Chapter 9 Nuclear Magnetic Resonance and Mass Spectrometry: Tools for Structure Determination

# Introduction

- Spectroscopy: the study of the interaction of energy with matter
  - → Energy applied to matter can be absorbed, emitted, cause a chemical change, or be transmitted
  - → Spectroscopy can be used to elucidate the structure of a molecule

## • Examples of Spectroscopy

- → Infrared (IR) Spectroscopy (Chapter 2)
  - Infrared energy causes bonds to stretch and bend
  - IR is useful for identifying functional groups in a molecule

#### → Nuclear Magnetic Resonance (NMR)

- Energy applied in the presence of a strong magnetic field causes absorption by the nuclei of some elements (most importantly, hydrogen and carbon nuclei)
- NMR is used to identify connectivity of atoms in a molecule

#### → Mass Spectrometry (MS)

- Molecules are converted to ions by one of several methods (including bombardment by a beam of electrons)
- P The ions formed may remain intact (as molecular ions, M+), or they may fragment
- P The resulting mixture of ions is sorted by mass/charge (*m/z*) ratio, and detected
- Molecular weight and chemical formula may be derived from the M+ and M+1 ions
- **Molecular structure may be deduced from the distribution of fragment ions**

# The Electromagnetic Spectrum

- → Electromagnetic radiation has the characteristics of both waves and particles
- → The wave nature of electromagnetic radiation is described by wavelength ( $\lambda$ ) or frequency (v)
- The relationship between wavelength (or frequency) and energy
   (E) is well defined

 $E = h\nu$ 

where  $h = \text{Planck's constant}, 6.63 = 10^{-34} \text{ J s}$ 

 $\nu =$ frequency (Hz)

$$E = \frac{hc}{v}$$

where c = velocity of light

Wavelength and frequency are inversely proportional (v= c/λ)
 The higher the frequency, the greater the energy of the wave
 The shorter the wavelength, the greater the energy of the wave

#### → NMR involves absorption of energy in the radiofrequency range



# Nuclear Magnetic Resonance (NMR) Spectroscopy

- ➔ The nuclei of protons (<sup>1</sup>H) and carbon-13 (<sup>13</sup>C), and certain other elements and isotopes, behave as if they were tiny bar magnets
- → When placed in a magnetic field and irradiated with radio frequency energy, these nuclei absorb energy at frequencies based on their chemical environments
- → NMR spectrometers are used to measure these absorptions
- Continuous-Wave (CW) NMR Spectrometers
  - → The oldest type of NMR spectrometer
  - The magnetic field is varied as the electromagnetic radiation is kept at a constant frequency
  - ➔ Different nuclei absorb the electromagnetic energy based on their chemical environment and produce peaks in different regions of the spectrum

## • Fourier Transform (FT) NMR Spectrometers

- The sample is placed in a constant (and usually very strong) magnetic field
- ➔ The sample is irradiated with a short pulse of radio frequency energy that excites nuclei in different environments all at once
- The resulting signal contains information about all of the absorbing nuclei at once
- → This signal is converted to a spectrum by a Fourier transformation
- → FT NMR allows signal-averaging, which leads to enhancement of real spectral signals versus noise
- The strong, superconducting magnets used in FTNMR spectrometers lead to greater sensitivity and much higher resolution than continuous wave instruments

## • Chemical Shift: Peak Position in an NMR Spectrum

- Nuclei in different chemical environments in a molecule will absorb at slightly different frequencies
- The position of the signals in the spectrum is called the "chemical shift"
- ➔ There are two reasons for differences in the magnetic environment for a proton
  - P The magnetic field generated by electrons circulating around the nucleus giving the signal
  - P Local magnetic fields generated by electrons elsewhere in the molecule

#### → Example: 1,4-dimethylbenzene



- P The spectrum is measured on a delta ( $\delta$ ) scale in units of parts per million (ppm)
- Lower frequency is to the left in the spectrum; these absorptions are said to be downfield
- Higher frequency is to the right in the spectrum: these absorptions are said to be upfield
- $\ref{P}$  The small signal at  $\delta$  0 corresponds to an internal standard called tetramethylsilane (TMS) used to calibrate the chemical shift scale
- P The number of signals in the spectrum corresponds to the number of unique sets of protons
- I,4-dimethylbenzene has protons in two unique environments and so shows two signals

- Integration of Peak Areas. The Integral Curve
  - → The area under each signal corresponds to the relative number of hydrogen atoms in each unique environment within a molecule
    - P The height of each step in the integral curve is proportional to the area of the signal underneath the step
- Signal Splitting
  - → The signal from a given proton will be split by the effect of magnetic fields associated with protons on adjacent carbons
  - → Characteristic peak patterns result from signal splitting that are related to the number of protons on adjacent carbons
  - → Example: 1,1,2-trichloroethane



# Nuclear Spin: The Origin of the Signal

- ➔ The nuclei of certain elements and isotopes have spin states that are quantized
- → <sup>1</sup>H has a spin quantum number I = 1/2 and has allowed spin states of +1/2 or -1/2
- → Other nuclei with I = 1/2 are <sup>13</sup>C, <sup>19</sup>F and <sup>31</sup>P and these also respond to an external magnetic field
- Nuclei with I = 0 do not have spin (<sup>12</sup>C and <sup>16</sup>O) and do not respond to an external magnetic field
- → The nuclei of NMR-active nuclei behave like tiny bar magnets
- ➔ In the absence of an external magnetic field these bar magnets are randomly orientated
- → In an external magnetic field they orient either with ( $\alpha$  spin state) or against ( $\beta$  spin state) the magnetic field



- Nuclei aligned with the magnetic field are lower in energy than those aligned against the field
- → The nuclei aligned with the magnetic field can be flipped to align against it if the right amount of energy is added ( $\Delta E$ )
- → The amount of energy required depends on the strength of the external magnetic field
  - P The stronger the external magnetic field, the higher the radio frequency energy required to flip the nuclear spin



- At (a) there is no external magnetic field and therefore no energy difference between the two states
- At (b) the external magnetic field is 1.41 Tesla and energy corresponding to a frequency of about 60MHz is needed to flip between the spin states
- At (c) the external magnetic field is 7.04 Tesla energy corresponding to a frequency of about 300MHz is needed to flip between the spin states Chapter 9

# Shielding and Deshielding of Protons

- Protons in an external magnetic field absorb at different frequencies depending on the electron density around that proton
- → High electron density around a nucleus shields the nucleus from the external magnetic field
  - Shielding causes absorption of energy at higher frequencies (more energy is required for this nucleus to flip between spin states) - the signals are upfield in the NMR spectrum
- → Lower electron density around a nucleus *deshields* the nucleus from the external magnetic field
  - P Deshielding causes absorption of energy at lower frequencies (less energy is required for this nucleus to flip between spin states) - the signals are downfield in the NMR spectrum



- → Electronegative atoms draw electron density away from nearby protons and therefore deshield them
- $\rightarrow$  Circulation of  $\pi$  electrons leads to a local induced magnetic field
  - P The induced field can reinforce or diminish the external field sensed by a proton (depending on the location of the proton), causing deshielding or shielding, respectively
  - $\ensuremath{\,{\scriptscriptstyle P}}$  Alkene and aromatic ring hydrogens are deshielded by the circulation of  $\pi$  electrons.
  - P A terminal alkyne hydrogen is shielded by the circulation of  $\pi$  electrons.



# Chemical Shift

- → Chemical shifts are measured in relation to the internal reference tetramethylsilane (TMS)
  - The protons of TMS are highly shielded because of the strong electron donating capability of silicon
  - P The signal for TMS is well away from most other proton absorptions

 $Si(CH_3)_4$ 

Tetramethylsilane (TMS)

→ The  $\delta$  scale for chemical shifts is independent of the magnetic field strength of the instrument (whereas the absolute frequency depends on field strength)

 $\delta = \frac{\text{(observed shift from TMS in hertz)} \times 10^{6}}{\text{(operating frequency of the instrument in hertz)}}$ 

→ Thus, the chemical shift in  $\delta$  units for protons on benzene is the same whether a 60 MHz or 300 MHz instrument is used

$$\delta = \frac{2181 \text{ Hz} \times 10^6}{300 \times 10^6 \text{ Hz}} = 7.27$$

$$\delta = \frac{436 \text{ Hz} \times 10^6}{60 \times 10^6 \text{ Hz}} = 7.27$$



# Chemical Shift Equivalent and Nonequivalent Protons

- ➔ To predict the number of signals to expect in an NMR spectrum it is necessary to determine how many sets of protons are in unique environments
- → Chemically equivalent protons are in the same environment and will produce only one signal

## • Homotopic Hydrogens

➔ Hydrogens are chemically equivalent or homotopic if replacing each one in turn by the same group would lead to an identical compound



#### • Enantiotopic and Diastereotopic Hydrogen Atoms

➔ If replacement of each of two hydrogens by some group leads to enantiomers, those hydrogens are enantiotopic

In the absence of a chiral influence, enantiotopic hydrogens have the same chemical shift and appear in the same signal



- ➔ If replacement of each of two hydrogens by some group leads to diastereomers, the hydrogens are diastereotopic
  - Diastereotopic hydrogens have different chemical shifts and will give different signals



# Signal Splitting: Spin-Spin Coupling

- The signal from a given proton will be split by the effect of magnetic fields associated with protons on adjacent carbons
- → Characteristic peak patterns result from signal splitting that are related to the number of protons on adjacent carbons
  - $\ref{eq:product}$  The effect of signal splitting is greatest between atoms separated by 3 or fewer  $\sigma$  bonds



*tert*-Butyl methyl ether (no signal splitting)

Signal splitting is not observed between homotopic or enantiotopic protons

CH<sub>3</sub>CH<sub>3</sub> (no signal splitting)

→ Signal splitting occurs only when two sets of protons have different chemical shifts (*i.e.*, are not chemical shift equivalent)

- → The magnetic field sensed by a proton ( $H_a$ ) being observed is affected by the magnetic moment of an adjacent proton ( $H_b$ )
  - $\ref{P}$  A proton (H\_b) can be aligned with the magnetic field or against the magnetic field, resulting in two energy states for H\_b
  - The observed proton (H<sub>a</sub>) senses the two different magnetic moments of H<sub>b</sub> as a slight change in the magnetic field; one magnetic moment reinforces the external field and one substracts from it
  - $\mathbb{P}$  The signal for H<sub>a</sub> is split into a doublet with a 1:1 ratio of peak areas
  - The magnitude of the splitting is called the coupling constant J<sub>ab</sub> and is measured in Hertz (Hz)



- → When two adjacent protons H<sub>b</sub> are coupled to H<sub>a</sub>, there are four possible combinations of the magnetic moments for the two H<sub>b</sub>s
  - Two of these combinations involve pairings of magnetic moments that cancel each other, causing no net displacement of signal
  - One combination of magnetic moments reinforces and another subtracts from the applied magnetic field
  - 𝑘 H<sub>a</sub> is split into a triplet having a 1:2:1 ratio of signal areas



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# → When three adjacent protons are coupled to H<sub>a</sub>, there are 10 possible combinations of the magnetic moments for the H<sub>b</sub>s

 Four unique orientations exist and so H<sub>a</sub> is split into a quartet with intensities 1:4:4:1



The general rule for splitting is that if there are n equivalent protons on adjacent atoms, these will split a signal into n + 1 peaks

#### → Coupled peaks have the same coupling constants J

P Comparison of coupling constants can help with the analysis of complex spectra

#### → Several factors complicate analysis of NMR spectra

- Peaks may overlap
- P Spin-spin coupling can be long-range (i.e., more than 3 bonds)

#### → Splitting patterns in aromatic groups can be confusing

A monosubstituted aromatic ring can appear as an apparent singlet or a complex pattern of peaks



- → Much more complex splitting can occur when two sets of adjacent protons split a particular set of protons
- $\rightarrow$  In the system below, H<sub>b</sub> is split by two different sets of hydrogens
  - :  $H_a$  and  $H_c$ 
    - P Theortically H<sub>b</sub> could be split into a triplet of quartets (12 peaks) but this complexity is rarely seen
    - P The spectrum of 1-nitropropane shows splitting of H<sub>b</sub> into only 6 peaks





# Proton NMR Spectra and Rate Processes

- → An NMR spectrometer is like a camera with a slow shutter speed
- → The NMR spectrometer will observe rapid processes as if they were a blur, *i.e.*, only an average of the changes will be seen
- When a <sup>1</sup>H NMR spectrum of very pure ethanol is taken, the hydroxyl proton is split into a triplet by the two adjacent hydrogens
- When an <sup>1</sup>H NMR of regular ethanol is taken the hydroxyl proton is a singlet
  - Impure ethanol contains acid and base impurities which catalyze the exchange of hydroxyl protons
  - P This rapid exchange is so fast that coupling to the adjacent CH<sub>2</sub> is not observed
  - P This process is called spin decoupling



# → Spin decoupling is typical in the <sup>1</sup>H NMR spectra of alcohols, amines and carboxylic acids

The proton attached to the oxygen or nitrogen normally appears as a singlet because of rapid exchange processes

# Carbon-13 NMR Spectroscopy

- $\rightarrow$  <sup>13</sup>C accounts for only 1.1% of naturally occurring carbon
  - <sup>P</sup> <sup>12</sup>C has no magnetic spin and produces no NMR signal

### • One Peak for Each Unique Carbon Atom

- → Since the <sup>13</sup>C isotope of carbon is present in only 1.1% natural abundance, there is only a 1 in 10,000 chance that two <sup>13</sup>C atoms will occur next to each other in a molecule
- → The low probability of adjacent <sup>13</sup>C atoms leads to no detectable carbon-carbon splitting
- →<sup>1</sup>H and <sup>13</sup>C do split each other, but this splitting is usually eliminated by adjusting the NMR spectrophotometer accordingly
  - P The process of removing the coupling of <sup>1</sup>H to an attached carbon is called broadband (BB) proton decoupling
- → Most <sup>13</sup>C NMR, therefore, consist of a single peak for each unique carbon

## • <sup>13</sup>C Chemical Shifts

→ Just as in <sup>1</sup>H NMR spectroscopy, chemical shifts in <sup>13</sup>C NMR depend on the electron density around the carbon nucleus

- P Decreased electron density causes the signal to move downfield (desheilding)
- P Increased electron density causes the signal to move upfield (*sheilding*)



- → Because of the wide range of chemical shifts, it is rare to have two <sup>13</sup>C peaks coincidentally overlap
- → A group of 3 peaks at δ 77 comes from the common NMR solvent deuteriochloroform and can be ignored

- Off-Resonance Decoupled Spectra
  - Broad-band decoupling removes all information about the number of hydrogens attached to each carbon
  - →Off-resonance decoupling removes some of the coupling of carbons to hydrogens so that the coupled peaks will not overlap
  - → Use of off-resonance decoupled spectra has been replaced by use of DEPT <sup>13</sup>C NMR

## • DEPT <sup>13</sup>C NMR

- → DEPT (distortionless enhanced polarization transfer) spectra are created by mathematically combining several individual spectra taken under special conditions
- → The final DEPT spectra explicitly show C, CH, CH<sub>2</sub>, and CH<sub>3</sub> carbons
- ➔ To simplify the presentation of DEPT data, the broadband decoupled spectrum is annotated with the results of the DEPT experiments using the labels C, CH, CH<sub>2</sub> and CH<sub>3</sub> above the appropriate peaks

### • Example: 1-chloro-2-propanol

→ (a) The broadband decoupled spectrum and (b) a set of DEPT spectra showing the separate CH,  $CH_2$ , and  $CH_3$  signals



## Introduction to Mass Spectrometry (MS)

- → A mass spectrometer produces a spectrum of masses based on the structure of a molecule.
- → A mass spectrum is a plot of the distribution of ion masses corresponding to the formula weight of a molecule and/or fragments derived from it
- The x-axis of a mass spectrum represents the masses of ions produced
- The y-axis represents the relative abundance of each ion produced
- → The pattern of ions obtained and their abundance is characteristic of the structure of a particular molecule



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## The Mass Spectrometer

- →One common type is the Electron Impact Mass Spectrometer (EI MS)
- Ionization (the formation of ions)
  - → A molecule is bombarded with a beam of high energy electrons
  - → An electron may be dislodged from the molecule by the impact, leaving a positively charged ion with an unpaired electron (a radical cation)
    - P This initial ion is called the molecular ion (M<sup>+</sup>) because it has the same molecular weight as the analyte

$$\begin{array}{c} \mathrm{H}: \overset{\mathbf{N}}{\mathrm{N}}: \mathrm{H} + e^{-} \longrightarrow \begin{bmatrix} \mathrm{H}: \mathrm{N}: \mathrm{H} \\ \mathrm{H} \end{bmatrix}^{+} & + 2 e \\ \overset{\mathbf{N}}{\mathrm{H}} \end{bmatrix}^{+} \end{array}$$

Molecular ion, M<sup>+</sup> (a radical cation)

- Fragmentation
  - → Excess vibrational energy is imparted to the molecular ion by collision with the electron beam this causes fragmentation
    - P The fragmentation pattern is highly characteristic of the structure of the molecule

$$\begin{array}{ccc} H: \stackrel{+}{N}: H \longrightarrow H: \stackrel{+}{N}: + H \cdot \\ \stackrel{+}{H} & H: \stackrel{+}{N}: - \rightarrow H: \stackrel{+}{N}: + H \cdot \\ \stackrel{+}{H^2} & H: \stackrel{+}{N}: - \rightarrow H: \stackrel{+}{N}: + H \cdot \\ \end{array}$$

### • Ion Sorting

- → The fragments are sorted according to their mass to charge ratio, (m/z)
- → Most of the fragments detected have charge +1; the net effect is sorting of the ions by mass (m/z, where z = +1)
- → The charged molecular ion (M<sup>+</sup>) and fragments pass through an analyzer that sorts the ions according to m/z
  - One method of sorting involves directing the ions through a curved tube that passes through a magnetic field; as the magnetic field is varied, ions of different m/z values successfully traverse the tube and reach the detector
- → After ion sorting the results are plotted as a spectrum with m/z on the horizontal axis and relative abundance of each ion on the vertical axis



## The Mass Spectrum

- Data from a mass spectrometer can be represented as a graph or table
- The most abundant (intense) peak in the spectrum is called the base peak and is assigned a normalized intensity of 100%
- → The masses are based on rounding of atom masses to the nearest whole number (in low resolution mass spectroscopy)
- → The data and fragmentation patterns for ammonia are as follows



P The base peak for ammonia is the molecular ion, but this is often not the case

# → The small peak at m/z 18 comes from the small amount of <sup>15</sup>N<sup>1</sup>H<sub>3</sub> because of the small natural abundance of <sup>15</sup>N compared to <sup>14</sup>N

Element	Most Common Isotope		Natural Abundance of Other Isotopes (Based on 100 Atoms of Most Common Isotope)			
Carbon Hydrogen Nitrogen Oxygen Fluorine Silicon	<sup>12</sup> C <sup>1</sup> H <sup>14</sup> N <sup>16</sup> O <sup>19</sup> F <sup>28</sup> Si	100 100 100 100 100 100	<sup>13</sup> C <sup>2</sup> H <sup>15</sup> N <sup>17</sup> O <sup>29</sup> Si	1.11 0.016 0.38 0.04 5.10	<sup>18</sup> O <sup>30</sup> Si	0.20 3.35
Phosphorus Sulfur Chlorine Bromine Iodine	<sup>31</sup> P <sup>32</sup> S <sup>35</sup> Cl <sup>79</sup> Br <sup>127</sup> l	100 100 100 100 100	<sup>33</sup> S <sup>37</sup> Cl <sup>81</sup> Br	0.78 32.5 98.0	<sup>34</sup> S	4.40

𝑘 This peak is called an M+1 peak

<sup>a</sup>Data obtained from Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; Wiley: New York, 1998; p 7.

# Determination of Molecular Formulas and Molecular Weights

- The Molecular Ion and Isotopic Peaks
  - → The presence of heavier isotopes one or two mass units above the common isotope yields small peaks at M<sup>+,</sup>+1 and M<sup>+,</sup>+2

 $M^+$  + 1 Elements:C, H, N $M^+$  + 2 Elements:O, S, Br, Cl

- → The intensity of the M<sup>+,</sup>+1 and M<sup>+,</sup>+2 peaks relative to the M peak can be used to confirm a molecular formula
- → Example: In the spectrum of methane one expects an M<sup>+,</sup>+1 peak of 1.17% based on a 1.11% natural abundance of <sup>13</sup>C and a 0.016% natural abundance of <sup>2</sup>H

 $1.11 + 4(0.016) \simeq 1.17\%$ 



# High-Resolution Mass Spectrometry

- → Low-resolution mass spectrometers measure m/z values to the nearest whole number
- → High-resolution mass spectrometers measure m/z values to three or four decimal places
- ➔ The high accuracy of the molecular weight calculation allows accurate determination of the molecular formula of a fragment

#### → Example

One can accurately pick the molecular formula of a fragment with a nominal molecular weight of 32 using high-resolution MS

 $O_2 = 2(15.9949) = 31.9898$ 

 $N_2H_4 = 2(14.0031) + 4(1.00783) + 32.0375$ 

 $CH_4O = 12.00000 + 4(1.00783) + 15.9949 = 32.0262$ 

Isotope	Mass	Isotope	Mass
<sup>1</sup> H	1.00783	<sup>19</sup> F	18.9984
<sup>2</sup> H	2.01410	<sup>32</sup> S	31.9721
<sup>12</sup> C	12.00000 (std)	<sup>33</sup> S	32.9715
<sup>13</sup> C	13.00336	<sup>34</sup> S	33.9679
<sup>14</sup> N	14.0031	<sup>35</sup> Cl	34.9689
<sup>15</sup> N	15.0001	<sup>37</sup> Cl	36.9659
<sup>16</sup> O	15.9949	<sup>79</sup> Br	78.9183
<sup>17</sup> O	16.9991	<sup>81</sup> Br	80.9163
<sup>18</sup> O	17.9992	127	126.9045

#### • The exact mass of certain nuclides is shown below

## Fragmentation

- ➔ In El mass spectrometry the molecular ion is highly energetic and can break apart (fragment)
- → Fragmentation pathways are predictable and can be used to determine the structure of a molecule
- → The processes that cause fragmentation are unimolecular
- The relative ion abundance is extremely important in predicting structures of fragments
- Fragmentation by Cleavage at a Single Bond
  - → Cleavage of a radical cation occurs to give a radical and a cation but only the cation is observable by MS
  - ➔ In general the fragmentation proceeds to give mainly the most stable carbocation
    - $\ref{P}$  In the spectrum of propane the peak at 29 is the base peak (most abundant) 100% and the peak at 15 is 5.6%

$$CH_{3}CH_{2} \stackrel{+}{\underset{-e^{-}}{\leftarrow}} CH_{3}CH_{2} \stackrel{+}{\underset{-e^{-}}{\leftarrow}} CH_{3} \stackrel{+}{\underset{$$

## • Fragmentation Equations

- → The M<sup>+.</sup> Ion is formed by loss of one of its most loosely held electrons

  - P Loosely held nonbonding electrons on nitrogen and oxygen, and  $\pi$  electrons in double bonds are common locations for an electron to be lost *(i.e., where the remaining unshared electron in M<sup>+,</sup> resides)*
- ➔ In molecules with only C-C and C-H bonds, the location of the lone electron cannot be predicted and the formula is written to reflect this using brackets

 $[CH_{3}CH_{2}CH_{3}]^{\ddagger} \longrightarrow CH_{3}CH_{2}^{+} + \cdot CH_{3}$  $[CH_{3}CH_{2}CH_{3}]^{\ddagger} \longrightarrow CH_{3}CH_{2} \cdot + \cdot CH_{3}$ 



#### → Example: The spectrum of hexane



#### → Example: spectrum of neopentane

- Fragmentation of neopentane shows the propensity of cleavage to occur at a branch point leading to a relatively stable carbocation
- The formation of the 3° carbocation is so favored that almost no molecular ion is detected



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# → Carbocations stabilized by resonance are also formed preferentially

Alkenes fragment to give resonance-stabilized allylic carbocations

$$CH_{2} = CH - CH_{2} - R \xrightarrow{\text{ionization}} CH_{2} \xrightarrow{+} CH \xrightarrow{-e^{-}} CH_{2} \xrightarrow{+} CH \xrightarrow{-e^{-}} CH_{2} \xrightarrow{+} CH_{2} \xrightarrow$$

- → Carbon-carbon bonds next to an atom with an unshared electron pair break readily to yield a resonance stabilized carbocation
  - P Z=N, O, or S R may be H

$$R - \ddot{Z} - CH_{2} - CH_{3} \xrightarrow{\text{ionization}} R - \ddot{Z} - \dot{Z} - CH_{2} + CH_{3} \xrightarrow{\text{fragmentation}} R - \ddot{Z} = CH_{2} + CH_{3}$$

$$R - \ddot{Z} - \dot{C}H_{2} + CH_{3} + CH_{$$

where Z = N, O, or S; R may also be H.

#### Carbon-carbon bonds next to carbonyl groups fragment readily to yield resonance stabilized acylium ions



→ Alkyl substituted benzenes often lose a hydrogen or alkyl group to yield the relatively stable tropylium ion



Other substituted benzenes usually lose their substitutents to yield a phenyl cation



#### • Fragmentation by Cleavage of 2 Bonds

→ The products are a new radical cation and a neutral molecule

→ Alcohols usually show an M<sup>+,</sup>-18 peak from loss of water



which can also be written as

$$[R-CH_2-CH_2-OH]^{\ddagger} \longrightarrow [R-CH=CH_2]^{\ddagger} + H_2O$$

$$M^{\ddagger} \qquad M^{\ddagger} - 18$$

Cycloalkenes can undergo a retro-Diels Alder reaction (section 13.11) to yield an alkadienyl radical cation



#### → Carbonyl compounds can undergo a *McLafferty Rearrangement*

**P** Y may be R, H, OH, OR etc.

