1



2

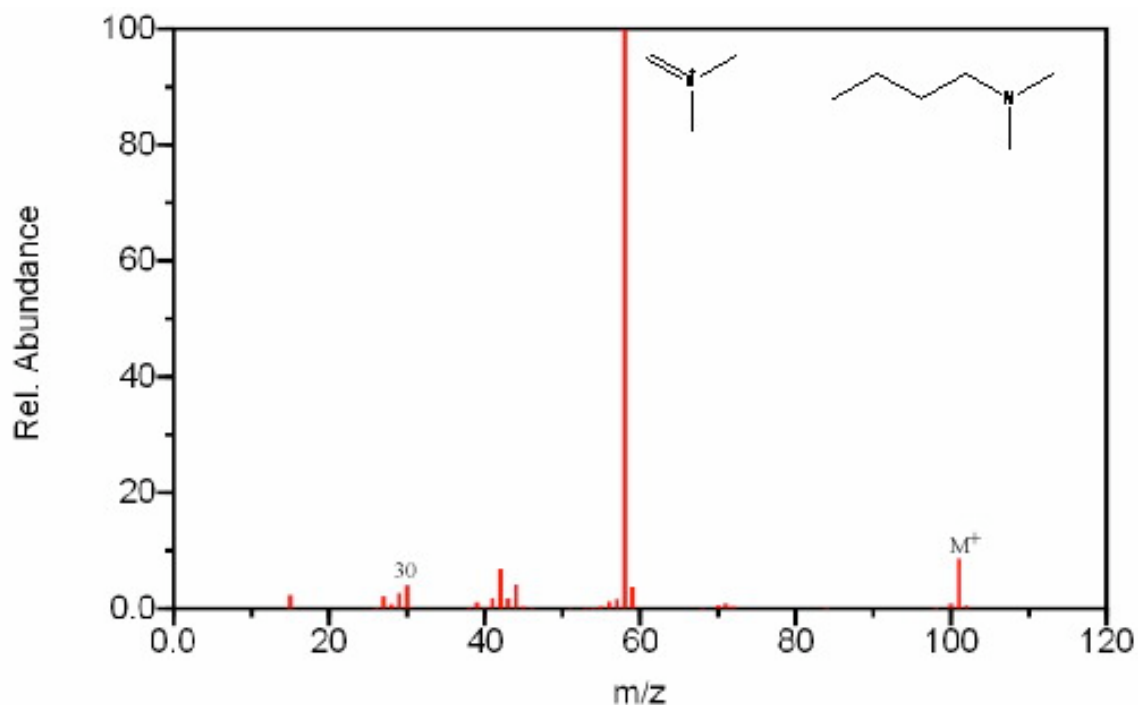
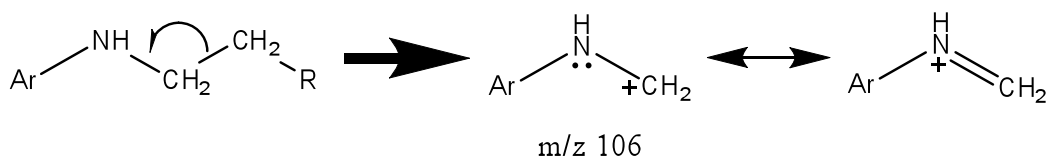


Figure 2.20 Fragmentation of Three Amines - The mass spectrum is easily recognized as an amine due to its odd molecular ion and the presence of even fragments. The base peak in each spectrum, due to  $\beta$  cleavage distinguishes between the primary, secondary, and tertiary amine.

Spectra from the NIST/EPA/NIH Mass Spectral Library. Reprinted with permission from NIST.

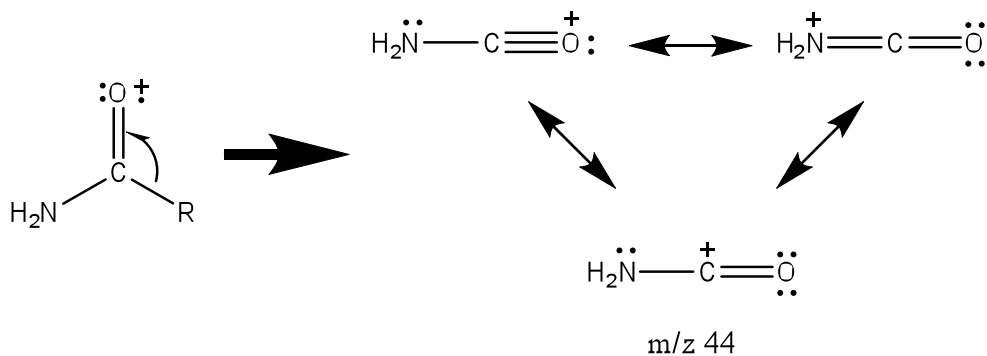
Cyclic amines produce a discernable molecular ion peak unless the  $\alpha$  carbon is substituted. The loss of hydrogen from the  $\alpha$  carbon is also a prominent peak. The ring is cleaved when the  $\beta$  bond is broken and subsequent alkene molecules fragment from the remaining ring structure.

The molecular ion of an aromatic amine is expectedly intense. The loss of the hydrogen atom bonded to the nitrogen gives a prominent peak at  $M - 1$ . Similar to ethers, the loss of HCN from the aniline ion produces peaks at  $C_5H_6$  and  $C_5H_5$ . Unlike ethers however, the hetero atom not the aromatic group controls the major pathways of fractionation resulting in  $\beta$  cleavage.

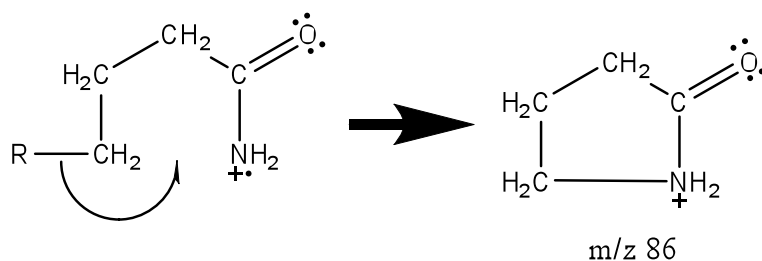


## 2.16 Fractionation of Amides

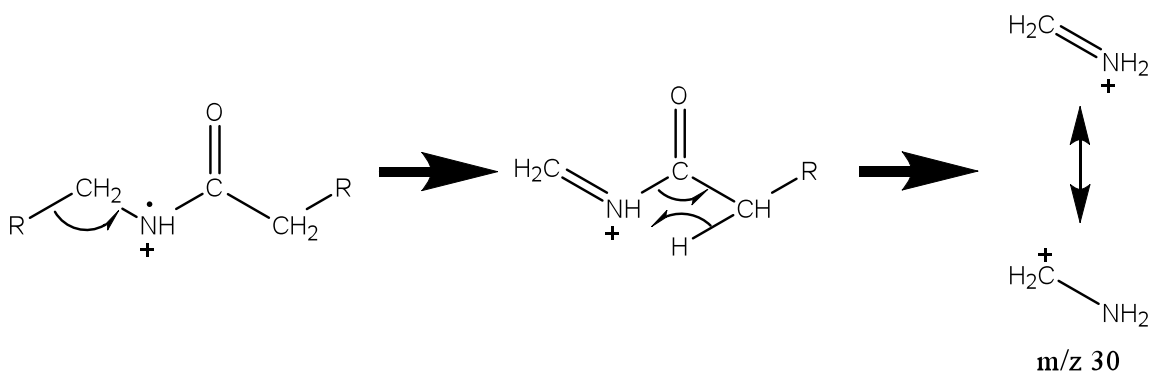
The molecular ion of most straight chain amides is usually discernable which allows the nitrogen atom to be identified. The fractionation pattern is dependent on the length of the alkyl chain and the degree of substitution of the nitrogen group. Primary amides give a prevalent peak from the McLafferty rearrangement.



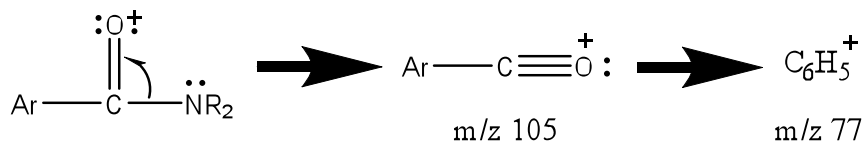
In primary amides that lack an abstractable hydrogen atom for the McLafferty rearrangement, this accounts for the base peak. In the other amides including secondary and tertiary, the base peak is created by the McLafferty rearrangement at m/z 59. Primary amines also produce a peak at m/z 86 as a result of the following cleavage.



When the alkyl groups bonded to the nitrogen are longer than two carbons, another rearrangement is discernable.



Aromatic amides have a more prominent molecular ion peak. The common fragments are characterized by the loss of  $\text{NR}_2$  to form a resonance stabilized cation followed by the subsequent loss of  $\text{CO}$ .

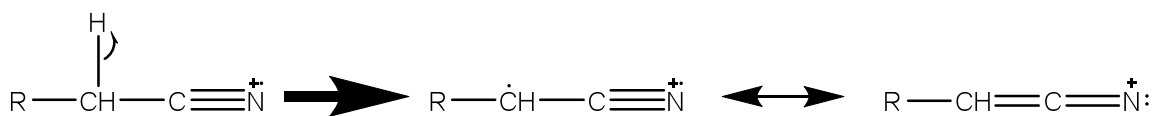


## 2.17 Fragmentation of Nitriles

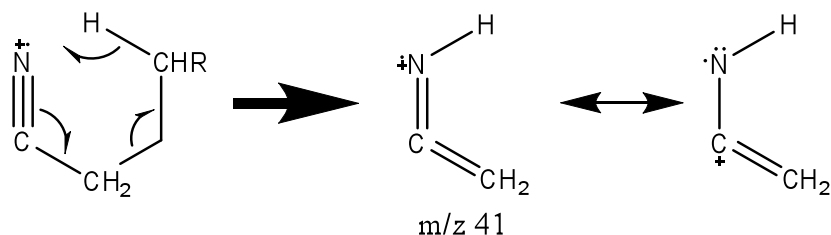
The presence of the nitrogen can usually be identified by the odd molecular weight according to the nitrogen rule (Section 2.3). This identification technique is usually unable to identify a nitrile because these compounds lack a molecular ion. The presence of a  $\text{M}-1$  peak complicates the identification of the



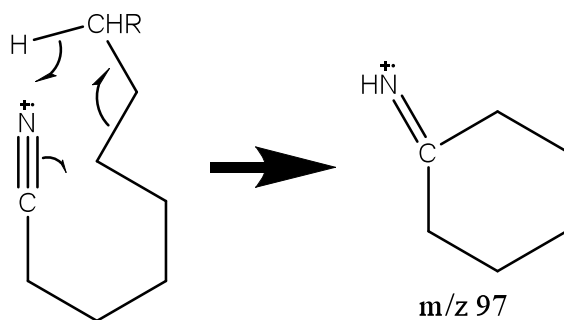
1 molecular ion. This peak is formed by a loss of an  $\alpha$  hydrogen to form a  
2 resonance stabilized cation.



6 A prominent and frequent base peak is the result of the McLafferty  
7 rearrangement at  $m/z$  41 in compounds whose  $\alpha$  carbon is not branched. This  
8 peak, however, is unable to confirm that a compound is a nitrile because  
9 hydrocarbon chains frequently form a peak at  $\text{C}_3\text{H}_5$ .



13 A unique peak at  $m/z$  97 is characteristic of nitriles that contain a straight  
14 chain of seven carbons or more.



## 18 2.18 Reviewing General Principals

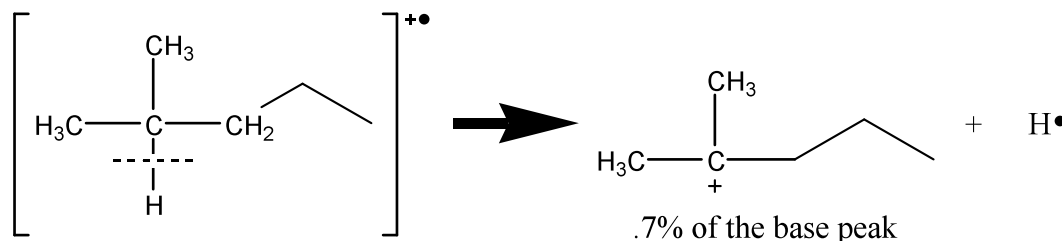
1       After surveying common compounds encountered in organic chemistry  
2 and their corresponding spectra we are able to make some generalizations about  
3 fractionation patterns. When dealing with a compound's molecular ion;

- 4  
5       1. The molecular ion of ethers, carboxylic acids, aldehydes, and nitrogen  
6       containing molecules such as amides and nitriles can be very faint or  
7       potentially absent. The molecular ion of alcohols and branched  
8       compounds is almost always undetected.
- 9       2. Increasing a compound's size or the branching of the alkyl portion will  
10      decrease the intensity of the molecular ion.
- 11      3. Cyclic structures, elements of unsaturation, and aromatic groups increase  
12      the intensity of the molecular ion.

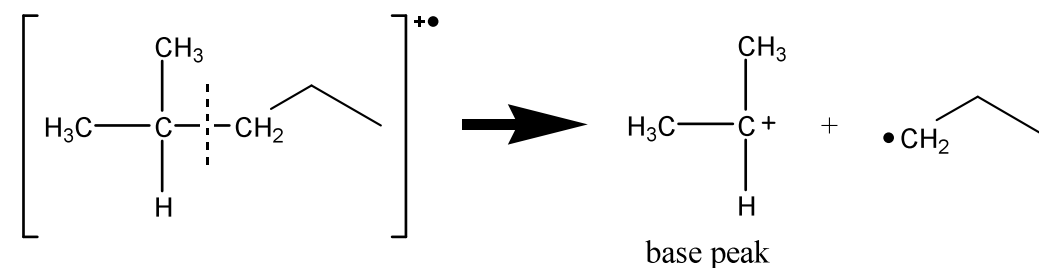
13  
14      Unknown compounds, in the absence of a reference standard, can often be  
15      more difficult but not impossible to discern given the prevalence of multiple  
16      fragments. The majority of compounds, however, will abide by the following  
17      rules.

- 18  
19      1. Resonance stabilized cations are favored because they help delocalize  
20      the positive charge throughout the molecule.
- 21      2. The cleavage of bonds is favored at substituted carbon atoms that  
22      produce the most stable cation. As a result, tertiary cations are favored  
23      over secondary which are favored over primary which are more stable  
24      than  $\text{CH}_3^+$ .
- 25      3. The longest chain is eliminated most frequently because the greater  
26      number of carbon atoms allows for the delocalization of the radical.
- 27      4. The combination of rule two and three can be good predictors of the  
28      prevalence of fragments. Achieving a balance between the stability of the  
29      radical and the cation produces the most prevalent peaks. The following  
30      example illustrates this point.

1



2



3

5. The  $\beta$  bond to the heteroatom is frequently broken since the heteroatom's non bonding electrons allow for resonance forms that stabilize the cation.

4

5

6. Rearrangements account for prominent peaks in the spectrum such as the loss of water from an alcohol or the McLafferty rearrangement.

6

7

8

Besides having a general set of guidelines that govern general fractionation, it is also important to be able to identify patterns that are indicative of particular functional groups. As a result, a condensed table of the commonly observed fragmentation patterns is listed in the table below.

9

10

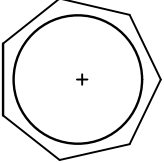
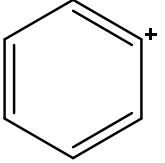
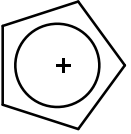
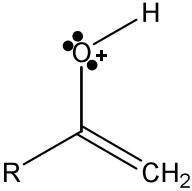
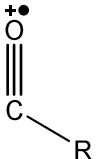
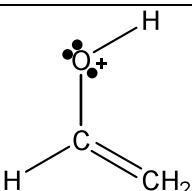
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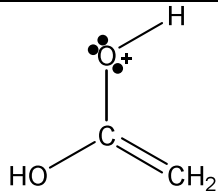
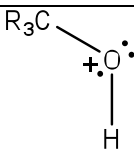
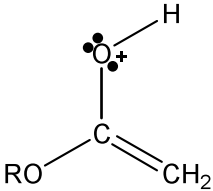
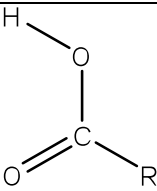
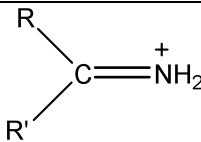
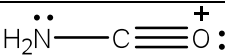
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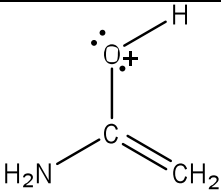
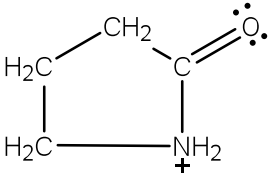
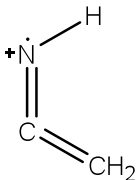
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Table 2.2 A Review of Common Fragmentation Patterns

| Functional Group       | Observed Fragments | M/Z Value       |
|------------------------|--------------------|-----------------|
| Straight Chain Alkanes | $C_nH_{2n+1}$      | 43, 57, 71, ... |
|                        | $M - CH_3$         | $M - 15$        |
|                        | $M - CH_2CH_3$     | $M - 29$        |
|                        | $M - CH_2CH_2CH_3$ | $M - 43$        |
| Branched Alkanes       | $C_nH_{2n}$        | Various         |
| Cyclic Alkanes         | $M - H_2C=CH_2$    | $M - 28$        |
| Alkenes                | $C_nH_{2n-1}$      | Various         |
|                        | $C_nH_{2n}$        | Various         |

|                  |   |         |
|------------------|---|---------|
| Aromatics        |    | 91      |
|                  |    | 77      |
|                  |    | 56      |
| Alcohols         | M – H <sub>2</sub> O  | M – 18  |
|                  | M – (H <sub>2</sub> O & H <sub>2</sub> C=CH <sub>2</sub> )                          | M – 46  |
|                  | M – (CH <sub>3</sub> & H <sub>2</sub> O)  | M – 33  |
| Primary Alcohols | CH <sub>2</sub> OH  | 31      |
| Ketones          |   | 43 + R  |
|                  |  | Various |
| Aldehydes        |  | 44      |
|                  | COH   | 29      |
|                  | M – H <sub>2</sub> O  | M – 18  |
|                  | M – H <sub>2</sub> C=CH <sub>2</sub>  | M – 28  |
|                  | M – H <sub>2</sub> C=CH–OH  | M – 44  |

|                  |   |             |
|------------------|---|-------------|
| Carboxylic Acids |    | 60          |
|                  | M – OH  | M – 17      |
|                  | M – CO <sub>2</sub> H   | M – 45      |
|                  | C <sub>n</sub> H <sub>2n-1</sub> O <sub>2</sub>                                     | 73, 87, ... |
| Ethers           | β cleavage  | various     |
|                  |    | various     |
| Esters           |    | 74, 88, ... |
|                  |  | various     |
|                  | R <sup>+</sup>  | various     |
|                  | R'—C≡O <sup>+</sup>   | various     |
| Amines           |  | various     |
|                  | C <sub>n</sub> H <sub>2n+2</sub> N  | 58, 72, ... |
| Primary Amines   | CH <sub>2</sub> NH <sub>2</sub>   | 30          |
| Amides           | CH <sub>2</sub> NH <sub>2</sub>   | 30          |
|                  |  | 44          |

|          |   |       |
|----------|---|-------|
|          |  | 59    |
|          |  | 86    |
| Nitriles | M - H   | M - 1 |
|          |  | 41    |

1

## 2 2.19 Searchable Databases

3

4 The proliferation of databases and the number of compounds that they  
5 contained has made the interpretation of spectra less important. These  
6 databases cover over 200,000 compounds, the two most commonly used  
7 databases are the one produced by the National Institute of Standards and  
8 Technology (NIST) along with the *Wiley Registry of Mass Spectral Data*. Using  
9 these databases can be of great assistance when performing routine analysis  
10 and sometimes are the only way to positively identify a particular compound.

11

12 These databases cannot be the exclusive tool that chemists rely on to  
13 interpret data. Like other tools, it is necessary to know when and how to use it.  
14 Databases are a perfect tool for performing routine analysis when the analyte  
15 and the reference standard have a high percent match. When the quality of the  
16 match becomes low, it is necessary to assess the validity of the database match.  
17 It is also necessary to understand these fractionation patterns when performing  
18 research especially when synthesizing new compounds that are not contained in

the published databases, and for which there is obviously no reference compound. Only the combination of manual interpretation along with the usage of a library can the composition of an unknown sample truly be discerned.

## 6.20 References

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Linstrom, P.; Mallard, W., Eds., NIST Chemistry WebBook, NIST. Standard Reference database Number 69, June 2005, National Institute of Standards and Technology, Gaithersburg MD, 20899 (<http://webbook.nist.gov>).

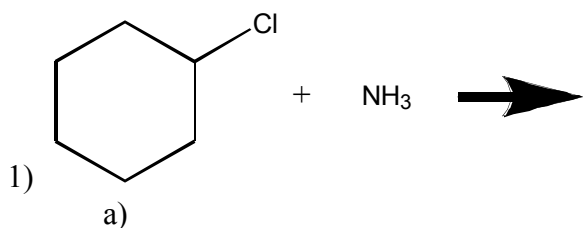
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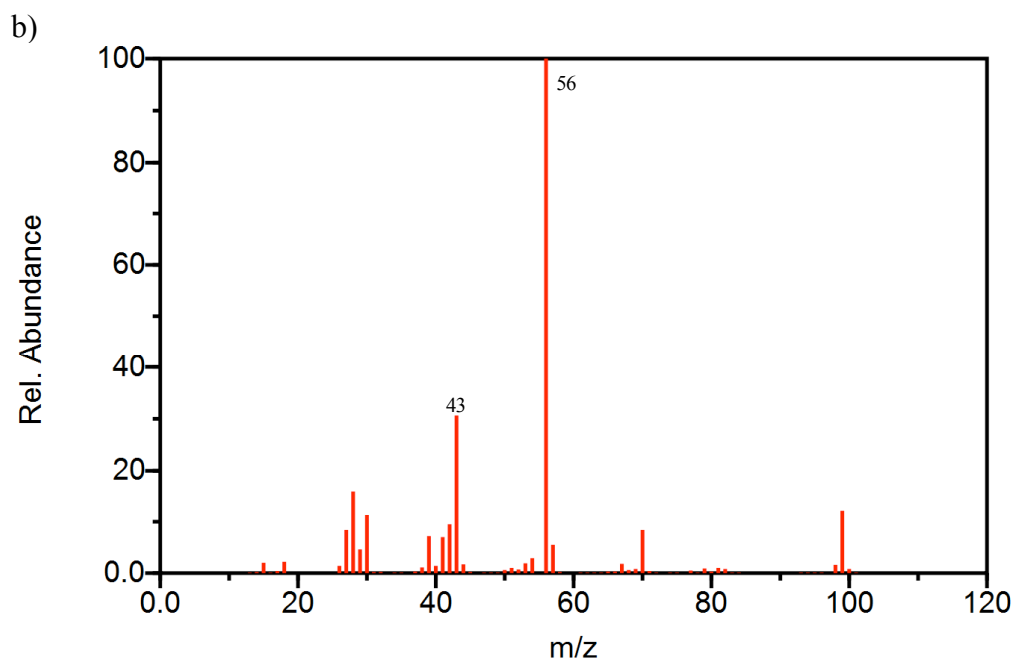
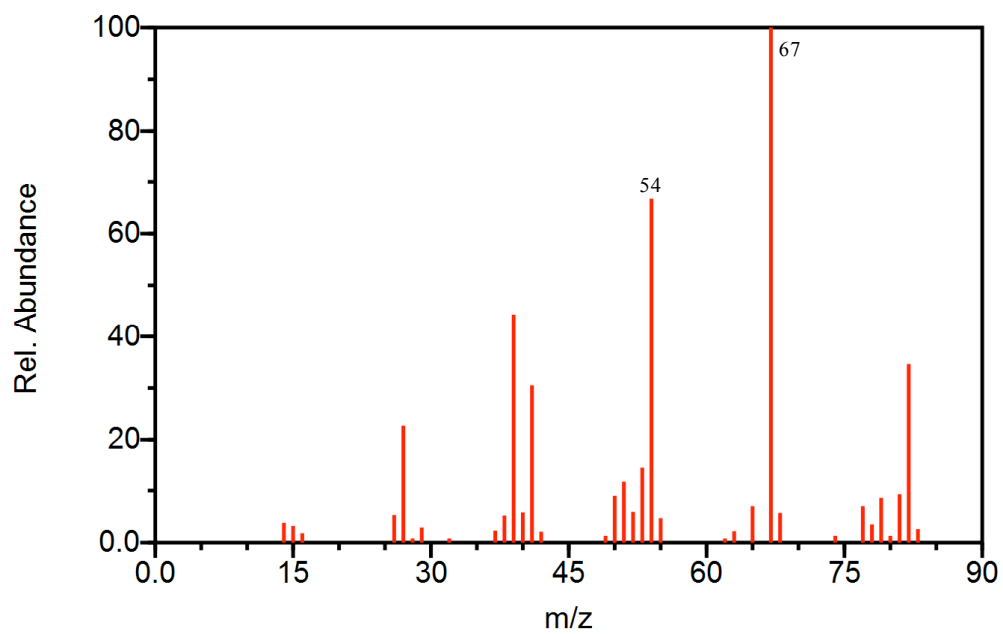
Silverstein R.; Bassler, G.; Morrill, T. Mass Spectrometry. *Spectrometric Identification of Organic Compounds*, 5th ed.; John Wiley & Sons: New York, 1991; 3-89.

Wade, L. Infrared Spectroscopy and Mass Spectrometry. *Organic Chemistry*, 6th ed.; Pearson Prentice Hall: New Jersey, 2006; 508-558.

## 6.21 Questions

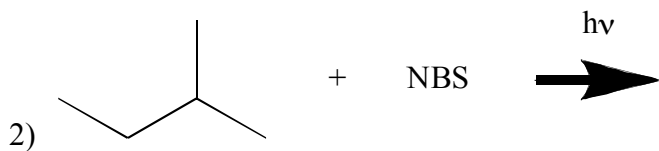
Determine the identity of the products of the given reaction by using the mass spectra. Then propose a likely mechanism of fragmentation for the numbered peaks.



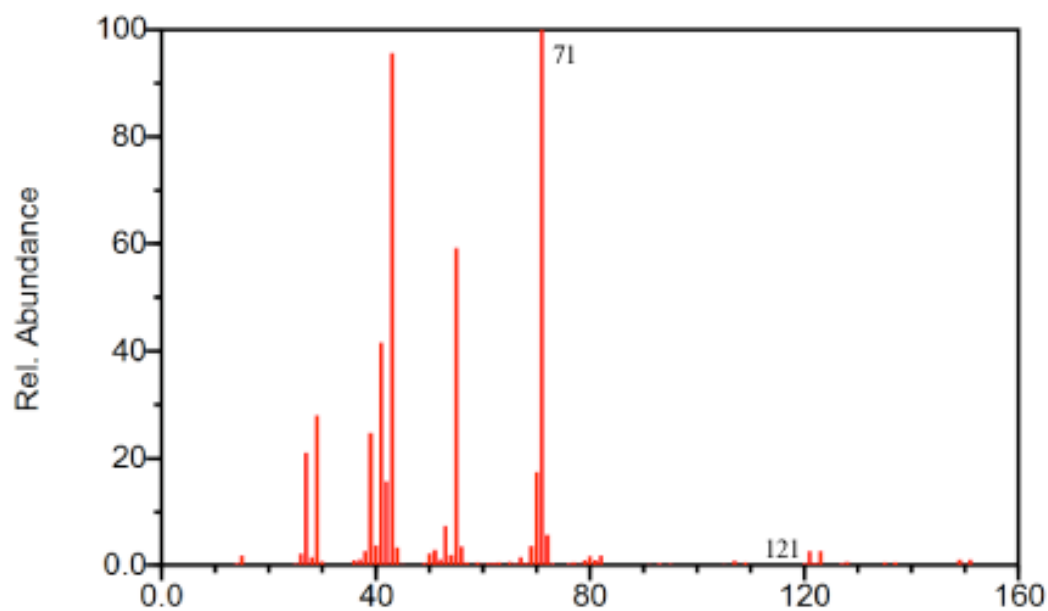


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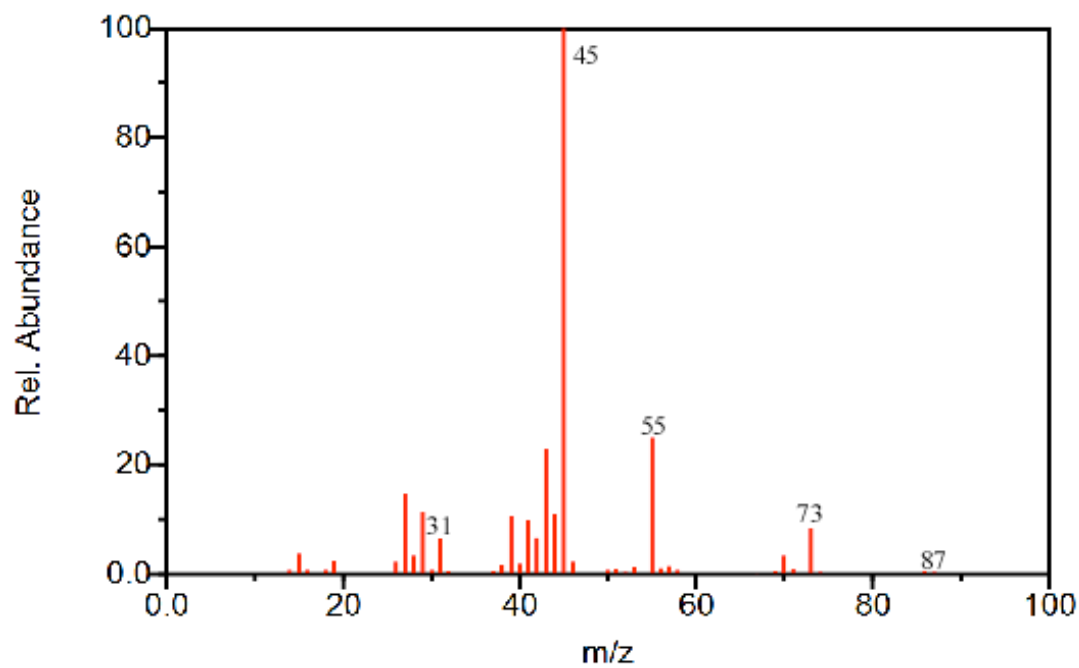
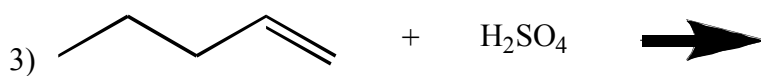
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m/z  
H<sub>2</sub>O

2

3

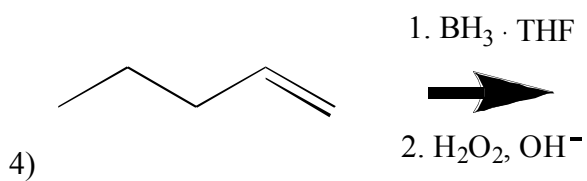
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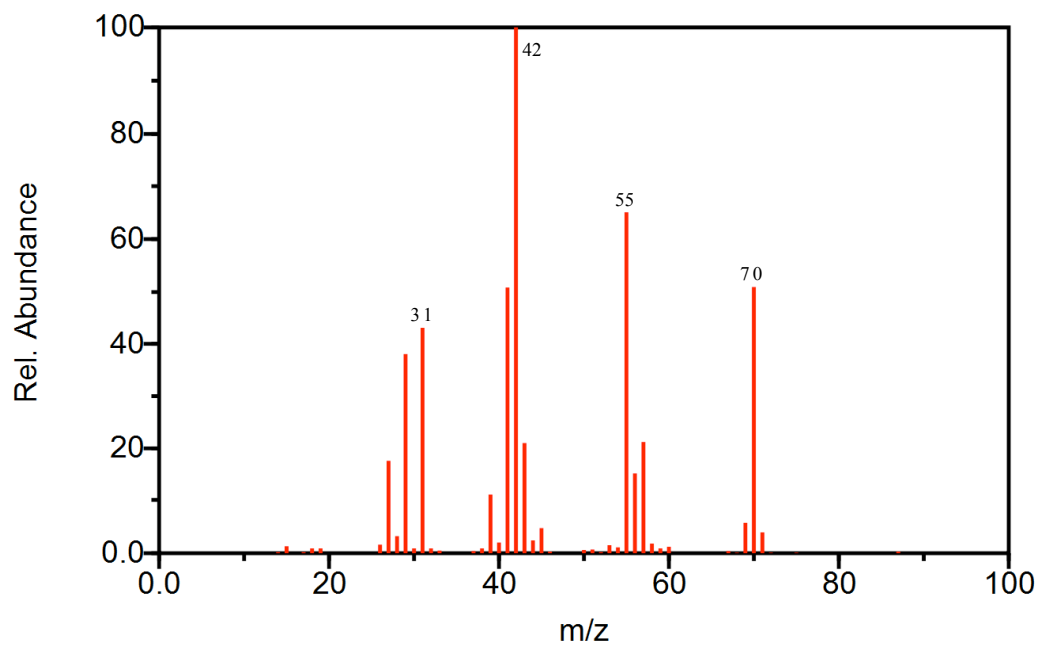
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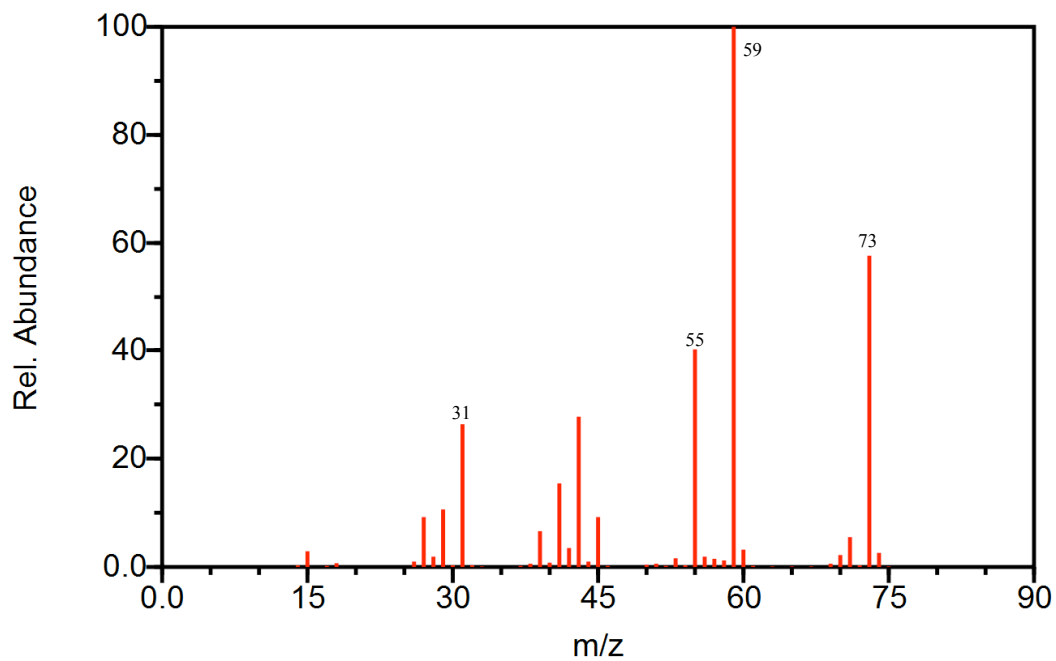
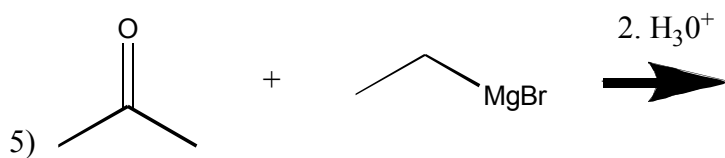


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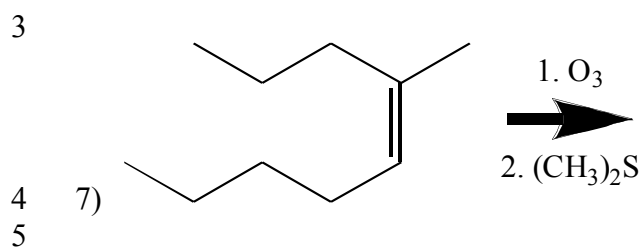
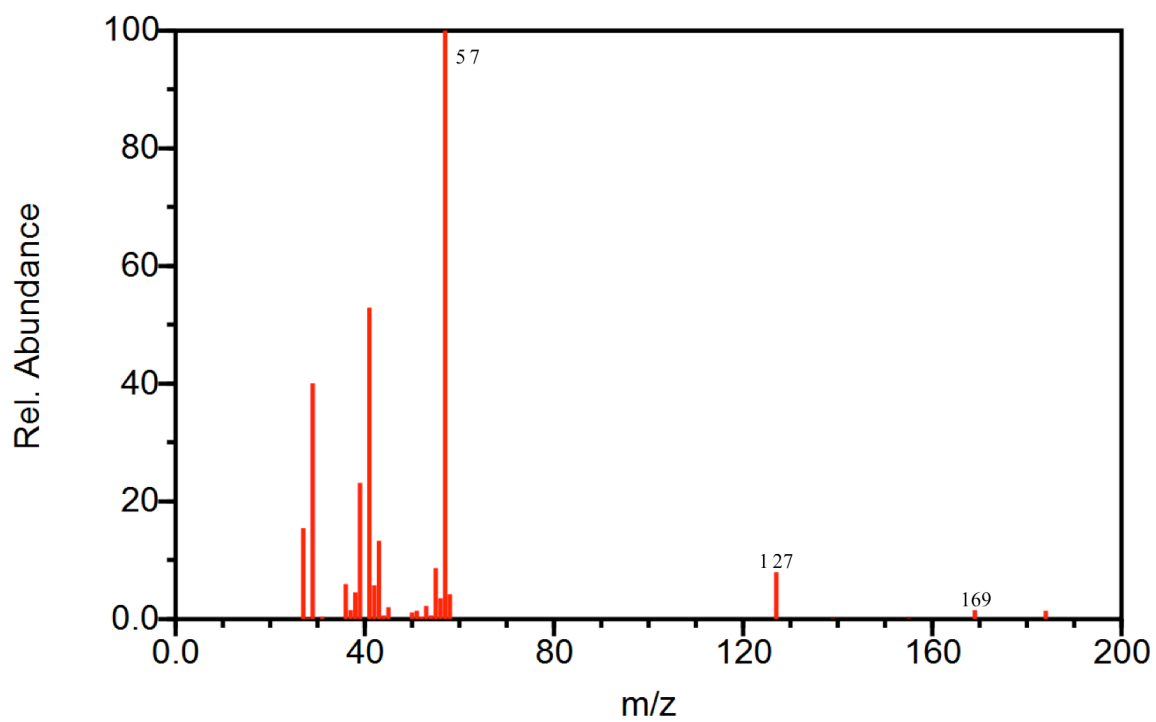
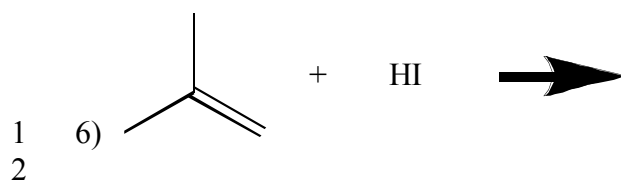
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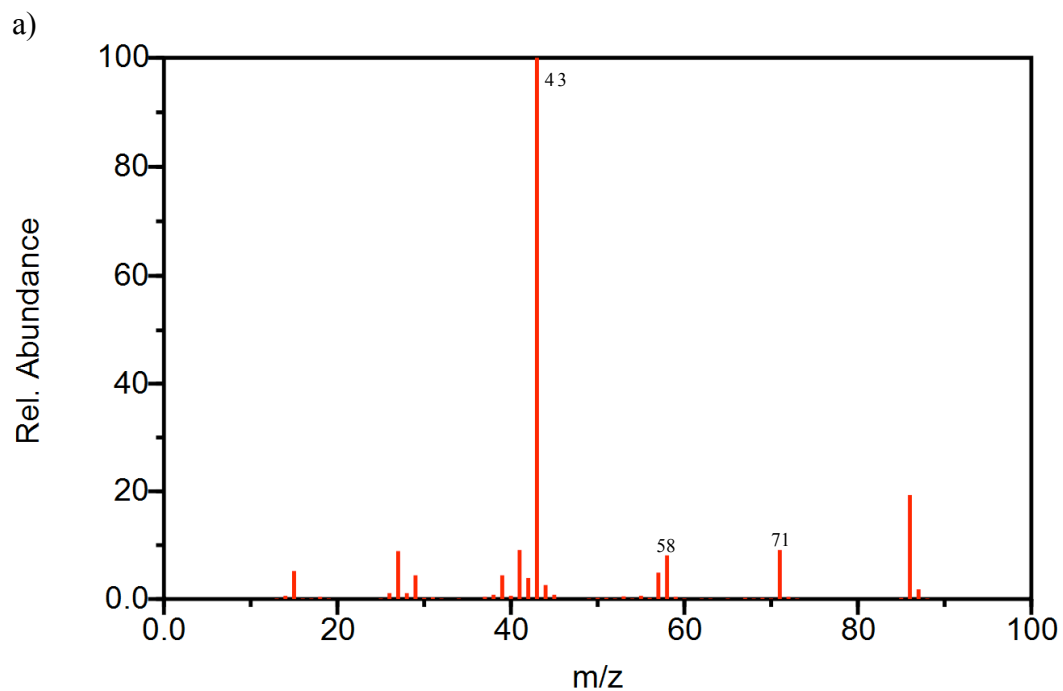
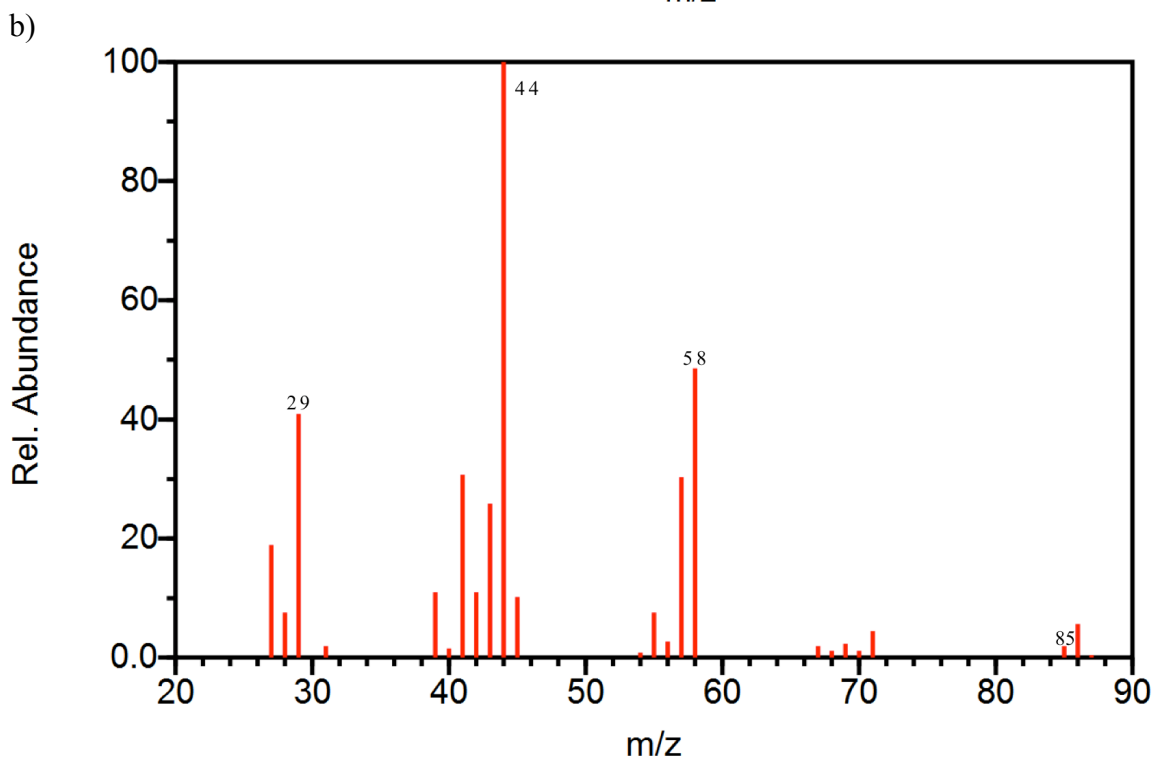
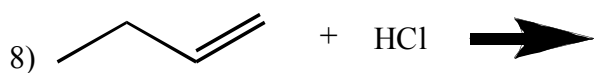


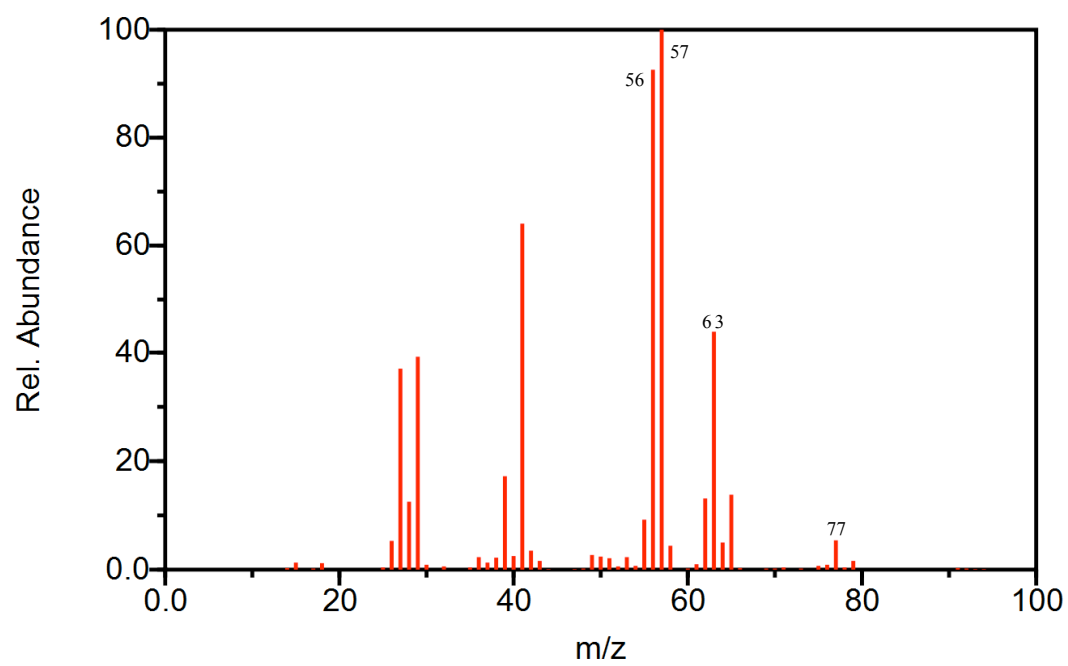
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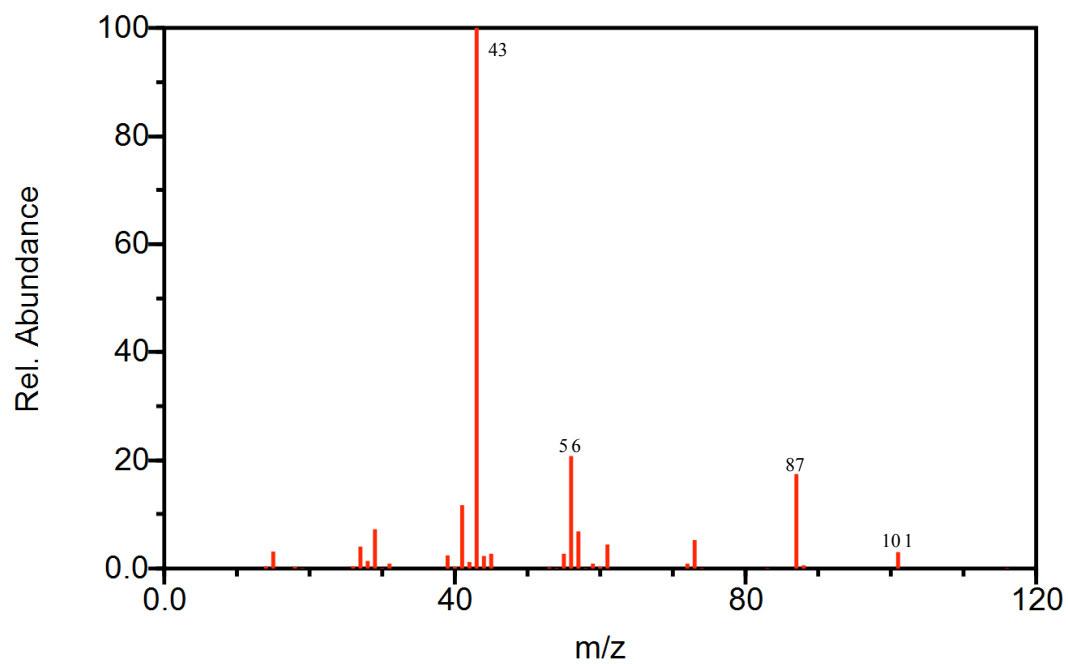
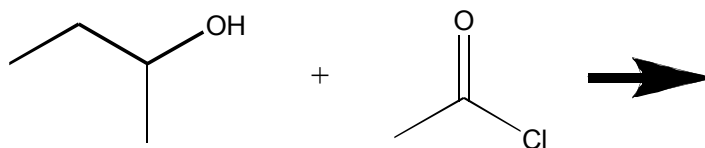
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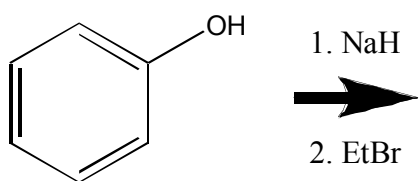
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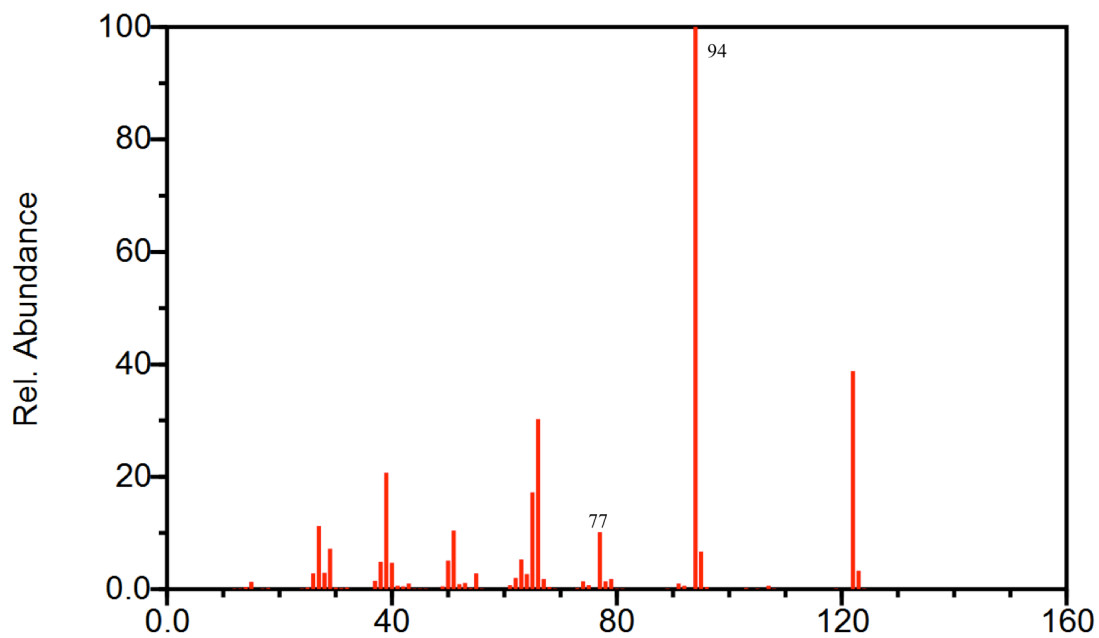


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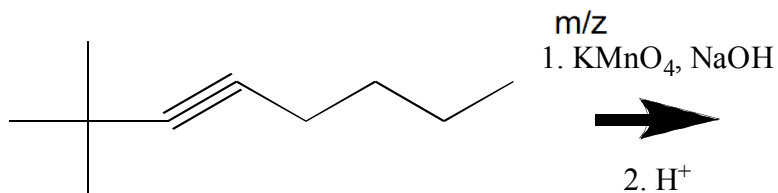
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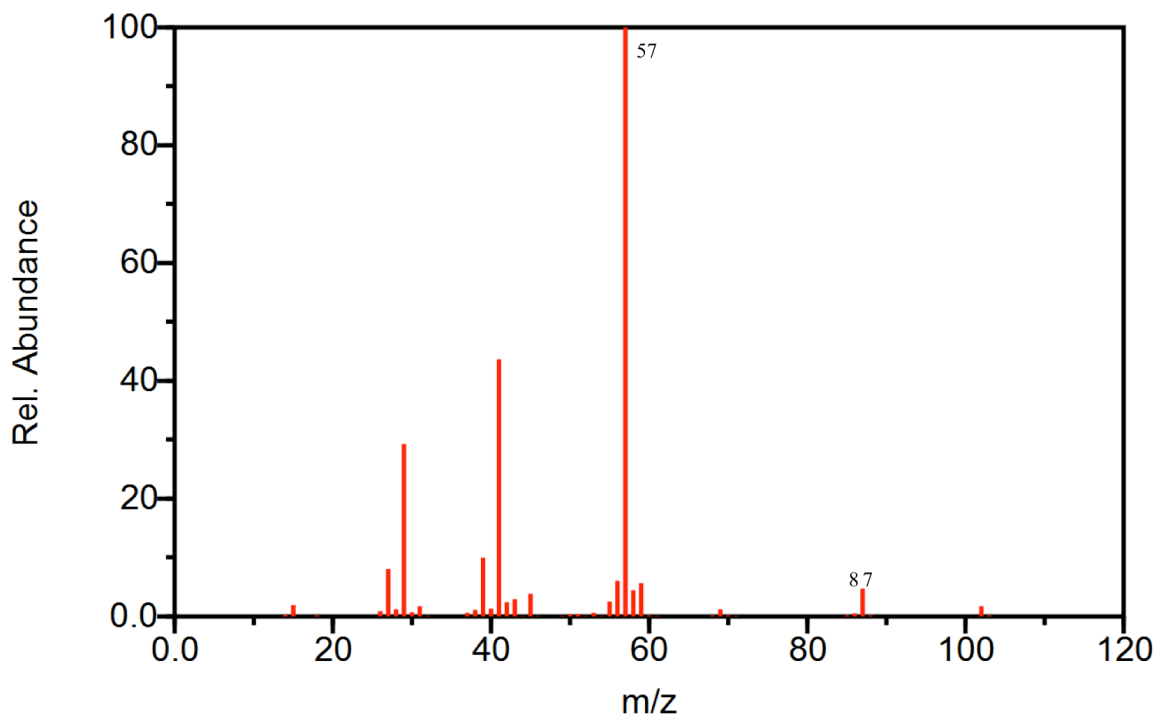
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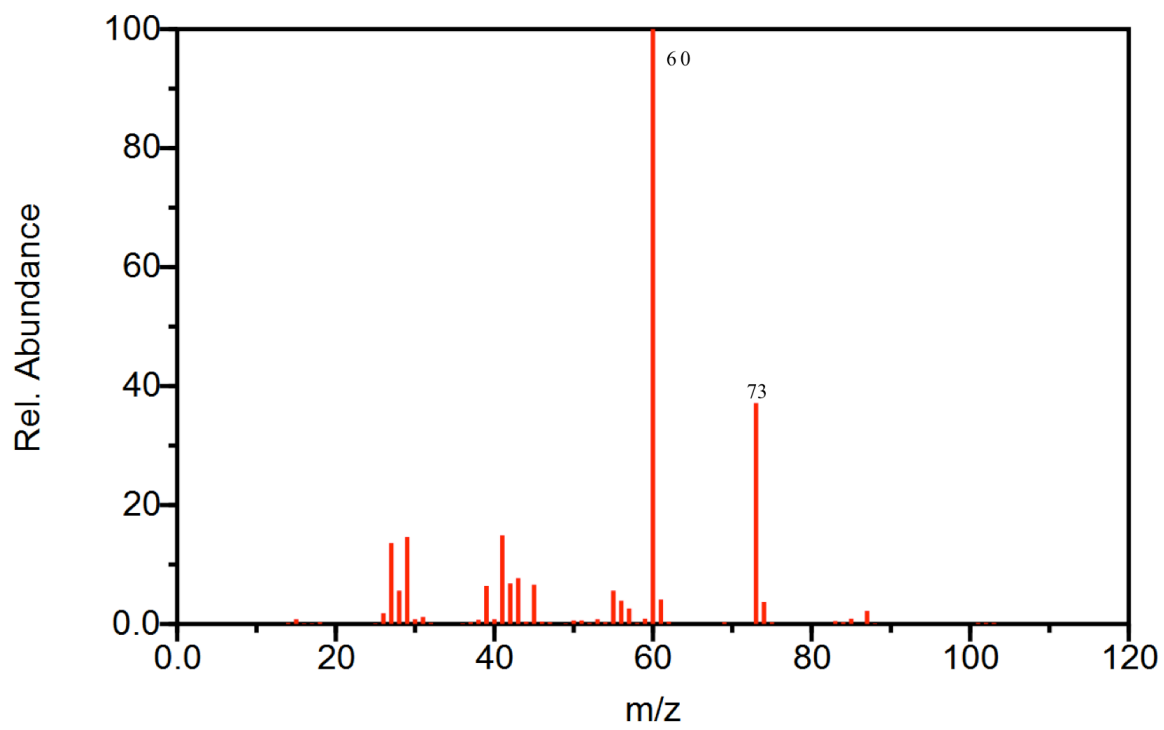
a)



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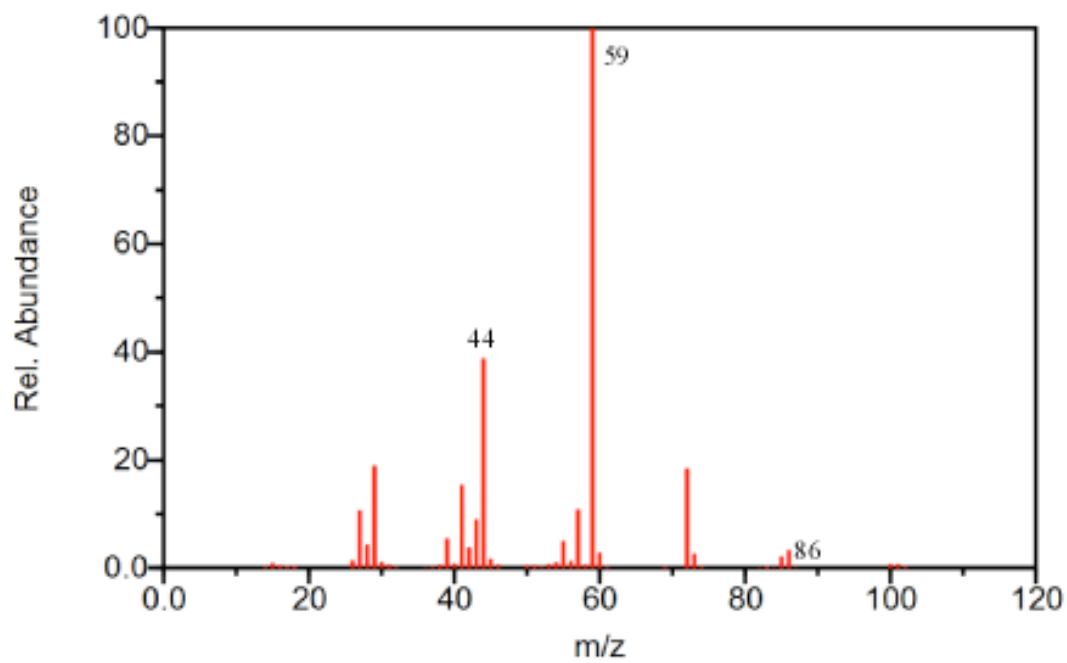
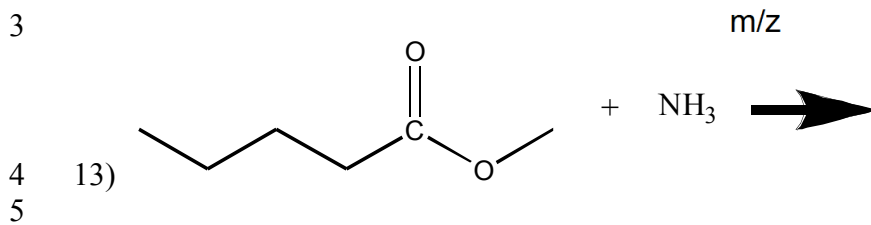
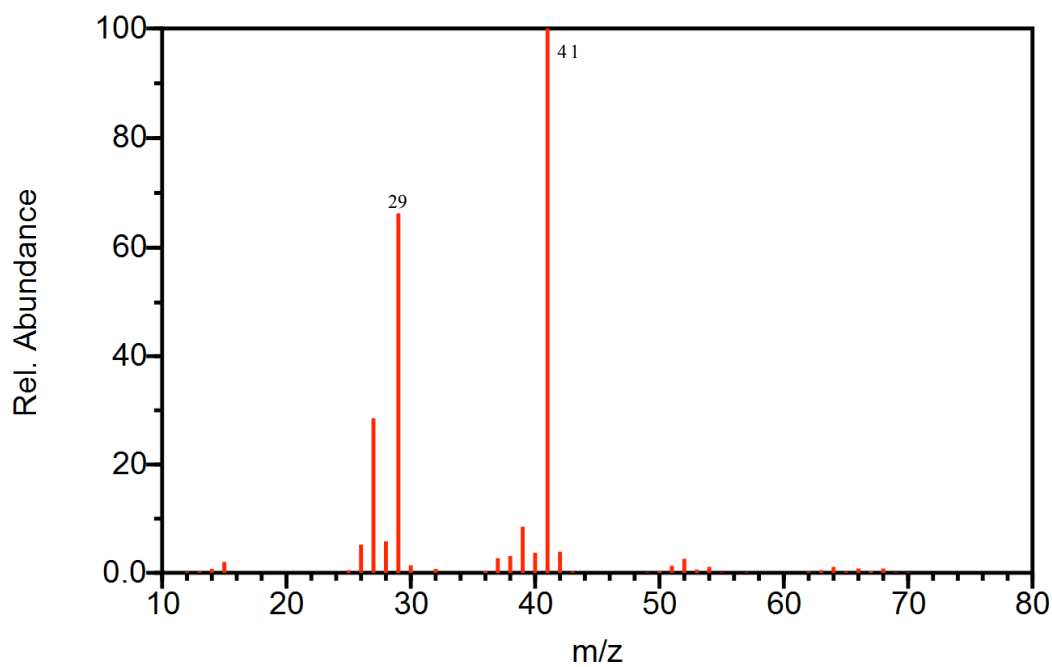
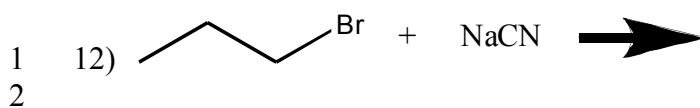
7

b)



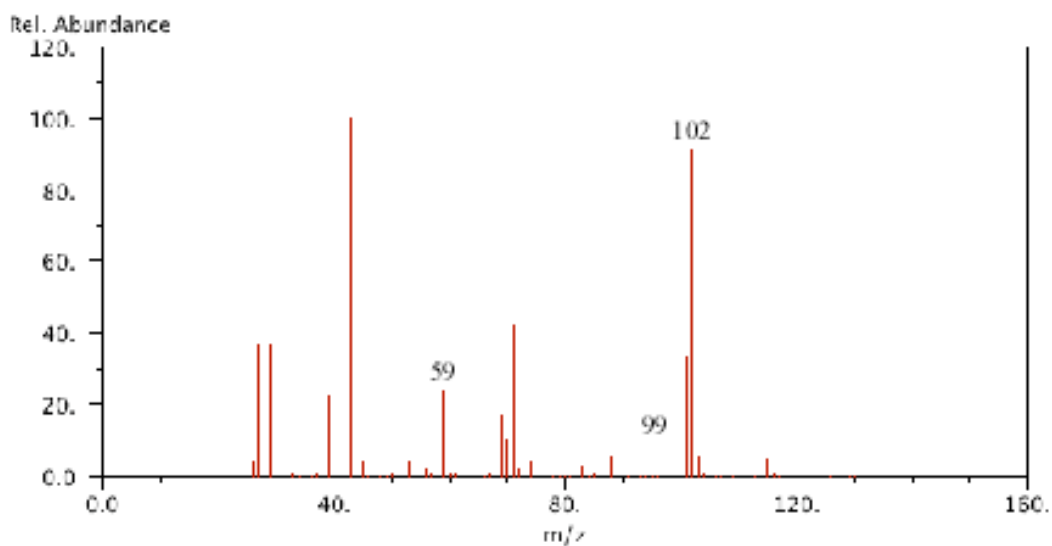
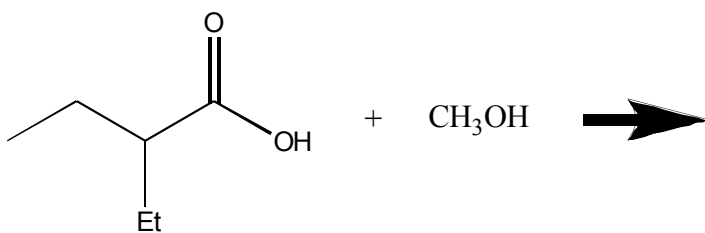
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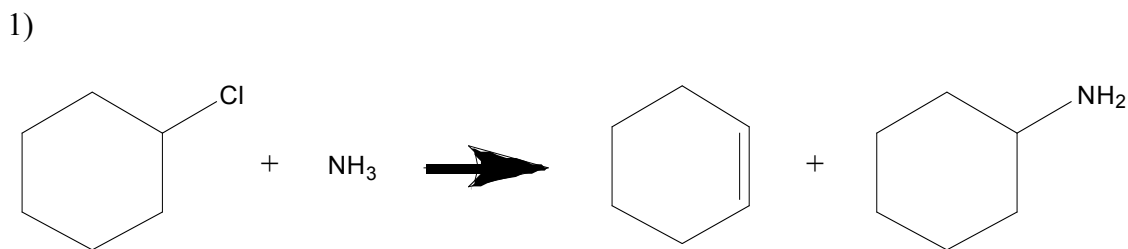


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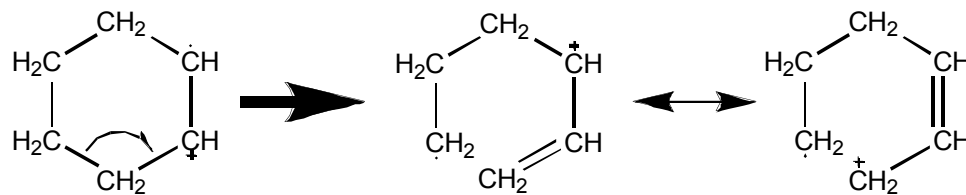
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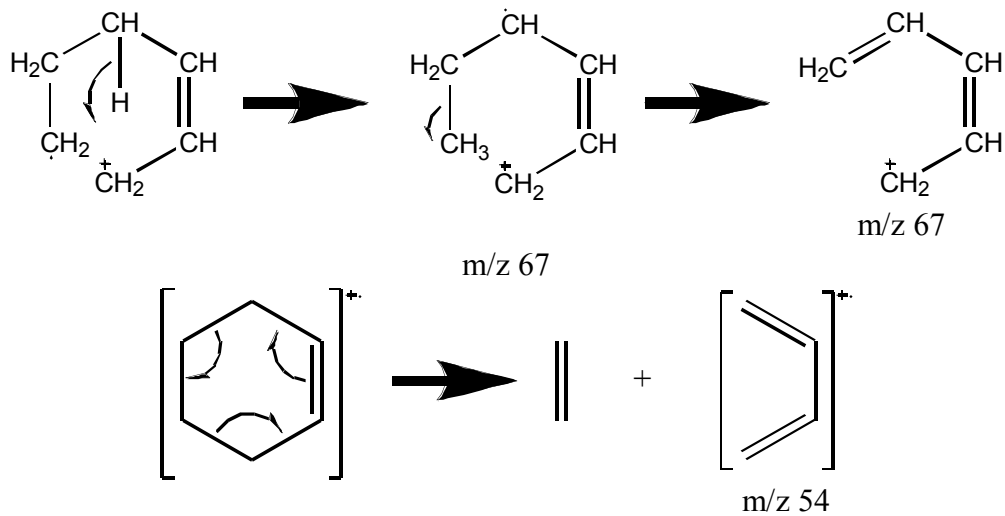


## 6.22 Problem Solutions

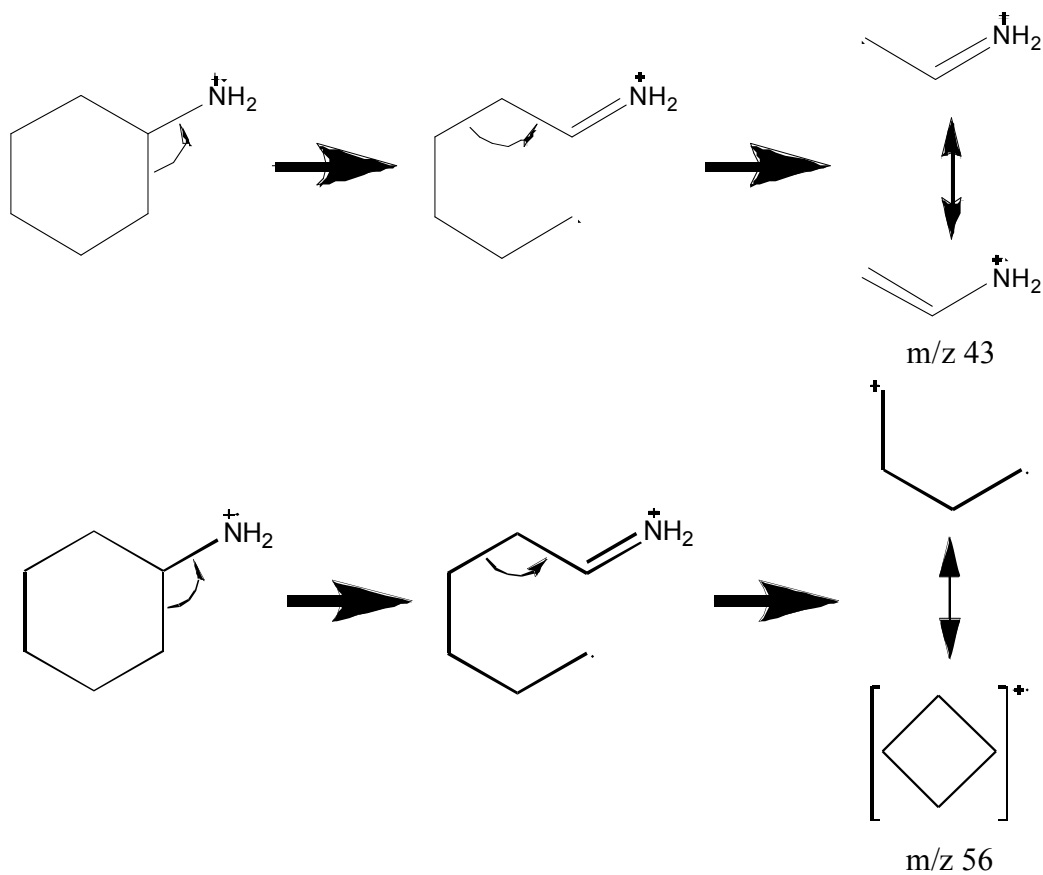


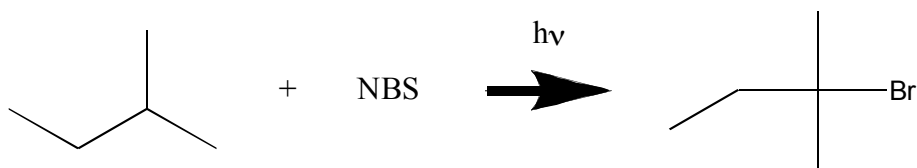
a) The  $M^+$  peak at 82 suggests that the spectrum is of cyclohexene.



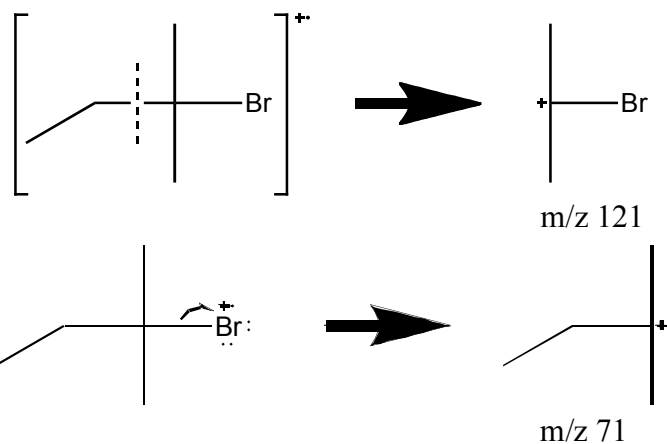


b) The odd  $M^+$  peak at 99 suggests the nitrogen containing compound cyclohexanamine.

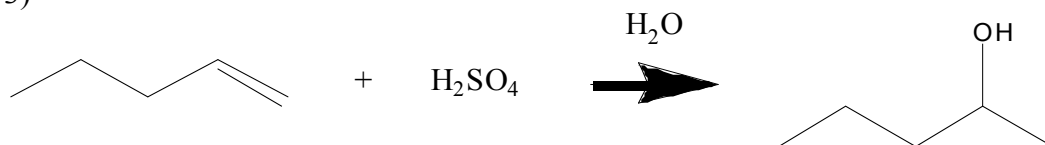




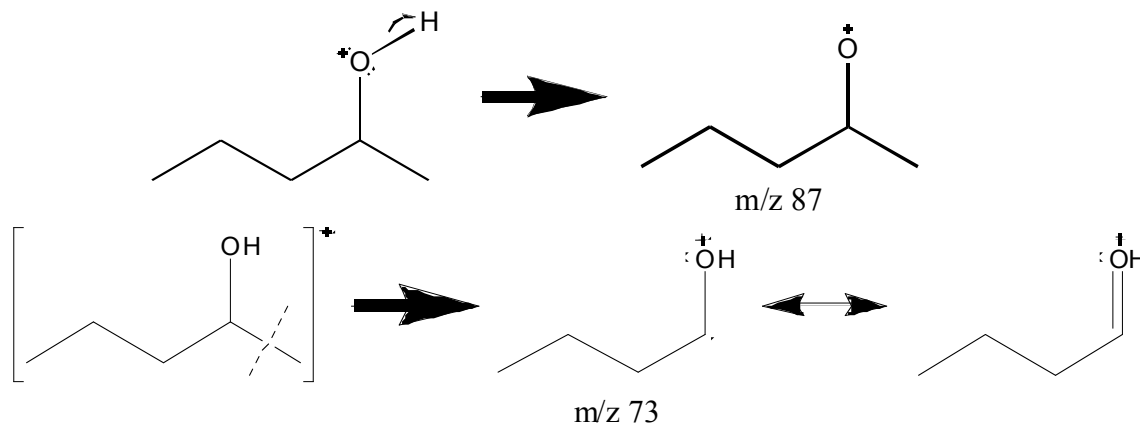
The pair of peaks at 121 and 123 as well as at 149 and 151 indicates that the compound contains bromine. These, in combination with other prominent fragments, suggest that the compound is 2-bromo-2-methylbutane.



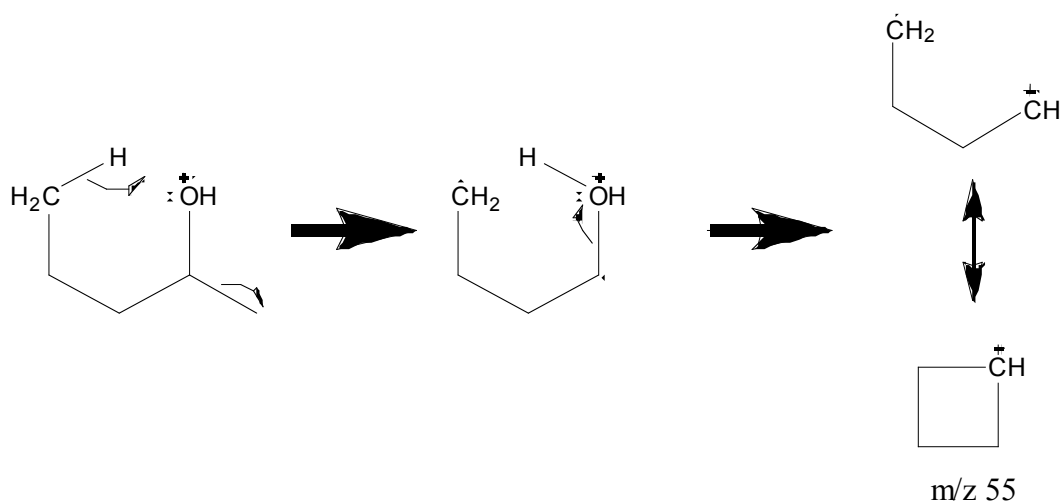
3)



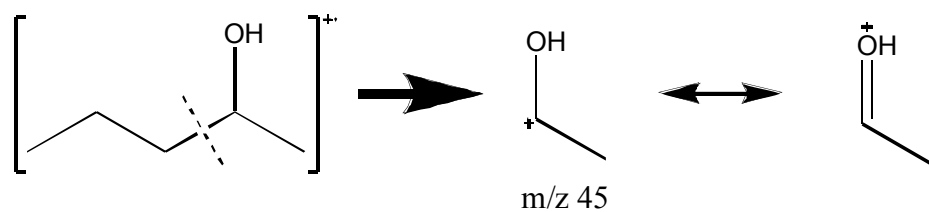
The peak at  $m/z$  87 is deceiving because it is not the molecular ion in this case. By utilizing other prominent peaks ( $m/z$  73 and 45) and our knowledge of organic chemistry, we can deduce that the mass spectrum is of 2-pentanol.



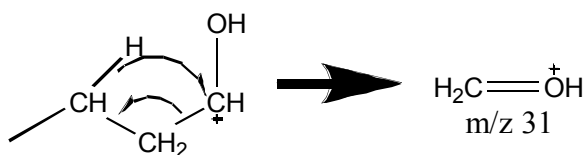
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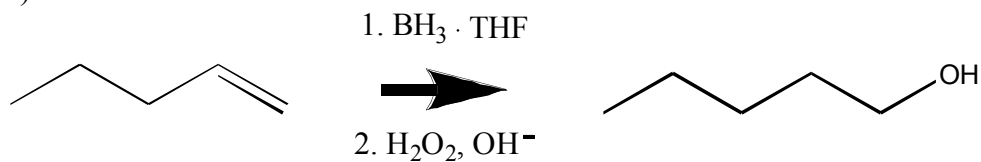


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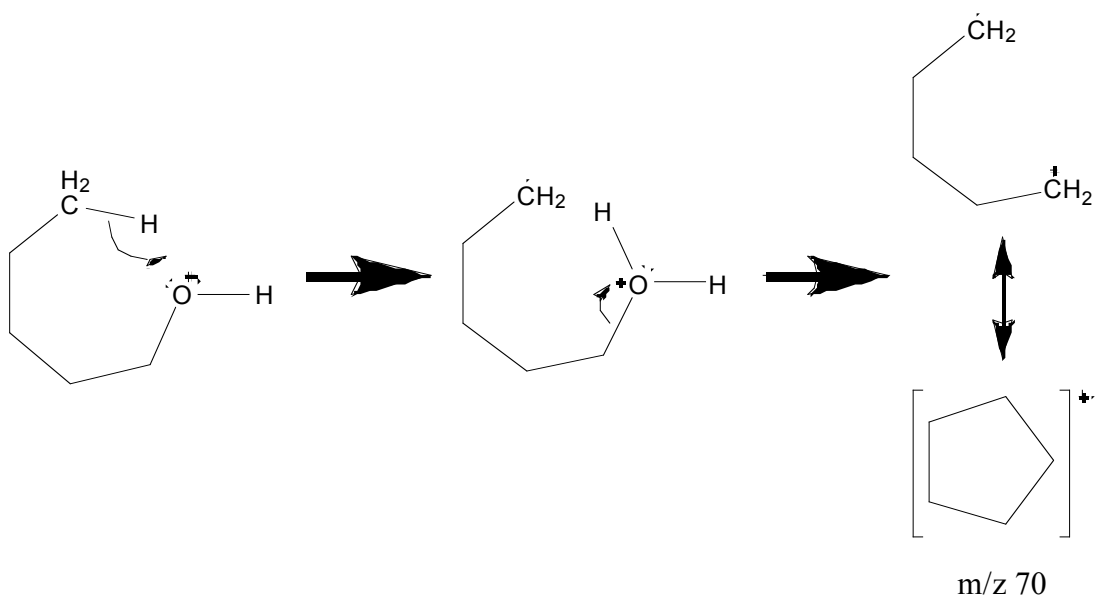
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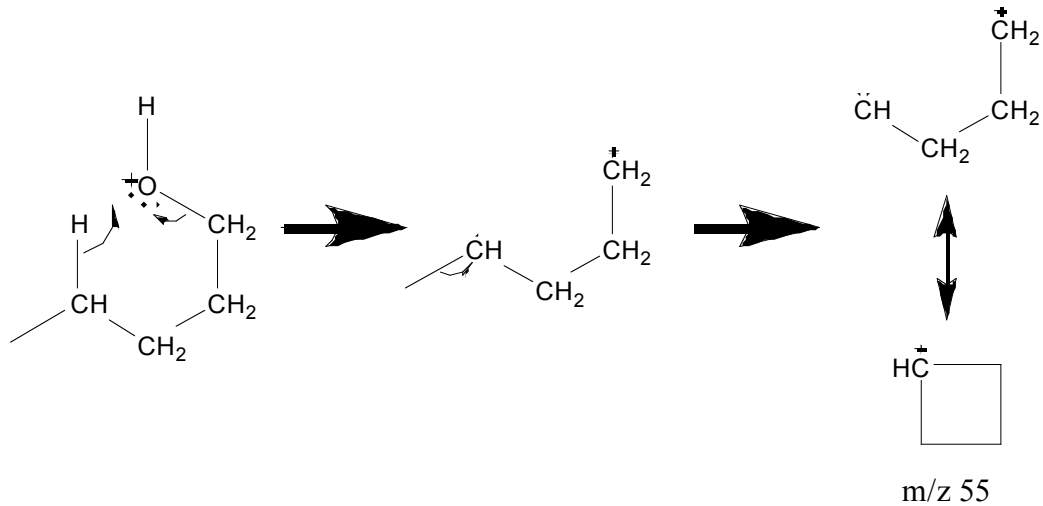
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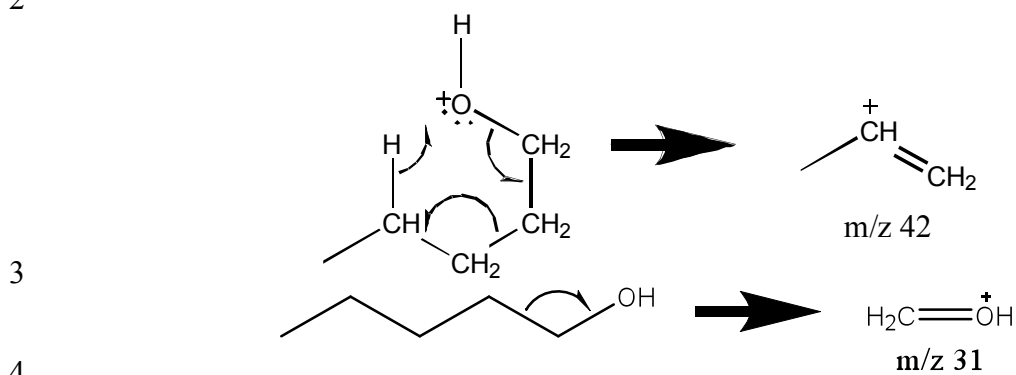
The molecular ion is missing from the spectrum which is to be expected from a straight chain alcohol. While it would be possible to determine the molecular weight from a soft ionization technique, the existence of other prominent peaks indicates that the spectrum is of 1-pentanol.



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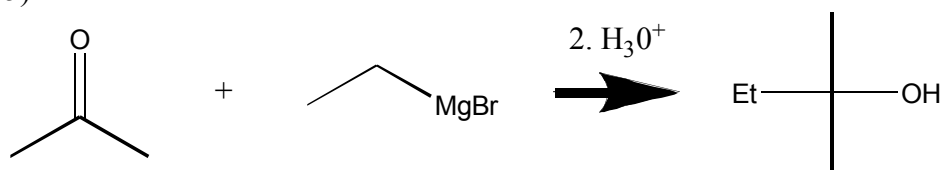


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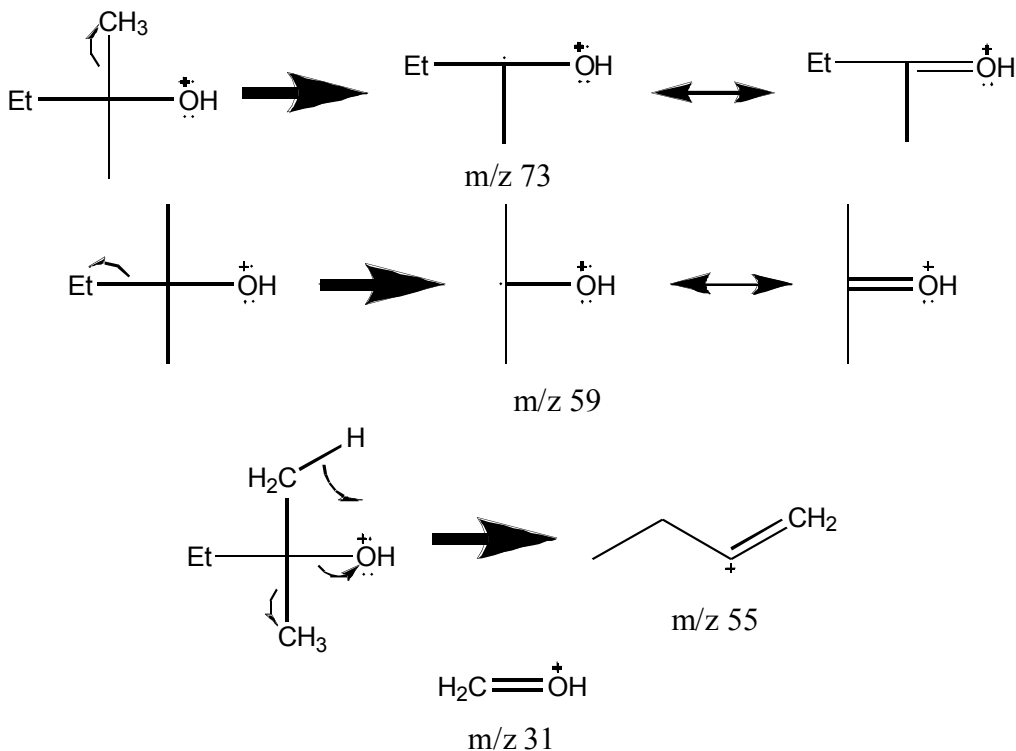
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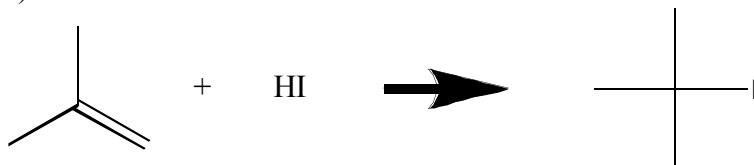
1 5)



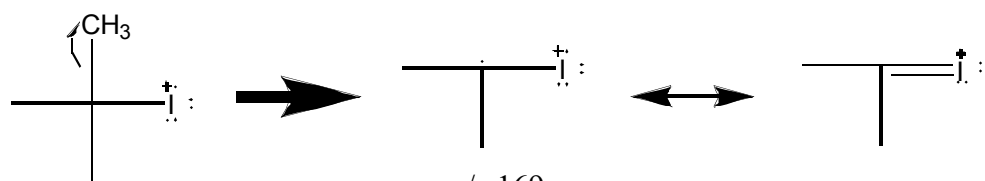
4 The molecular ion is missing from the spectrum which is to be expected. The existence  
5 of other prominent peaks indicates that the spectrum is of 2-methyl-2-butanol.  
6



13 6)



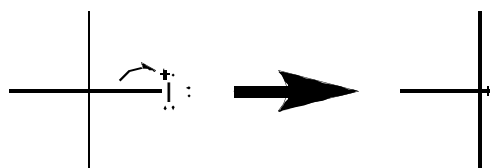
16 The molecular ion at 184 as well as the large gap in the spectrum in combination with the  
17 peak at 127 indicates that the spectrum contains iodine and can be attributed to tert-butyl  
18 iodide.  
19



m/z 169

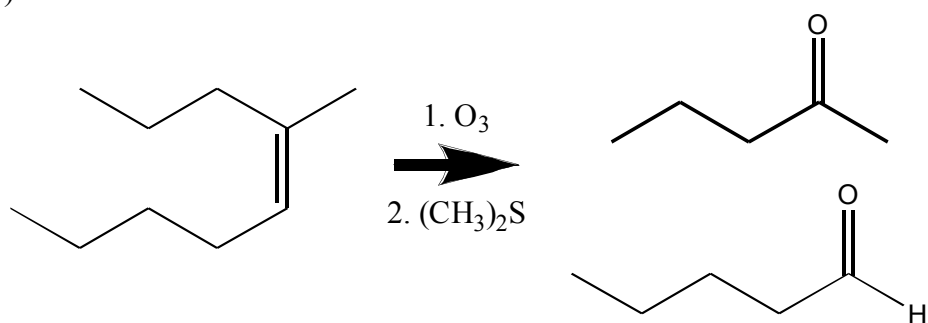
$\text{I}^+$

m/z 127

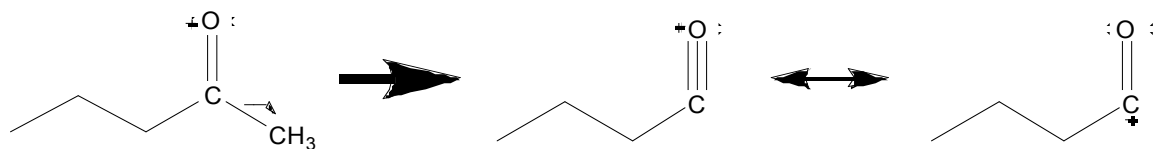


m/z 57

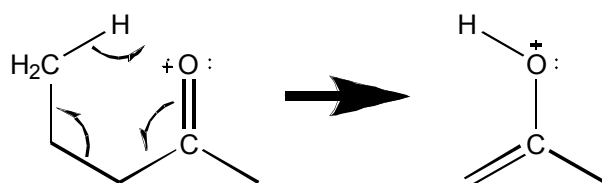
7)



a) The molecular ion at 86 doesn't help distinguish compound a from b. The more intense molecular ion suggests that a) is the ketone, 2-pentanone, rather than the aldehyde.

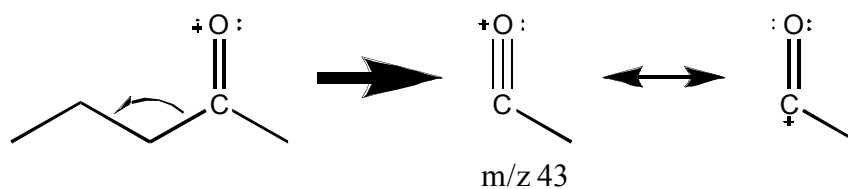


m/z 71

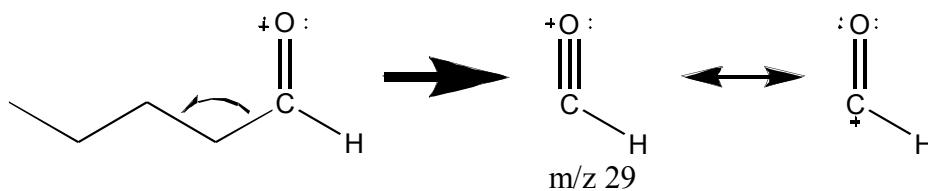
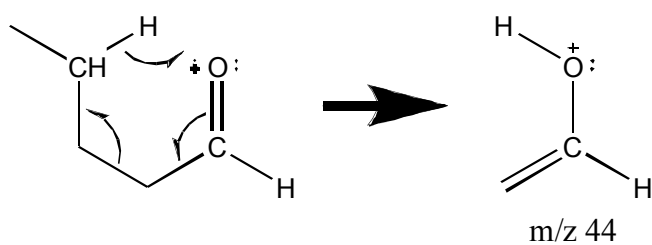
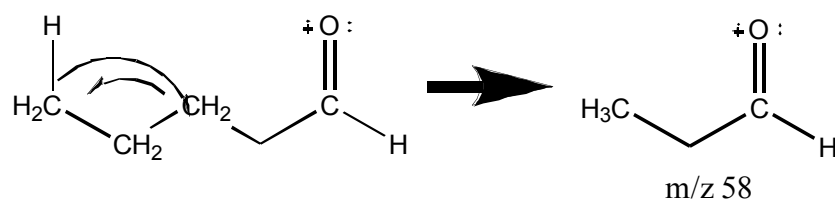
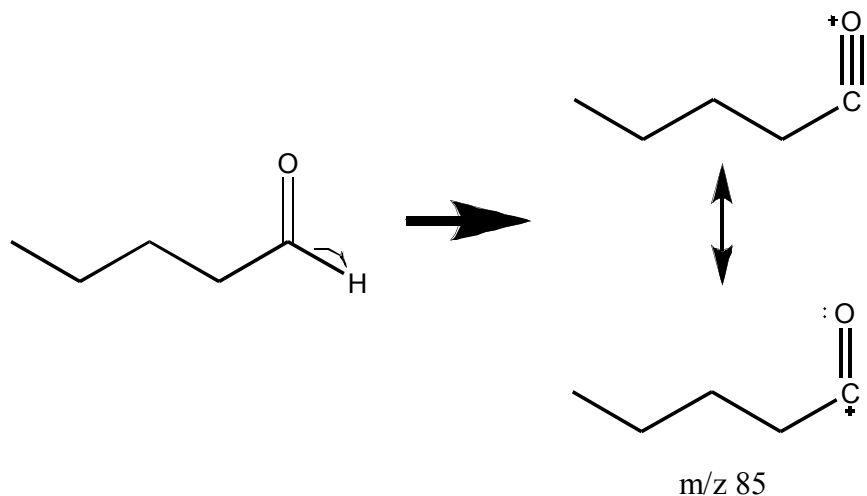


m/z 58

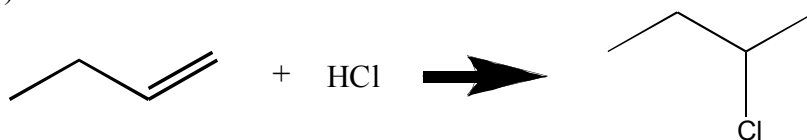




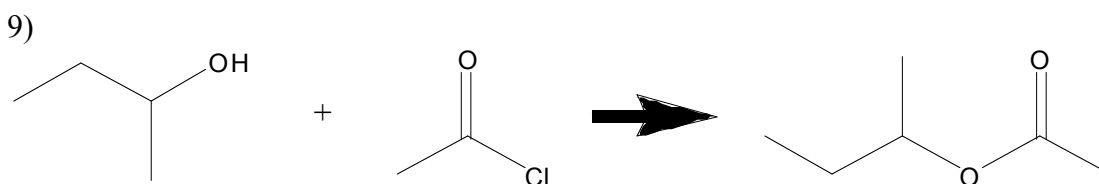
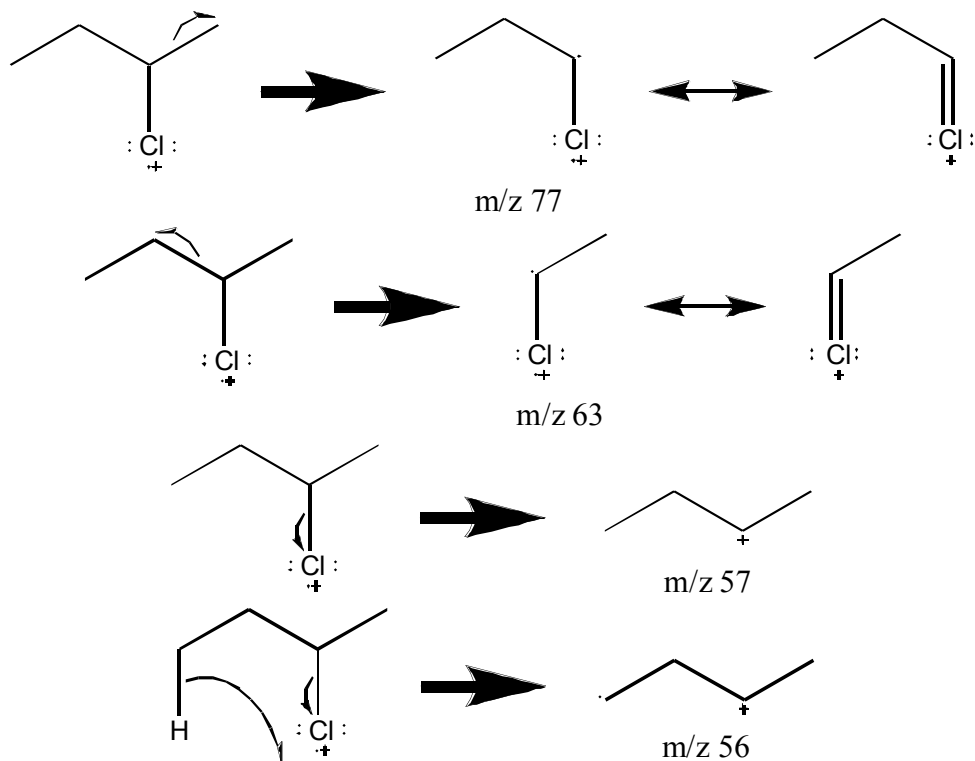
b) The presence of the M-1 peak helps to indicate that compound b) is the aldehyde, pentanal.



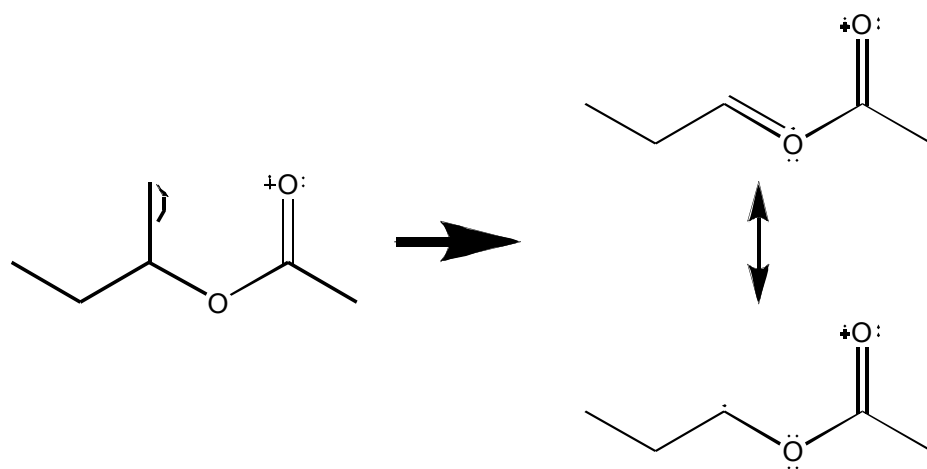
8)



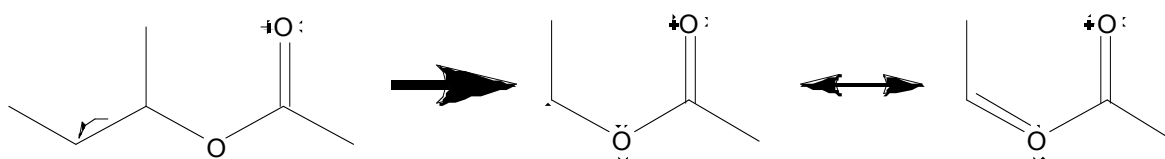
While the molecular ion is absent from the spectrum, the peaks at  $m/z$  77 and 63 indicate the presence of a chlorine atom in the sample indicating that the compound is 2-chlorobutane.



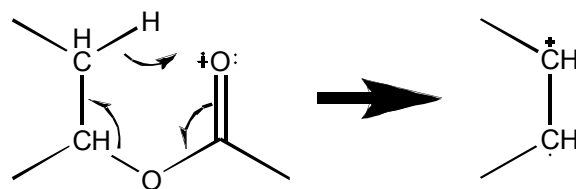
While the molecular ion is absent, the other prominent peaks indicate both the functional group and the hydrocarbon structure of the compound sec-butyl acetate.



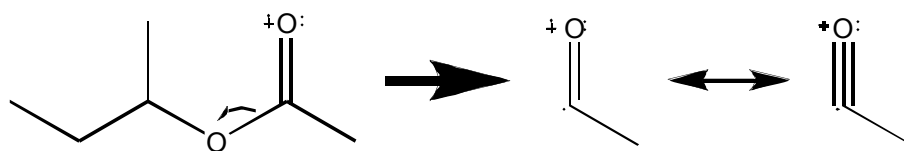
m/z 101



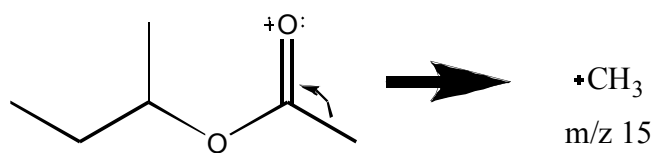
m/z 87



m/z 56



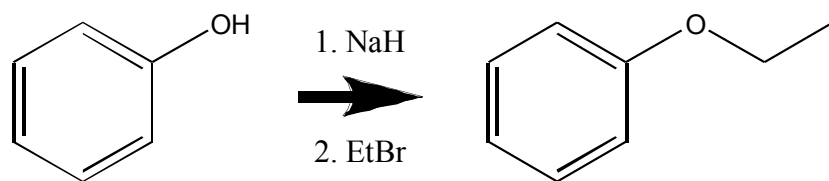
m/z 43



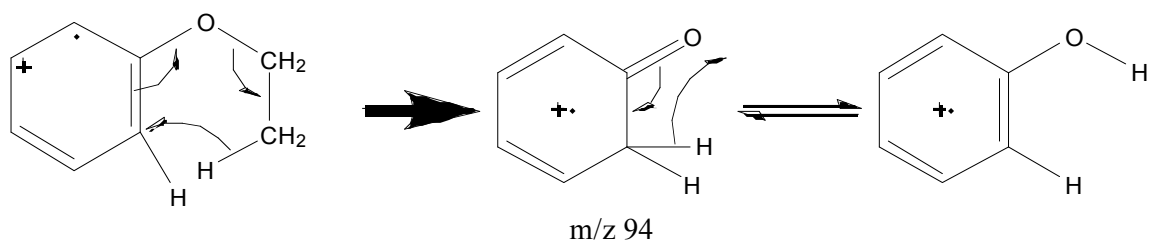
$^+\text{CH}_3$

m/z 15

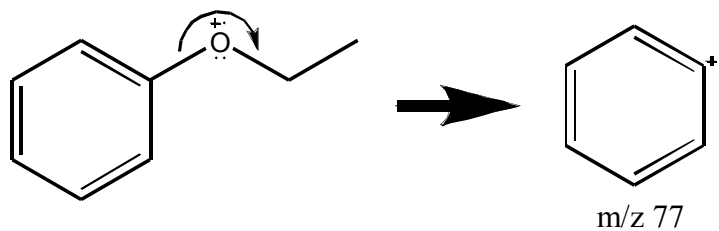
10)



1 The molecular ion of this ether is stabilized by the aromatic group. At m/z 122 it  
2 indicates that the spectrum is of ethoxybenzene.  
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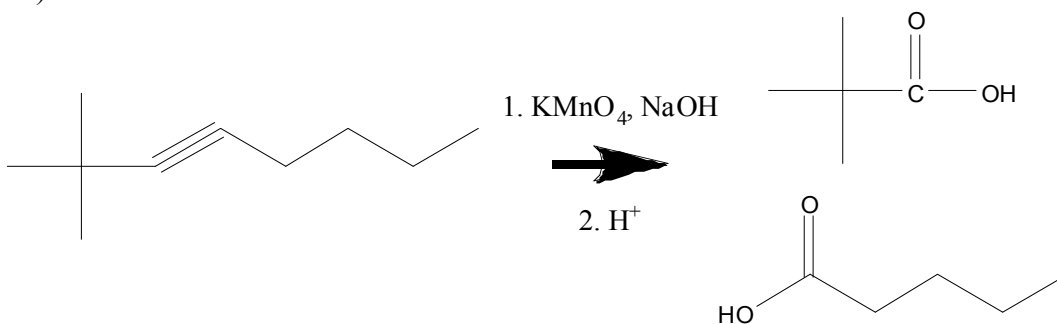
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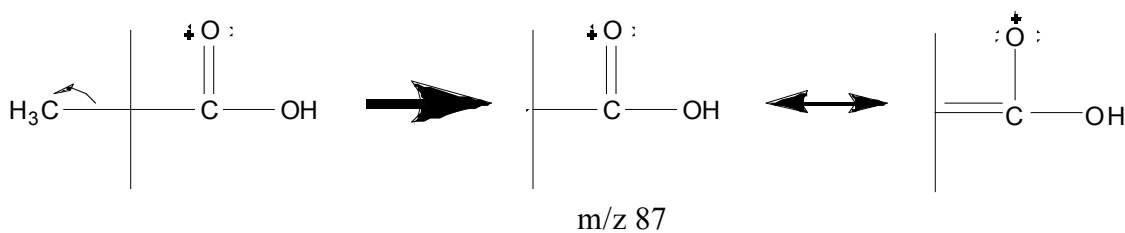
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a) The molecular ion at 102 fails to distinguish between the two expected carboxylic acids. The prevalent peaks at  $m/z$  87 and 57 as indicates that the compound is pivalic acid.



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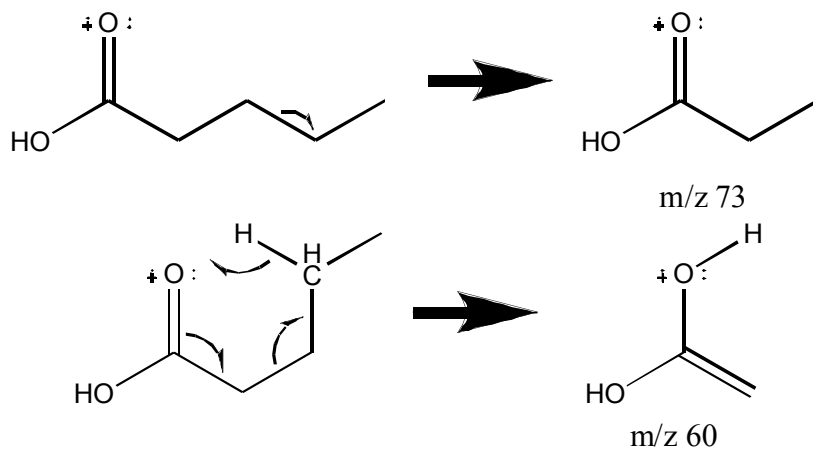
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b) The missing molecular ion can be expected from a carboxylic acid. The prevalent peaks at  $m/z$  73 and 60 indicates that the compound is pentanoic acid.



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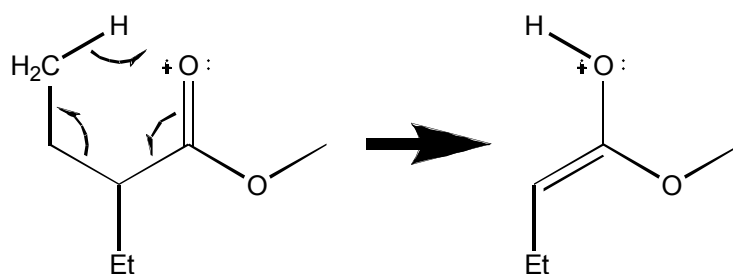
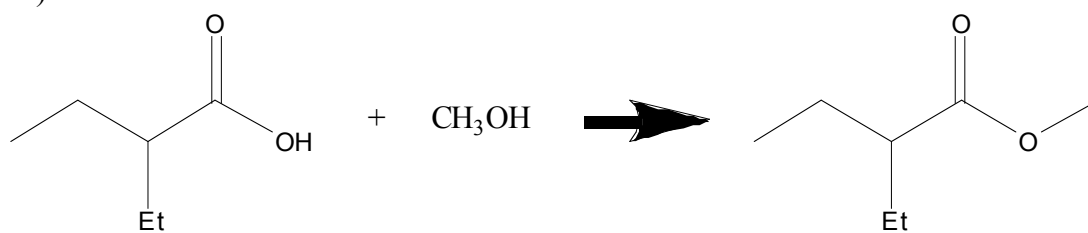
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1 14)



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