

Chapter 12

12.1 Write as many molecular formulas as you can for compounds that have the following molecular ions in their mass spectra. Assume that all the compounds contain C and H and that O may or may not be present.

(a) $M^+=86$

Solution: C_6H_{14} $C_5H_{10}O$ $C_4H_8O_2$ $C_3H_4O_3$

(b) $M^+=128$

Solution: $C_{10}H_8$ C_9H_{20} C_9H_4O $C_8H_{16}O$ $C_7H_{12}O_2$ $C_6H_8O_3$ $C_5H_4O_4$

(c) $M^+=156$

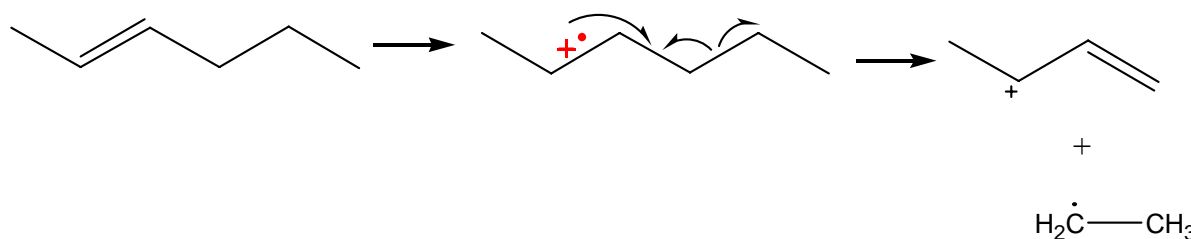
Solution: $C_{12}H_{12}$ $C_{11}H_{24}$ $C_{11}H_8O$ $C_{10}H_{20}O$ $C_{10}H_4O_2$ $C_9H_{16}O_2$ $C_8H_{12}O_3$ $C_7H_8O_4$ $C_6H_4O_5$

12.2 The male sex hormone testosterone contains C, H, and O and has a mass of 288.2089 amu as determined by high-resolution mass spectrometry. What is the molecular formula of testosterone?

Solution: $C_{19}H_{28}O_2$

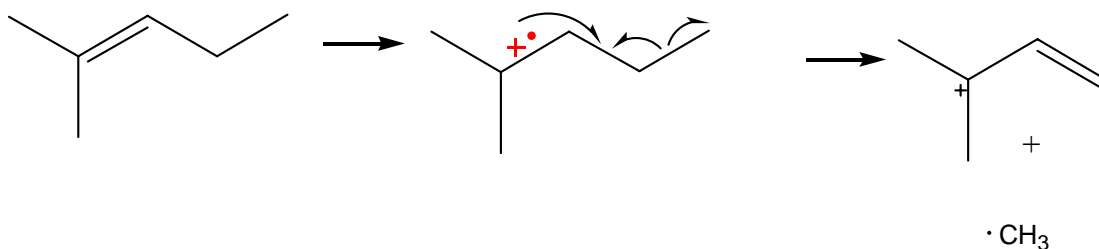
12.3 Two mass spectra are shown. One corresponds to 2-methyl-2-pentene; the other, to 2-hexene. Which is which? Explain.

Solution:



Sample B shows a base peak at $m/z=55$, corresponds to the loss of a $-CH_2CH_3$ (29 mass units) from the molecular ion. But sample A has only a small peak at $m/z=55$.

While it's hard for 2-methyl-2-pentene to lose a $-CH_2CH_3$ unit.



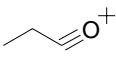
Conversely, sample A shows a big peak at $m/z=69$, corresponds to the loss of a $-CH_3$ (15 mass units) from the molecular ion. But sample B has only a small peak at $m/z=69$.


Base peak ($m/z=41$) will be the allylic cation. Molecular ion loses 43 mass units step by step, not in a single way (no propyl group could be lost in a single step).

12.4 What are the masses of the charged fragments produced in the following cleavage pathways?

(a) Alpha cleavage of 2-pentanone.

Solution:

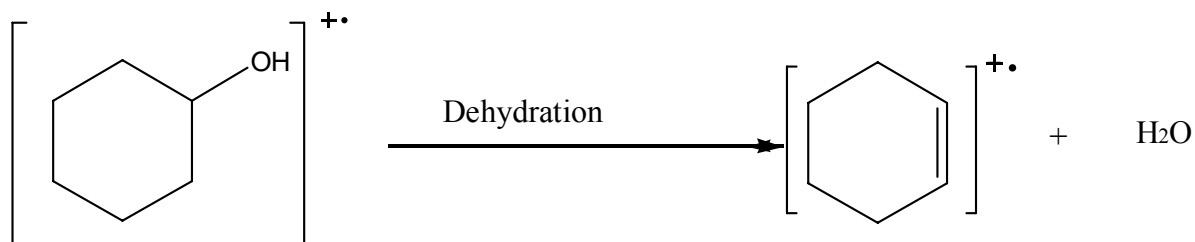
Loss of $-\text{CH}_3$ (15 mass units) : 71 

Loss of $-\text{CH}_2\text{CH}_2\text{CH}_3$ (43 mass units) 

(b) Dehydration of cyclohexanol

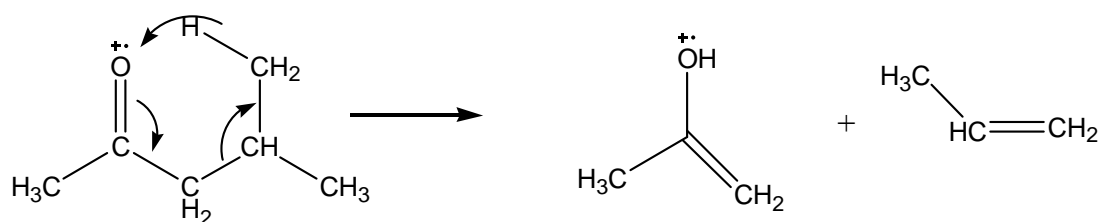
Solution :

Loss of H_2O : $100-18=82$

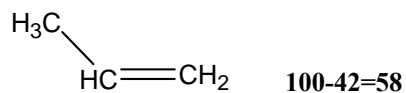


(c) McLafferty rearrangement of 4-methyl-2-pentanone.

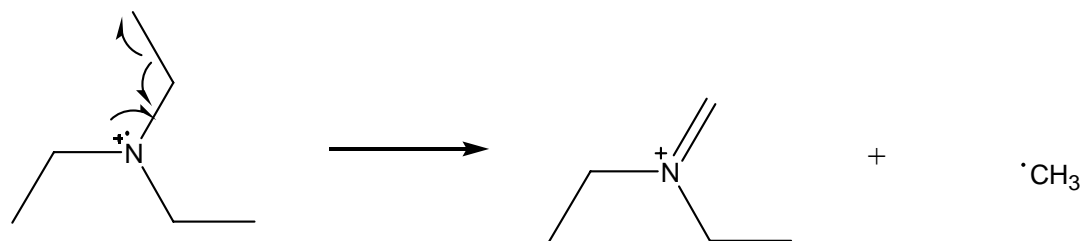
Solution:



Loss of

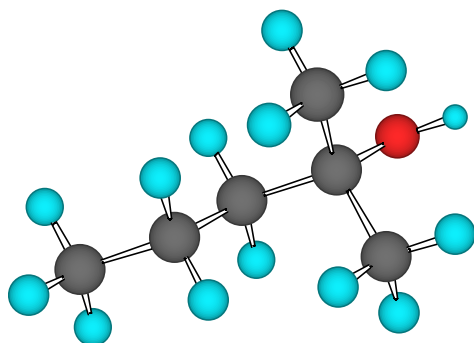


(d) Alpha cleavage of triethylamine.

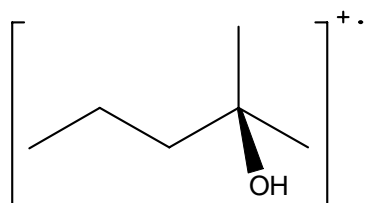


Loss of $-\text{CH}_3$ (15 mass units): $101-15=86$

12.5 List the masses of the parent ion and of several fragments you might expect to find in the mass spectrum of the following molecule (red=O):



Solution:

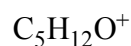
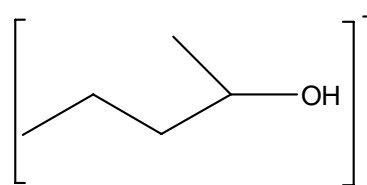


Exact Mass: 102.10

Mol. Wt.: 102.17

m/e: 102.10 (100.0%), 103.11 (6.9%)

C, 70.53; H, 13.81; O, 15.66

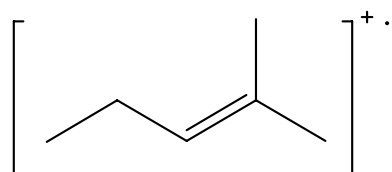


Exact Mass: 88.09

Mol. Wt.: 88.15

m/e: 88.09 (100.0%), 89.09 (5.8%)

C, 68.13; H, 13.72; O, 18.15



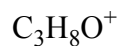
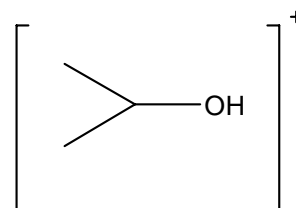
Exact Mass: 84.09

Mol. Wt.: 84.16

m/e: 84.09 (100.0%), 85.10

(6.9%)

C, 85.63; H, 14.37



Exact Mass: 60.06

Mol. Wt.: 60.09

m/e: 60.06 (100.0%), 61.06 (3.5%)

C, 59.96; H, 13.42; O, 26.62

12.6 Which has higher energy, infrared radiation with $\lambda=1.0 \times 10^{-6}\text{m}$ or an X ray with $\lambda=3.0 \times 10^{-9}\text{m}$?

Solution: It will be obvious that the X ray has higher energy .

12.7 Which has the higher energy, radiation with $\nu=4.0 \times 10^9\text{Hz}$ or radiation with $\lambda=9.0 \times 10^{-6}\text{m}$?

Solution:

$$E_1 = h\nu = 6.626 \times 10^{-34} \times 4.0 \times 10^9 \text{ J} = 2.65 \times 10^{-24} \text{ J}$$

$$E_2 = hc/\lambda = 6.626 \times 10^{-34} \times 3.0 \times 10^8 \div 9.0 \times 10^{-6} \text{ J} = 2.21 \times 10^{-20} \text{ J}$$

Definitely the radiation with $\lambda=9.0 \times 10^{-6}\text{m}$ has a more higher energy.

12.8 It is useful to develop a feeling for the amounts of energy that is corresponding to different parts of the electromagnetic spectrum. Calculate the energies of each of the following kinds of radiation

using the relationships

$$E = 1.20 \times 10^{-4} \text{ kJ/mol} / \lambda(\text{m}) \quad \text{and} \quad \nu = c/\lambda$$

- (a) A gamma ray with $\lambda = 5.0 \times 10^{-11} \text{ m}$
- (b) An X ray with $\lambda = 3.0 \times 10^{-9} \text{ m}$
- (c) Ultraviolet light with $\nu = 6.0 \times 10^{15} \text{ Hz}$
- (d) Visible light with $\nu = 7.0 \times 10^{14} \text{ Hz}$
- (e) Infrared radiation with $\lambda = 2.0 \times 10^{-5} \text{ m}$
- (f) Microwave radiation with $\nu = 1.0 \times 10^{11} \text{ Hz}$

Solution

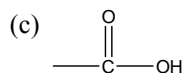
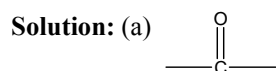
- (a) $E_2 = N_A hc/\lambda = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 3.0 \times 10^8 \div 5.0 \times 10^{-11} \text{ kJ/mol} = 2.4 \times 10^6 \text{ kJ/mol}$
- (b) $E_2 = N_A hc/\lambda = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 3.0 \times 10^8 \div 3.0 \times 10^{-9} \text{ kJ/mol} = 4.0 \times 10^4 \text{ kJ/mol}$
- (c) $E_1 = N_A h\nu = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 6.0 \times 10^{15} \text{ kJ/mol} = 2.4 \times 10^3 \text{ kJ/mol}$
- (d) $E_1 = N_A h\nu = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 7.0 \times 10^{14} \text{ kJ/mol} = 2.8 \times 10^2 \text{ kJ/mol}$
- (e) $E_2 = N_A hc/\lambda = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 3.0 \times 10^8 \div 2.0 \times 10^{-5} \text{ kJ/mol} = 6.0 \text{ kJ/mol}$
- (f) $E_1 = N_A h\nu = 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 1.0 \times 10^{11} \text{ kJ/mol} = 4.0 \times 10^{-2} \text{ kJ/mol}$

12.9 Because IR absorptions can be expressed either in micrometers or in wavenumbers, it's useful to be able to interconvert between units. Do the following conversions.

- (a) $3.10 \mu\text{m}$ to cm^{-1} **Solution: $3.10 \mu\text{m} = 3225 \text{ cm}^{-1}$**
- (b) $5.85 \mu\text{m}$ to cm^{-1} **Solution: $5.85 \mu\text{m} = 1710 \text{ cm}^{-1}$**
- (c) 2250 cm^{-1} to μm **Solution: $2250 \text{ cm}^{-1} = 4.44 \mu\text{m}$**

12.10 Refer to Table 12.1, and make educated guesses about what functional groups the following molecules might contain:

- (a) A compound with a strong absorption at 1710 cm^{-1}
- (b) A compound with a strong absorption at 1540 cm^{-1}
- (c) A compound with strong absorption at 1720 cm^{-1} and at $2500\text{--}3100 \text{ cm}^{-1}$



12.11 How might you use IR spectroscopy to distinguish between the following pairs of isomers?

- (a) $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OCH_3 (b) Cyclohexane and 1-hexene
- (b) $\text{CH}_3\text{CH}_2\text{COOH}$ and $\text{HOCH}_2\text{CH}_2\text{CHO}$

Solution : (a) $\text{CH}_3\text{CH}_2\text{OH}$ has a strong and broad H-O absorption at 3400 to 3650 cm^{-1} while the CH_3OCH_3 without this absorption.

(b) 1-hexene has a C=C at $1640\text{--}1680 \text{ cm}^{-1}$, while the cyclohexane without this absorption.

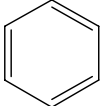
(c) $\text{CH}_3\text{CH}_2\text{COOH}$ has a strong and broad O-H absorption at $2500\text{--}3100 \text{ cm}^{-1}$, while $\text{HOCH}_2\text{CH}_2\text{CHO}$ has a strong O-H absorption at $3400\text{--}3650 \text{ cm}^{-1}$.

12.12 The IR spectrum of phenylacetylene is shown in Figure 12.15. What absorption bands can you

identify?

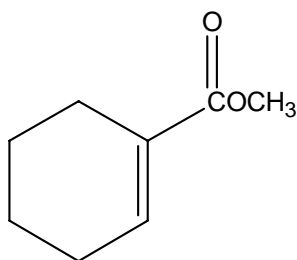
Solution: 3300 cm^{-1} $\text{—C}\equiv\text{C—H}$ absorption

3030 cm^{-1} aromatics $\text{—}\overset{\text{H}}{\text{C}}=\text{}$ absorption (weak)

$1450\text{--}1600\text{ cm}^{-1}$  absorption
 $2100\text{--}2260\text{ cm}^{-1}$ $\text{—C}\equiv\text{C—}$ absorption

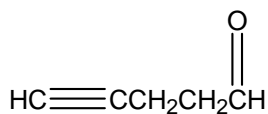
12.13 Where might the following compounds have IR absorption?

(a)



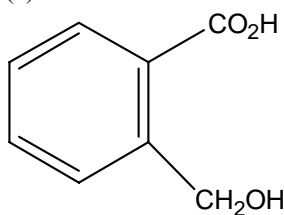
Solution: $\text{C}=\text{C}$ $1640\text{--}1680\text{ cm}^{-1}$
 $\text{C}=\text{O}$ 1715 cm^{-1}

(b)



Solution: $\text{C}\equiv\text{C}$ $2100\text{--}2260\text{ cm}^{-1}$
 $\equiv\text{C-H}$ 3300 cm^{-1}
 $\text{C}=\text{O}$ 1730 cm^{-1}

(c)

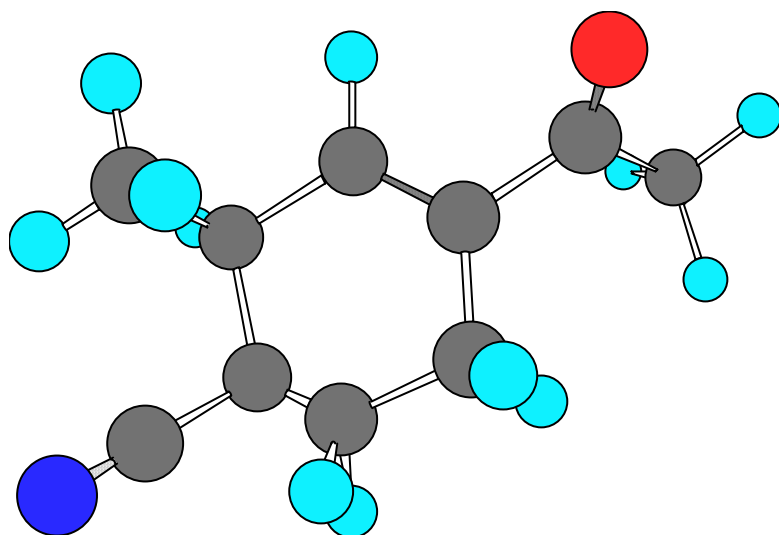


Solution: —OH (alcohol) $3400\text{--}3650\text{ cm}^{-1}$
 —OH (carboxylic acid) $2500\text{--}3100\text{ cm}^{-1}$
 $\text{C}=\text{O}$ 1715 cm^{-1}



$1660\text{--}2000\text{ cm}^{-1}$ $1450\text{--}1600\text{ cm}^{-1}$

12.14 Where might the following compound have IR absorptions? (Red=O, blue=N)

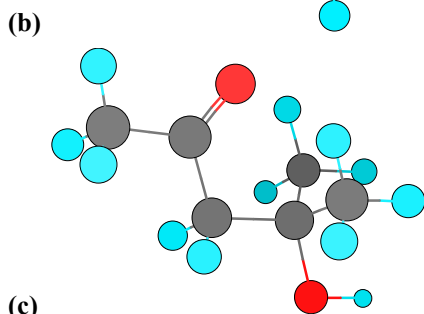
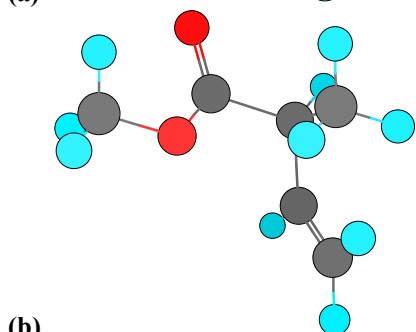
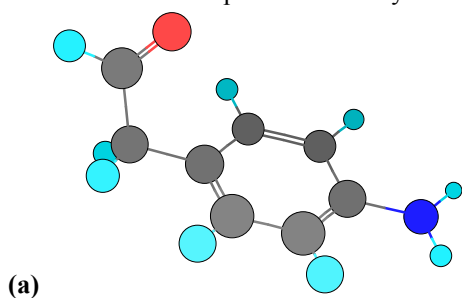


Solution: $\text{N}\equiv\text{C}$ 2210~2260 cm^{-1}

$\text{C}=\text{O}$ 1690 cm^{-1}

$\text{C}=\text{C}$ 1640~1680 cm^{-1}

12.15: Where in the IR spectrum would you expect each of the following molecules to absorb?



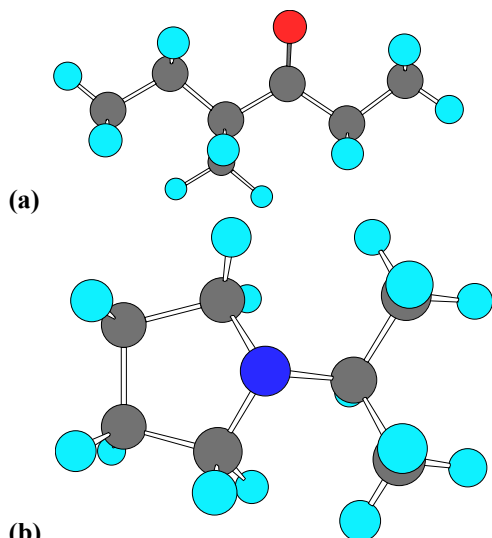
Solution:

(a): 1730 cm^{-1} ($\text{C}=\text{O}$), 1540 cm^{-1} (NO_2) and 1450-1600 cm^{-1} (benzene)

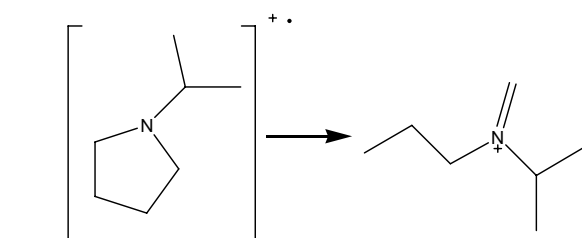
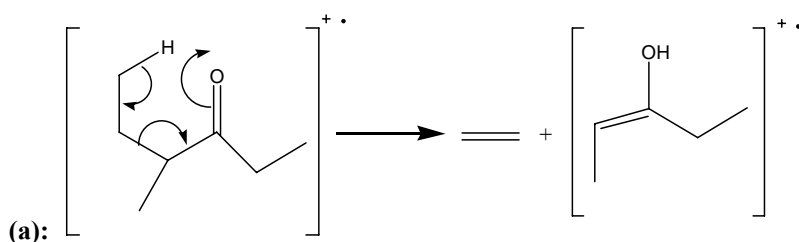
(b): 1640-1680 cm^{-1} ($\text{RCH}=\text{CH}_2$) and 1735 cm^{-1} ($\text{C}=\text{O}$)

(c): 1715 cm^{-1} ($\text{C}=\text{O}$) and 3400-3650 cm^{-1} ($\text{O}-\text{H}$)

12.16 Show structure of the likely fragments you would expect in the mass spectra of the following molecules.



Solution:



12.17 Write the molecular formulas of all hydrocarbons corresponding to the following molecular ions. How many degrees of unsaturation (double bonds and/or rings) are indicated by each formula?

(a) $M^+ = 86$

Solution:

Formula	Degrees of Unsaturation
C_7H_2	7
C_6H_{14}	0

(b) $M^+ = 110$

Solution:

Formula	Degrees of Unsaturation
C_9H_2	9
C_8H_{14}	2

(c) $M^+=146$

Solution:

Formula	Degrees of Unsaturation
$C_{12}H_2$	12
$C_{11}H_{14}$	5

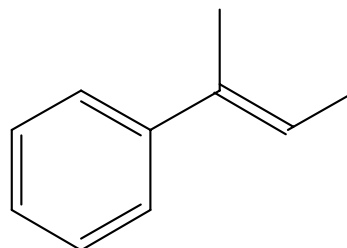
(d) $M^+=190$

Solution:

Formula	Degrees of Unsaturation
$C_{15}H_{10}$	11
$C_{14}H_{22}$	4

12.18 Draw the structure of a molecule that is consistent with the mass-spectral data in each of the following molecules:

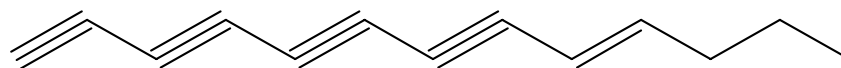
(a) A hydrocarbon with $M^+=132$



Solution: The formula is $C_{10}H_{12}$, one of the isomers is

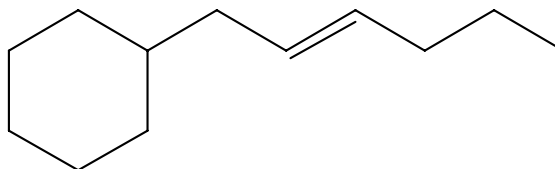
(b) A hydrocarbon with $M^+=166$

Solution: The formula is $C_{13}H_{10}$ or $C_{12}H_{22}$, one of the isomers of $C_{13}H_{10}$ is

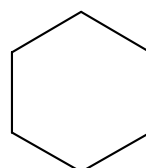


and one of the

isomers of $C_{12}H_{22}$ is



(c) A hydrocarbon with $M^+=84$



Solution: The formula is C_6H_{12} , one of the isomers is

12.19: Write molecular formulas for compounds that show the following molecular ions in their high-resolution mass spectra. Assume that C, H, N and O might be present, and use the exact atomic masses described in Section 12.2. (a) $M^+ = 98.0844$; (b) $M^+ = 123.0320$.

Solution: (a): As $M_H = 1.00783$, $M_C = 12.00000$, $M_N = 14.00307$, $M_O = 15.99491$, $M^+ / M_C = 8.1745$; so the probable molecular formulas are C_7H_{14} or $C_6H_{10}O$, but the exact mass spectra of $C_6H_{10}O$ is 98.0732 which is not the same as M^+ , so the exact molecular formula is C_7H_{14} .

(b): $M^+ / M_C = 10.1693$; as the residual is an odd number so there should be a N, the probable molecular formulas are $C_8H_{13}N$ or $C_6H_5NO_2$, but the exact mass spectra of $C_8H_{13}N$ is not the same as M^+ , so the exact molecular formula is $C_6H_5NO_2$.

12.20: Camphor, a saturated monoketone from the Asian camphor tree, is used among other things as a moth repellent and as a constituent of embalming fluid. If camphor has $M^+ = 152.1201$ by high-resolution mass spectrometry, what is its molecular formula? How many rings does camphor have?

Solution: As the camphor is a monoketone, and $M^+ / M_C = 12.6767$, so the molecular formula should be $C_{10}H_{16}O$, so the number of rings = $(10 \times 2 - 16) / 2 = 2$.

12.21 The nitrogen rule of mass spectrometry says that a compound containing an odd number of nitrogens has an odd-numbered molecular ion. Conversely, a compound containing an even number of nitrogens has an even-numbered M^+ peak. Explain.

Solution: Nitrogen is trivalent, thus requiring an odd number of hydrogen atoms in a molecular. So a compound containing an odd number of nitrogens has an odd-numbered molecular ion. Conversely, a compound containing an even number of nitrogens has an even-numbered M^+ peak.

12.22 In light of the nitrogen rule mentioned in Problem 12.21, what is the molecular formula of pyridine, $M^+ = 79$?

Solution: The molecular formula of pyridine: C_5H_5N

12.23 Nicotine is a diamino compound isolated from dried tobacco leaves. Nicotine has two rings and $M^+ = 162.1157$ by high-resolution mass spectrometry. Give a molecular formula for nicotine, and calculate the number of double bonds.

Solution: The molecular formula of nicotine is $C_{10}H_{14}N_2$ and it has 3 double bonds.

12.24 The hormone cortisone contains C, H, and O, and shows a molecule ion at $M^+ = 360.1937$ by high-resolution mass spectrometry. What is the molecular formula of cortisone? (The degree of unsaturation of cortisone is 8)

Solution: The molecular formula is $C_{21}H_{28}O_5$

12.25 Halogenated compounds are particularly easy to identify by their mass spectra because both chlorine and bromine occur naturally as mixtures of two abundant isotopes. Chlorine occurs as ^{35}Cl (75.8%) and ^{37}Cl (24.2%); bromine occurs as ^{79}Br (50.7%) and ^{81}Br (49.3%). At what masses do the molecular ions occur for the following formulas? What are the relative percentages of the each molecular ion?

(a) Bromomethane, CH₃Br

Solution:

Molecular ion	CH₃⁷⁹Br⁺	CH₃⁸¹Br⁺
m/z	94	96
Relative percentage	50.7%	49.3%

(b) 1-Chlorohexane, C₆H₁₃Cl

Solution:

Molecular ion	C₆H₁₃³⁵Cl⁺	C₆H₁₃³⁷Cl⁺
m/z	120	122
Relative percentage	75.8%	24.2%

12.26 Molecular ions can be particularly complex for polyhalogenated compounds. Taking the natural abundance of Cl into account (See Problem 12.25), calculate the masses of the molecular ions of the following formulas. What are the relative percentages of each ion?

(a) Chloroform, CHCl₃

Solution:

Molecular ion	CH³⁵Cl₃⁺	CH³⁷Cl³⁵Cl₂⁺	CH³⁵Cl³⁷Cl₂⁺	CH³⁷Cl₃⁺
m/z	118	120	122	124
Relative percentage	43.55%	47.71%	13.32%	1.42%

(b) Freon 12, CF₂Cl₂ (Fluorine occurs only as ¹⁹F.)

Solution:

Molecular ion	CF₂³⁵Cl₂⁺	CF₂³⁵Cl³⁷Cl⁺	CF₂³⁷Cl₂⁺
m/z	120	122	124
Relative percentage	57.46%	36.69%	5.90%

12.27 By knowing the natural abundances of minor isotopes, it's possible to calculate the relative heights of M⁺ and M+1 peaks. If ¹³C has a natural abundance of 1.10%, what are the relative heights of the M⁺ and M+1 peaks in the mass spectrum of benzene, C₆H₆?

Solution: The M+1 peak is 6.6%(1.1%*6) as high as the M⁺ peak.

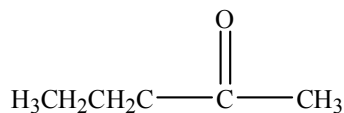
12.28 Propose structures for compounds that fit the following data:

(a) A ketone with M⁺=86 and fragments at m/z=71 and m/z=43

(b) An alcohol with M⁺=88 and fragments at m/z=73, m/z=70, and m/z=59

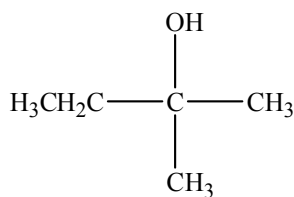
Solution:

(a)



(-CH₃: 86-71=15; -CH₂CH₂CH₃: 86-43=43;)

(b)

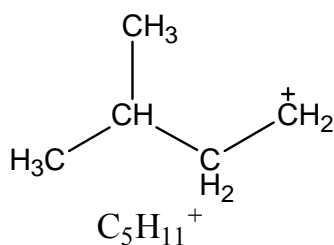


(-CH₃: 88-73=15; H₂O: 88-70=18; -CH₂CH₃: 88-59=29)

12.29 2-Methylpentane (C₆H₁₄) has the mass spectrum shown. Which peak represents M⁺? Which is the base peak? Propose structures for fragment ions of *m/z* =71, 57, 43 and 29. Why does the base peak have mass it does?

Solution:

The molecule weight of 2-Methylpentane (C₆H₁₄) is about 86, so the final peak represents M⁺ according to its molecular weight. The base peak is the peak with *m/z* =43. The structure of fragment ions shows in the following structure:

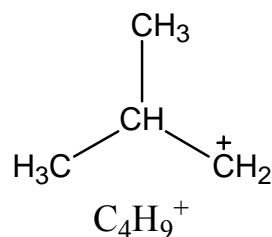


Exact Mass: 71.09

Mol. Wt.: 71.14

m/e: 71.09 (100.0%), 72.09 (5.7%)

C, 84.42; H, 15.59

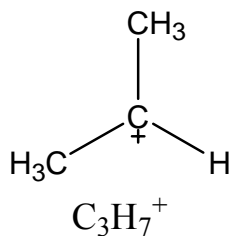


Exact Mass: 57.07

Mol. Wt.: 57.11

m/e: 57.07 (100.0%), 58.07 (4.4%)

C, 84.12; H, 15.88

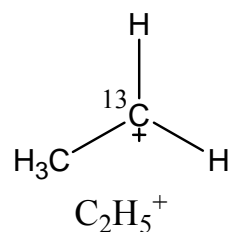


Exact Mass: 43.05

Mol. Wt.: 43.09

m/e: 43.05 (100.0%), 44.06 (3.4%)

C, 83.63; H, 16.38

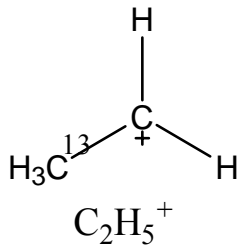


Exact Mass: 29.04

Mol. Wt.: 29.06

m/e: 29.04 (100.0%), 30.04 (2.2%)

C, 82.66; H, 17.34



Exact Mass: 29.04

Mol. Wt.: 29.06

m/e:

C, 82.66; H, 17.34

The base peak is the peak that the carbocation with the molecular weight of 43, as it's the most stable carbocation in the process.

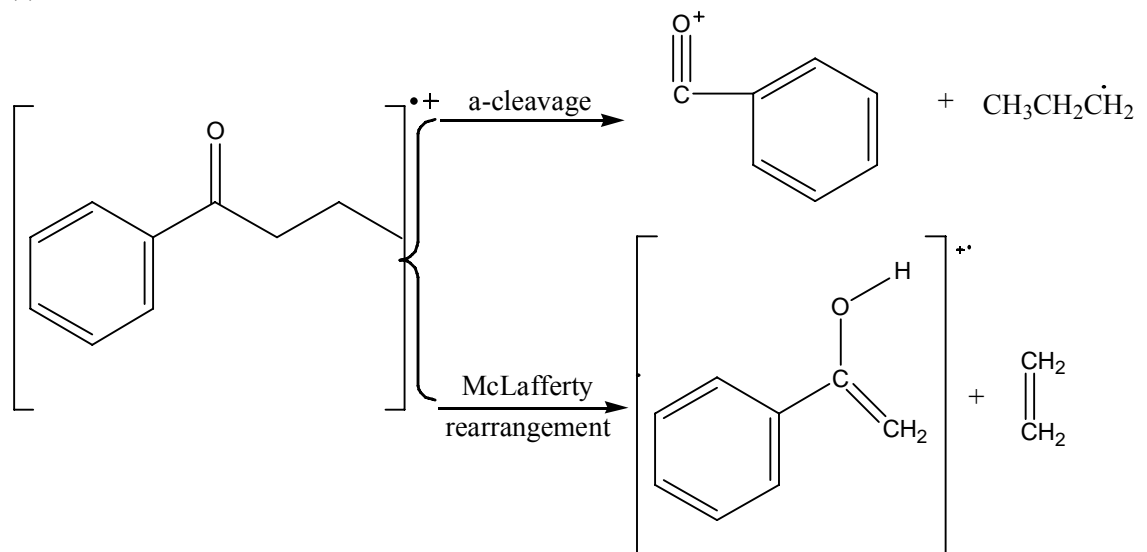
12.30 Assume that you are in a laboratory carrying out the catalytic hydrogenation of cyclohexene to cyclohexane. How would you use a mass spectrometer to determine when the reaction is finished?

Solution:

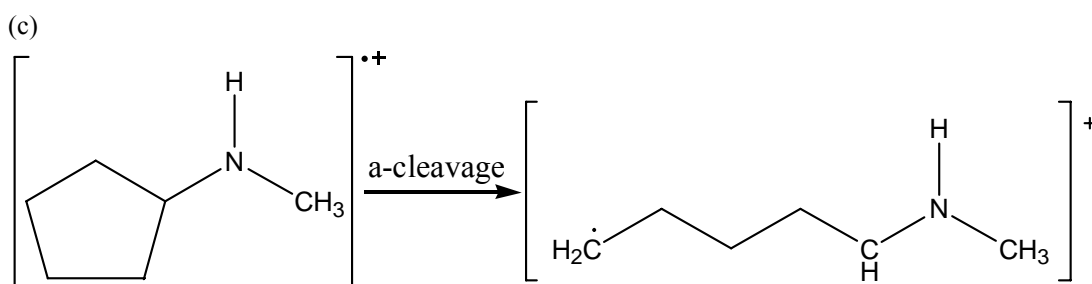
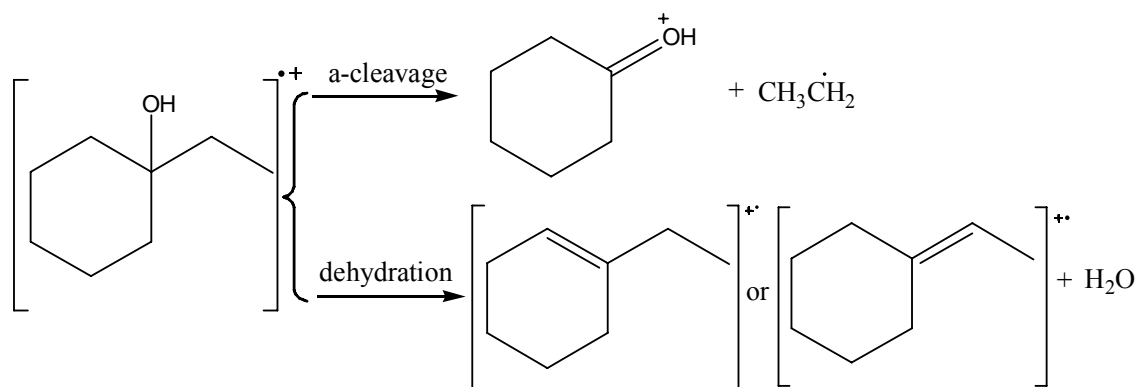
GC-MS should be used.

12.31 What fragments might you expect in the mass spectra of the following compounds?

(a)



(b)



12.32 Convert the following IR absorption values from micrometers to wavenumbers:

- (a) An alcohol, $2.98\mu\text{m}$
 $\nu = 1/\lambda = 3355.7\text{cm}^{-1}$
- (b) An ester, $5.81\mu\text{m}$
 $\nu = 1/\lambda = 1721.2\text{cm}^{-1}$
- (c) A nitrile, $4.93\mu\text{m}$
 $\nu = 1/\lambda = 2028.4\text{cm}^{-1}$

12.33 Convert the following IR absorption values from wavenumbers to micrometers:

- (a) A cyclopentanone, 1755cm^{-1} (b) An amine, 3250cm^{-1}
- (c) An aldehyde, 1725cm^{-1} (d) An acid chloride, 1780cm^{-1}

Solution: (a) $\lambda = 1/1755\text{ cm}^{-1} = 0.5698\text{mm}$
 (b) $\lambda = 1/3250\text{ cm}^{-1} = 0.3077\text{mm}$
 (c) $\lambda = 1/1725\text{ cm}^{-1} = 0.5797\text{mm}$
 (d) $\lambda = 1/1780\text{ cm}^{-1} = 0.5618\text{mm}$

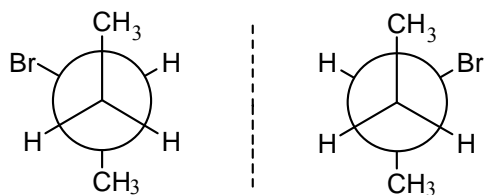
12.34 How might you use IR spectroscopy to distinguish among the three isomers 1-butyne, 1,3-butadiene, and 2-butyne?

Solution: To 1, 3-butadiene, there will be two strong absorption at 3020-3100 and 1640-1680

To 1-butyne, there will be two strong absorption at 3300 and 2100-2260.

To 2-butyne, there will be a strong absorption at 2100-2260 but not 3300.

12.35 Would you expect two enantiomers such as (R)-2-bromobutane and (S)-2-bromobutane to have identical or different IR spectra? Explain.



Solution: Identical. The reason: the enantiomers are mirror-image compounds, so every allowed vibration of one compound has its mirror-image vibration of the other compound, and the two mirror-image vibrations will have the same absorption.

12.36 Would you expect two diastereomers such as meso-2,3-dibromobutane and (2R,3S)-dibromobutane to have identical or different IR spectra? Explain.



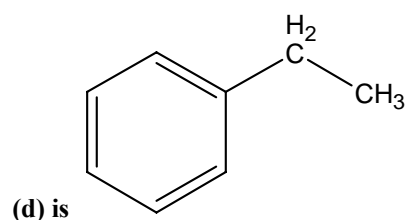
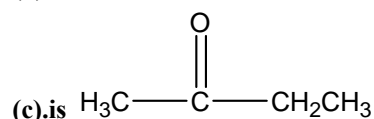
Solution: Different. The reason: Diastereomers are not mirror-image compounds, so every bond of one compound can't find another bond of the other compound that has the identical circumstance, and the absorptions of the two compounds obviously are different.

12.37: Propose structures for compounds that meet the following description:

- (a) C_5H_8 , with IR absorptions at 3300 and 2150 cm^{-1}
- (b) C_4H_8O , with a strong IR absorption at 3400 cm^{-1}
- (c) C_4H_8O , with a strong IR absorption at 1715 cm^{-1}
- (d) C_8H_{10} , with IR absorption at 1600 and 1500 cm^{-1}

Solution: (a) is $HC\equiv CCH_2CH_2CH_3$

(b) is $H_3CHC=CHCH_2OH$



12.38: How could you use infrared spectroscopy to distinguish between the following pairs of isomers?

- (a) $HC\equiv CCH_2NH_2$ and $H_3CH_2CC\equiv N$
- (b) CH_3COCH_3 and CH_3CH_2CHO

Solution: (a): $HC\equiv CCH_2NH_2$, with IR absorption at 3300 and $2100\text{--}2260\text{ cm}^{-1}$

$H_3CH_2CC\equiv N$, with a strong IR absorption at $2210\text{--}2260\text{ cm}^{-1}$

(b) CH_3COCH_3 with a strong IR absorption at 1715 cm^{-1}

CH_3CH_2CHO with a strong IR absorption at 1730 cm^{-1}

12.39 Two infrared spectra are shown. One is the spectrum of cyclohexane, and the other is the spectrum of cyclohexene. Identify them, and explain your answer.

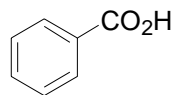
Solution: (b) is the spectrum of cyclohexene because it shows a characteristic

C=C absorption at 1640 cm^{-1} and a vinylic =C-H absorption at 3020 cm^{-1} .

12.40 At what approximate positions might the following compounds show IR absorptions?

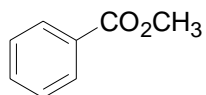
Solution:

(a)



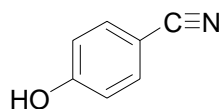
	3030	weak
	1660~2000	weak
	1450~1600	medium
C=O	1670~1780	strong
O-H	2500~3100	strong, very broad

(b)



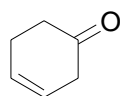
	3030	weak
	1660~2000	weak
	1450~1600	medium
C=O	1670~1780	strong
—CH ₃	2850~2960	medium to strong

(c)



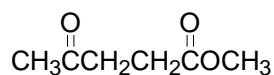
	3030	weak
	1660~2000	weak
	1450~1600	medium
O-H	2500~3100	strong, very broad
-C≡N	2210~2260	medium

(d)



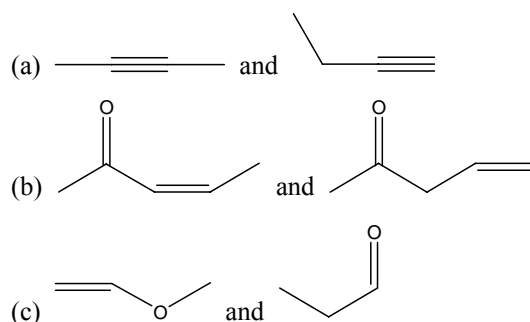
C=O	1670~1780	strong
C=C	1640~1680	medium
=C-H	3020~3100	medium

(e)



C-H	2850~2960	medium to strong
C=O	1670~1780	strong
C-O	1050~1150	strong

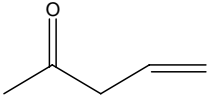
12.41 How would you use infrared spectroscopy to distinguish between the following pairs of constitutional isomers?

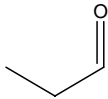
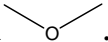


Solution:

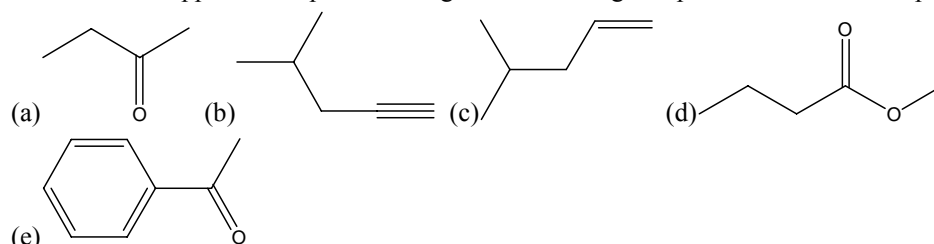
(a). has a strong absorption at the position of 3300cm^{-1} of $\equiv\text{C}-\text{H}$.

(b). has a special strong absorption at 1690cm^{-1} of $\text{C}=\text{O}$ because of the

conjugation π bond, and  should have separated typical absorption of $\text{C}=\text{O}$ and $\text{C}=\text{C}$.

(c).  has a distinguishing absorption at 1730cm^{-1} of aldehydes which is different from those of $\text{C}=\text{C}$ and .

12.42 At what approximate positions might the following compounds show IR absorptions?

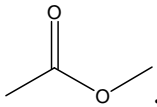


Solution:

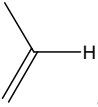
(a). Absorption: $1670\text{-}1780\text{cm}^{-1}$ of $\text{C}=\text{O}$.

(b). Absorption: 3300cm^{-1} of $\text{C}\equiv\text{C}-\text{H}$; $2100\text{-}2260\text{cm}^{-1}$ of $\text{C}\equiv\text{C}$.

(c). Absorption: $3020\text{-}3100\text{cm}^{-1}$ of $\text{C}=\text{C}-\text{H}$; $1640\text{-}1680\text{cm}^{-1}$ of $\text{C}=\text{C}$.

(d). Absorption: 1735cm^{-1} of typical .

(e). Absorption: 1690cm^{-1} of $\text{C}=\text{O}$ next to the aromatic ring; $1450\text{-}1600\text{cm}^{-1}$ and

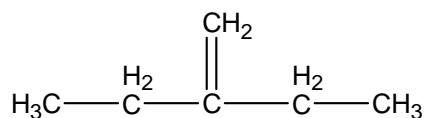
$1660\text{-}2000\text{cm}^{-1}$ (should be overlapped) of benzene ring; 3030cm^{-1} of .

12.43 Assume you are carrying out the dehydration of 1-methylcyclohexanol to yield 1-methylcyclohexene. How could you use infrared spectroscopy to determine when the reaction is complete?

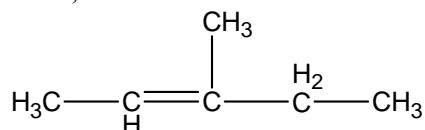
Solution: When there is no absorption in the area of $3400\text{-}3650$ where O-H has absorption peak, it shows that the reaction is complete.

12.44. Assume that you are carrying out the base-induced dehydrobromination of 3-bromo-3-methylpentane to yield an alkene. How could you use IR spectroscopy to tell which of two possible elimination products is formed?

Solution: Because $\text{R}_2\text{C}=\text{CH}_2$ has a big absorption in the 890cm^{-1} , we only need to find whether there is an absorption in the 890cm^{-1} , if there is an absorption, the product will be



if not, it is



12.45 Which is stronger, the C=O bond in an ester (1735cm^{-1}) or the C=O bond in a saturated ketone (1715cm^{-1})? Explain.

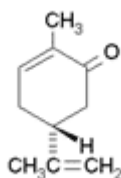
Solution: $1735 > 1715$, so the C=O bond in an ester (1735cm^{-1}) is stronger than the C=O bond in a saturated ketone (1715cm^{-1}). Strong bonds vibrate at a higher energy and a higher frequency.

12.46 Carvone is an unsaturated ketone responsible for the odor of spearmint. If carvone has $M^+ = 150$ in its mass spectrum and contains three double bonds and one ring, what is its molecular formula?

Solution: $\text{C}_{10}\text{H}_{14}\text{O}$

12.47 Carvone (Problem 12.46) has an intense infrared absorption at 1690cm^{-1} . what kind of ketone does carvone contain?

Solution: carvone contains ketone next to a double bond. As follow:



12.48 The mass spectrum (a) and the infrared spectrum (b) of an unknown hydrocarbon are shown. Propose as many structures as you can.

Solution:

IR:

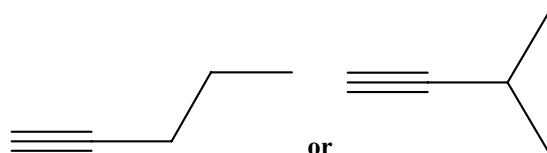
- The region from 3500 to 3000cm^{-1} corresponding to absorptions caused by $\equiv\text{C}-\text{H}$
- The region from 2200 to 2000cm^{-1} is where $\text{C}\equiv\text{C}$ stretching occurs.

So there is a terminal $\text{C}\equiv\text{C}-\text{H}$ in the molecule.

MS:

The base peak is $m/z = 67$. It is not the M^+ because the mass of hydrocarbon can not be odd. So the M^+ might be 68 or 82.

If M^+ 's mass is 68, the formula might be C_5H_8 , and the structure may be



If the loss of a methyl radical from the molecule gives rise to the base peak, the mass of the molecule is $67+15=82$, which is hexyne. The structure might be

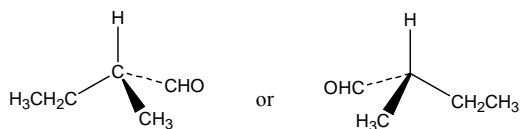
12.50 Propose structures for compounds that meet the following descriptions:

(a) An optically active compound $C_5H_{10}O$ with an IR absorption at 1730 cm^{-1}

(b) An non-optically active compound C_5H_9N with an IR absorption at 2215 cm^{-1}

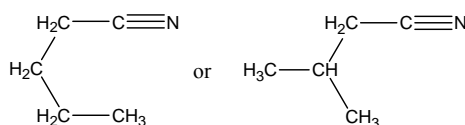
Solution:

(a) Saturated aldehyde absorb at 1730 cm^{-1} , and the compound is optically active, so the possible structure is:

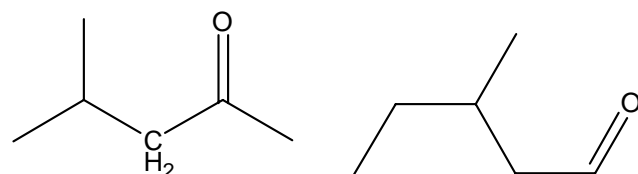


(b) Nitriles ($-C\equiv N$) absorb at 2215 cm^{-1} and the compound is non-optically active.

The possible structure is:



12.51 4-Methyl-2-pentanone and 3-methylpentanal are isomers. Explain how you could tell them apart, both by mass spectrometry and by infrared spectroscopy.



4-Methyl-2-pentanone

3-methylpentanal

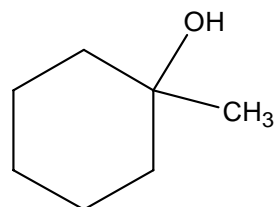
solution:

by mass spectrometry : we can get different base peak to tell them apart

by infrared spectroscopy: the aldehyde absorb at 1730 cm^{-1} , while the ketone absorb at 1715 cm^{-1}

12.52 Grignard reagents undergo a general and very useful reaction with ketones. Methylmagnesium bromide, for example, reacts with cyclohexanone to yield a product with the formula $C_7H_{14}O$. What is the structure of this product if it has an IR absorption at 3400 cm^{-1} ? (See Section 17.6)

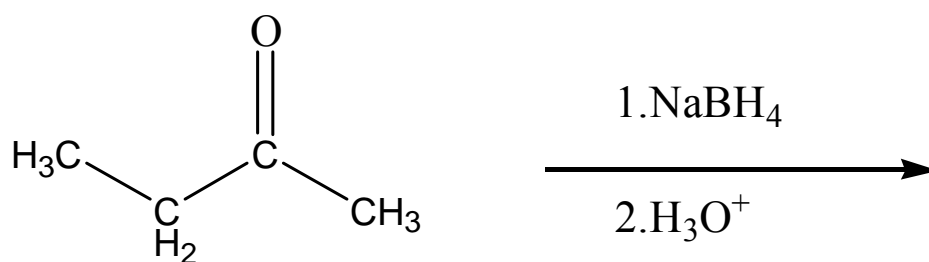
Solution:



The hydroxy group results in the IR absorption at 3400 cm^{-1} .

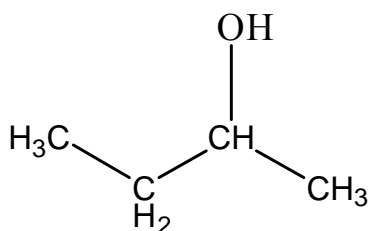
12.53 Ketones undergo a reduction when treated with sodium borohydride, $NaBH_4$. What's the structure of the compound produced by reaction of 2-Butanone with $NaBH_4$ if it has an IR

absorption at 3400cm^{-1} and $M^+ = 74$ in the mass spectrum?(See Section 17.5)



Solution:

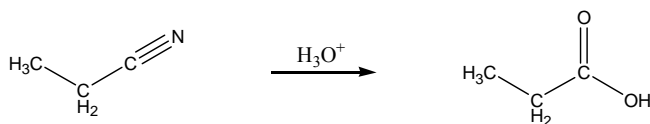
Cause the Function Group O-H's Band position is $3400\sim 3650$, so there should be a -OH group in the product. And $M^+ = 74$, which indicates that the product should be $\text{C}_4\text{H}_{10}\text{O}$. So the structure of



the product should be

12.54 Nitriles, $\text{R}-\text{CN}$, undergo a hydrolysis reaction when heated with aqueous acid. What is the structure of the compound produced by hydrolysis of propanenitrile, $\text{CH}_3\text{CH}_2\text{CN}$, if it has IR absorption at 2500cm^{-1} and 1710cm^{-1} and has $M^+ = 74$?

Solution:



The IR absorption between 2500cm^{-1} and 1710cm^{-1} shows the $\text{C}=\text{O}$ functional group. By calculating the molecular mass, the product is an acid.