

Chapter 12 – Structure Determination: Mass Spectrometry and Infrared Spectroscopy

Chapter Outline

I. Mass Spectrometry (Sections 12.1 – 12.4).

A. General features of mass spectrometry (Section 12.1).

1. Purpose of mass spectrometry.
 - a. Mass spectrometry is used to measure the molecular weight of a compound.
 - b. Mass spectrometry can also provide information on the structure of an unknown compound.
2. Technique of mass spectrometry.
 - a. A small amount of sample is vaporized into the *ionization source* and is bombarded by a stream of high-energy electrons.
 - b. An electron is dislodged, producing a cation radical.
 - c. Most of the cation radicals fragment; the fragments may be positively charged or neutral.
 - d. In the *deflector*, a strong magnetic field deflects the positively charged fragments, which are separated by m/z ratio.
 - e. A *detector* records the fragments as peaks.
3. Important terms.
 - a. The mass spectrum is presented as a bar graph, with masses (m/z) on the x axis and intensity on the y axis.
 - b. The base peak is the tallest peak and is assigned an intensity of 100%.
 - c. The parent peak, or molecular ion (M^+), corresponds to the unfragmented cation radical.
 - d. In large molecules, the base peak is often not the molecular ion.

B. Interpreting mass spectra (Sections 12.2 – 12.4).

1. Molecular weight (Section 12.2).
 - a. Mass spectra can frequently provide the molecular weight of a sample.
 - i. Double-focusing mass spectrometers can provide mass measurements accurate to 0.0005 amu.
 - ii. Some samples fragment so easily that M^+ is not seen.
 - b. If you know the molecular weight of the sample, you can often deduce its molecular formula.
 - c. There is often a peak at $M+1$ that is due to contributions from ^{13}C and ^2H .
2. Fragmentation patterns of hydrocarbons.
 - a. Fragmentation patterns can be used to identify a known compound, because a given compound has a unique fragmentation "fingerprint".
 - b. Fragmentation patterns can also provide structural information.
 - i. Most hydrocarbons fragment into carbocations and radicals.
 - ii. The positive charge remains with the fragment most able to stabilize it.
 - iii. It is often difficult to assign structures to fragments.
 - iv. For hexane, major fragments correspond to the loss of methyl, ethyl, propyl, and butyl radicals.
3. Fragmentation patterns of common functional groups (Section 12.3).
 - a. Alcohols.
 - i. Alcohols can fragment by alpha cleavage, in which a C–C bond next to the –OH group is broken.

The products are a cation and a radical.
 - ii. Alcohols can also dehydrate, leaving an alkene cation radical with a mass 18 units less than M^+ .

- b. Amines also undergo alpha cleavage, forming a cation and a radical.
 - c. Carbonyl compounds.
 - i. Aldehydes and ketones with a hydrogen 3 carbons from the carbonyl group can undergo the McLafferty rearrangement.
The products are a cation radical and a neutral alkene.
 - ii. Aldehydes and ketones also undergo alpha cleavage, which breaks a bond between the carbonyl group and a neighboring carbon.
The products are a cation and a radical.
- C. Mass spectrometry in biological systems: TOF instruments (Section 12.4).
- 1. Time-of-flight instruments are used to produce charged molecules with little fragmentation.
 - 2. The ionizer can be either ESI or MALDI.
 - a. In an ESI source, the sample is dissolved in a polar solvent and sprayed through a steel capillary tube.
 - i. As the sample exits, it is subjected to a high voltage, which protonates the sample.
 - ii. The solvent is evaporated, yielding protonated sample molecules.
 - b. In a MALDI source, the sample is absorbed onto a matrix compound.
 - i. The matrix compound is ionized by a burst of laser light.
 - ii. The matrix compound transfers energy to the sample, protonating it.
 - 3. The samples are focused into a small packet and given a burst of energy.
Each molecule moves at a velocity that depends on the square root of its mass.
 - 4. The analyzer is an electrically grounded tube that detects the molecules by velocity.
- II. Spectroscopy and the electromagnetic spectrum (Section 12.5).
- A. The nature of radiant energy.
- 1. Different types of electromagnetic radiation make up the electromagnetic spectrum.
 - 2. Electromagnetic radiation behaves both as a particle and as a wave.
 - 3. Electromagnetic radiation can be characterized by three variables.
 - a. The wavelength (λ) measures the distance from one maximum to the next.
 - b. The frequency (ν) measures the number of wave maxima that pass a fixed point per unit time.
 - c. The amplitude is the height measured from the midpoint to the maximum.
 - 4. Wavelength times frequency equals the speed of light.
 - 5. Electromagnetic energy is transmitted in discrete energy bundles called quanta.
 - a. $\epsilon = h \times \nu$
 - b. Energy varies directly with frequency but inversely with wavelength.
 - c. $E = 1.20 \times 10^{-2} \text{ kJ/mol} \div \lambda \text{ (cm)}$ for a "mole" of photons.
- B. Electromagnetic radiation and organic molecules.
- 1. When an organic compound is struck by a beam of electromagnetic radiation, it absorbs radiation of certain wavelengths, and transmits radiation of other wavelengths.
 - 2. If we determine which wavelengths are absorbed and which are transmitted, we can obtain an absorption spectrum of the compound.
For an infrared spectrum:
 - i. The horizontal axis records wavelength.
 - ii. The vertical axis records percent transmittance.
 - iii. The baseline runs across the top of the spectrum.
 - iv. Energy absorption is a downward spike.
 - 3. The energy a molecule absorbs is distributed over the molecule.
 - 4. There are many types of spectroscopies that differ in the region of the electromagnetic spectrum that is being used.

III. Infrared Spectroscopy (Sections 12.6 – 12.8).

A. Infrared radiation (Section 12.6).

1. The infrared (IR) region of the electromagnetic spectrum extends from 7.8×10^{-7} m to 10^{-4} m.
 - a. Organic chemists use the region from 2.5×10^{-6} m to 2.5×10^{-5} m.
 - b. Wavelengths are usually given in μm , and frequencies are expressed in wavenumbers, which are the reciprocal of wavelength.
 - c. The useful range of IR radiation is 4000 cm^{-1} to 400 cm^{-1} ; this corresponds to energies of 48.0 kJ/mol to 4.80 kJ/mol.
2. IR radiation causes bonds to stretch and bend and causes other molecular vibrations.
3. Energy is absorbed at a specific frequency that corresponds to the frequency of the vibrational motion of a bond.
4. If we measure the frequencies at which IR energy is absorbed, we can find out the kinds of bonds a compound contains and identify functional groups.

B. Interpreting IR spectra (Sections 12.7 – 12.8).

1. General principles (Section 12.7).
 - a. Most molecules have very complex IR spectra.
 - i. This complexity means that each molecule has a unique fingerprint that allows it to be identified by IR spectroscopy.
 - ii. Complexity also means that not all absorptions can be identified.
 - b. Most functional groups have characteristic IR absorption bands that don't change from one compound to another.
 - c. The significant regions of IR absorptions :
 - i. 4000 cm^{-1} – 2500 cm^{-1} corresponds to absorptions by C–H, O–H, and N–H bonds.
 - ii. 2500 cm^{-1} – 2000 cm^{-1} corresponds to triple-bond stretches.
 - iii. 2000 cm^{-1} – 1500 cm^{-1} corresponds to double bond stretches.
 - iv. The region below 1500 cm^{-1} is the fingerprint region, where many complex bond vibrations occur.
 - d. The frequency of absorption of different bonds depends on two factors:
 - i. The strength of the bond.
 - ii. The difference in mass between the two atoms in the bond.
2. IR spectra of some common functional groups (Section 12.8).
 - a. Alkanes.
 - i. C–C absorbs at 800 – 1300 cm^{-1} .
 - ii. C–H absorbs at 2850 – 2960 cm^{-1} .
 - b. Alkenes.
 - i. =C–H absorbs at 3020 – 3100 cm^{-1} .
 - ii. C=C absorbs at 1650 – 1670 cm^{-1} .
 - iii. RCH=CH₂ absorbs at 910 and 990 cm^{-1} .
 - iv. R₂C=CH₂ absorbs at 890 cm^{-1} .
 - c. Alkynes.
 - i. –C≡C– absorbs at 2100 – 2260 cm^{-1} .
 - ii. ≡C–H absorbs at 3300 cm^{-1} .
 - d. Aromatic compounds.
 - i. =C–H absorbs at 3030 cm^{-1} .
 - ii. Ring absorptions occur at 1660 – 2000 cm^{-1} and at 1450 – 1600 cm^{-1} .

- e. The alcohol O–H bond absorbs at 3400–3650 cm^{-1} .
- f. The N–H bond of amines absorbs at 3300–3500 cm^{-1} .
- g. Carbonyl compounds.
 - i. Saturated aldehydes absorb at 1730 cm^{-1} ; unsaturated aldehydes absorb at 1705 cm^{-1} .
 - ii. Saturated ketones absorb at 1715 cm^{-1} ; unsaturated ketones absorb at 1690 cm^{-1} .
 - iii. Saturated esters absorb at 1735 cm^{-1} ; unsaturated esters absorb at 1715 cm^{-1} .

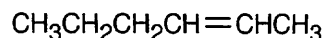
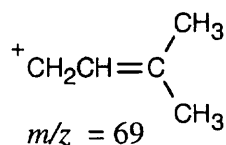
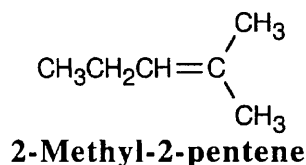
Solutions to Problems

12.1 If the isotopic masses of the atoms C, H, and O had integral values of 12 amu, 1 amu and 16 amu, many molecular formulas would correspond to a molecular weight of 288 amu. Because isotopic masses are not integral, however, only one molecular formula is associated with a molecular ion at 288.2089 amu.

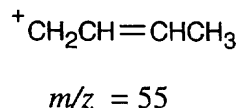
To reduce the number of possible formulas, assume that the difference in molecular weight between 288 and 288.2089 is due mainly to hydrogen. Divide 0.2089 by 0.00783, the amount by which the atomic weight of one ^1H atom differs from 1. The answer, 26.67, gives a "ballpark" estimate of the number of hydrogens in testosterone. Then, divide 288 by 12, to determine the maximum number of carbons. Since $288 \div 12 = 24$, we know that testosterone can have no more than 22 carbons if it also includes hydrogen and oxygen. Make a list of *reasonable* molecular formulas containing C, H and O whose mass is 288 and which contain 20–30 hydrogens. Tabulate these, and calculate their exact masses using the values in the text. The only possible formula for testosterone is $\text{C}_{19}\text{H}_{28}\text{O}_2$.

Molecular formula	Isotopic mass			
	Mass of carbons	Mass of hydrogens	Mass of oxygens	Mass of molecular ion
$\text{C}_{20}\text{H}_{32}\text{O}$	240.0000 amu	32.2504 amu	15.9949 amu	288.2453 amu
$\text{C}_{19}\text{H}_{28}\text{O}_2$	228.0000	28.2191	31.9898	288.2089
$\text{C}_{18}\text{H}_{24}\text{O}_3$	216.0000	24.1879	47.9847	288.1726

12.2



2-Hexene

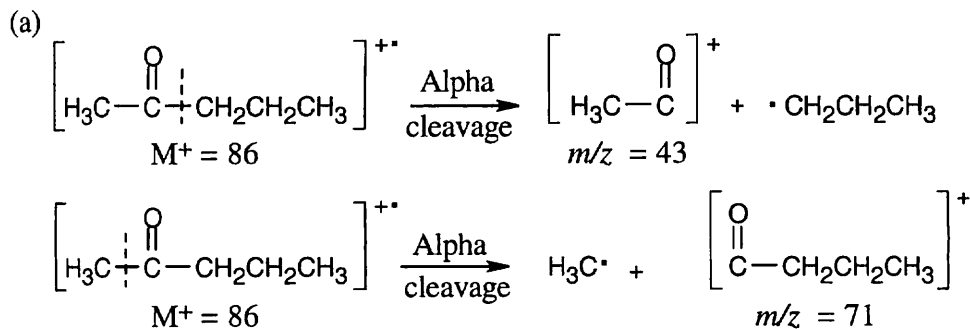


Fragmentation occurs to a greater extent at the weakest carbon–carbon bonds, producing a relatively stable cation. Spectrum (a), which has a dominant peak at $m/z = 69$, corresponds to 2-methyl-2-pentene, and spectrum (b), which has $m/z = 55$ as its base peak, corresponds to 2-hexene.

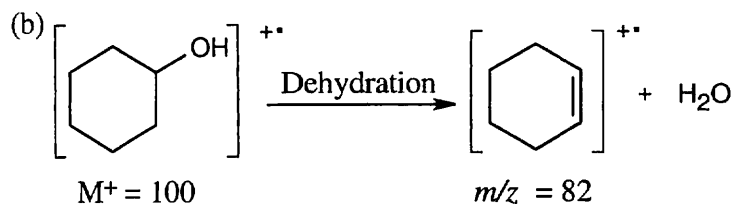
- 12.3 Strategy:** In a mass spectrum, the molecular ion is both a cation and a radical. When it fragments, two kinds of cleavage can occur. (1) Cleavage can form a radical and a cation (the species observed in the mass spectrum). Alpha cleavage shows this type of pattern. (2) Cleavage can form a neutral molecule and a different radical cation (the species observed in the mass spectrum). Alcohol dehydration and the McLafferty rearrangement show this cleavage pattern.

For each compound, calculate the mass of the molecular ion and identify the functional groups present. Draw the fragmentation products and calculate their masses.

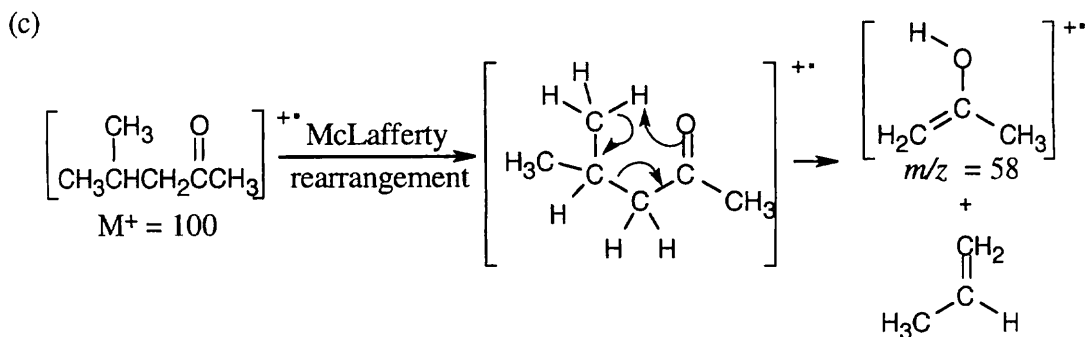
Solution:



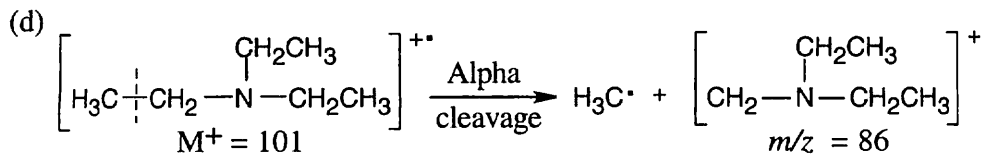
In theory, alpha cleavage can take place on either side of the carbonyl group to produce cations with $m/z = 43$ and $m/z = 71$. In practice, cleavage occurs on the more substituted side of the carbonyl group, and the first cation, with $m/z = 43$, is observed.



Dehydration of cyclohexanol produces a cation radical with $m/z = 82$.



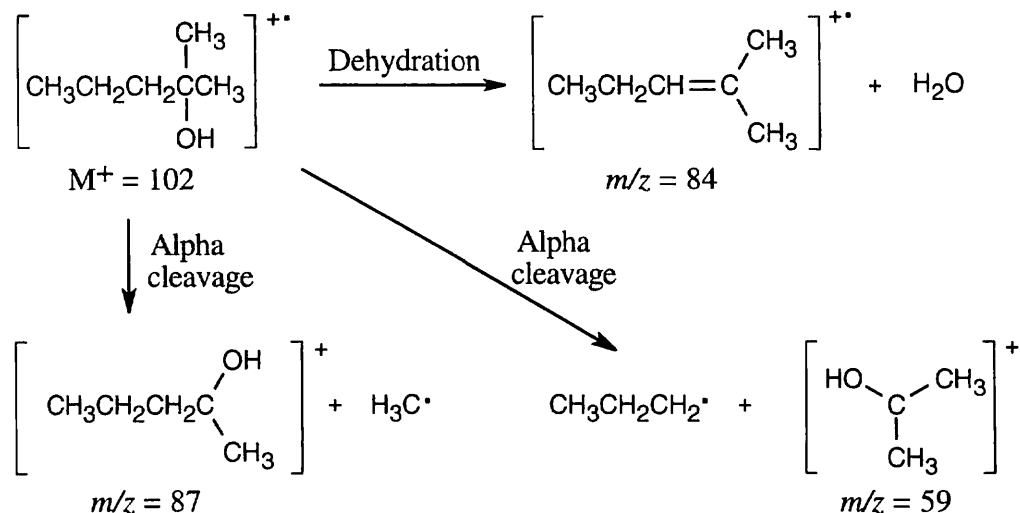
The cation radical fragment resulting from McLafferty rearrangement has $m/z = 58$.



Alpha cleavage of triethylamine yields a cation with $m/z = 86$.

- 12.4 Strategy:** Identify the functional groups present in the molecule and recall the kinds of fragmentations those functional groups produce. 2-Methyl-2-pentanol produces fragments that result from both dehydration and from alpha cleavage. Two different alpha cleavage products are possible.

Solution:



- 12.5 Strategy:** We know that: (1) energy increases as wavelength decreases, and (2) the wavelength of X-radiation is smaller than the wavelength of infrared radiation. Thus, we estimate that an X ray is of higher energy than an infrared ray.

Solution:

$$\epsilon = h\nu = hc/\lambda; \quad h = 6.62 \times 10^{-34} \text{ J}\cdot\text{s}; \quad c = 3.00 \times 10^8 \text{ m/s}$$

for $\lambda = 10^{-6} \text{ m}$ (infrared radiation):

$$\epsilon = \frac{(6.62 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{1.0 \times 10^{-6} \text{ m}} = 2.0 \times 10^{-19} \text{ J}$$

for $\lambda = 3.0 \times 10^{-9} \text{ m}$ (X radiation):

$$\epsilon = \frac{(6.62 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{3.0 \times 10^{-9} \text{ m}} = 6.6 \times 10^{-17} \text{ J}$$

Confirming our estimate, the calculation shows that an X ray is of higher energy than infrared radiation.

Convert radiation in m to radiation in Hz by the equation:

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{9.0 \times 10^{-6} \text{ m}} = 3.3 \times 10^{13} \text{ Hz}$$

The equation $\epsilon = h\nu$ shows that the greater the value of ν , the greater the energy. Thus, radiation with $\nu = 3.3 \times 10^{13} \text{ Hz}$ ($\lambda = 9.0 \times 10^{-6} \text{ m}$) is higher in energy than radiation with $\nu = 4.0 \times 10^9 \text{ Hz}$.

12.6

- (a) $E = \frac{1.20 \times 10^{-4} \text{ kJ/mol}}{\lambda \text{ (in m)}} = \frac{1.20 \times 10^{-4} \text{ kJ/mol}}{5.0 \times 10^{-11}} = 2.4 \times 10^6 \text{ kJ/mol}$ for a gamma ray.
- (b) $E = 4.0 \times 10^4 \text{ kJ/mol}$ for an X ray.
- (c) $\nu = \frac{c}{\lambda}$; $\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^8 \text{ m/s}}{6.0 \times 10^{15} \text{ Hz}} = 5.0 \times 10^{-8} \text{ m}$
 $E = \frac{1.20 \times 10^{-4} \text{ kJ/mol}}{5.0 \times 10^{-8}} = 2.4 \times 10^3 \text{ kJ/mol}$ for ultraviolet light
- (d) $E = 2.8 \times 10^2 \text{ kJ/mol}$ for visible light.
- (e) $E = 6.0 \text{ kJ/mol}$ for infrared radiation
- (f) $E = 4.0 \times 10^{-2} \text{ kJ/mol}$ for microwave radiation.

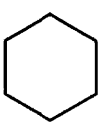
12.7 (a) A compound with a strong absorption at 1710 cm^{-1} contains a carbonyl group and is either a ketone or aldehyde.

(b) A compound with a nitro group has a strong absorption at 1540 cm^{-1} .

(c) A compound showing both carbonyl (1720 cm^{-1}) and -OH ($2500\text{--}3000 \text{ cm}^{-1}$ broad) absorptions is a carboxylic acid.

12.8 **Strategy:** To use IR spectroscopy to distinguish between isomers, find a strong IR absorption that is present in one isomer but absent in the other.

Solution:

- (a)
- | | |
|--|-------------------------------------|
| <chem>CH3CH2OH</chem> | <chem>CH3OCH3</chem> |
| Strong hydroxyl band | No band in the region |
| at $3400\text{--}3640 \text{ cm}^{-1}$ | $3400\text{--}3640 \text{ cm}^{-1}$ |
- (b)
- | | |
|--|---|
| <chem>CH3CH2CH2CH2CH=CH2</chem> |  |
| Alkene bands at | |
| $3020\text{--}3100 \text{ cm}^{-1}$ and | |
| at $1640\text{--}1680 \text{ cm}^{-1}$. | No bands in alkene region. |
- (c)
- | | |
|--|-------------------------------------|
| <chem>CH3CH2CO2H</chem> | <chem>HOCH2CH2CHO</chem> |
| Strong, broad band | Strong band at |
| at $2500\text{--}3100 \text{ cm}^{-1}$ | $3400\text{--}3640 \text{ cm}^{-1}$ |

12.9 Based on what we know at this point, we can identify four absorptions in this spectrum.

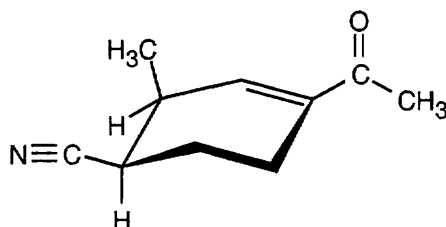
- (a) Absorptions in the region 1450 cm^{-1} – 1600 cm^{-1} are due to aromatic ring $\text{C}=\text{C}$ motions.
- (b) The absorption at 2100 cm^{-1} is due to a $\text{C}\equiv\text{C}$ stretch.
- (c) Absorptions in the range 3000 cm^{-1} – 3100 cm^{-1} are due to aromatic ring $\text{C}=\text{H}$ stretches.
- (d) The absorption at 3300 cm^{-1} is due to a $\text{C}\equiv\text{H}$ stretch.

12.10 (a) An ester next to a double bond absorbs at 1715 cm^{-1} . The alkene double bond absorbs at 1640 – 1680 cm^{-1} .

(b) The aldehyde carbonyl group absorbs at 1730 cm^{-1} . The alkyne $\text{C}\equiv\text{C}$ bond absorbs at 2100 – 2260 cm^{-1} , and the alkyne $\text{H}-\text{C}\equiv$ bond absorbs at 3300 cm^{-1} .

(c) The most important absorptions for this compound are due to the alcohol group (a broad, intense band at 3400 – 3650 cm^{-1}) and to the carboxylic acid group, which has a $\text{C}=\text{O}$ absorption in the range 1710 – 1760 cm^{-1} and a broad $\text{O}-\text{H}$ absorption in the range 2500 – 3100 cm^{-1} . Absorptions due to the aromatic ring [3030 cm^{-1} (w) and 1450 – 1600 cm^{-1} (m)] may also be seen.

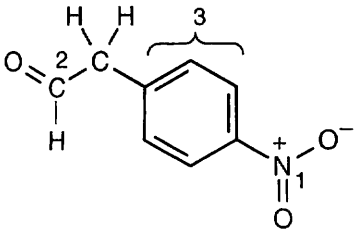
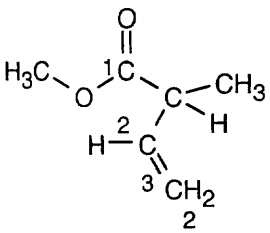
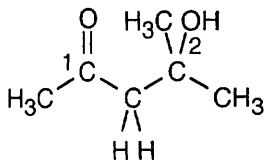
12.11



The compound contains nitrile and ketone groups, as well as a carbon–carbon double bond. The nitrile absorption occurs at 2210 – 2260 cm^{-1} . The ketone shows an absorption at 1690 cm^{-1} , a lower value than usual because the ketone is next to the double bond. The double bond absorption occurs at 1640 – 1680 cm^{-1} .

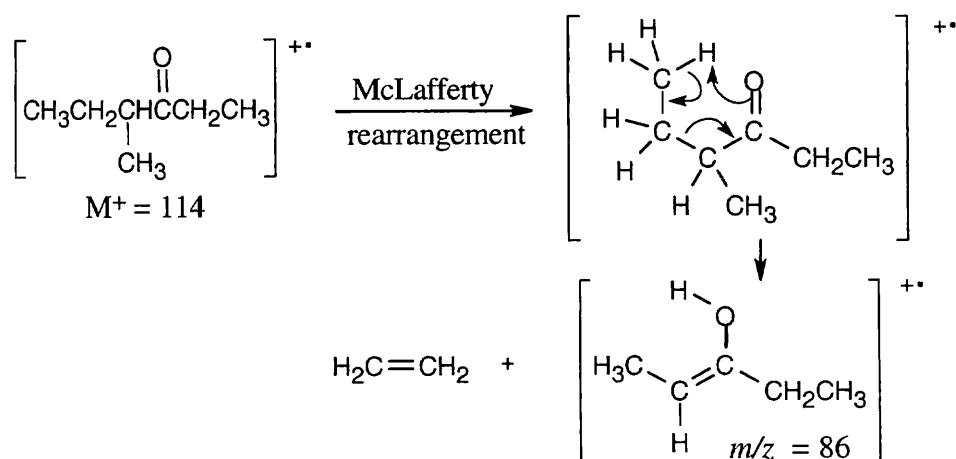
Visualizing Chemistry

12.12

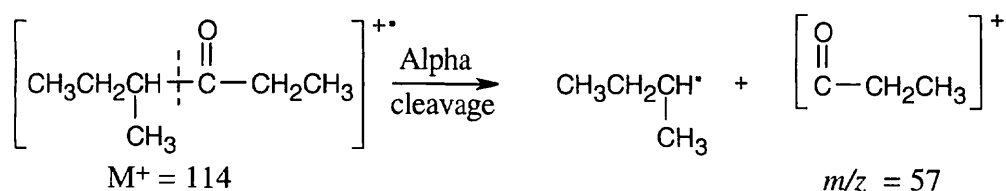
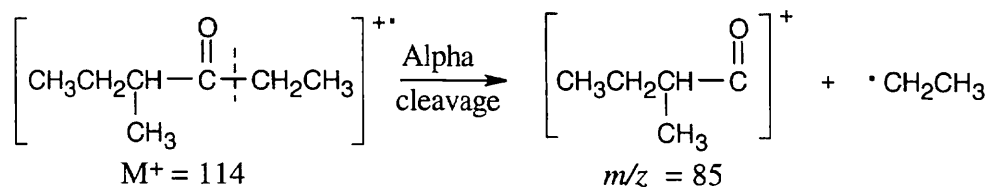
Compound	Significant IR Absorption	Due to:
(a) 	1540 cm ⁻¹ 1730 cm ⁻¹ 3030 cm ⁻¹ , 1450–1600 cm ⁻¹	nitro group (1) aldehyde (2) aromatic ring C–H(3) aromatic ring C=C(3)
(b) 	1735 cm ⁻¹ 3020–3100 cm ⁻¹ 910 cm ⁻¹ , 990 cm ⁻¹	ester (1) vinyl stretch C–H(2) C=CH ₂ bend(3)
(c) 	1715 cm ⁻¹ 3400–3650 cm ⁻¹	ketone (1) alcohol (2)

12.13 (a) The mass spectrum of this ketone shows fragments resulting from both McLafferty rearrangement and alpha cleavage.

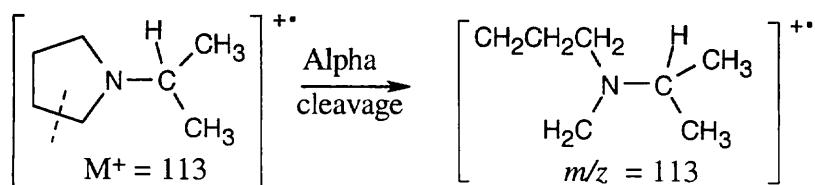
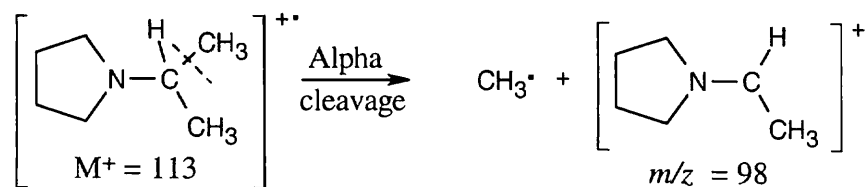
McLafferty rearrangement:



Alpha cleavage:



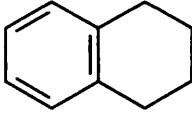
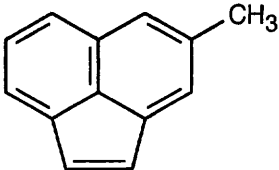
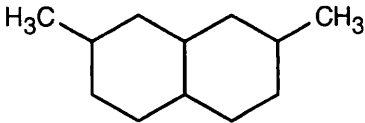
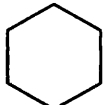
(b) Two different fragments can arise from alpha cleavage of this amine:



The second product results from cleavage of a bond in the five-membered ring.

Additional Problems

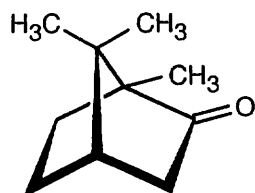
12.14

M^+	Molecular Formula	Degree of Unsaturation	Possible Structure
(a) 132	$C_{10}H_{12}$	5	
(b) 166	$C_{13}H_{10}$	9	
	$C_{12}H_{22}$	2	
(c) 84	C_6H_{12}	1	

12.15 (a) The compound contains no more than 7 carbons. As in Problem 12.1, divide the mass to the right of the decimal point by 0.00783 to arrive at an approximate value for the number of hydrogens (10.7). Since the compound has an even mass (and an even number of hydrogens), it contains an even number of nitrogens, or no nitrogens. The two most likely formulas are $C_6H_{10}O$ ($M^+ = 98.0732$) and $C_5H_{10}N_2$ ($M^+ = 98.0844$). The latter formula agrees precisely with the given molecular ion.

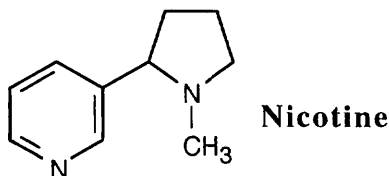
(b) The compound contains no more than 9 carbons, and 4.1 hydrogens. The number of hydrogens must be odd, since M^+ is odd. Assume the molecule has 5 hydrogens, and adjust the numbers of nitrogens and oxygens until you arrive at the correct value for M^+ . The formula is $C_6H_5NO_2$.

12.16 Reasonable molecular formulas for camphor are $C_{10}H_{16}O$, $C_9H_{12}O_2$, $C_8H_8O_3$. The actual formula, $C_{10}H_{16}O$ ($M^+ = 152.1201$), corresponds to three degrees of unsaturation. The ketone functional group accounts for one of these. Since camphor is a saturated compound, the other two degrees of unsaturation are due to two rings.



Camphor

- 12.17** Carbon is tetravalent, and nitrogen is trivalent. If a C–H unit (formula weight 13) is replaced by an N atom (formula weight 14), the molecular weight of the resulting compound increases by one. Since all neutral hydrocarbons have even-numbered molecular weights (C_nH_{2n+2} , C_nH_{2n} , and so forth) the resulting nitrogen-containing compounds have odd-numbered molecular weights. If two C–H units are replaced by two N atoms, the molecular weight of the resulting compound increases by two and remains an even number.
- 12.18** Because M^+ is an odd number, pyridine contains an odd number of nitrogen atoms. If pyridine contained one nitrogen atom (atomic weight 14) the remaining atoms would have a formula weight of 65, corresponding to $-C_5H_5$. C_5H_5N is, in fact, the molecular formula of pyridine.
- 12.19** Subtract the isotopic mass of the two nitrogens from the value of M^+ , and divide the quantity to the right of the decimal point by 0.00783 to find the approximate number of hydrogens in nicotine. The molecular formula of nicotine is $C_{10}H_{14}N_2$. To find the equivalent hydrocarbon formula, subtract the number of nitrogens from the number of hydrogens. The equivalent hydrocarbon formula of nicotine, $C_{10}H_{12}$, indicates five degrees of unsaturation — two of them due to the two rings and the other three due to three double bonds.



- 12.20** Use the technique described in Problem 12.1 to find the molecular formula of cortisone. Cortisone contains approximately 25 hydrogens. Make a table of possible molecular formulas for cortisone that have around 25 hydrogens and calculate the exact molecular weights corresponding to these formulas.

Molecular formula	Isotopic mass			
	Mass of carbons	Mass of hydrogens	Mass of oxygens	Mass of molecular ion
$C_{27}H_{20}O$	324.0000 amu	20.1565 amu	15.9949 amu	360.1514 amu
$C_{25}H_{28}O_2$	300.0000	28.2191	31.9898	360.2089
$C_{24}H_{24}O_3$	288.0000	24.1878	47.9847	360.1725
$C_{21}H_{28}O_5$	252.0000	28.2191	79.9746	360.1937

The molecular weight of $C_{21}H_{28}O_5$ corresponds to the observed molecular weight of cortisone. (Note that only the last formula has the correct degree of unsaturation, 8).

12.21 In order to simplify this problem, neglect the ^{13}C and ^2H isotopes in determining the molecular ions of these compounds.

(a) The formula weight of $-\text{CH}_3$ is 15, and the atomic masses of the two bromine isotopes are 79 and 81. The two molecular ions of bromoethane occur at $M^+ = 94$ (50.7%) and $M^+ = 96$ (49.3%).

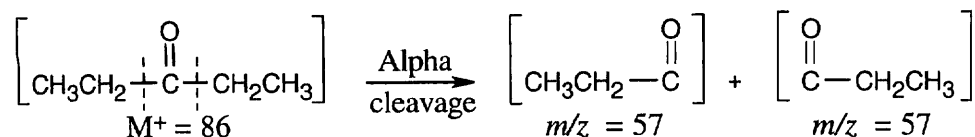
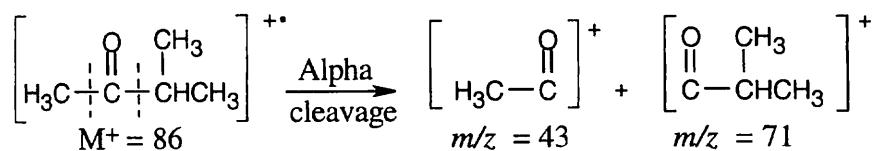
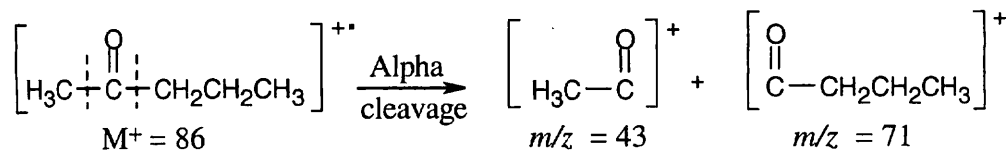
(b) The formula weight of $-\text{C}_6\text{H}_{13}$ is 85, and the atomic masses of the two chlorine isotopes are 35 and 37. The two molecular ions of 1-chlorohexane occur at $M^+ = 120$ (75.8%) and $M^+ = 122$ (24.2%).

12.22 Each carbon atom has a 1.10% probability of being ^{13}C and a 98.90% probability of being ^{12}C . The ratio of the height of the ^{13}C peak to the height of the ^{12}C peak for a one-carbon compound is $(1.10/98.9) \times 100\% = 1.11\%$. For a six-carbon compound, the contribution to $(M+1)^+$ from ^{13}C is $6 \times (1.10/98.9) \times 100\% = 6.66\%$. For benzene, the relative height of $(M+1)^+$ is 6.66% of the height of M^+ .

A similar line of reasoning can be used to calculate the contribution to $(M+1)^+$ from ^2H . The natural abundance of ^2H is 0.015%, so the ratio of a ^2H peak to a ^1H peak for a one-hydrogen compound is 0.015%. For a six-hydrogen compound, the contribution to $(M+1)^+$ from ^2H is $6 \times 0.015\% = 0.09\%$.

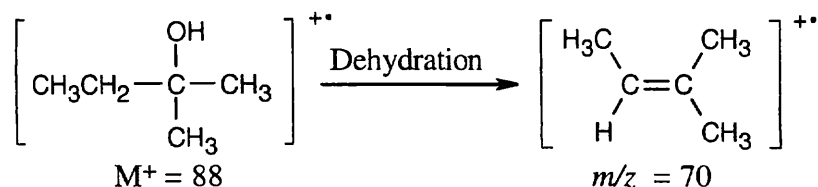
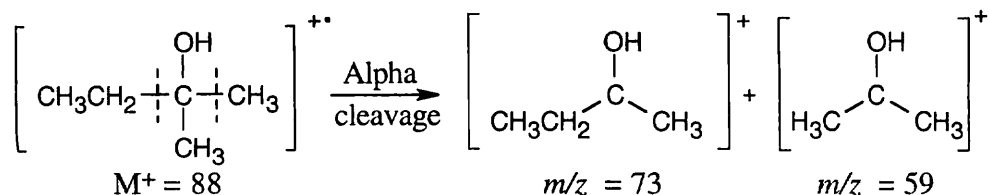
For benzene, $(M+1)^+$ is 6.75% of M^+ . Notice that ^2H contributes very little to the size of $(M+1)^+$.

12.23 (a) The molecular formula of the ketone is $\text{C}_5\text{H}_{10}\text{O}$, and the fragments correspond to the products of alpha cleavage (McLafferty rearrangement fragments have even-numbered values of m/z). Draw all possible ketone structures, show the charged products of alpha cleavage, and note which fragments correspond to those listed.

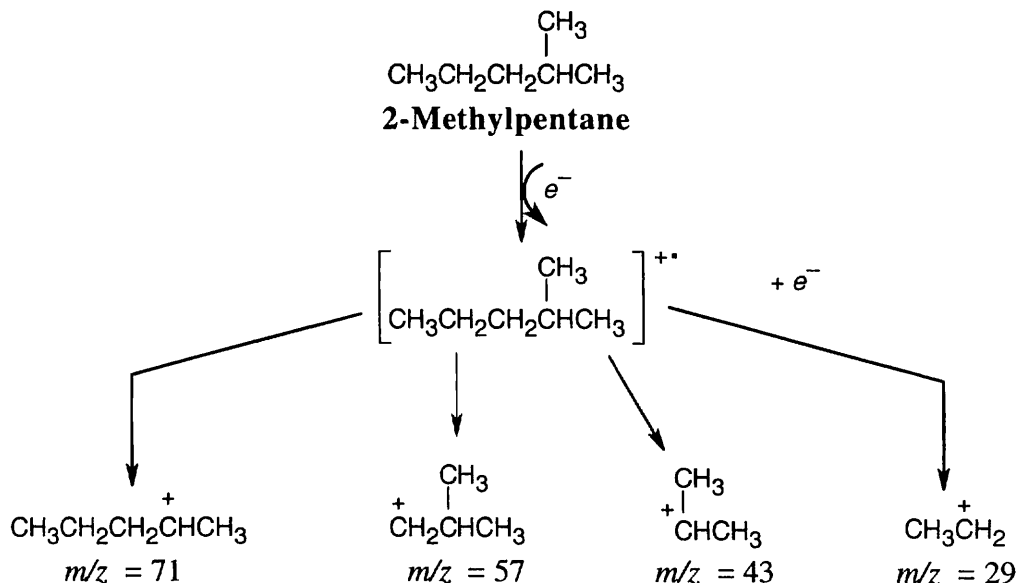


Either of the first two compounds shows the observed fragments in its mass spectrum.

(b) $C_5H_{12}O$ is the formula of an alcohol with $M^+ = 88$. The fragment at $m/z = 70$ is due to the product of dehydration of M^+ . The other two fragments are a result of alpha cleavage. Draw the possible C_5 alcohol isomers, and draw their products of alpha cleavage. The tertiary alcohol shown fits the data.



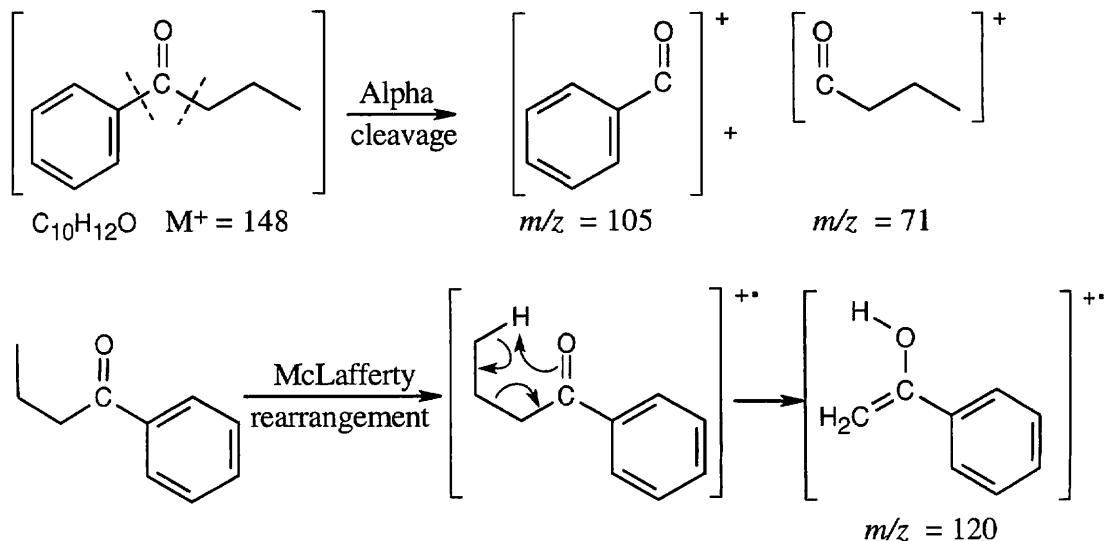
12.24



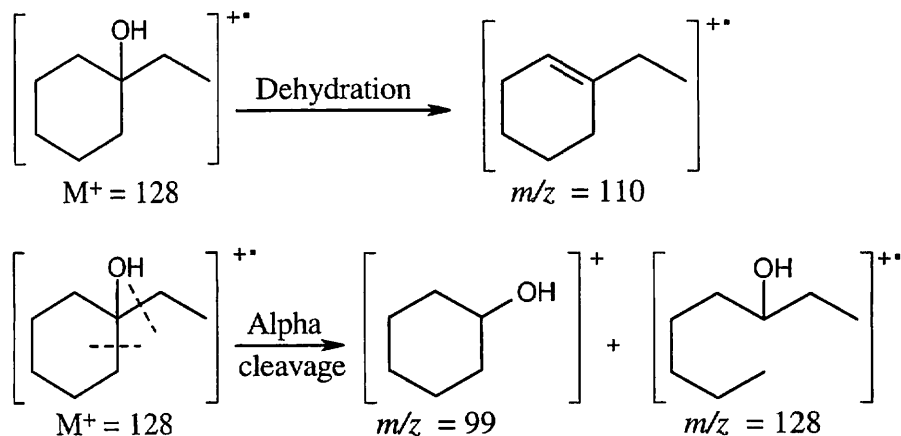
The molecular ion, at $m/z = 86$, is present in very low abundance. The base peak, at $m/z = 43$, represents a stable secondary carbocation.

12.25 Before doing the hydrogenation, familiarize yourself with the mass spectra of cyclohexene and cyclohexane. Note that M^+ is different for each compound. After the reaction is underway, inject a sample from the reaction mixture into the mass spectrometer. If the reaction is finished, the mass spectrum of the reaction mixture should be superimposable with the mass spectrum of cyclohexane.

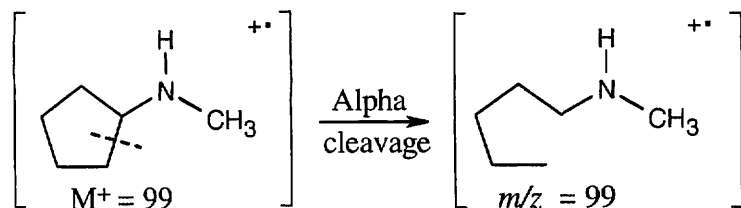
12.26 (a) This ketone shows mass spectrum fragments that are due to alpha cleavage and to the McLafferty rearrangement. The molecular ion occurs at $M^+ = 148$, and major fragments have $m/z = 120$, 105, and 71. (Note that only charged species are shown.)



(b) The fragments in the mass spectrum of this alcohol ($\text{C}_8\text{H}_{16}\text{O}$) result from dehydration and alpha cleavage. Major fragments have m/z values of 128 (the same value as the molecular ion), 110, and 99.



(c) Amines fragment by alpha cleavage. In this problem, cleavage occurs in the ring, producing a fragment with the same value of m/z as the molecular ion (99).



12.27 $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ shows absorptions at $2100\text{--}2260\text{ cm}^{-1}$ ($\text{C}\equiv\text{C}$) and at 3300 cm^{-1} ($\text{C}\equiv\text{C}\text{--H}$) that are due to the terminal alkyne bond.

$\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$ has absorptions in the regions $1640\text{--}1680\text{ cm}^{-1}$ and $3020\text{--}3100$ that are due to the double bonds. It also shows absorptions at 910 cm^{-1} and 990 cm^{-1} that are due to monosubstituted alkene bonds. No absorptions occur in the alkyne region.

$\text{CH}_3\text{C}\equiv\text{CCH}_3$. For reasons we won't discuss, symmetrically substituted alkynes such as 2-butyne do not show a $\text{C}\equiv\text{C}$ bond absorption in the IR. This alkyne is distinguished from the other isomers in that it shows no absorptions in either the alkyne or alkene regions.

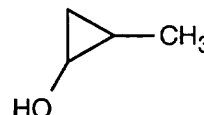
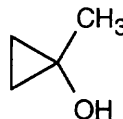
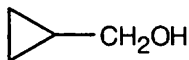
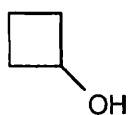
12.28 Two enantiomers have identical physical properties (other than the sign of specific rotation). Thus, their IR spectra are also identical.

12.29 Since diastereomers have different physical properties and chemical behavior, their IR spectra are also different.

12.30 (a) Absorptions at 3300 cm^{-1} and 2150 cm^{-1} are due to a terminal triple bond. Possible structures:

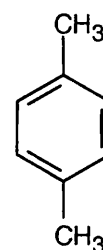
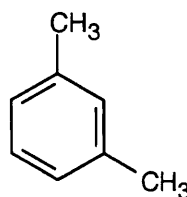
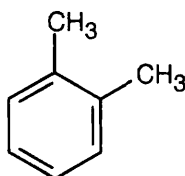
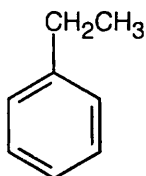


(b) An IR absorption at 3400 cm^{-1} is due to a hydroxyl group. Since no double bond absorption is present, the compound must be a cyclic alcohol.



(c) An absorption at 1715 cm^{-1} is due to a ketone. The only possible structure is $\text{CH}_3\text{CH}_2\text{COCH}_3$.

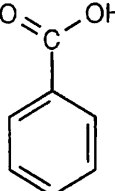
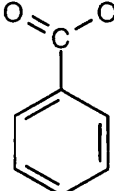
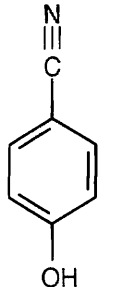
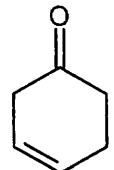
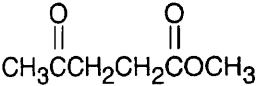
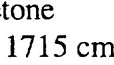
(d) Absorptions at 1600 cm^{-1} and 1500 cm^{-1} are due to an aromatic ring. Possible structures:



- 12.31 (a) $\text{HC}\equiv\text{CCH}_2\text{NH}_2$
 Alkyne absorptions at 3300 cm^{-1} , $2100\text{--}2260\text{ cm}^{-1}$
 Amine absorption at $3300\text{--}3500\text{ cm}^{-1}$
- $\text{CH}_3\text{CH}_2\text{C}\equiv\text{N}$
 Nitrile absorption at $2210\text{--}2260\text{ cm}^{-1}$
- (b) CH_3COCH_3
 Strong ketone absorption at 1715 cm^{-1}
- $\text{CH}_3\text{CH}_2\text{CHO}$
 Strong aldehyde absorption at 1730 cm^{-1}

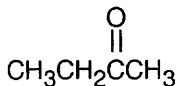
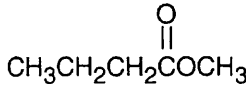
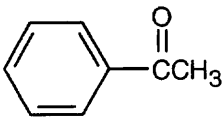
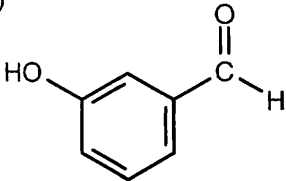
12.32 Spectrum (b) differs from spectrum (a) in several respects. Note in particular the absorptions at 715 cm^{-1} (strong), 1140 cm^{-1} (strong), 1650 cm^{-1} (medium), and 3000 cm^{-1} (medium) in spectrum (b). The absorptions at 1650 cm^{-1} ($\text{C}=\text{C}$ stretch) and 3000 cm^{-1} ($=\text{C}\text{--H}$ stretch) can be found in Table 12.1. They allow us to assign spectrum (b) to cyclohexene and spectrum (a) to cyclohexane.

12.33 Only absorptions with medium to strong intensity are listed.

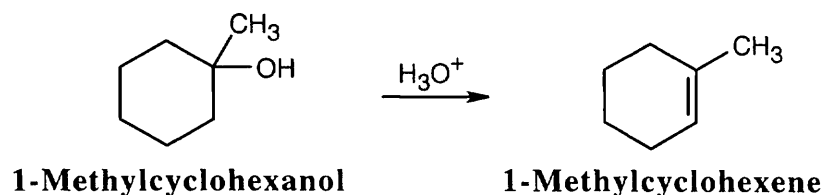
- (a)  aromatic ring $\text{C}=\text{C}$ $1450\text{--}1600\text{ cm}^{-1}$
 aromatic ring $\text{C}\text{--H}$ 3030 cm^{-1}
 carboxylic acid $\text{C}=\text{O}$ $1710\text{--}1760\text{ cm}^{-1}$
 carboxylic acid $\text{O}\text{--H}$ $2500\text{--}3100\text{ cm}^{-1}$
- (b)  aromatic ring $\text{C}=\text{C}$ $1450\text{--}1600\text{ cm}^{-1}$
 aromatic ring $\text{C}\text{--H}$ 3030 cm^{-1}
 aromatic ester 1715 cm^{-1}
- (c)  aromatic ring $\text{C}=\text{C}$ $1450\text{--}1600\text{ cm}^{-1}$
 aromatic ring $\text{C}\text{--H}$ 3030 cm^{-1}
 alcohol $\text{O}\text{--H}$ $3400\text{--}3650\text{ cm}^{-1}$
 nitrile $\text{C}\equiv\text{N}$ $2210\text{--}2260\text{ cm}^{-1}$
- (d)  alkene $\text{C}=\text{C}$ $1640\text{--}1680\text{ cm}^{-1}$
 alkene $=\text{C}\text{--H}$ $3020\text{--}3100\text{ cm}^{-1}$
 ketone 1715 cm^{-1}
- (e)  ester 1735 cm^{-1}
-  ketone 1715 cm^{-1}

- 12.34 (a) $\text{CH}_3\text{C}\equiv\text{CCH}_3$ exhibits no terminal $\equiv\text{C}\text{--H}$ stretching vibration at 3300 cm^{-1} , as $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ does.
- (b) $\text{CH}_3\text{COCH}=\text{CHCH}_3$, a ketone next to a double bond, shows a strong ketone absorption at 1690 cm^{-1} ; $\text{CH}_3\text{COCH}_2\text{CH}=\text{CH}_2$ shows a ketone absorption at 1715 cm^{-1} and monosubstituted alkene absorptions at 910 cm^{-1} and 990 cm^{-1} .
- (c) $\text{CH}_3\text{CH}_2\text{CHO}$ exhibits an aldehyde band at 1730 cm^{-1} ; $\text{H}_2\text{C}=\text{CHOCH}_3$ shows characteristic monosubstituted alkene absorptions at 910 cm^{-1} and 990 cm^{-1} .

12.35

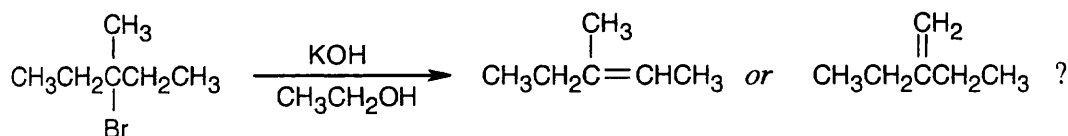
<i>Compound</i>	<i>Distinguishing Absorption</i>	<i>Due to:</i>
(a) 	1715 cm ⁻¹	C=O (ketone)
(b) $(\text{CH}_3)_2\text{CHCH}_2\text{C}\equiv\text{CH}$	2100–2260 cm ⁻¹ 3300 cm ⁻¹	C≡C C≡C–H
(c) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}=\text{CH}_2$	910 cm ⁻¹ , 990 cm ⁻¹ 1640–1680 cm ⁻¹ 3020–3100 cm ⁻¹	RCH=CH ₂ C=C =C–H
(d) 	1735 cm ⁻¹	C=O (ester)
(e) 	1690 cm ⁻¹ 1450–1600 cm ⁻¹ 3030 cm ⁻¹	ketone next to aromatic ring aromatic ring aromatic ring
(f) 	1710 cm ⁻¹ 3400–3650 cm ⁻¹ 1450–1600 cm ⁻¹ 3030 cm ⁻¹	aldehyde next to aromatic ring alcohol aromatic ring aromatic ring

12.36



The infrared spectrum of the starting alcohol shows a broad absorption at 3400–3640 cm⁻¹ due to an O–H stretch. The alkene product exhibits medium intensity absorbances at 1645–1670 cm⁻¹ and at 3000–3100 cm⁻¹. Monitoring the disappearance of the alcohol absorption makes it possible to decide when reaction is complete. It is also possible to monitor the appearance of the alkene absorptions.

12.37



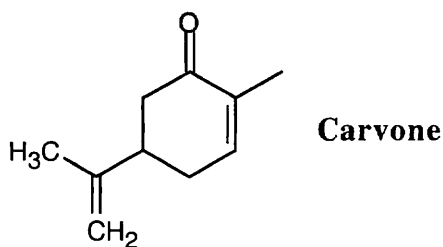
3-Bromo-3-methylpentane 3-Methyl-2-pentene 2-Ethyl-1-butene

The IR spectra of both products show the characteristic absorptions of alkenes in the regions $3020\text{--}3100\text{ cm}^{-1}$ and 1650 cm^{-1} . However, in the region $700\text{--}1000\text{ cm}^{-1}$, 2-ethyl-1-butene shows a strong absorption at 890 cm^{-1} that is typical of 2,2-disubstituted $\text{R}_2\text{C}=\text{CH}_2$ alkenes. The presence or absence of this peak should help to identify the product. (3-Methyl-2-pentene is the major product of the dehydrobromination reaction.)

12.38 The following expressions are needed:

$\epsilon = h\nu = hc/\lambda = hc\tilde{\nu}$, where $\tilde{\nu}$ is the wavenumber. The last expression shows that, as $\tilde{\nu}$ increases, the energy needed to cause IR absorption increases, indicating greater bond strength. Thus an ester $\text{C}=\text{O}$ bond ($\tilde{\nu} = 1735\text{ cm}^{-1}$) is stronger than a ketone $\text{C}=\text{O}$ bond ($\tilde{\nu} = 1715\text{ cm}^{-1}$).

- 12.39** Possible molecular formulas containing carbon, hydrogen, and oxygen and having $M^+ = 150$ are $\text{C}_{10}\text{H}_{14}\text{O}$, $\text{C}_9\text{H}_{10}\text{O}_2$, and $\text{C}_8\text{H}_6\text{O}_3$. The first formula has four degrees of unsaturation, the second has five degrees of unsaturation, and the third has six degrees of unsaturation. Since carvone has three double bonds (including the ketone) and one ring, $\text{C}_{10}\text{H}_{14}\text{O}$ is the correct molecular formula for carvone.



- 12.40** The intense absorption at 1690 cm^{-1} is due to a ketone next to a double bond.

- 12.41** The peak of maximum intensity (base peak) in the mass spectrum occurs at $m/z = 67$. This peak does *not* represent the molecular ion, however, because M^+ of a hydrocarbon must be an even number. Careful inspection reveals the molecular ion peak at $m/z = 68$. $M^+ = 68$ corresponds to a hydrocarbon of molecular formula C_5H_8 with a degree of unsaturation of two.

Fairly intense peaks in the mass spectrum occur at $m/z = 67, 53, 40, 39$, and 27 . The peak at $m/z = 67$ corresponds to loss of one hydrogen atom, and the peak at $m/z = 53$ represents loss of a methyl group. The unknown hydrocarbon thus contains a methyl group.

Significant IR absorptions occur at 2130 cm^{-1} ($-\text{C}\equiv\text{C}-$ stretch) and at 3320 cm^{-1} ($=\text{C}-\text{H}$ stretch). These bands indicate that the unknown hydrocarbon is a terminal alkyne. Possible structures for C_5H_8 are $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$ and $(\text{CH}_3)_2\text{CHC}\equiv\text{CH}$. [1-Pentyne is correct.]

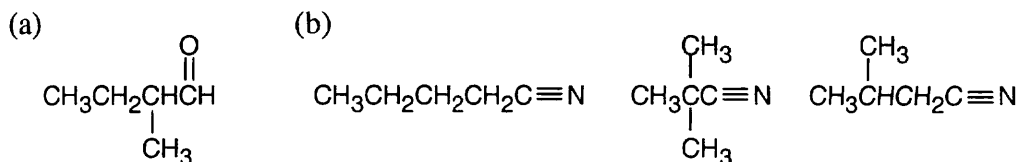
12.42 The molecular ion, $M^+ = 70$, corresponds to the molecular formula C_5H_{10} . This compound has one double bond or ring.

The base peak in the mass spectrum occurs at $m/z = 55$. This peak represents loss of a methyl group from the molecular ion and indicates the presence of a methyl group in the unknown hydrocarbon. All other peaks occur with low intensity.

In the IR spectrum, it is possible to distinguish absorptions at 1660 cm^{-1} and at 3000 cm^{-1} due to a double bond. (The 2960 cm^{-1} absorption is rather hard to detect because it occurs as a shoulder on the alkane C–H stretch at $2850\text{--}2960\text{ cm}^{-1}$.)

Since no absorptions occur in the region $890\text{ cm}^{-1}\text{--}990\text{ cm}^{-1}$, we can exclude terminal alkenes as possible structures. The remaining possibilities for C_5H_{10} are $CH_3CH_2CH=CHCH_3$ and $(CH_3)_2C=CHCH_3$. [2-Methyl-2-butene is correct.]

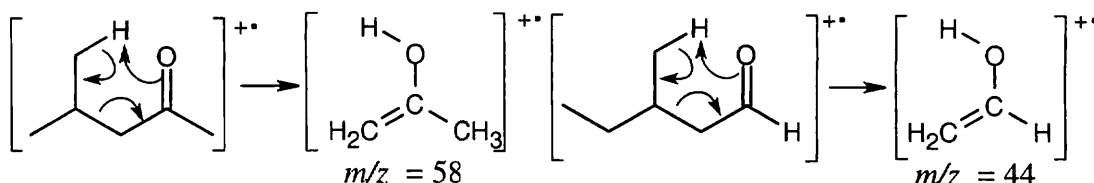
12.43



12.44 The simplest way to distinguish between the two isomers is by taking their IR spectra. The aldehyde carbonyl group absorbs at 1730 cm^{-1} , and the ketone carbonyl group absorbs at 1715 cm^{-1} .

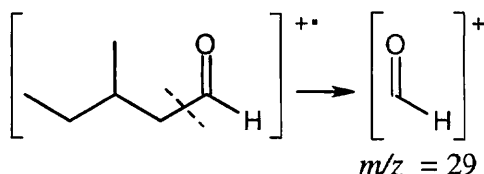
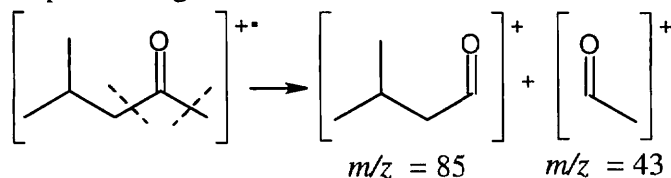
The mass spectra of the two isomers also differ. Like ketones, aldehydes also undergo alpha cleavage and McLafferty rearrangements.

McLafferty rearrangement:



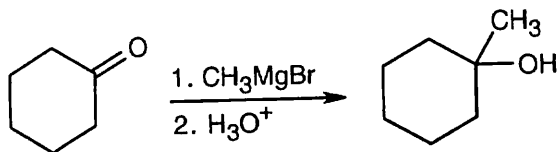
The fragments from the McLafferty rearrangements differ in values of m/z .

Alpha cleavage:



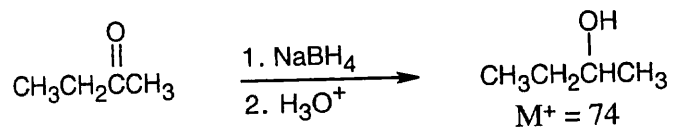
The fragments resulting from alpha cleavage also differ in values of m/z .

12.45

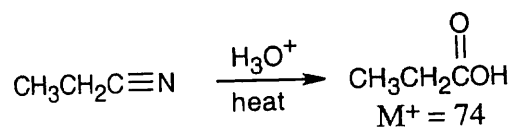


The absorption at 3400 cm^{-1} is due to a hydroxyl group.

12.46



12.47



The absorption at 1710 cm^{-1} is due to the carbonyl group of a carboxylic acid, and the absorption at $2500\text{--}3100\text{ cm}^{-1}$ is due to the --OH group of the carboxylic acid.