

Organic Chemistry 2 Primer 2021

Rhett C. Smith, Ph.D.

Tania Houjeiry, Ph.D.

Andrew G. Tennyson, Ph.D.

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BY RHETT C. SMITH, TANIA HOUJEIRY, AND ANDREW G. TENNYSON

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Executive Editor: Rhett C. Smith, Ph.D. You can reach him through our office at: IQ@protonguru.com

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Lesson VII.8. Introduction to Mass Spectrometry

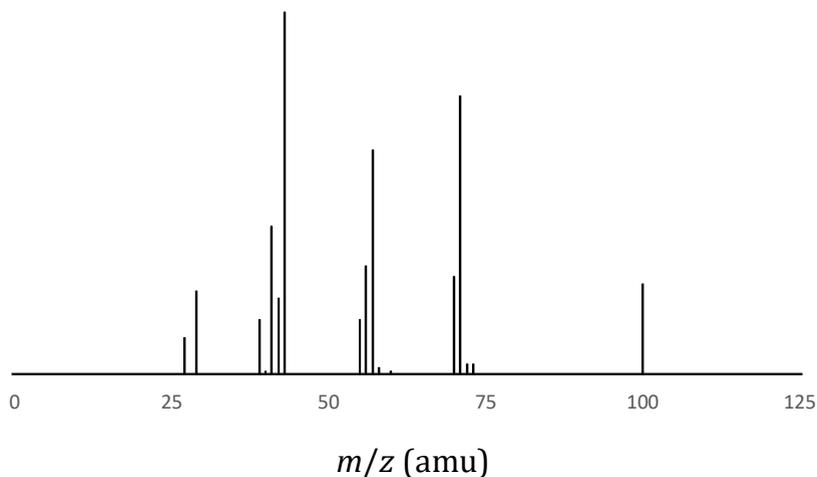
Lesson VII.8.1 Formation, Separation, and Detection of Molecular Ions

Mass spectrometry is a technique that can be used to determine the molecular weight of a molecule as well as the molecular weight of some of the pieces of the molecule that form when it is fragmented by the application of energy. Knowing the molecular weight and the mass of specific fragments of the molecule can be used in conjunction with the other analytical techniques we have seen in Lessons VII.1-7 to assist in characterizing molecules.

Electronic detectors can most easily detect charged, rather than neutral, species. For this reason, the first step in mass spectrometry is creating ions from neutral molecules. The ion that is made by taking one electron away from the neutral molecule has the same molecular weight as the neutral molecule that we are trying to examine. This molecule is called the **molecular ion**. We have seen some ways to make ions by chemical reactions (for example, by heterolysis). A molecular ion can also be formed by "ionizing" a molecule, a process which removes an electron from or adds an electron to a neutral molecule to afford a cationic or anionic molecular ion, respectively. If only a single electron is removed from or added to a neutral molecule, the resulting molecular ion is a "radical cation" or "radical anion".

Mass spectrometric analysis of an analyte is a three-step process involving the formation, separation, and detection of molecular ions. The ionization technique most commonly employed for small organic molecules is "electron ionization" (EI), whereby an analyte molecule in the vapor phase is bombarded by a stream of high-energy electrons, which dislodges an electron from the analyte molecule to afford a cationic molecular ion, which is abbreviated as "[M]⁺". Although there are other mass spectrometry techniques, in this course we will assume all spectra come from the EI process.

After the various ions have been formed, a mass spectrometer employs one or more internal electric and/or magnetic fields to separate the ions according to their mass-to-charge (m/z) ratios. An electromagnetic field will deflect the path of a traveling ion to a greater extent if m is smaller (lighter molecules) or z is larger (higher charges). In this manner, a mass spectrometer is able to separate and select ions based on their m/z ratios. The final stage of the mass spectrometry experiment is detection, whereby the separated ions either impact a detector element (which imparts a charge to the detector) or pass by a detector element (which induces an electric current). Because neutral species carry no Coulombic charges, they are undetectable. The typical mass spectrum shows a plot of intensity (y -axis) versus m/z (x -axis). In this book, z is always one, so the numeric value on the x -axis corresponds to the value of the molecular weight of the fragment giving the peak. A typical mass spectrum is shown below:



Lesson VII.8.2 Predicting Molecular Ion Structure

As a general rule, it is hardest to remove an electron from a σ -bonding orbital than π -bonding orbital, and it is easiest to remove electrons from a non-bonding orbital (i.e., a lone pair). Therefore, ionization will remove an electron from a lone pair before a π -bond, and it will remove an electron from a π -bond before a σ -bond. Removal of an e^- from a lone pair leaves behind a radical cationic charge ($\bullet+$) on that individual atom. Removal of an e^- from a π -bond leaves behind a cationic charge (+) on one atom of the π -bond and a radical charge (\bullet) on the other atom. Radical stability has a greater impact than cation stability, so the + and \bullet will be preferentially be situated according to maximize radical stability. Keep in mind that ionization is a high-energy process that occurs in the gas phase, so other species with the radical in less stable positions can also be formed by ionization, but usually in lower yields. If the molecule is an alkane, simply draw square brackets around the molecule and place the $\bullet+$ symbol at the top on the outside of the right bracket (there is no convenient way to represent σ -bonds which contain only 1 electron). In general, drawing the $\bullet+$ localized to a specific atom or group of atoms is preferred, because it makes understanding fragmentation mechanisms more intuitively accessible.

Lesson VII.8.3 Isotopic Abundance and Molecular Mass

When converting mass to moles in organic lab, our calculation of the molecular weight will use 12.011 as the atomic mass of carbon. However, this number is the average mass of a carbon atom. No actual carbon atom weight 12.011 amu. Instead, 98.9% of all the carbon atoms in the Universe have a mass of 12.000 and the remaining 1.1% have a mass of 13.003. Consider this from a different perspective: in a sample of 100 CH_4 molecules, 99 will have a carbon with a mass of 12.000 and the 100th will have a carbon with a mass of 13.003. Ionizing this sample of 100 CH_4 molecules will generate 99 molecular ions with an m/z ratio of 16 and 1 molecular ion with an m/z ratio of 17. Clearly, we will see a huge peak in the mass spectrum at 16 amu and only a small peak at 17 amu.

Although there are some exceptions we will cover in subsequent lessons, for the purposes of sophomore organic chemistry you only need to consider the atomic mass of the most abundant isotope of each element when calculating the molecular masses of the various molecular ions and descendant fragments. In other words, if you observe a molecular ion peak with an m/z value of 170.21, and you know from other techniques that the analyte only has hydrogen and carbon atoms, you would only use the atomic mass of hydrogen-1 (1.0) and the atomic mass of carbon-12 (12.0) when calculating the number of hydrogen and carbon atoms present in that ion.

Lesson VII.8.4 Isotopic Peaks

In Lesson VII.8.3, we saw that many of the elements found in organic molecules essentially have only one isotope. Notable absences from the table in that lesson were chlorine and bromine. Whereas fluorine is 100% fluorine-19, chlorine is 76% chlorine-35 and 24% chlorine-37, and bromine is 51% bromine-81 and 49% bromine-81. As a result, a molecular ion or fragment that contains either Cl or Br will exhibit two prominent peaks, called the " m " and " $m+2$ " peaks because they differ by 2 units of m/z . Thus, if you are given a mass spectrum of an unknown compound and you observe the m and $m+2$ pattern for some of peaks, you should immediately conclude that the unknown compound contains one or more chlorine or bromine atoms.

Lesson VII.9. Introduction to Fragmentation Mechanisms

Lesson VII.9.1 What is Fragmentation and Why Does It Occur?

In the context of mass spectrometry (MS), fragmentation is a term that describes when a molecular ion breaks apart into 2 or more lower-molecular weight components. Because fragmentation processes can involve the breakage and formation of σ -bonds, it is useful to think of fragmentation processes as chemical reactions. Bombardment of a molecule with high-energy electrons transfers a significant amount of energy to that molecule, thus a molecular ion formed by EI will often undergo multiple fragment processes.

Why do molecular ions generated by a mass spectrometer undergo fragmentation? Keep in mind that every atom in nearly every organic molecule has an octet, so ionizing a molecule means that some atom(s) will no longer have a complete octet. We know that an atom that lacks a complete octet is much higher in energy than an atom that has a complete octet, so the ionization of a molecule affords a higher energy species, so we have to add a lot of energy to get fragmentation to occur. As we mentioned in the previous lesson, ionization is a very high-energy process that occurs in the gas phase, so a $\bullet+$ species can fragment to make the more stable $+$ (with less stable \bullet) or the more stable \bullet (with less stable $+$). In general, the energetically *preferred* fragmentation pathway is determined by cation stability, but other fragmentation pathways are still energetically *accessible* under MS experimental conditions. These fragments formed from the molecular ion can themselves undergo fragmentation reactions, which can result in complicated MS data that provide tremendous insight into molecular structure.

Although there are some exceptions, the molecular ion (which has an odd number of e^-) typically fragments into an even-electron cation and an odd-electron radical. The even-electron cations then typically fragment into other even-electron species. Keep in mind that each of the following mechanisms were formulated on the basis of experimental data – chemists made observations on how molecules fragmented and then proposed mechanisms to explain how those fragments formed; it would have been difficult to hypothesize the proper fragmentation of these molecules without the MS data.

Lesson VII.9.2 Fragmentation via Bond Heterolysis and/or Bond Homolysis

Fragmentation of a molecular ion into one or more molecules requires the breakage of bonds (new bonds can also be formed, but some bonds must be broken). Bond breakage can occur by heterolysis or homolysis (1 e^- in a bond is transferred to one atom, and the other e^- is transferred to the other atom).

To illustrate how a molecular ion may fragment via heterolysis, consider a dialkyl ether as an example. Ionization places the $\bullet+$ on the O, because the e^- in the lone pairs on O are more energetically accessible than the e^- in any of the σ -bonds. One of the C–O bonds then breaks heterolytically to place the 2 e^- on the O, resulting in a carbocation and an O-centered radical. This bond heterolysis is preferred because it affords a C-centered cation instead of an O-centered cation, the former being more stable due to the lower electronegativity of carbon. Do not forget that cations and radicals can rearrange!

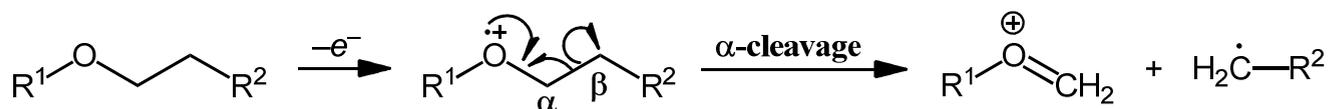
Lesson VII.9.4 Inductive Cleavage

The simplest fragmentation mechanism is "inductive cleavage", which refers to breakage of a bond between the atom bearing the $\bullet+$ character and the α -atom, and it may occur either heterolytically or homolytically. The fragmentation of the dialkyl ether and aryl alkyl ether we showed in Lesson VII.9.2 are examples of inductive cleavage by heterolysis and homolysis, respectively.

Lesson VII.9. α -Cleavage

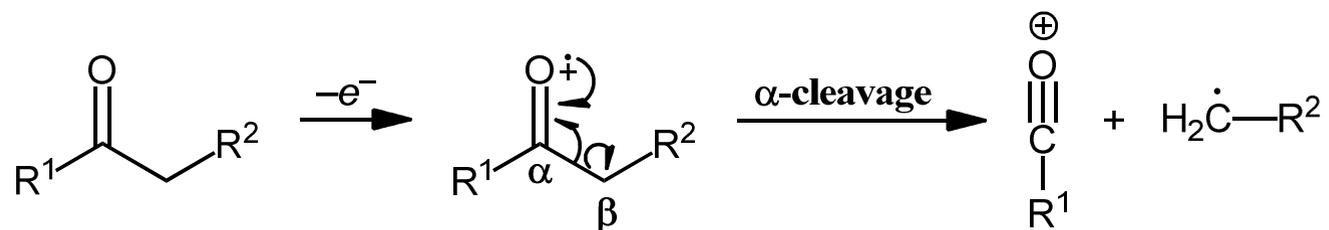
In α -cleavage, the bond between the α - and β -positions is broken, and **the α -atom stays with the original fragment**.

For our first example, let us revisit a dialkyl ether. Ionization again places the $\bullet+$ on the O atom. Next, the bond between the α -carbon and the β -carbon breaks homolytically:



The driving force for this reaction is that every atom in the cationic fragment has a complete octet.

For our second example, consider a dialkyl ketone. Ionization places the $\bullet+$ on the O atom, and the bond between the α -carbon and the β -carbon breaks homolytically:



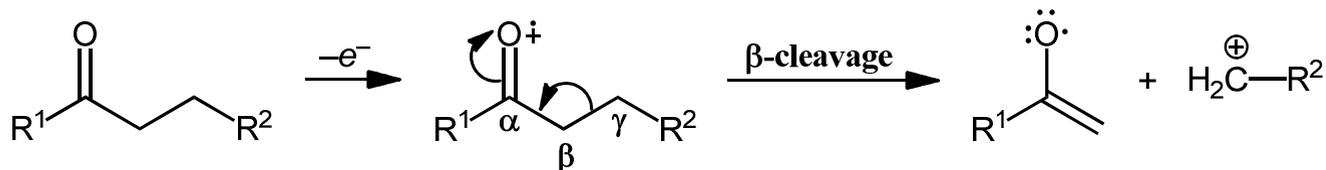
Again, the driving force for this reaction is that every atom in the cationic fragment has a complete octet.

Lesson VII.9.6 β -Cleavage

In β -cleavage, the bond between the β - and γ -positions is broken, whereby **the atoms at the α - and the β -positions stay with the original fragment**.

For an example, let us revisit a dialkyl ketone. Ionization again places the $\bullet+$ on the O atom, but now the bond between the α -carbon and the β -carbon breaks heterolytically. The $2 e^-$ from this bond moves in between C_α and C_β to form a $C=C$ bond, and the $C_\alpha-O$ π -bond breaks heterolytically to place those $2 e^-$ in an additional lone pair on O, which affords an enol with \bullet character on the O. The other fragment is a carbocation with the $+$ charge on C_γ . Although the cationic fragment produced by β -cleavage lacks a complete octet, the radical character on the other fragment is stabilized by

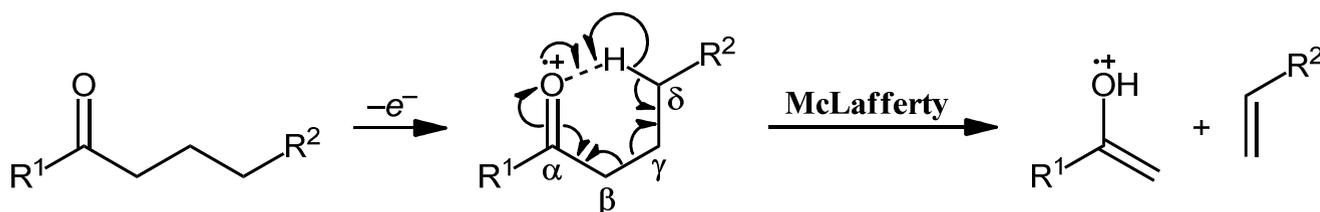
delocalization. In general, β -cleavage is less common than either α -cleavage or the McLafferty rearrangement that we are about to discuss.



Lesson VII.9.7 McLafferty Rearrangement

The McLafferty rearrangement refers to a fragmentation process in which bond cleavage (typically β -cleavage) is accompanied by H transfer (typically from the δ -carbon) and proceeds through a cyclic 6-membered transition state. The McLafferty rearrangement is typically associated with carbonyl-based functional groups, although we will see that other functional groups exhibit similar rearrangements.

We will continue using a dialkyl ketone as our example. Ionization again places the $\bullet+$ on the O atom, but now one of the alkyl chains is sufficiently long that it places a C–H bond (specifically at C δ) in close proximity to the O $^+$. A six-membered arrangement of atoms participates in the McLafferty rearrangement to form a stable neutral alkene and a resonance-stabilized cation:

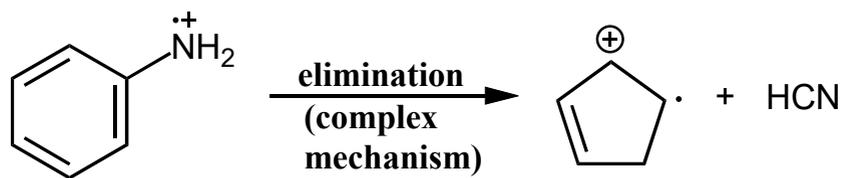


Lesson VII.9.2.8 Retro Diels–Alder

Another fragmentation mechanism that proceeds through a cyclic 6-membered transition state is termed "retro Diels–Alder". In retro Diels–Alder, a 6-membered cycle comprising one or more atoms bearing $\bullet+$ character is converted into one 4-membered chain, which retains the $\bullet+$ character, and one 2-membered chain, which is neutral.

Lesson VII.9.2.9 Elimination

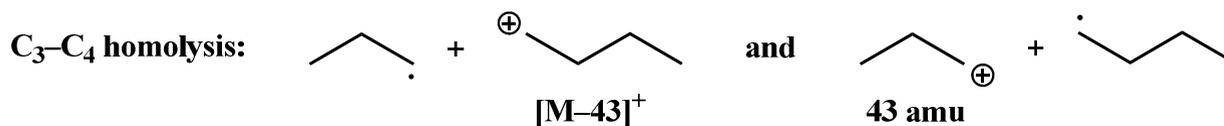
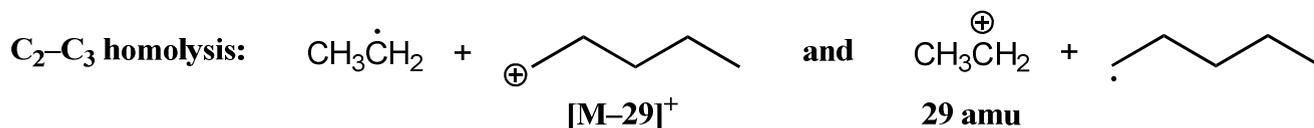
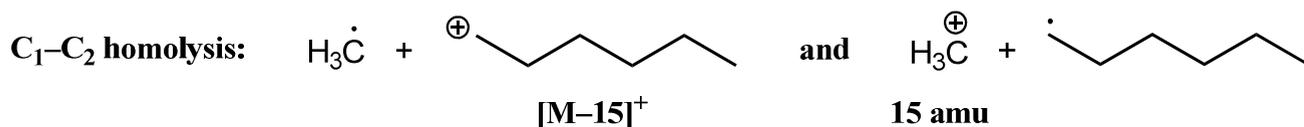
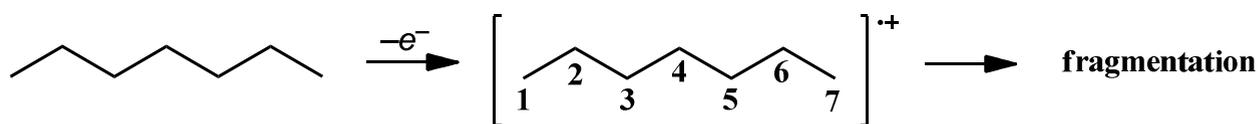
Elimination, in the context of fragmentation during a mass spectrometry experiment, simply refers to a process in which one molecule fragments into two molecules, where one of the molecules is usually (but not always) expelled as a low molecular weight neutral molecule. Sometimes drawing an arrow-pushing mechanism for an elimination process is easy, as is the case with $[\text{R}-\text{CH}_2-\text{C}\equiv\text{O}]^+$, and sometimes it is beyond our abilities in this course, as is the case with $[\text{PhNH}_2]^{++}$, shown below:



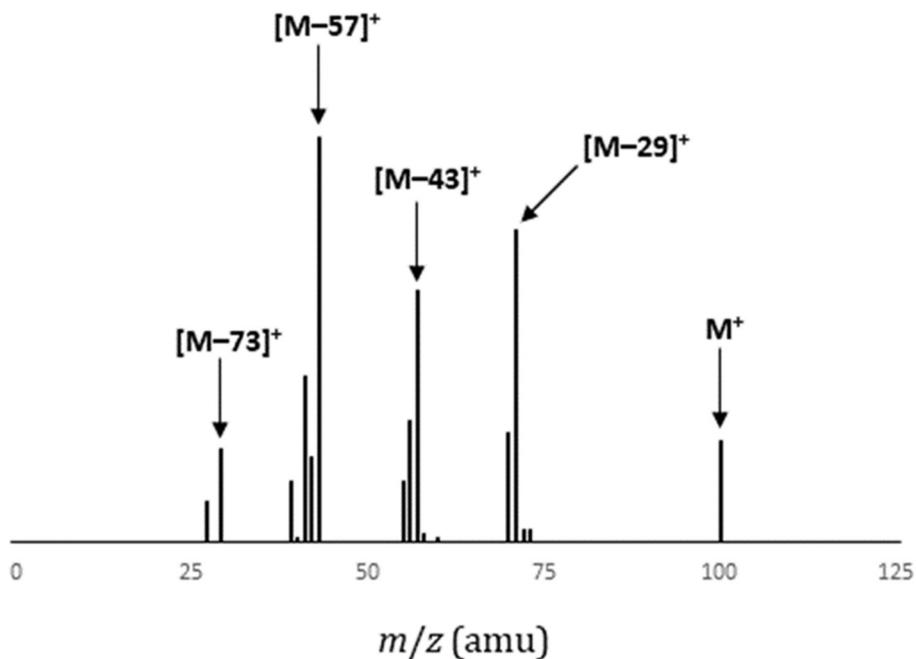
Lesson VII.10 Fragmentation of Alkanes

Lesson VII.10.1 Linear Alkanes

The M^+ peak is typically visible for linear alkanes, although its intensity decreases with increasing alkane length. There is no convenient way to draw the radical cation formed by ionization of an alkane, so we typically represent it with square brackets. The molecular ion can fragment along any of the C–C bonds, usually in a way that places the radical on the smaller fragment and the cation on the larger fragment. A feature that is characteristic for alkanes is a series of peaks separated by 14 amu, the mass of CH_2 . In general, there will be the M^+ peak, then a peak corresponding to $[M-15]^+$, then $[M-29]^+$, and so on. Note that the $[M-15]^+$ peak is derived from the loss of CH_3^\bullet , the least stable radical, so the $[M-15]^+$ peak is usually very weak and is sometimes absent entirely. Lastly, it is possible for $\text{H}_2\text{C}=\text{CH}_2$ to eliminate from one of the cationic fragments. The various fragments for *n*-heptane are shown below.

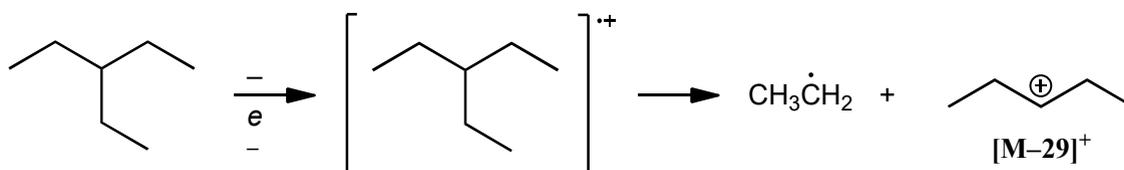
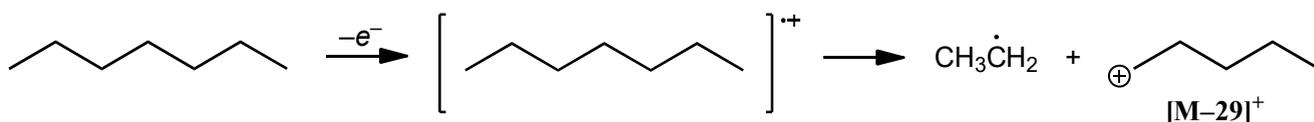


The mass spectrum of *n*-heptane shows prominent peaks for the cationic fragments delineated above:

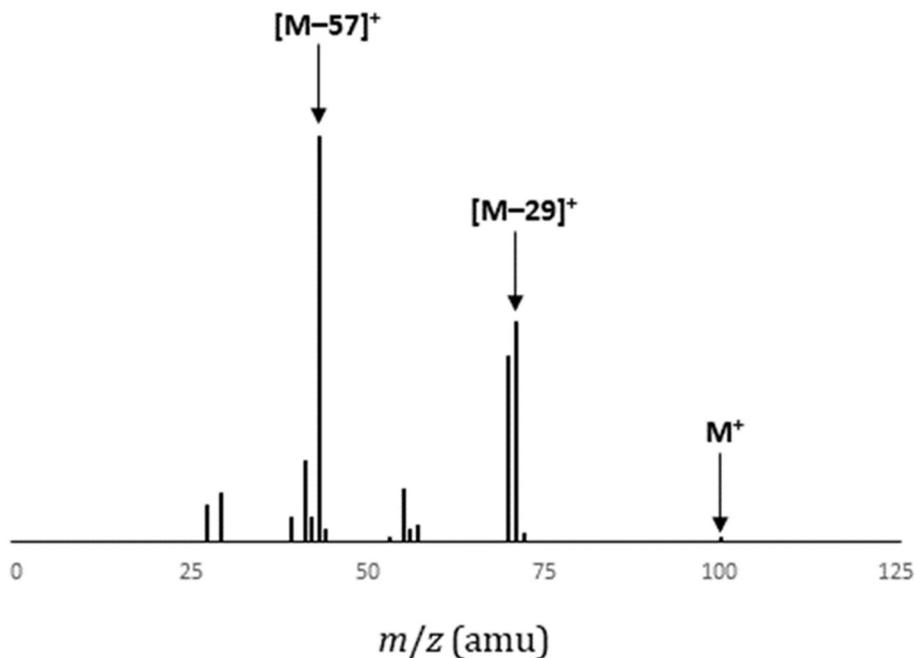


Lesson VII.10.2 Branched Alkanes

The M^+ peak for branched alkanes is typically smaller than for linear alkanes, and may be absent entirely. Like a linear alkane, the molecular ion for a branched alkane can fragment along any of the C–C bonds, but fragmentation is more favored at the branching sites because it affords more stable carbocations. Similarly, the MS of a branched alkane will exhibit a series of peaks separated by 14 amu, the mass of CH_2 , but the relative intensities will be different than in a linear alkane. For example, both *n*-heptane and 3-ethylpentane will exhibit $[M-29]^+$ peaks at 71 amu, but this peak in the MS of 3-ethylpentane will have much higher relative intensity because it is derived from a more stable 2° cation. In general, the fragmentation patterns for branched alkanes are highly conserved with those for linear alkanes, with the only differences primarily being different relative peak intensities.

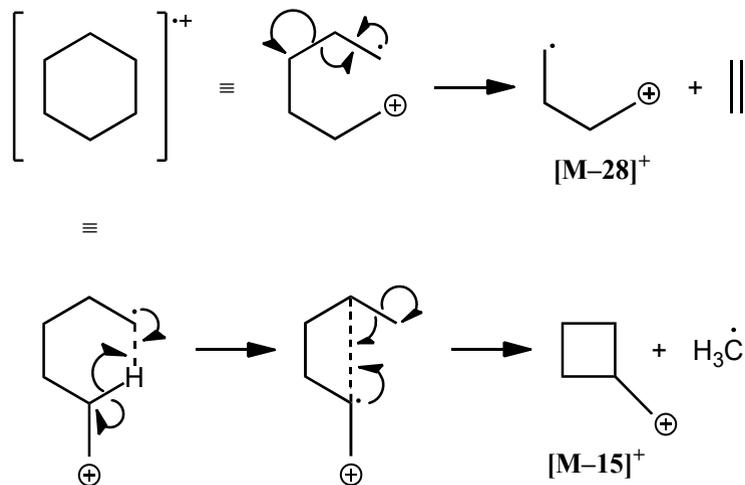


The mass spectrum of 3-ethylpentane shows prominent peaks for the cationic fragments delineated above:

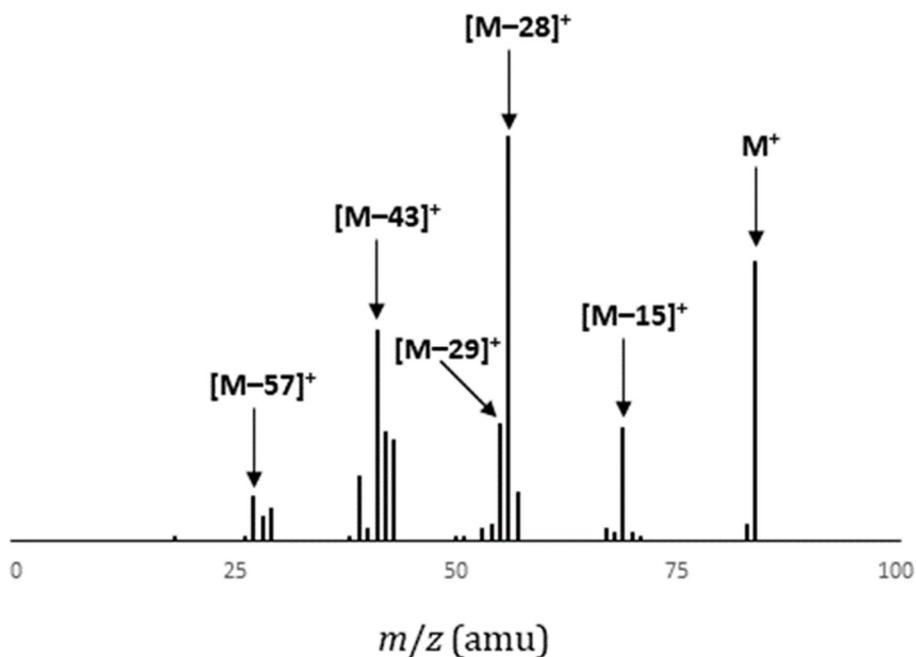


Lesson VII.10.3 Cycloalkanes

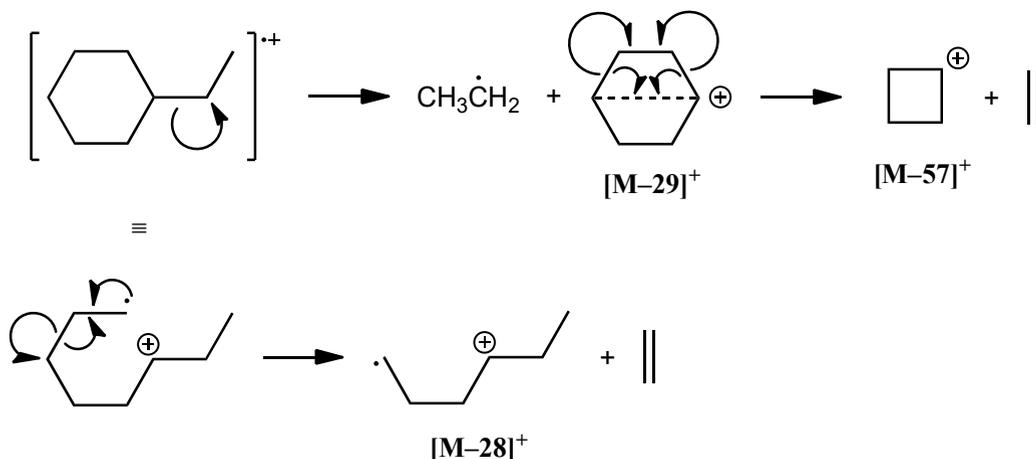
The M^+ peak for cycloalkanes is typically more intense than for either linear or branched alkanes, with intensities higher for unbranched cycloalkanes compared to branched cycloalkanes. With an unbranched cycloalkane, the two major fragments are formed by loss of $H_2C=CH_2$ and CH_3^{\bullet} , with amu values of $[M-28]^+$ and $[M-15]^+$, respectively. Mechanisms are shown below for the fragmentation of the cyclohexane molecular ion.



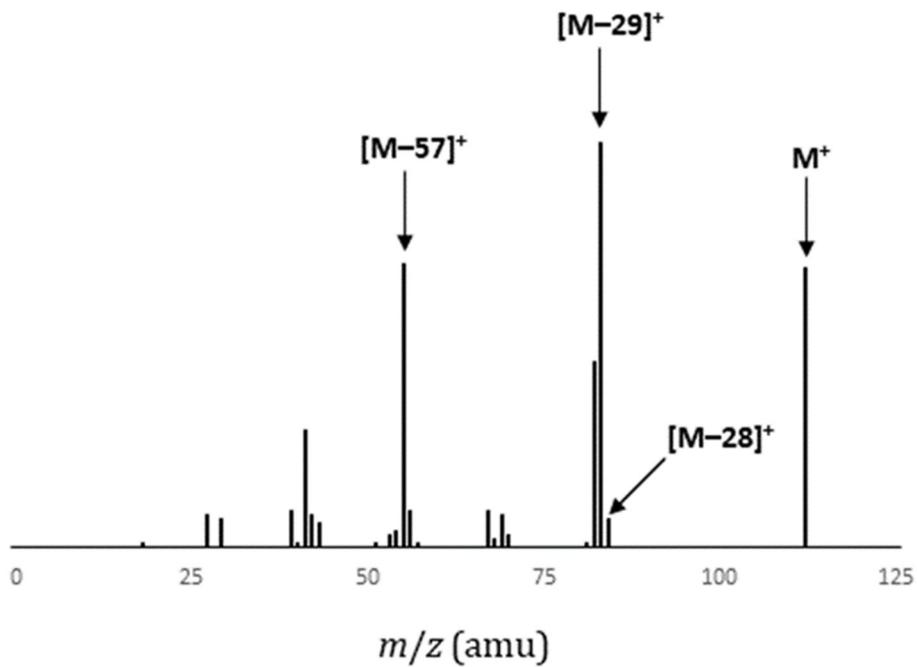
The mass spectrum of cyclohexane shows prominent peaks for the cationic fragments delineated above:



With a branched cycloalkane, loss of the side-chain as an alkyl radical is a major fragmentation pathway, and the resulting carbocation can subsequently eliminate $\text{H}_2\text{C}=\text{CH}_2$. However, keep in mind that the parent radical cation can also eliminate $\text{H}_2\text{C}=\text{CH}_2$. Mechanisms are shown below for the various fragmentation modes for the ethylcyclopentane molecular ion. In general, if a cycloalkane has an alkyl side chain, it will not exhibit an $[M-15]^+$ peak due to CH_3^\bullet release and ring contraction, unless the side chain is a methyl group, in which case an $[M-15]^+$ peak will be present, but instead will arise from side chain heterolysis.



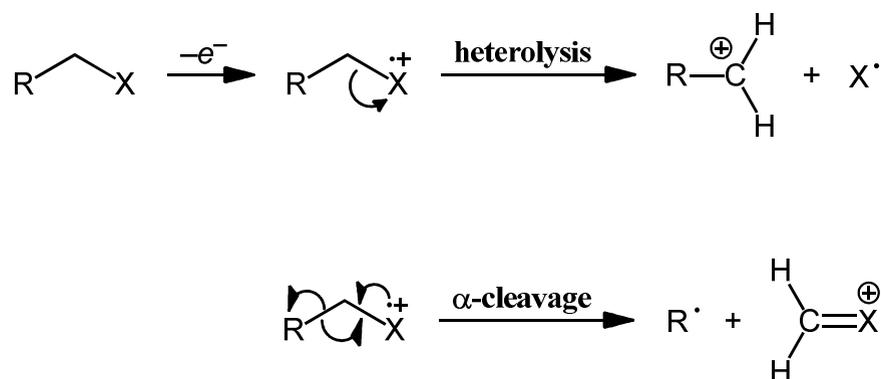
The mass spectrum of ethylcyclohexane shows prominent peaks for the cationic fragments delineated above:



Lesson VII.11. Fragmentation of Heteroatom-Containing Aliphatics

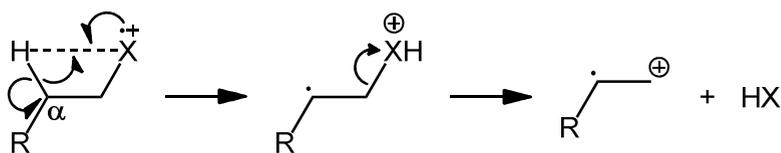
Lesson VII.11.1 Halogenated Alkanes

The molecular ion formed by ionization of a halogenated aliphatic (saturated molecule) has the radical cation character localized on the halogen (it is easier to remove an electron from a lone pair than from a bonding orbital). Remember that the presence and relative intensity of any $M+2$ peaks will inform you of the identity of the halogen! One fragmentation mechanism involves heterolytic cleavage of the C–X bond, placing both e^- on the departing halogen, affording a carbocation and a halogen radical. This process is most favorable when $X = \text{I}$ and is least favorable when $X = \text{F}$. Alternatively, the molecular ion could undergo α -cleavage to afford an alkyl radical and a halonium species. This process will favor formation of the largest possible alkyl radical. When $X = \text{I}$, an additional fragmentation mode is the release of I^+ , which exhibits a peak at 127 amu.

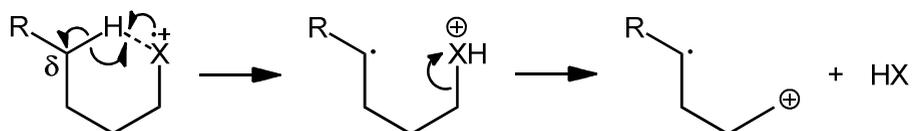


Elimination of HX from the molecular ion can also occur, which produces another radical cation. This process is most favorable when $X = \text{F}$ and is least favorable when $X = \text{I}$. The H-atom can come from either C_α or C_δ , and is referred to as 1,2-elimination or 1,4-elimination, respectively. Note, however, that the mass loss is identical for both elimination mechanisms, so it is impossible to determine which mechanism is occurring using only mass spec.

1,2-elimination

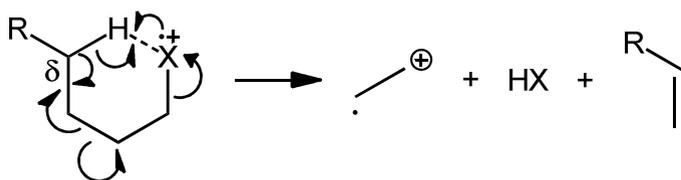


1,4-elimination

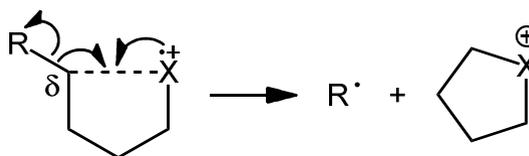


Any alkyl halide that features a hydrogen atom at the δ -position can also undergo a double elimination reaction, which eliminates HX and an alkene, leaving behind a radical cation. Lastly, in alkyl halides that have non-hydrogen substituents at the δ -position, a σ -bond can form between the halogen and C_δ , accompanied by homolytic cleavage of the $C_\delta-C_\epsilon$ bond, to form a cyclic halonium in a process termed δ -cyclization. Remember that the alkyl fragments themselves can also fragment.

double elimination



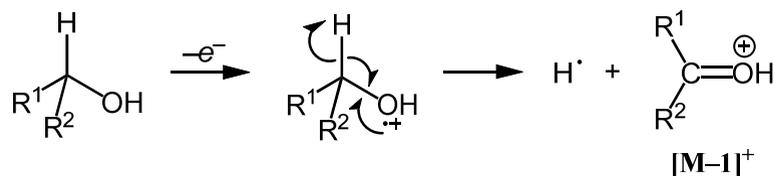
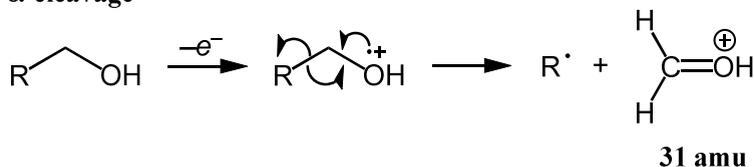
δ -cyclization



Lesson VII.11.2 Alcohols

Ionization of an alcohol places the radical cation character on the oxygen atom. The M^+ peak is generally weak for 1° and 2° alcohols, and is often absent for 3° alcohols. Occasionally, a 1° or 2° alcohol may exhibit an $[M-1]^+$ peak due to α -cleavage of an H-atom. Alcohols undergo many of the same fragmentation mechanisms as alkyl halides. Some notable differences are that alcohols rarely undergo heterolysis (to release HO^\bullet) or δ -cyclization. Primary alcohols display a prominent peak at 31 amu.

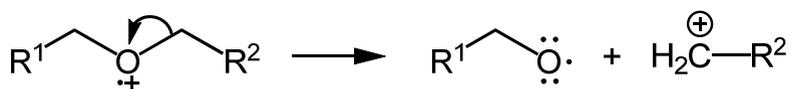
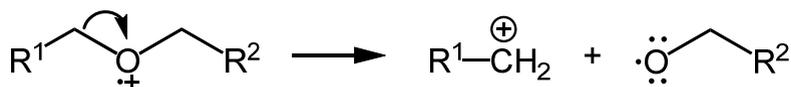
α -cleavage



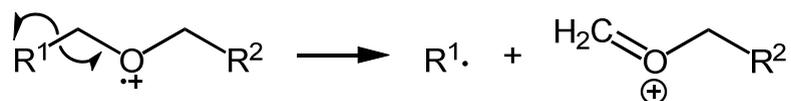
Lesson VII.11.3 Ethers

Ionization of an ether places the radical cation character on the oxygen atom. In general, the M^+ peak is stronger and there are fewer types of fragmentation mechanisms for an ether compared to an alcohol with the same molecular formula (principal modes are α -cleavage, there is generally no 1,2- or 1,4-elimination). These fragmentation modes can occur on either side of the oxygen, but keep in mind that O–C homolysis will not occur unless there is something that can stabilize an oxygen with only 6 valence electrons (e.g., delocalization across any aryl ring).

heterolysis

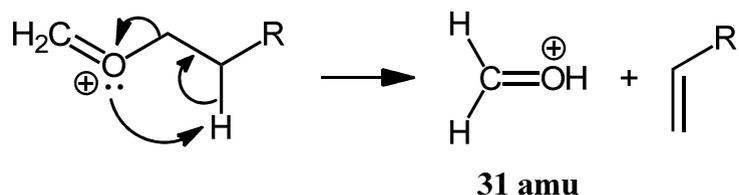


α -cleavage



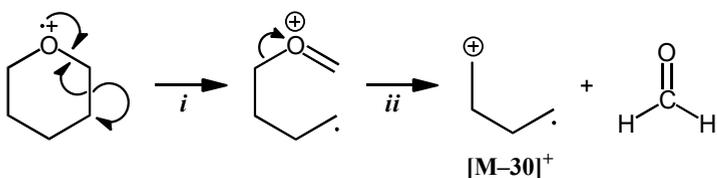
Note that ethers of the general formula $R^1CH_2OCH_2R^2$ will give a prominent peak at 31 amu, the same as with 1° alcohols, because the product of α -cleavage can subsequently rearrange. As a result, the presence of a peak at 31 amu is not unambiguous for 1° alcohols.

rearrangement

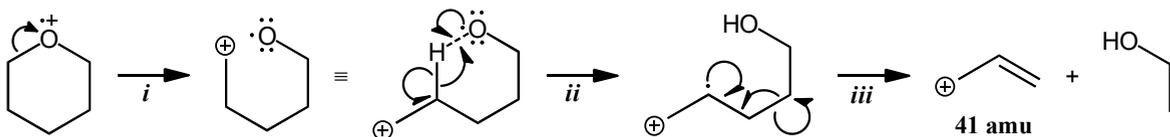


Interestingly, cyclic ethers exhibit peaks at $[M-30]^+$ due to the elimination of $H_2C=O$, and those with ring sizes greater than 4 exhibit peaks at 41 amu from the allyl cation! Larger allyl cations can also be observed, depending on the size of the ring. These processes are illustrated for tetrahydropyran here:

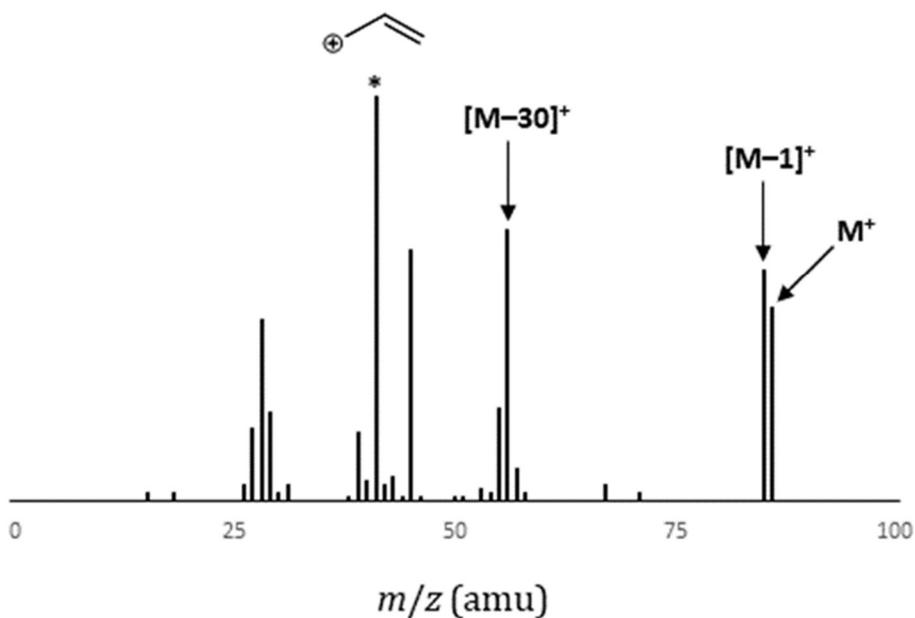
α -cleavage (i) then elimination (ii)



heterolysis (i), rearrangement (ii), then elimination (iii)



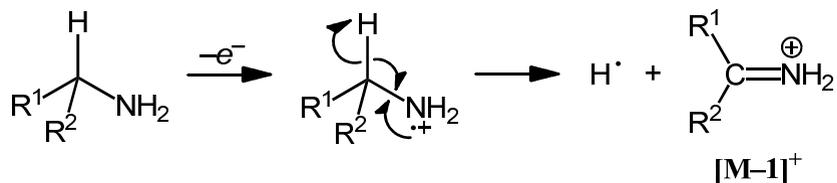
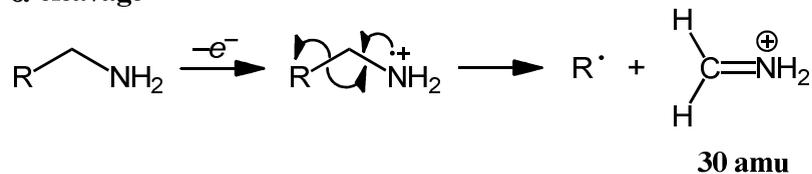
The mass spectrum of cyclohexanol shows prominent peaks for the cationic fragments delineated above:



Lesson VII.11.4 Amines

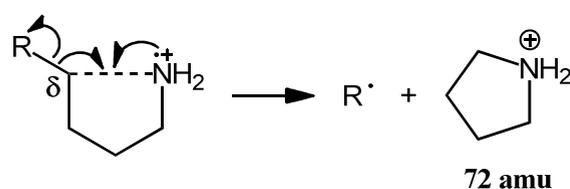
The radical cation character in the molecular ion of an amine is localized on the nitrogen atom. The M^+ peak is typically weak or absent, but an $[M-1]^+$ peak is often observable. Like ethers, the principal fragmentation modes involve α -cleavage. Primary amines often exhibit peaks at 30 amu.

α -cleavage



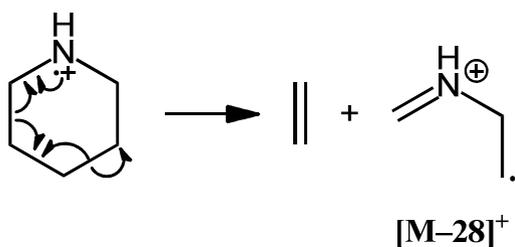
Amines can undergo δ -cyclization, and will exhibit peaks at 72 amu if there are no substituents at the α -, β -, or γ -positions. However, amines generally do not eliminate NH_3 (either by itself or via double elimination).

δ -cyclization

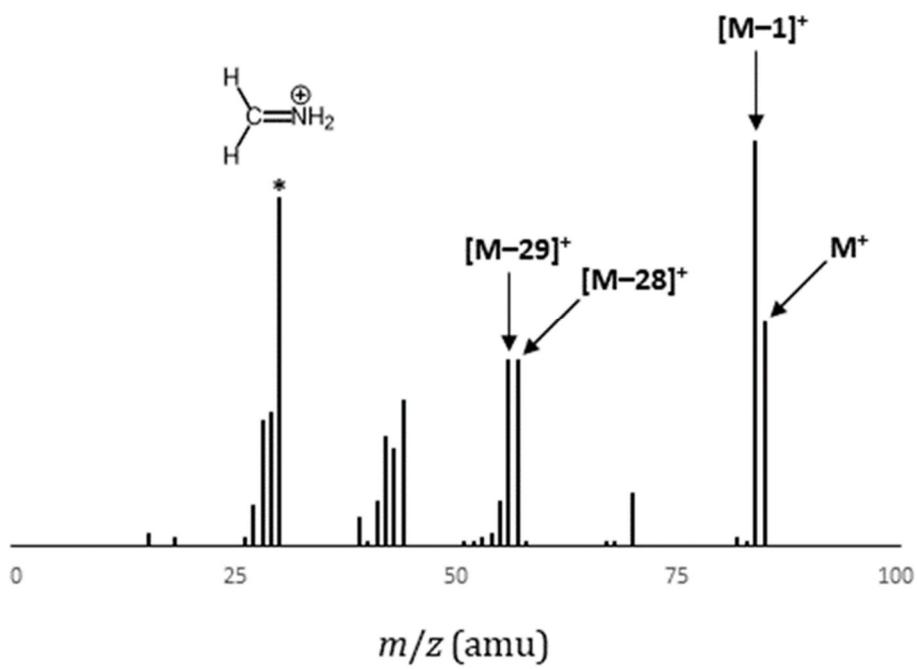


Cyclic amines display stronger M^+ and $[M-1]^+$ peaks, but their fragmentation patterns are much more complicated to interpret. However, a common feature of most cyclic amines is an $[M-28]^+$ peak, corresponding to the elimination of ethylene, as shown for piperidine below:

elimination



The mass spectrum of piperidine shows prominent peaks for the cationic fragments delineated above:

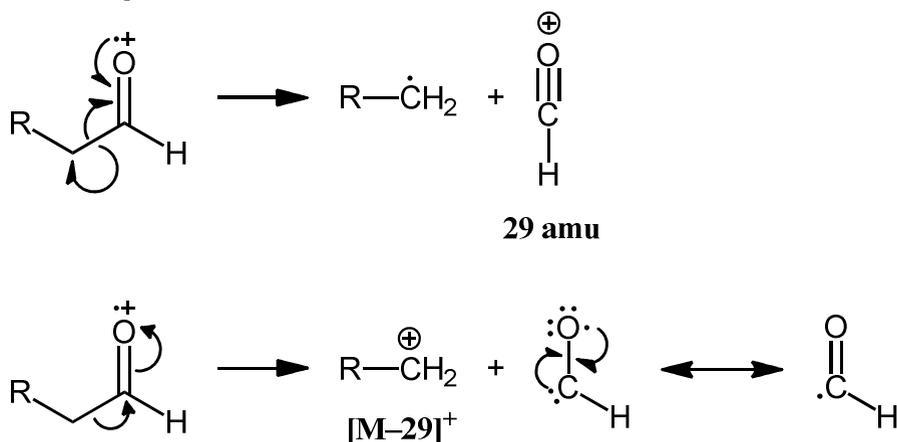


Lesson VII.12. Fragmentation of Carbonyl-Containing Molecules

Lesson VII.12.1 Aldehydes

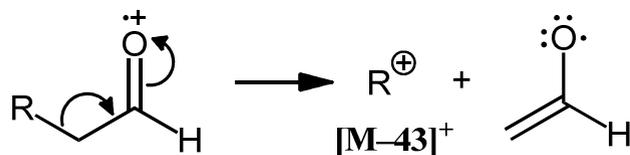
The molecular ion of any carbonyl-containing functional group carries the radical cation character on the oxygen atom belonging to the carbonyl unit. In aldehydes, the M^+ and $[M-1]^+$ peaks are usually very weak or absent. The fragmentation modes are generally limited to α -cleavage to form an alkyl radical and the $[O=C-H]^+$ cation (29 amu). However, 29 amu also corresponds to the molecular weight for the $CH_3CH_2^+$ cation, so the presence of a peak at 29 amu is not diagnostic for either $[O=C-H]^+$ or $CH_3CH_2^+$ cations. Alternatively, α -cleavage can form an $[M-29]^+$ alkyl cation and $[O=C-H]^{\bullet}$ radical. Do not forget that any alkyl cation fragments formed can themselves fragment or rearrange.

α -cleavage



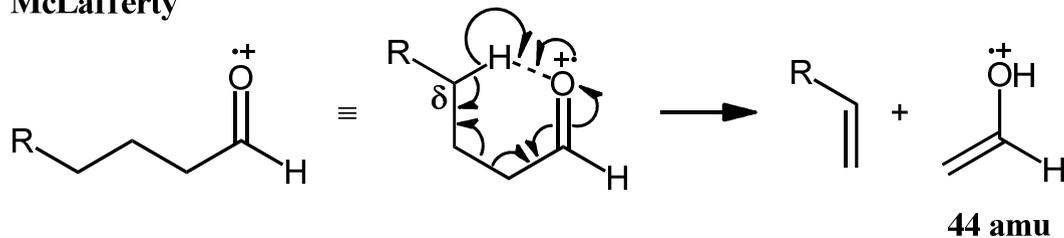
β -cleavage can occur in aldehydes to give $[M-43]^+$ peaks, but this is not as favorable as α -cleavage. If α -substituents are present, the mass loss will be greater than 43 amu.

β -cleavage



Aldehydes longer than propanal can also undergo a McLafferty rearrangement to afford a neutral alkene and 44 amu radical cation (or higher if α -substituents are present). Interestingly, aldehydes with long alkyl chains also exhibit $[M-18]^+$ peaks due to the elimination of H_2O , but the mechanism by which this occurs is unclear.

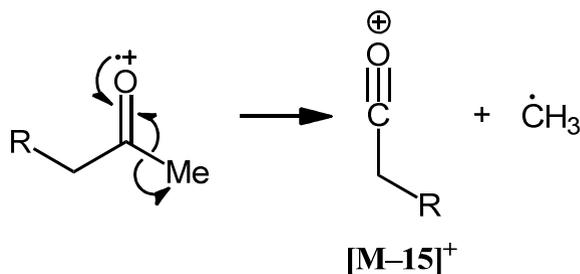
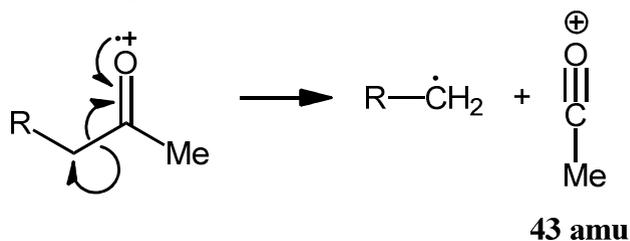
McLafferty



Lesson VII.12.2 Ketones

In contrast to aldehydes, M^+ peaks are visible for most ketones. Ketones fragment in ways similar to aldehydes, namely via α -cleavage, but no H_2O elimination peaks are observed even with very long alkyl chains. Note that α -cleavage can occur on both sides of the carbonyl unit. Methyl alkyl ketones show prominent peaks at 43 amu corresponding to the acylium cation $[O=C-CH_3]^+$, but this mass is identical to that of the $CH_3CH_2CH_2^+$ cation, so this peak is not diagnostic for either species. For some $[O=C-R]^+$ fragments, CO can eliminate to afford an alkyl cation that is 28 amu lighter, but this is a relatively minor pathway, and 28 amu is also identical to the mass of $H_2C=CH_2$, so it is not diagnostic for either elimination pathway.

α -cleavage

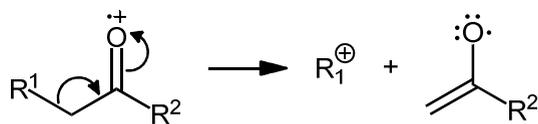


elimination

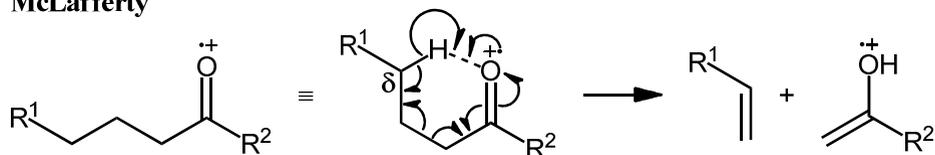


Ketones can undergo β -cleavage, but it is not as common as α -cleavage. If one alkyl substituent has 3 or more carbons, a McLafferty rearrangement is also possible.

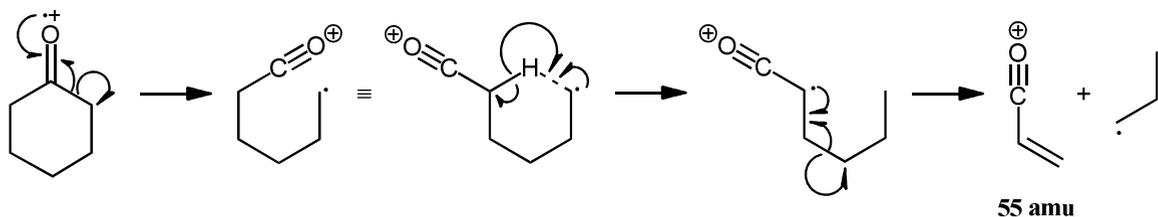
β -cleavage



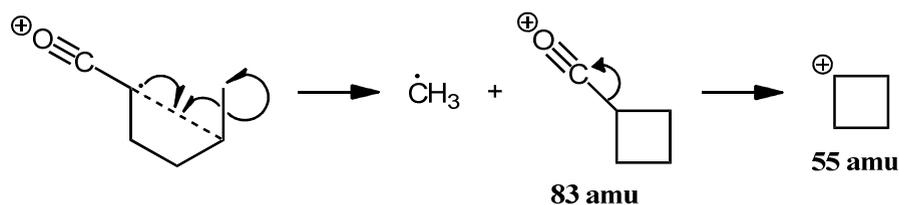
McLafferty



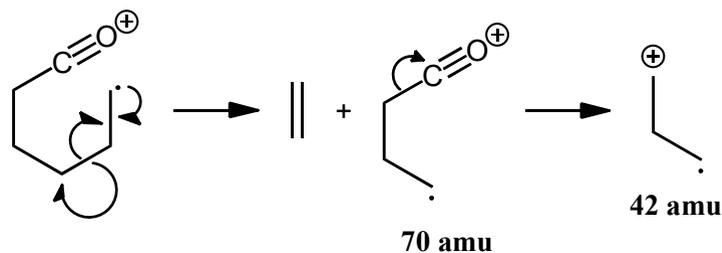
Cyclic ketones exhibit much stronger M^+ peaks than acyclic ketones. Although the fragmentation patterns are more complex, the fragmentation mechanisms are similar to those with cyclic alcohols. We show cyclohexanone below as an example. One C_α - C_β bond breaks homolytically to afford a cationic $O=C$ moiety and a carbon radical. This acyclic species can rearrange by 3 different mechanisms. The radical can abstract H^\bullet from adjacent to the $O=C$ moiety, which then fragments to eliminate an alkyl radical and yield a 55 amu cation. This 55 amu cation can subsequently eliminate CO.



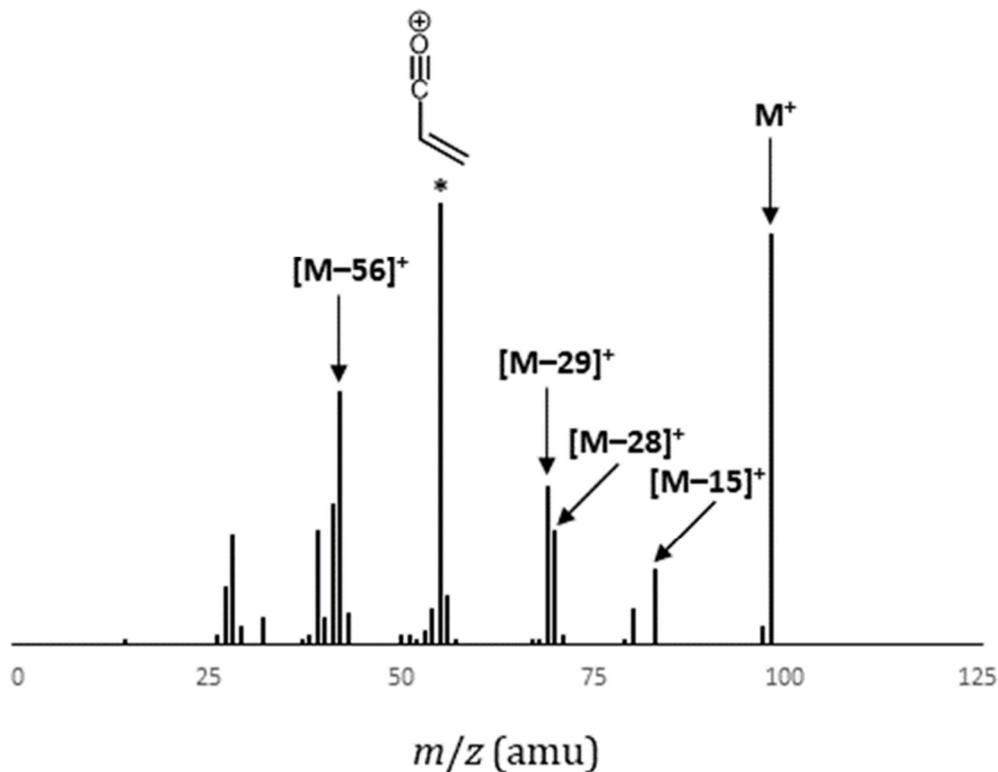
Alternatively, this H^\bullet abstraction can be followed by a cyclization and elimination of an alkyl radical to afford an 83 amu cation. This cation can also subsequently eliminate CO.



Lastly, the initial radical cation can eliminate $H_2C=CH_2$ (derived from C_β and C_γ) to afford another radical cation, which can further eliminate CO to yield an alkyl radical cation.



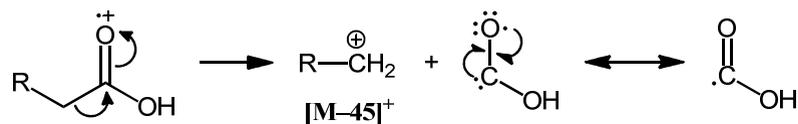
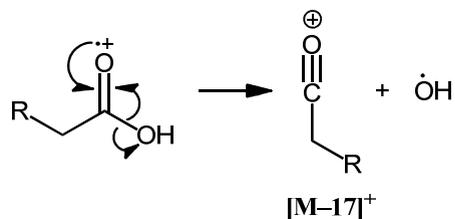
The mass spectrum of cyclohexanone does shows prominent peaks for the cationic fragments delineated above:



Lesson VII.12.3 Carboxylic Acids

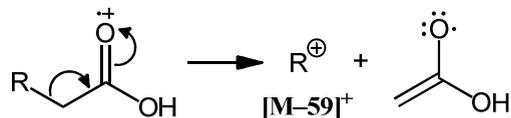
Carboxylic acids generally do not exhibit observable M^+ peaks, and drawing mechanisms for some of the more prominent fragments is non-trivial. An $[M-17]^+$ peak from α -cleavage to release HO^\bullet is often present, albeit with low intensity. Alternatively, α -cleavage on the other side of the carbonyl would release a $[CO_2H]^\bullet$ radical and afford an $[M-45]^+$ alkyl cation. However, this is the same mass loss as if α -cleavage to release HO^\bullet were followed by elimination of CO .

α -cleavage

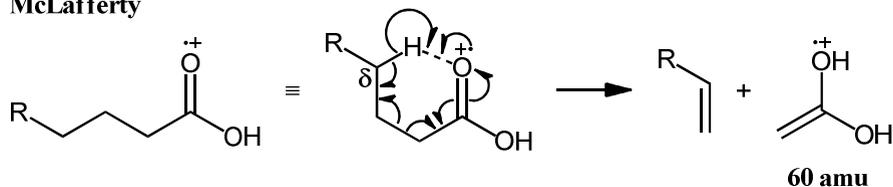


β -cleavage can occur in carboxylic acids to give $[\text{M}-59]^+$ peaks, and this is usually more favorable than α -cleavage. In general, the most intense peak observed for carboxylic acids is at 60 amu, which is produced by a McLafferty rearrangement.

β -cleavage

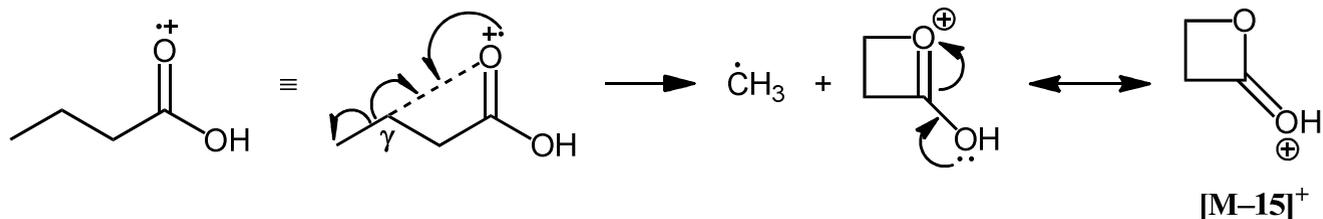


McLafferty

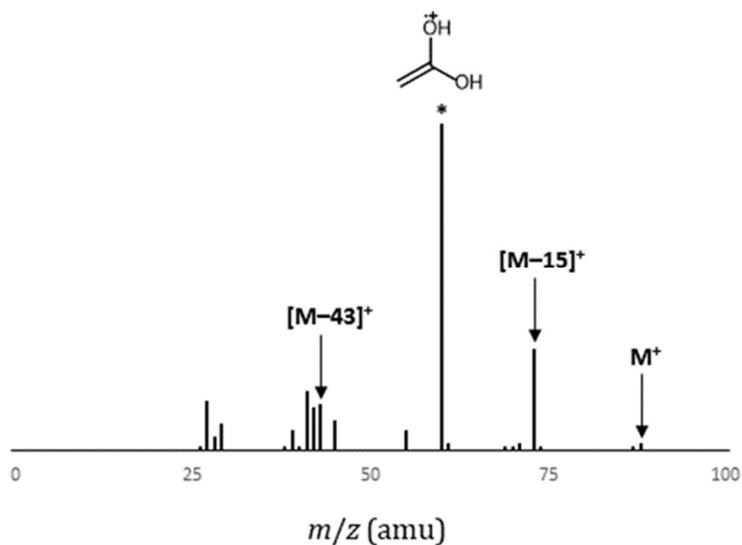


Interestingly, carboxylic acids show peaks consistent with γ -cyclization, despite the fact that neither aldehydes nor ketones do. Butyric, pentanoic, and hexanoic acids, for example, exhibit prominent $[\text{M}-15]^+$, $[\text{M}-29]^+$, and $[\text{M}-43]^+$ peaks, respectively.

γ -cyclization



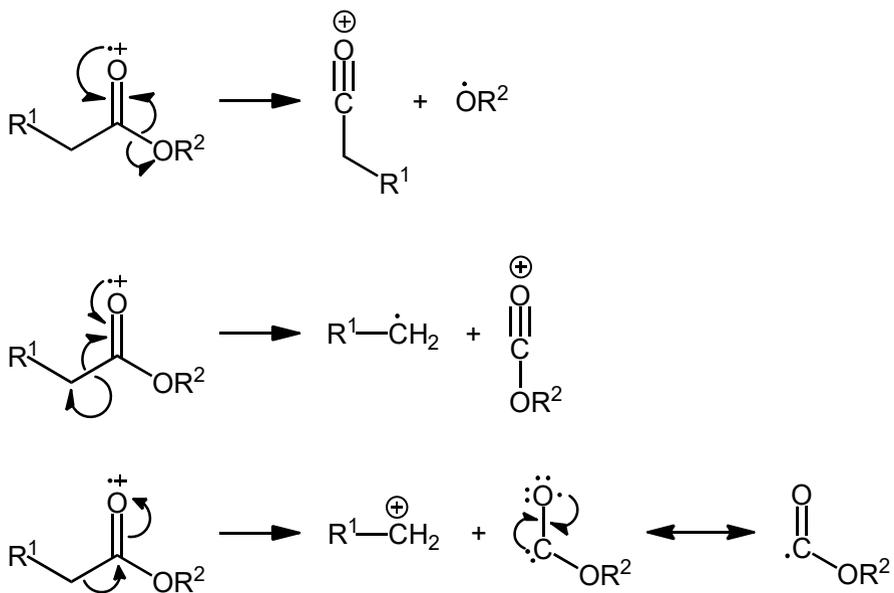
The mass spectrum of butanoic acid shows prominent peaks for the cationic fragments delineated above:



Lesson VII.12.4 Esters

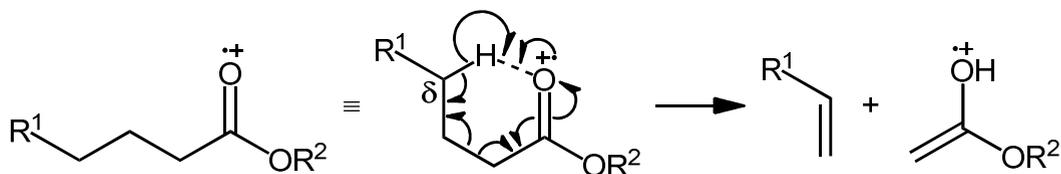
Esters may exhibit weak M^+ peaks and they undergo a greater variety of fragmentation pathways than carboxylic acids. For example, α -cleavage can occur on either side of the carbonyl unit of an ester, and the alkyl chain can depart as either a radical or a cation, so there are 3 permutations of α -cleavage. In contrast to aldehydes, ketones, and acids, β -cleavage is rarely observed.

α -cleavage

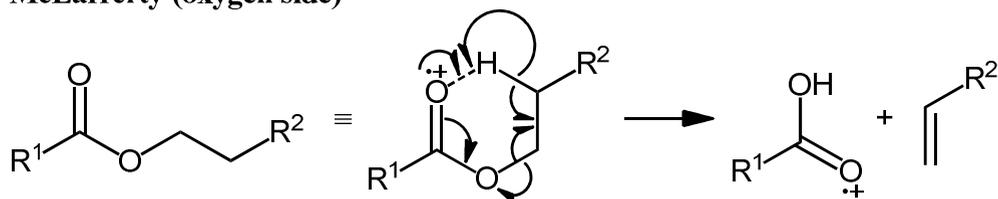


The most prominent peak observed with an ester is derived from a McLafferty rearrangement, but keep in mind that this can occur on either side of the carbonyl unit if the alkyl chains are sufficiently long.

McLafferty (carbonyl side)

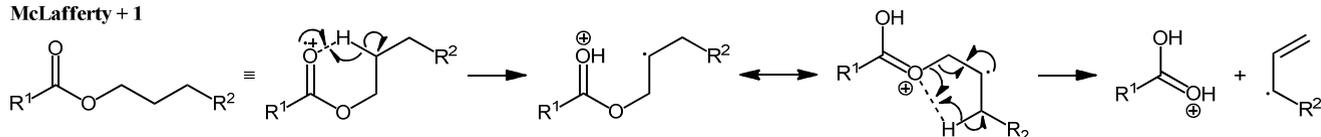


McLafferty (oxygen side)



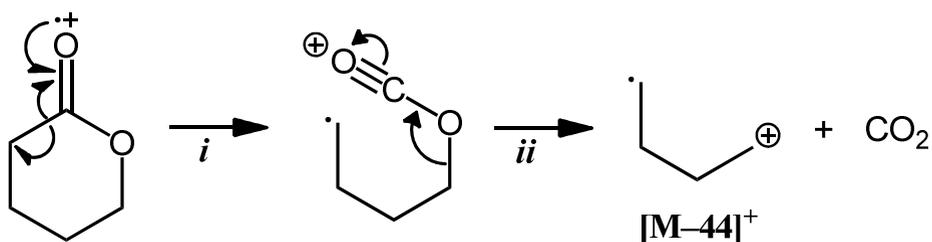
If the alkyl chains on both the "carbonyl side" and the "oxygen side" of sufficient length, then McLafferty rearrangement will occur exclusively on the "oxygen side". If McLafferty rearrangement does occur on the "oxygen side", it will be accompanied by a so-called "McLafferty + 1" peak, which will have significantly greater intensity than the regular McLafferty peak.

McLafferty + 1



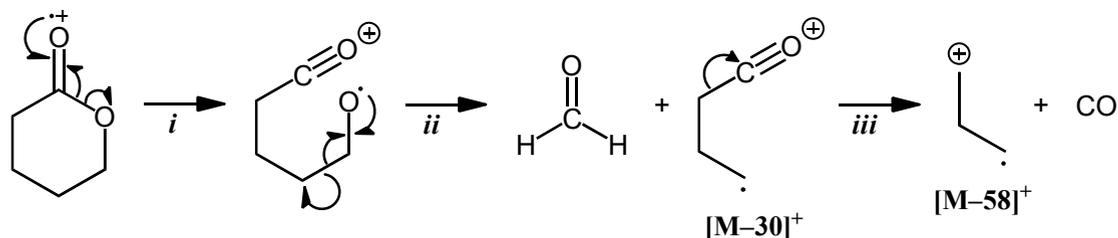
Cyclic esters are more commonly known as lactones, and these exhibit much stronger M^+ peaks than their acyclic counterparts. Lactone fragmentation is determined by whether α -cleavage occurs on the "carbonyl side" or the "oxygen side". If α -cleavage occurs on the "carbonyl side", it will be followed by elimination of CO_2 to give an alkyl radical cation at $[M-44]^+$. Consider the fragmentation of δ -valerolactone:

α -cleavage (i) then elimination (ii)

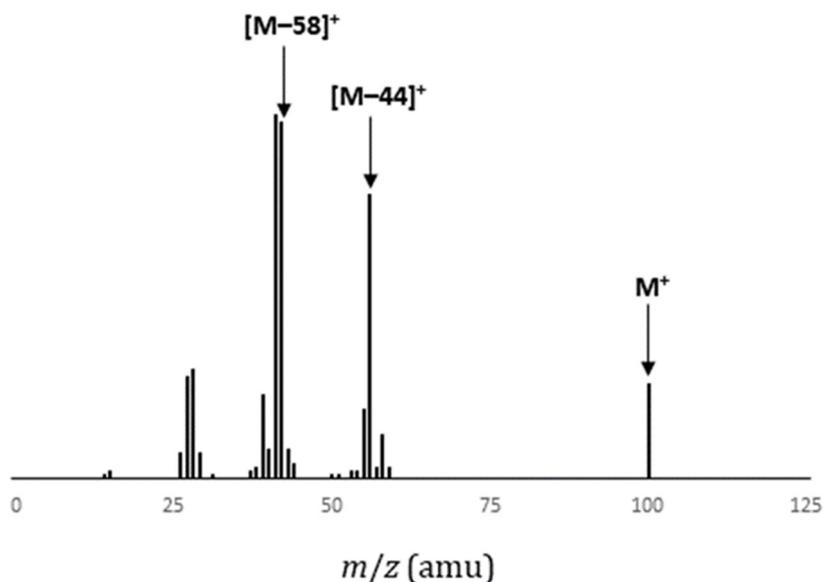


If α -cleavage instead occurs on the "oxygen side", it will be followed by elimination of $\text{H}_2\text{C}=\text{O}$, like we observed with cyclic ethers, to give an alkyl radical and cationic carbonyl at $[\text{M}-30]^+$. This species can fragment further by eliminating CO to produce an alkyl radical cation at $[\text{M}-58]^+$.

α -cleavage (i) then elimination (ii,iii)

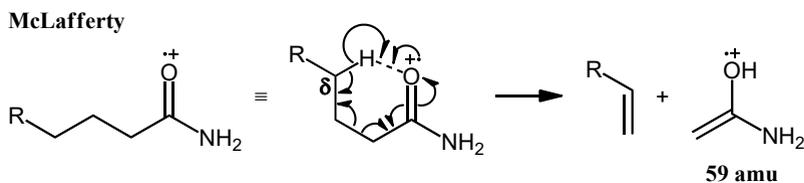
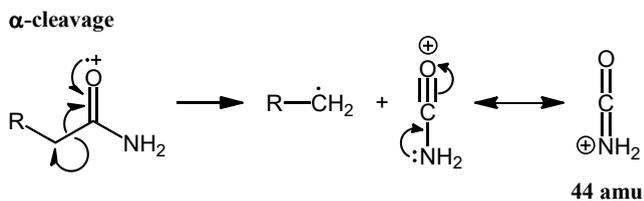


The mass spectrum of δ -valerolactone shows prominent peaks for the cationic fragments delineated above:



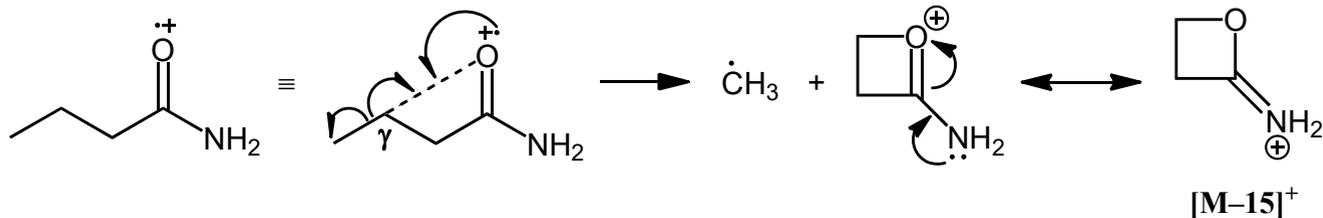
Lesson VII.12.5 Amides

Primary amides (those without N-alkyl substituents) typically do not exhibit M^+ peaks, and the major fragmentation pathways are α -cleavage to form the $[\text{O}=\text{C}=\text{NH}_2]^+$ ion at 44 amu and McLafferty rearrangement to yield a 59 amu radical cation. β -cleavage is generally not observed. Like carboxylic acids, 1° amides exhibit peaks consistent with γ -cyclization: butyramide, valeramide, and hexanamide, for example, exhibit prominent $[\text{M}-15]^+$, $[\text{M}-29]^+$, and $[\text{M}-43]^+$ peaks, respectively.

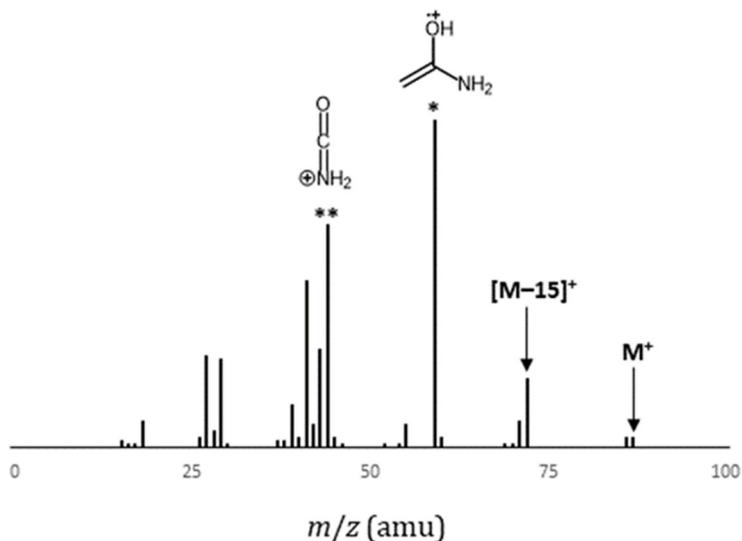


Similar to carboxylic acids, 1° amides also exhibit peaks consistent with γ -cyclization: butyramide, valeramide, and hexanamide, for example, exhibit prominent $[M-15]^+$, $[M-29]^+$, and $[M-43]^+$ peaks, respectively. The fragmentation of amides is illustrated by butyramide:

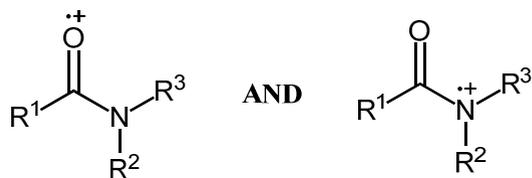
γ -cyclization



The mass spectrum of cyclohexanol shows prominent peaks for the cationic fragments delineated above:

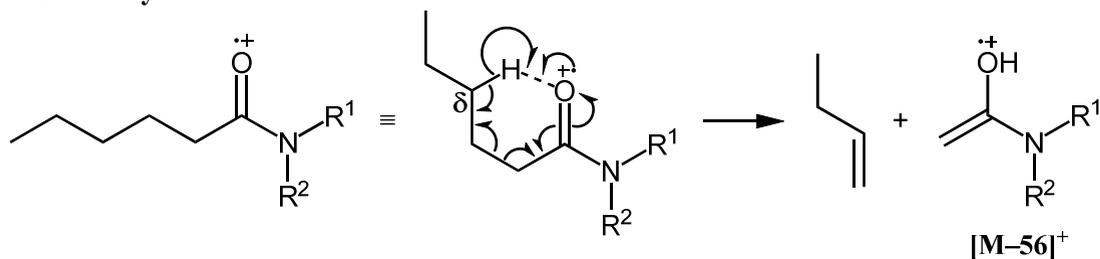


If *N*-alkyl substituents are present, then the M^+ peak is typically strong, and is often accompanied by an $[M-1]^+$ peak. The fragmentation of 2° and 3° amides is significantly more complex than their 1° counterparts. To understand their fragmentation patterns, it is useful to consider that there two distinct isomers can be formed by ionization, one with the radical cation character localized on the oxygen and the other with the $\bullet+$ on the nitrogen.

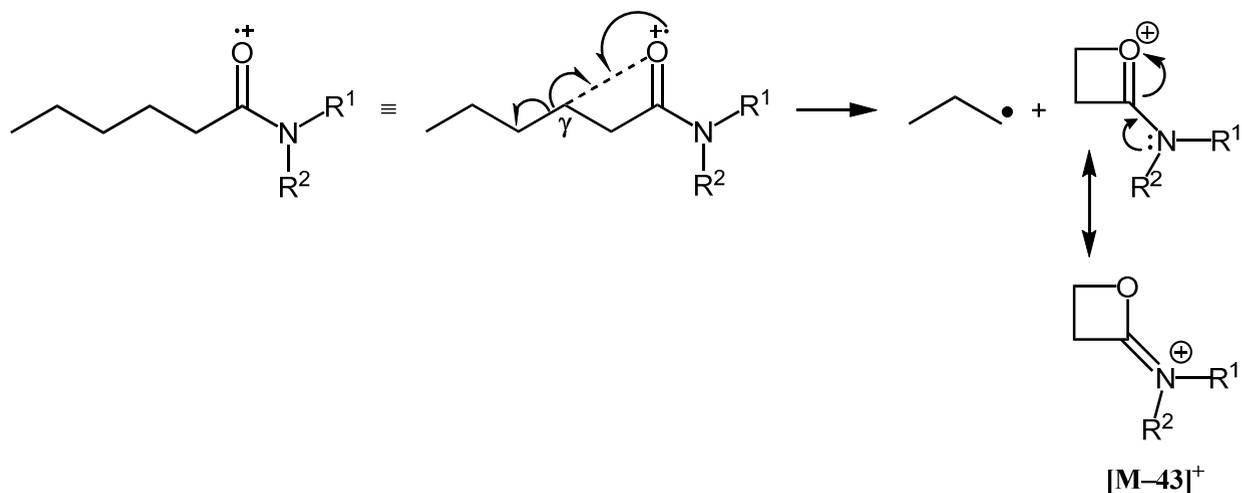


As expected, fragmentation of the isomer with the $\bullet+$ on the oxygen is similar to what is observed with 1° amides (i.e., McLafferty, and γ -cyclization), however it generally does not undergo α -cleavage on the carbonyl side of the amide functional group.

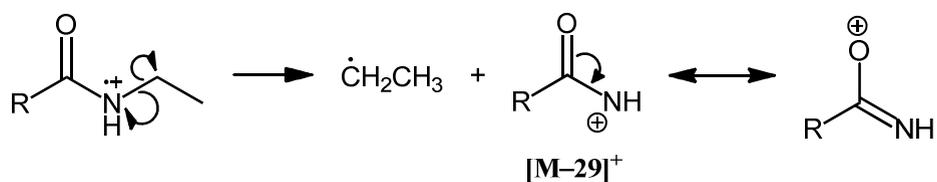
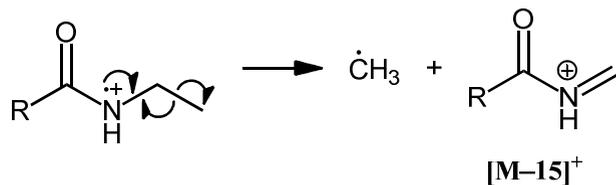
McLafferty



γ -cyclization



The isomer with the $\bullet+$ on the nitrogen can undergo homolysis and α -cleavage.

homolysis **α -cleavage**

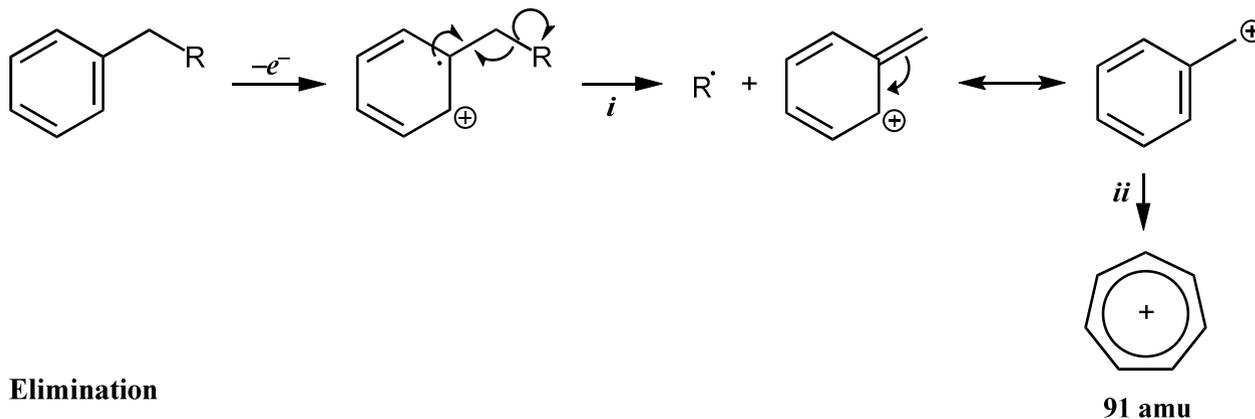
Depending on the N-alkyl substituent(s), some 2° and 3° amides exhibit peaks at 30 and 44 amu, corresponding to the $[\text{H}_2\text{C}=\text{NH}_2]^+$ and $[\text{O}=\text{C}=\text{NH}_2]^+$ ions, respectively. However, attempting to draw an arrow pushing mechanism for the formation of these fragments can be extremely challenging.

Lesson VII.13. Fragmentation of Arenes

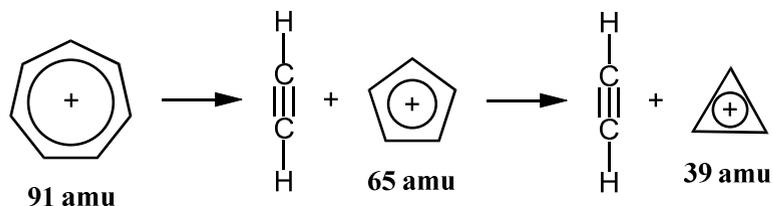
Lesson VII.13.1 Alkyl Substituents Only

If only an alkyl substituent is present on an arene, the radical cation character of the molecular ion resides in the π -system of the arene. The M^+ peak is typically strong, and the principal fragmentation mode is α -cleavage to form, after rearrangement, the tropylium cation (91 amu). Interestingly, $[C_7H_7]^+$ can release acetylene ($H-C\equiv C-H$, $\Delta M = -26$) to afford the $[C_5H_5]^+$ cation, which can also eliminate acetylene to afford the cyclopropenyl cation.

α -cleavage (i) then rearrangement (ii)

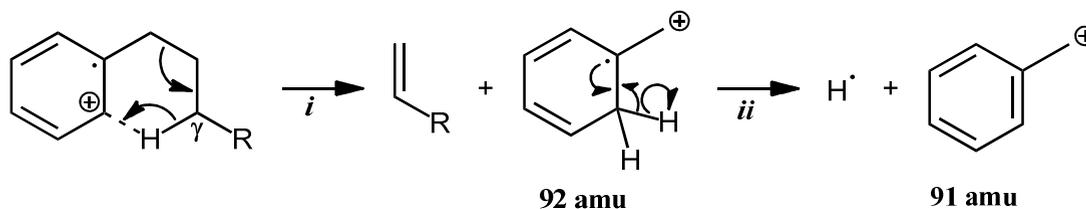


Elimination



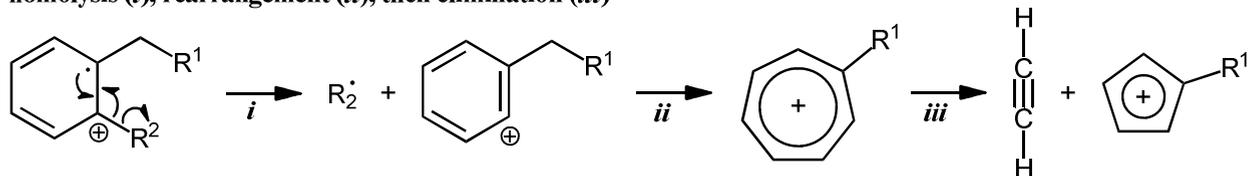
If there are hydrogen atoms at the γ -position of the alkyl chain, the molecular ion can undergo a McLafferty rearrangement. Note this affords a 92 amu radical cation, which we know will readily lose H^\cdot to yield the 91 amu benzyl cation, which can subsequently rearrange to tropylium.

McLafferty (i) then elimination (ii)



An arene with two alkyl substituents can additionally undergo homolysis of one of the arene–alkyl bonds, the driving force being the formation of a substituted tropylium (which can then undergo multiple successive eliminations of acetylene).

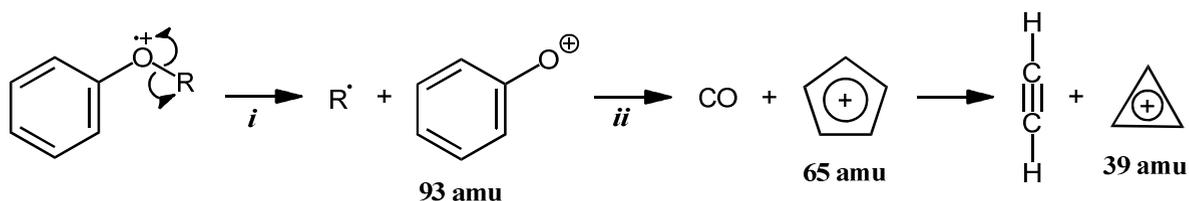
homolysis (i), rearrangement (ii), then elimination (iii)



Lesson VII.13.2 Heteroatom Attached to Arene

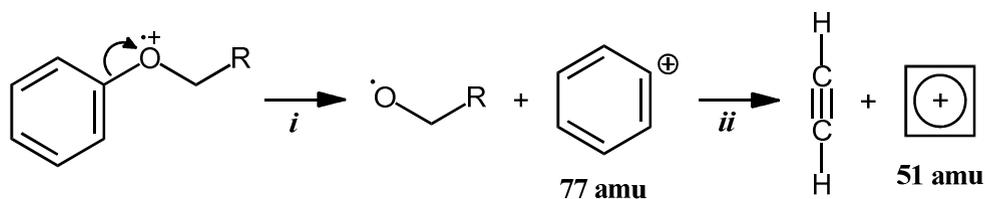
In an aryl alkyl ether, the radical cation character is primarily localized on the oxygen atom. The M^+ peak for these compounds is typically very strong. The parent ion can undergo homolysis of the oxygen–alkyl bond to generate the phenoxonium cation $[\text{PhO}]^+$, and this + charge is stabilized by delocalization across the ring. The phenoxonium cation can then eliminate $\text{C}\equiv\text{O}$ to afford $[\text{C}_5\text{H}_5]^+$, and we have already seen that this ion can fragment further.

homolysis (i) then elimination (ii)



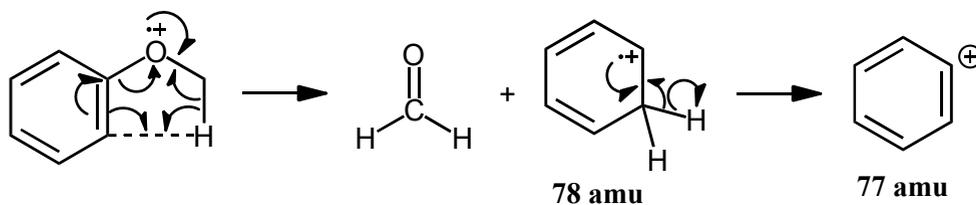
When the alkyl substituent is ethyl or larger, heterolysis of the aryl–oxygen bond can also occur, affording the phenyl cation (77 amu). Similar to $[\text{C}_7\text{H}_7]^+$, the phenyl cation can eliminate acetylene to generate $[\text{C}_4\text{H}_3]^+$ (51 amu).

heterolysis (i) then elimination (ii)

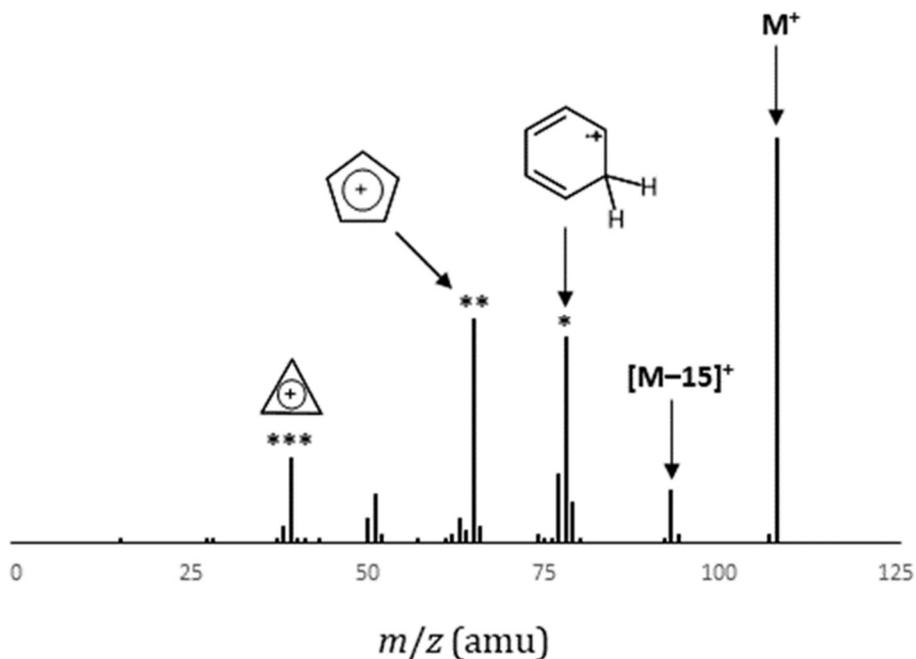


When the alkyl substituent is methyl, a rearrangement to eliminate H_2CO occurs instead, and the resulting phenyl radical cation (78 amu) will readily lose H^\bullet to afford the phenyl cation.

elimination

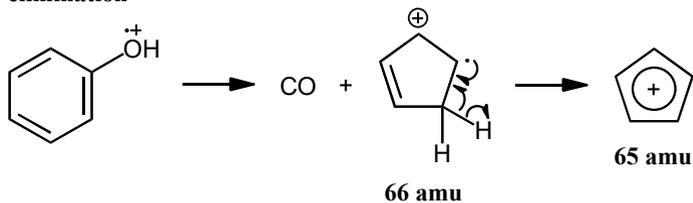


The mass spectrum of anisole reflects the fragmentation pathways described above:



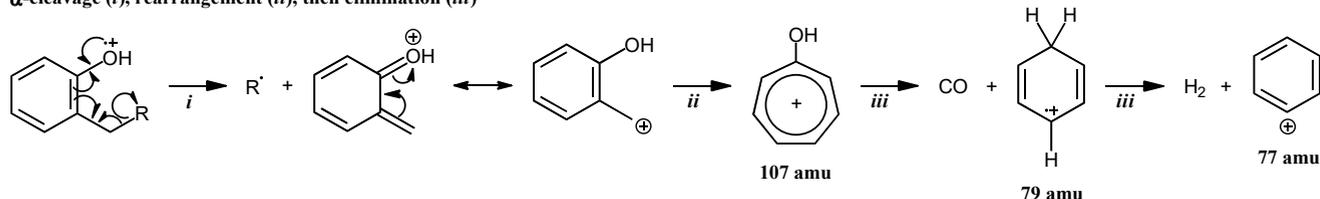
Aryl alcohols exhibit more complicated fragmentation patterns that cannot be represented as easily with arrow pushing mechanisms. Phenol, for example, displays a prominent M^+ peak, but it also displays an $[M-28]^+$ peak, which corresponds to the elimination of CO. This affords a radical cation with a mass of 66 amu, which can lose H^\bullet to yield the $[C_5H_5]^+$ cation (65 amu) and its descendant ions.

elimination

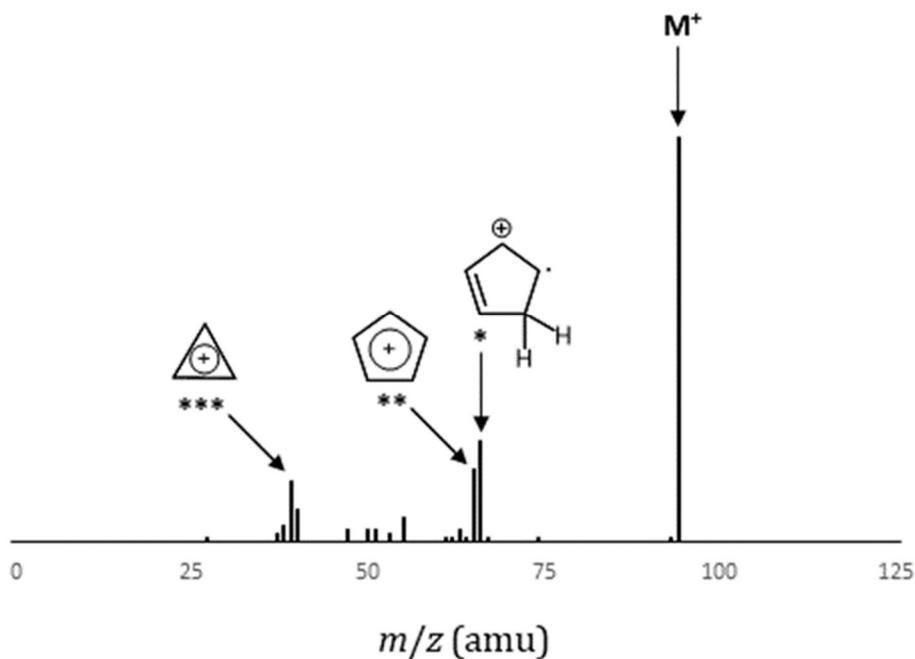


Aryl alcohols with alkyl substituents also undergo α -cleavage at the alkyl substituent, followed by a rearrangement to give hydroxytropylium (107 amu). This ion can eliminate CO to afford the $[\text{C}_6\text{H}_7]^+$ ion (79 amu), which can then eliminate H_2 to afford the phenyl cation (77 amu).

α -cleavage (i), rearrangement (ii), then elimination (iii)

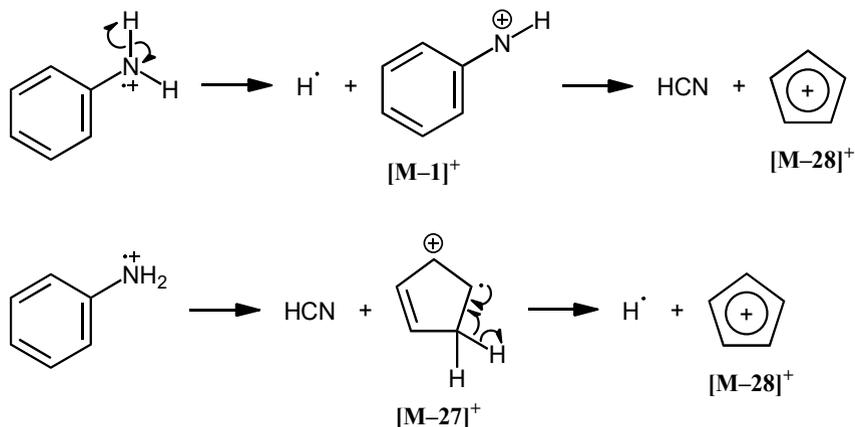


The mass spectrum of phenol reflects the fragmentation pathways described above:

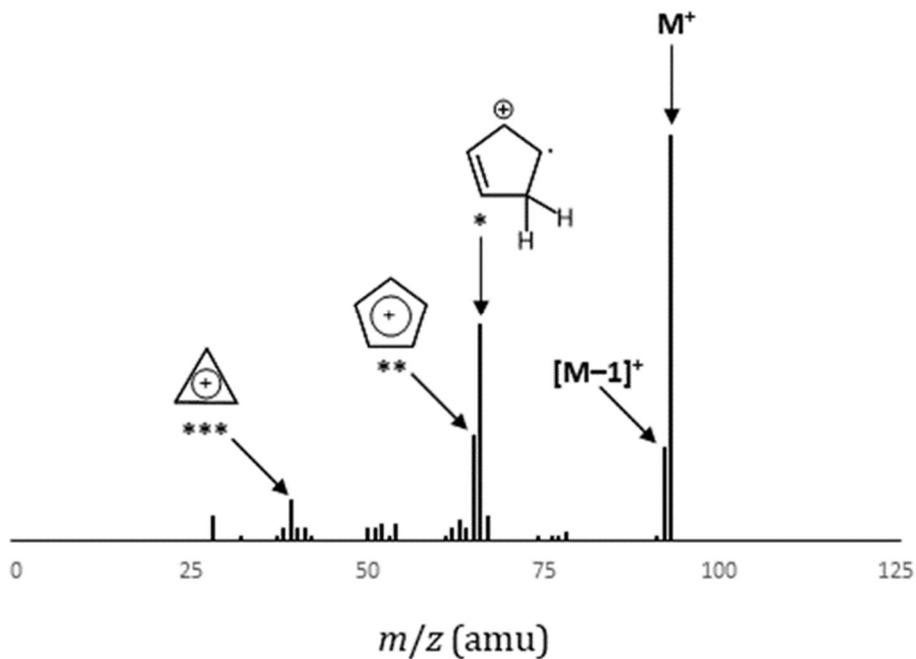


Anilines present strong $[\text{M}-1]^+$ peaks due to loss of H^\cdot in addition to prominent M^+ peaks. Note that the structure of the $[\text{M}-1]^+$ fragment is similar to that of the phenoxonium cation, which we previously learned could eliminate CO. Analogously, the $[\text{M}-1]^+$ fragment of an aniline can eliminate $\text{H}-\text{C}\equiv\text{N}$ (27 amu) to afford a peak at $[\text{M}-28]^+$. The parent ion can also eliminate HCN to afford a peak at $[\text{M}-27]^+$, which can subsequently lose H^\cdot and be converted into the $[\text{M}-28]^+$ fragment. In the case of aniline itself, we note these fragments are identical to the 65 and 66 amu fragments observed with phenol.

elimination

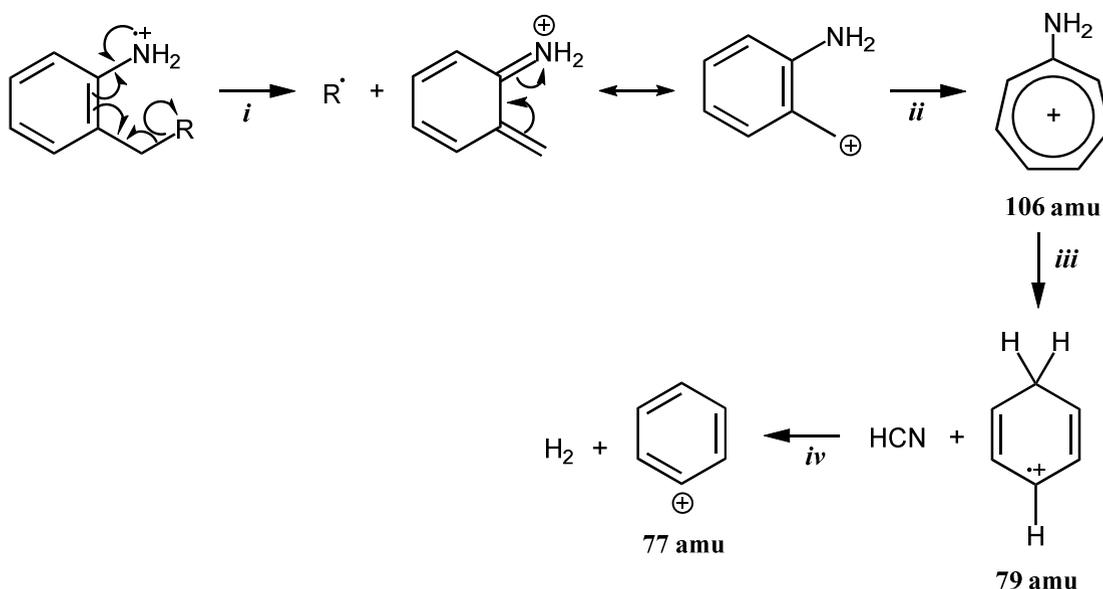


The mass spectrum of aniline reflects the fragmentation pathways described above:



Anilines with alkyl substituents on the arene can undergo α -cleavage followed by rearrangement to give the aminotropylium ion (106 amu). Similar to hydroxytropylium, aminotropylium can eliminate HCN to yield the familiar $[C_6H_7]^+$ ion, which can further fragment by losing H_2 to give the phenyl cation at 77 amu.

α -cleavage (i), rearrangement (ii), then elimination (iii)

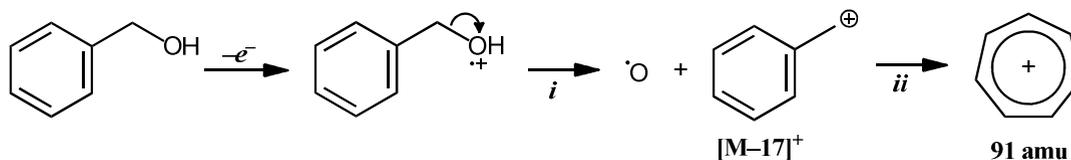


Anilines with *N*-alkyl substituents likewise undergo α -cleavage, rearrangement, and elimination to give the same peaks at 106, 79, and 77 amu, but generating an arrow-pushing mechanism for these processes is more challenging.

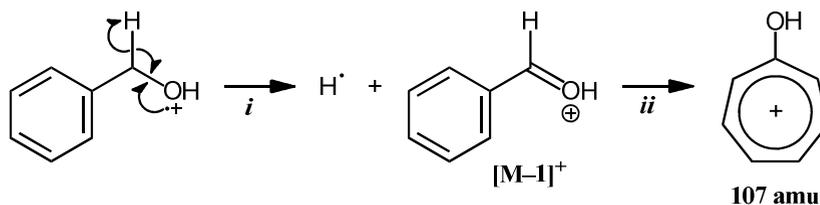
Lesson VII.13.3 Heteroatom at a Benzylic Position

The molecular ion for a compound with a heteroatom at a benzylic position features radical cation character at that heteroatom, which typically results in a strong M^+ peak. Benzyl alcohols can lose $HO\cdot$ via heterolysis and $H\cdot$ via α -cleavage. Both heterolysis and α -cleavage can subsequently be followed by rearrangement to afford tropylium and hydroxytropylium ions, respectively, which can undergo further elimination reactions (as we saw in the last lesson).

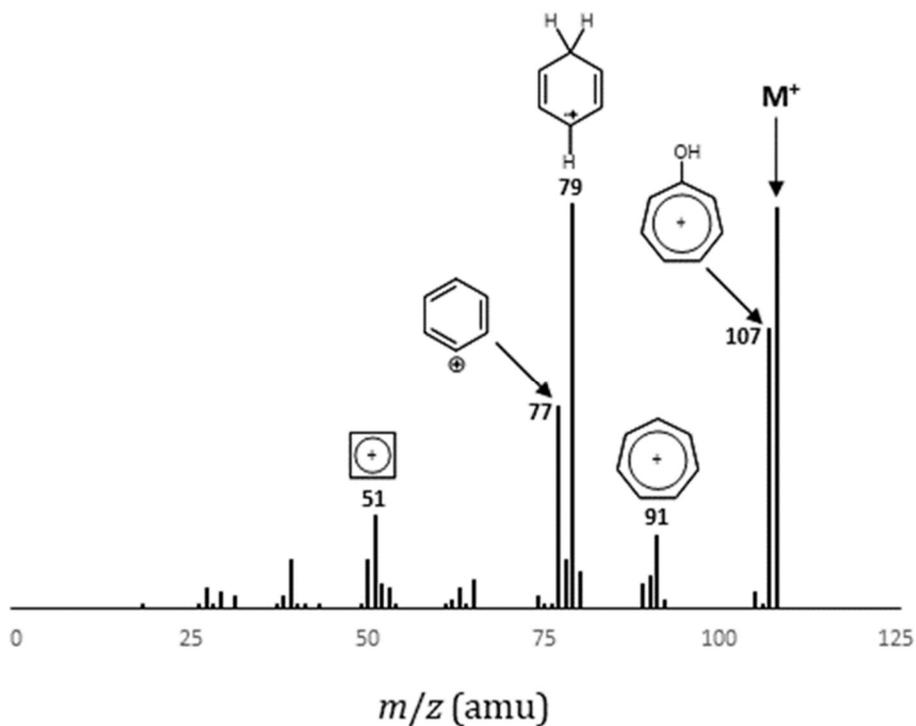
heterolysis (i) then rearrangement (ii)



α -cleavage (i) then rearrangement (ii)

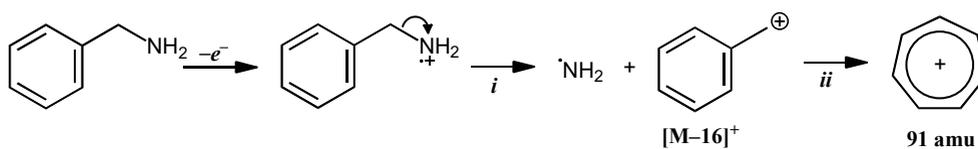


The mass spectrum of benzyl alcohol reflects the fragmentation pathways described above:

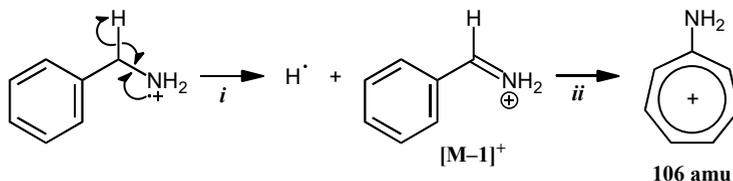


Benzylamines likewise lose H₂N[•] via heterolysis and H[•] via α -cleavage, which can be followed by rearrangement to afford tropylium and aminotropylium ions, respectively. Do not forget that these ions can also undergo subsequent elimination reactions.

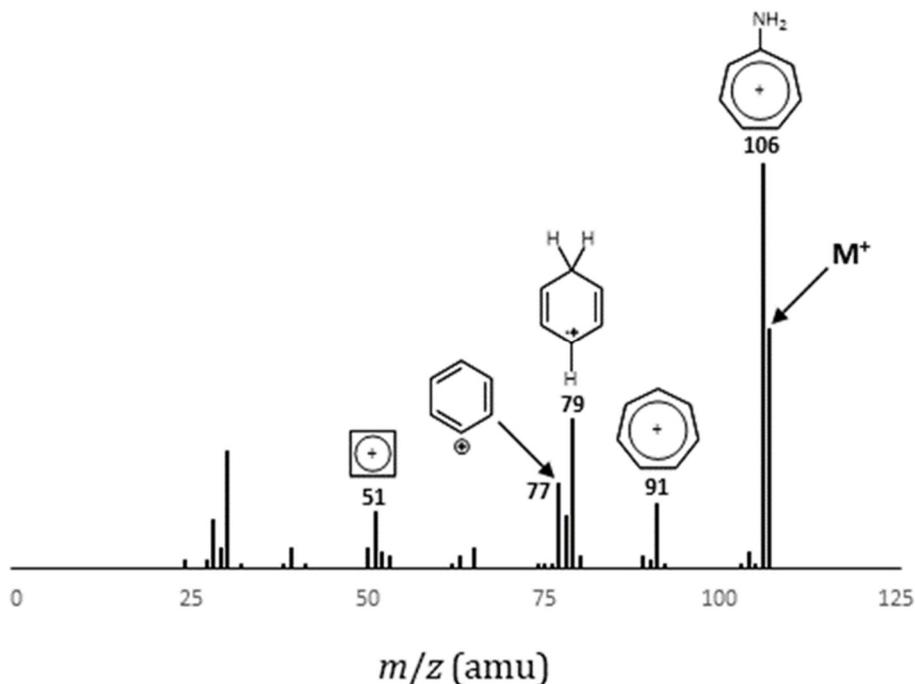
heterolysis (i) then rearrangement (ii)



α -cleavage (i) then rearrangement (ii)

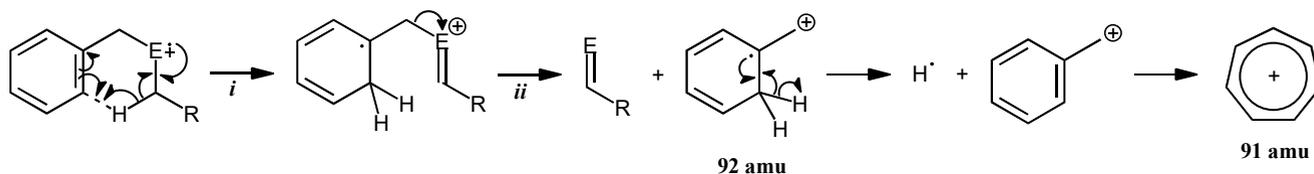


The mass spectrum of benzyl amine reflects the fragmentation pathways described above:



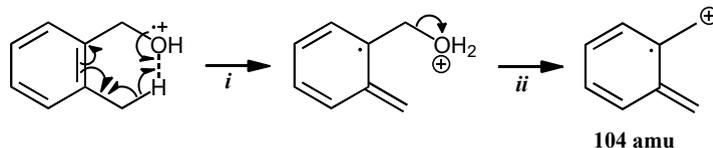
If an O-alkyl or N-alkyl substituent is present, the tropylium peak will be significantly more intense because RO^{\cdot} and RHN^{\cdot} are significantly more stable than HO^{\cdot} and H_2N^{\cdot} , which makes heterolysis of the C–O and C–N bonds more favorable. A prominent peak at 92 amu may also be observed, which can be assigned to a fragment formed by a McLafferty-like process, i.e., intramolecular H^{\cdot} transfer via a cyclic 6-membered transition state followed by elimination (shown below for $E = O$ or NR'). As might be expected, this 92 amu radical cation will readily lose H^{\cdot} to afford the familiar tropylium ion.

rearrangement (i) then elimination (ii)

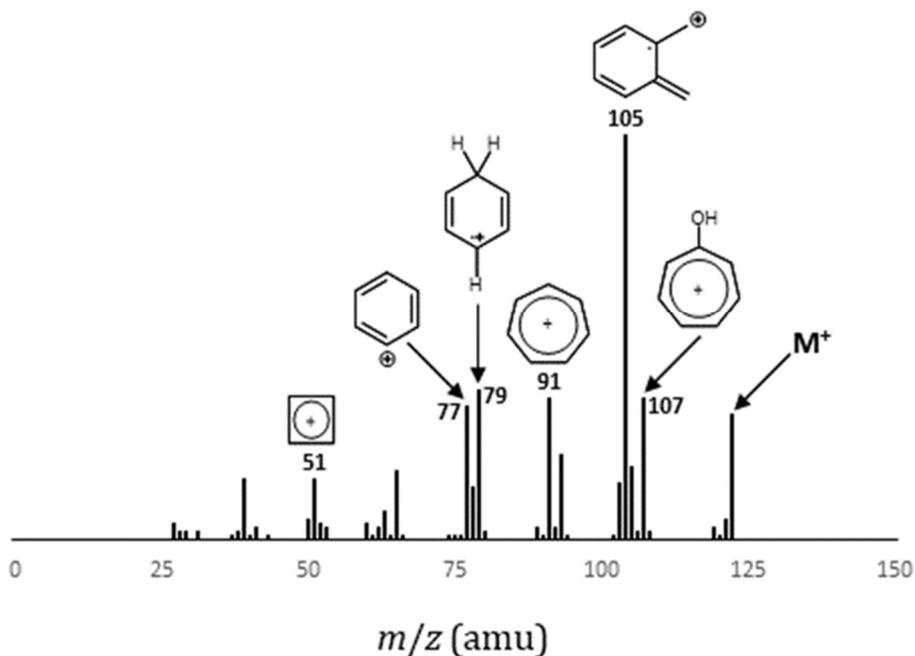


If an alkyl substituent is instead present on the arene of a benzylic alcohol or benzylamine, additional peaks appear at $[M-18]^+$ due to loss of H_2O or $[M-17]^+$ due to loss of NH_3 , respectively, via elimination. With 2-methylbenzyl alcohol, for example, the most intense peak is at 104 amu, corresponding to $[M-18]^+$. This fragment is formed from the molecular ion via intramolecular H^{\cdot} transfer via a 6-membered cyclic transition state followed by dissociation of H_2O to afford a radical cation.

rearrangement (i) then elimination (ii)



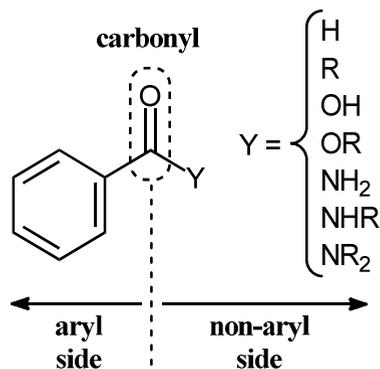
Unsurprisingly, the relative intensity of the peak at 104 amu decreases when the methyl substituent goes from the 2- to the 3- to the 4-position. The mass spectrum of 2-methylbenzyl alcohol reflects the fragmentation pathways described above:



A similar mechanism occurs in the elimination of NH_3 from appropriately substituted benzylamines.

Lesson VII.13.4 Carbonyl at a Benzylic Position

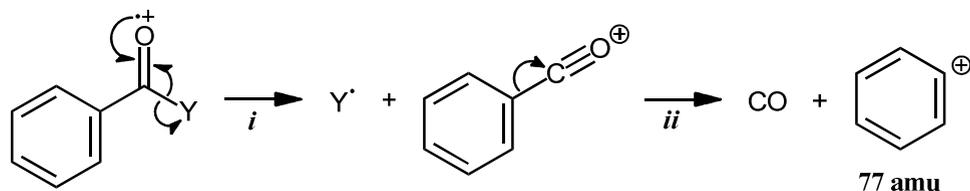
To discuss the fragmentation of molecules with carbonyl groups at the benzylic position, it is first convenient to introduce some shorthand terms to simplify our discussion in this Lesson. We will divide these molecules along the location of the carbonyl subunit. The side with the aryl ring will be referred to as the "aryl side" and the other side will be cleverly and creatively termed the "non-aryl side". Note that the identity of Y will vary based on the identity of the functional group: aldehydes (H), ketones (R), carboxylic acids (OH), esters (OR), and amides (NH_2 , NHR, NR_2).



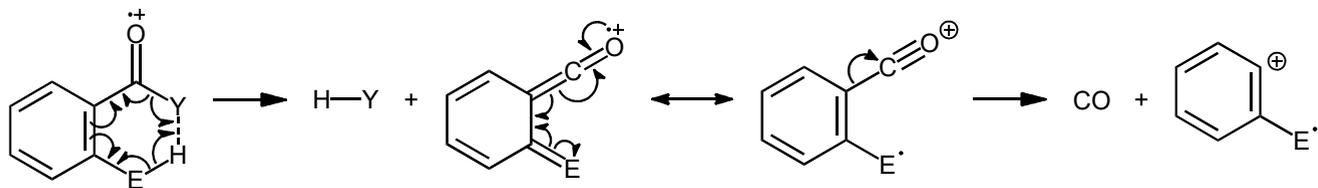
Each of these classes of molecules will undergo some fragmentation processes that are identical to what we have previously covered and some that are new. Essentially, the fragmentation pathways of the non-aryl side are identical to what we have previously covered with the non-aryl molecules. As a result, in this Lesson, we only need to discuss the fragmentation pathways involving the aryl side, and these are conserved for all identities of Y.

The primary fragmentation pathway for these types of molecules is α -cleavage along the C–Y bond, which releases Y^{*} and the [Ph–C≡O]⁺ cation. This cation can eliminate CO to afford the familiar phenyl cation at 77 amu, which itself can undergo subsequent elimination reactions.

α -cleavage (i) then elimination (ii)



If a substituent –EH is located *ortho* to the carbonyl-based functional group, where E can be CH₂, CHR, CR₂, O, NH, or NHR, then an additional fragmentation pathway becomes available. First, H–Y can eliminate, leaving behind a ketene (i.e., a molecule containing a C=C=O moiety) radical cation. We can draw another resonance structure for this radical cation, which illustrates the next fragmentation reaction, specifically the elimination of CO.



E = CH₂, CHR, CR₂
O, NH, NR

Lesson VII.14. Fragmentation of Alkenes

Lesson VII.14.1 Linear Alkenes

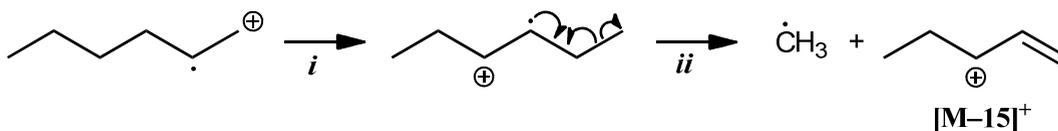
Ionization of an alkene removes an electron from the C–C π -bond, which places the radical on one of the alkene carbons and the + on the other alkene carbon. Because these electrons are so much easier to remove than those in C–C and C–H σ -bonds, the M^+ peak for an alkene is generally much stronger than for an alkane. To understand the fragmentation modes, let us consider 1-hexene specifically. We can draw the molecular ion with the + on the less substituted carbon and the \cdot on the more substituted carbon. We can then see how α -cleavage would release an allyl cation (41 amu).

α -cleavage

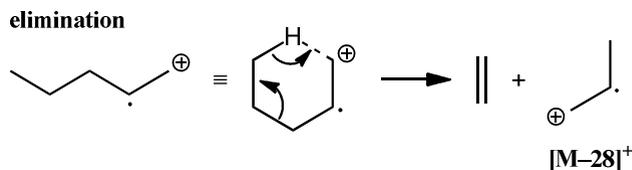


Due to the high energies involved in the mass spectrometry experiment, the position of the C=C bond will freely migrate over all the carbons. As a result, **every** alkene will show a peak at 41 amu due to the allyl cation. Aside from that, the fragmentation pattern for alkenes is similar to alkanes: there will be a peak at $[M-15]^+$ due to loss of $\cdot\text{CH}_3$, at $[M-29]^+$ due to loss of $\cdot\text{CH}_3\text{CH}_2$, etc. Drawing a mechanism for these fragments can only be done after the position of the C=C bond has moved.

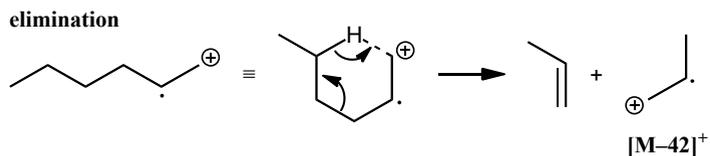
rearrangement (i) then α -cleavage (ii)



All alkenes exhibit an $[M-28]^+$ peak due to the elimination of $\text{H}_2\text{C}=\text{CH}_2$, which can occur via a McLafferty-like rearrangement (shown below for 1-pentene).

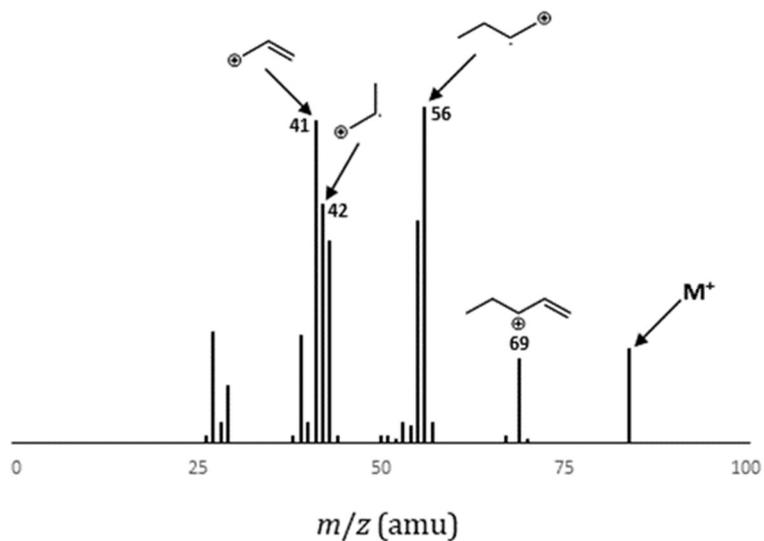


Alkenes longer than pentene can, in addition to eliminating $\text{H}_2\text{C}=\text{CH}_2$, also eliminate longer-chain alkenes, such as propene, butene, etc., depending on the initial chain length:

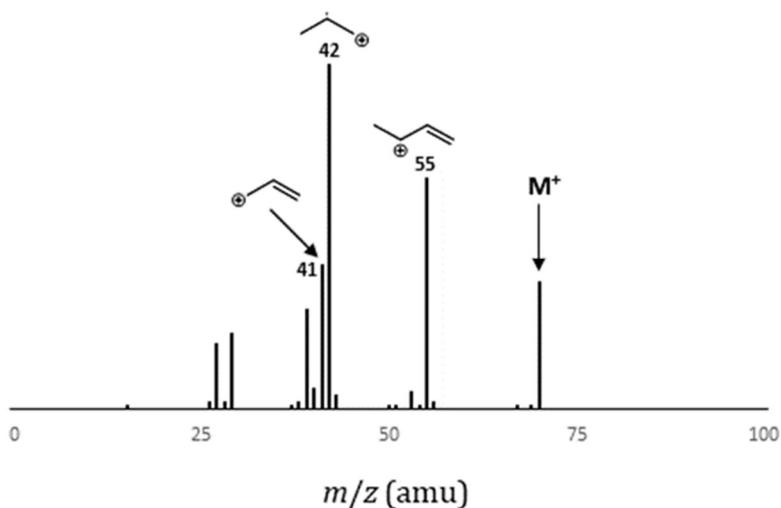


It is important to emphasize that **all** alkenes exhibit an $[M-28]^+$ peak, but it is not always possible to draw a McLafferty-like rearrangement or other mechanism that would make sense given the initial molecule (e.g., 2-methyl-2-butene). The mass spectrum of 1-hexene and 1-pentene illustrate the above-mentioned fragmentation pathways.

MS for 1-hexene:



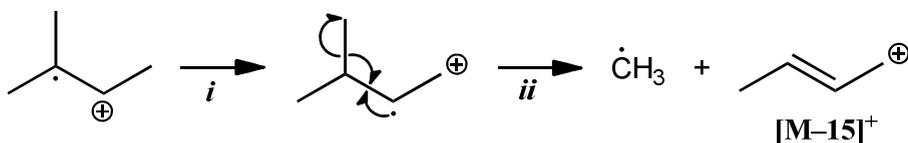
MS for 1-pentene:



Lesson VII.14.2 Branched Alkenes

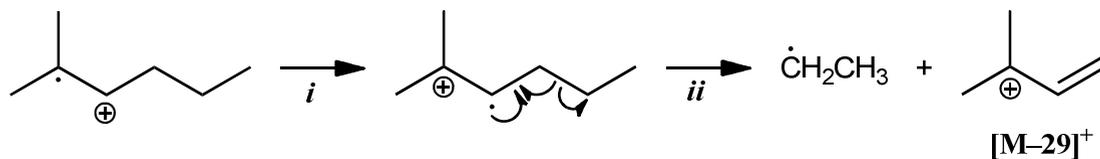
Branched alkenes also exhibit M^+ peaks, as well as many of the same fragmentation peaks as linear alkenes, e.g., 41 amu (allyl cation), $[M-15]^+$, $[M-28]^+$, $[M-29]^+$, etc. However, the relative intensity of the α -cleavage peaks will differ between branched and linear alkenes. One reason is that α -cleavage will occur more readily at any branched sites (similar to alkane behavior), thus the corresponding peaks will be more intense.

rearrangement (i) then α -cleavage (ii)



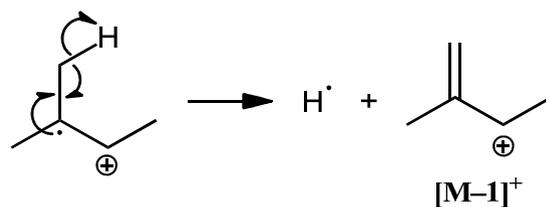
Analogously, a carbocation will be stabilized to a greater extent at a more substituted carbon, so any α -cleavage process that affords an allylic cation at a more substituted carbon will be more favorable.

rearrangement (i) then α -cleavage (ii)



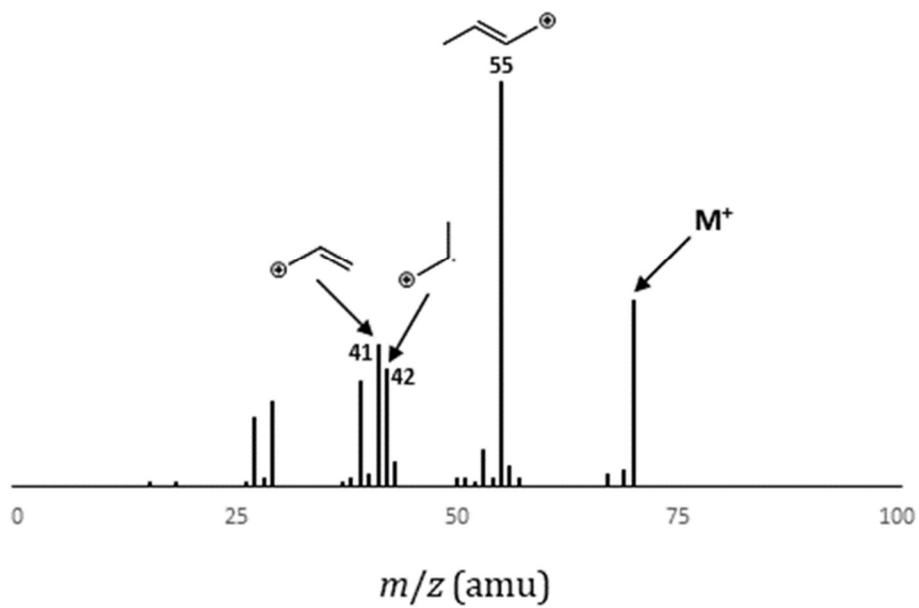
Molecules with a branch attached to an alkene carbon can occasionally exhibit $[M-1]^+$ peaks with weak intensity due to α -cleavage of H^{\cdot} .

α -cleavage



The MS for 2-methyl-2-butene demonstrates fragmentation in branched alkenes, and is shown on the following page.

MS for 2-methyl-2-butene

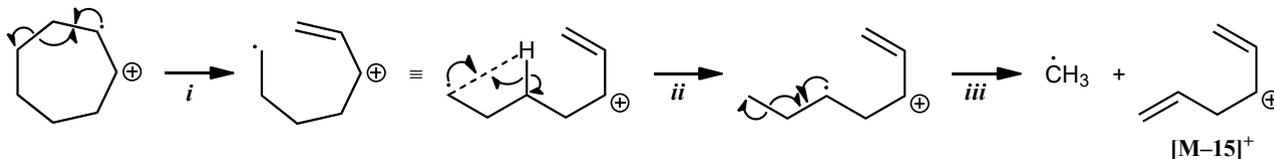


Lesson VII.14.3 Cycloalkenes

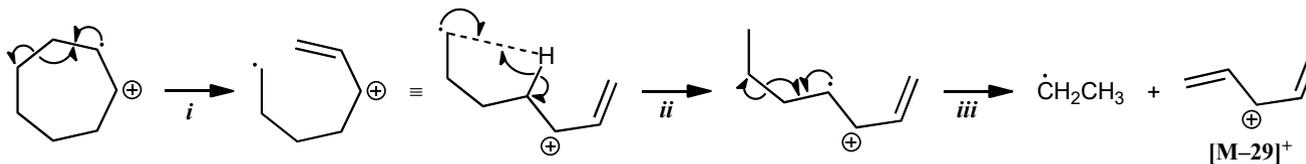
Cycloalkenes exhibit more intense M^+ peaks than acyclic alkenes, for the same reasons that M^+ peaks are more intense for cycloalkanes than acyclic alkanes. Cycloalkenes also exhibit significantly $[M-1]^+$ peaks than acyclic alkenes.

Interestingly, cycloalkenes still exhibit peaks at $[M-15]^+$, $[M-29]^+$, etc., consistent with elimination of alkyl radicals, despite the fact that there are no CH_3 groups in any of these molecules. Shown below are mechanisms for the elimination of $\cdot CH_3$ and $\cdot CH_2CH_3$ from cycloheptene.

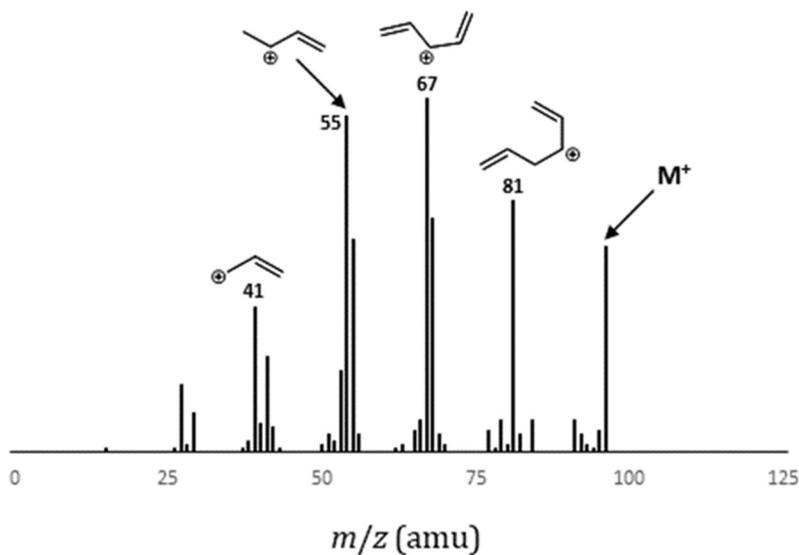
α -cleavage (i), rearrangement (ii), then elimination (iii)



α -cleavage (i), rearrangement (ii), then elimination (iii)



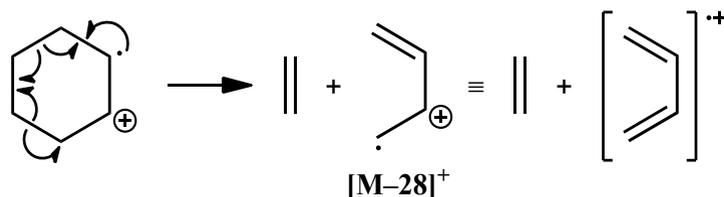
The MS for cycloheptene further demonstrates these fragmentation pathways:



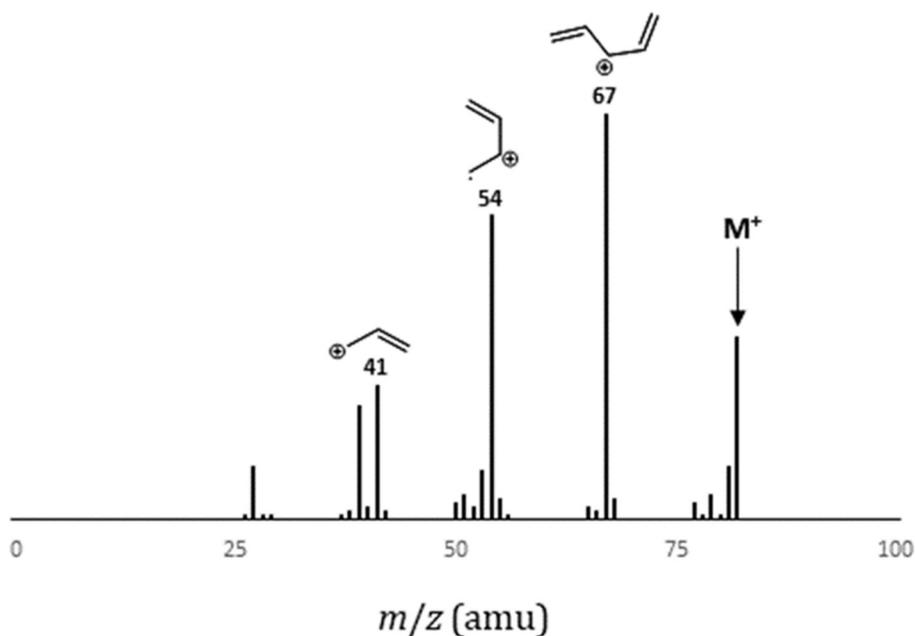
However, cyclopentene also exhibits $[M-15]^+$ and $[M-29]^+$ peaks, and cyclohexene also exhibits an $[M-29]^+$ peak, even though it is not possible to draw analogous mechanisms to form these fragments from these molecules. Likewise, **all** cycloalkenes exhibit peaks at 41 amu from the allyl cation.

Cyclohexene can undergo a retro Diels-Alder reaction to eliminate $H_2C=CH_2$ and yield an $[M-28]^+$ peak. It should be noted that this type of reaction can only occur with 6-membered rings. It is sometimes convenient to draw the radical cation using the square bracket convention, as it more readily depicts the diene fragment generated upon retro Diels-Alder release of the dienophile. Substituted cyclohexenes may eliminate alkenes larger than ethylene.

retro Diels-Alder



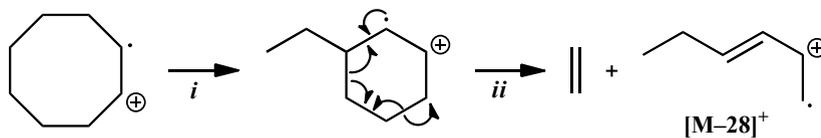
Here is the MS for cyclohexene:



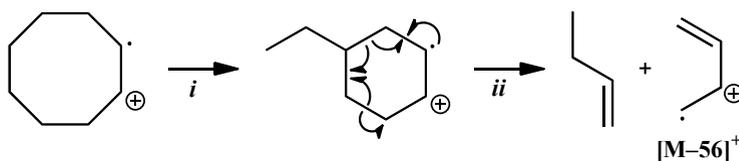
Interestingly, cycloalkenes larger than cyclohexene still exhibit $[M-28]^+$ peaks, despite the fact that they lack the necessary geometry to undergo retro Diels-Alder. One possible way to draw a mechanism is to consider rearrangement of the initial radical cation (feasible at the high energies of typical mass spectrometry experiments). For example, we could draw the rearrangement of an 8-membered ring into

an ethyl-substituted 6-membered ring, which would be capable of retro Diels-Alder. It is then possible to draw retro Diels-Alder reactions that eliminate either ethylene (28 amu) or 1-butene (56 amu). Indeed, cyclooctene exhibits intense $[M-28]^+$ and $[M-56]^+$ peaks.

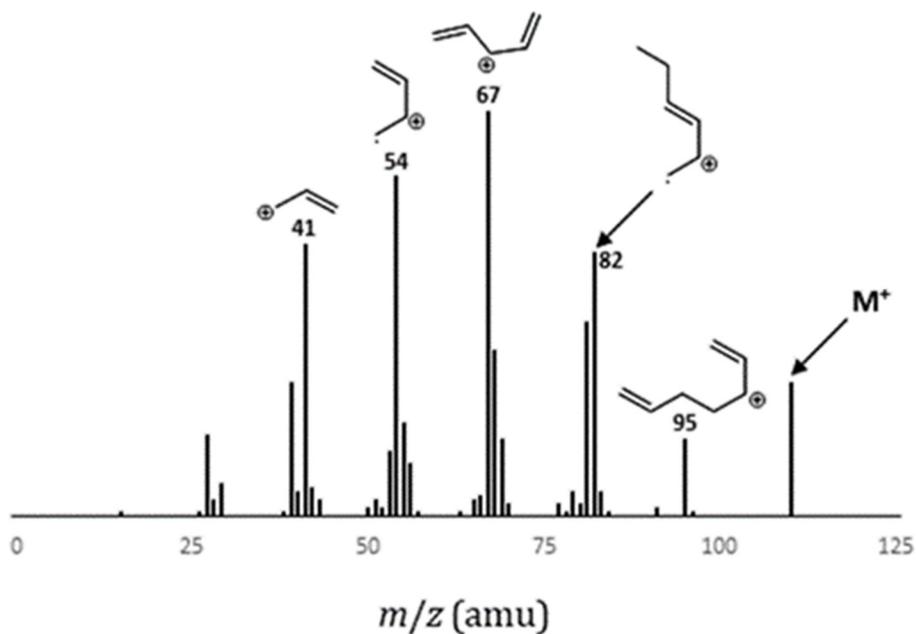
rearrangement (i) then retro Diels-Alder (ii)



rearrangement (i) then retro Diels-Alder (ii)



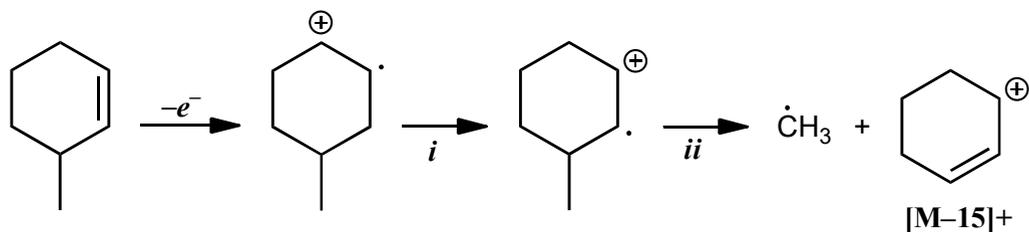
The MS for cyclooctene reflects these fragmentation pathways:



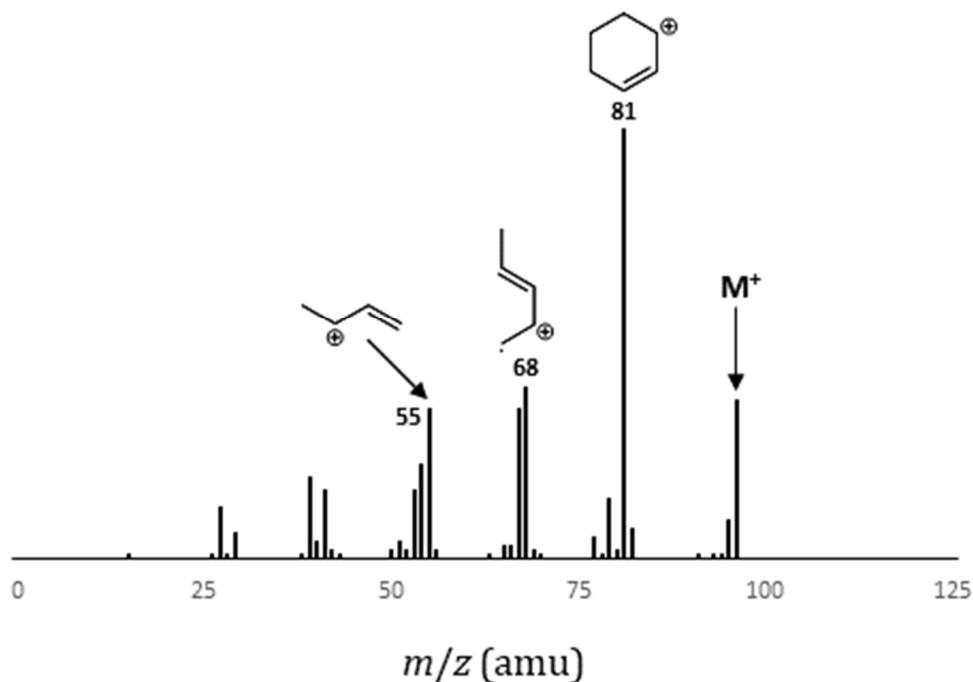
Lesson VII.14.4 Branched Cycloalkenes

Cycloalkenes with alkyl substituents on the ring undergo all of the same fragmentation reactions as those without alkyl substituents. However, a branched cycloalkene also undergoes α -cleavage to release the alkyl substituent as R^\bullet , and it is this fragmentation process that usually produces the most intense peak. Keep in mind that the position of the C=C bond freely migrates, so the location of the \bullet and $+$ may shift. As an example, 3-methyl-1-cyclohexene is shown below.

rearrangement (i) then α -cleavage (ii)



The MS for 3-methyl-1-cyclohexene further demonstrates these fragmentation pathways:

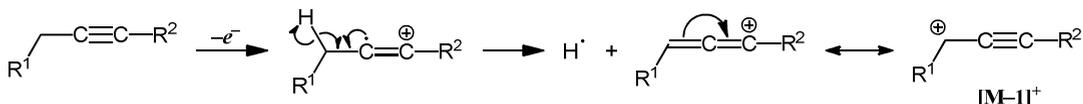


Lesson VII.15. Fragmentation of Other Unsaturated Molecules

Lesson VII.15.1 Alkynes

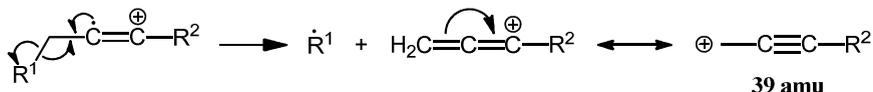
Similar to an alkene, ionization of an alkyne removes an electron from a C–C π -bond, which places the radical on one alkyne carbon and the + on the other. The M^+ peak for an alkyne is more intense than for an alkane, but the M^+ peak is much weaker for terminal alkynes than for internal alkynes. Whereas alkenes typically do not exhibit $[M-1]^+$ peaks, alkynes frequently exhibit $[M-1]^+$ peaks, which can be attributed to α -cleavage of a C–H bond to afford a propargylic carbocation.

α -cleavage



Alternatively, α -cleavage could instead release an alkyl radical. If $R^2 = \text{H}$, a characteristic peak can be observed at 39 amu. However, the position of the $\text{C}\equiv\text{C}$ bond can migrate, so a peak at 39 amu is even observed with internal alkynes, therefore its presence cannot be interpreted as evidence that the analyte is a terminal alkyne.

α -cleavage

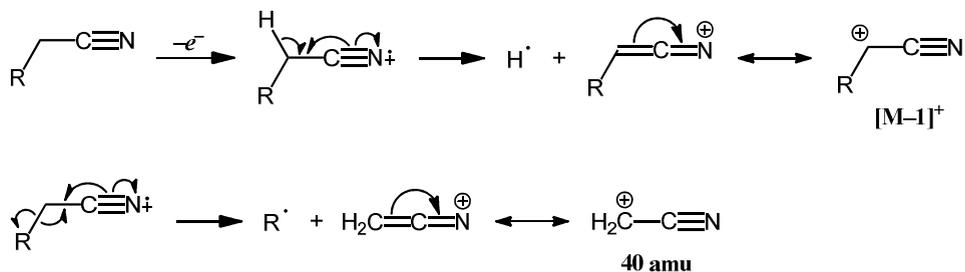


Keep in mind that the alkyl components of alkynes can still undergo alkane fragmentation reactions, so much of the mass spectrum of an alkyne will comprise $[M-15]^+$, $[M-29]^+$, etc., peaks.

Lesson VII.15.2 Nitriles

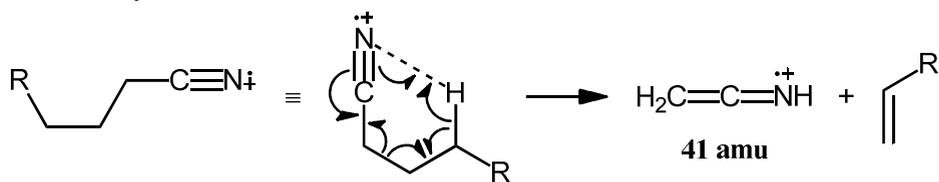
The $\bullet+$ on a nitrile is localized on the N, rather than spread over a C–N π -bond, because e^- in lone pairs are higher in energy (and thus easier to remove) than e^- in π -bonds. However, mass spectra and fragmentation modes of nitriles are highly conserved with those of alkynes, although M^+ peak intensities are generally lower for nitriles than alkynes. Nitriles readily undergo α -cleavage to release H^\bullet or alkyl radicals, although peaks from the latter are typically of lower intensity than in alkynes.

α -cleavage



In addition, a nitrile can undergo a McLafferty-like rearrangement to eliminate an alkene and afford a radical cation at 41 amu, which is often one of the most intense peaks.

McLafferty



Lastly, a nitrile can also eliminate HCN (giving an M-27 peak) to leave behind an alkyl radical cation, but this peak is generally weak.