Chapter 15
Infrared Spectroscopy and Mass Spectrometry

Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 15. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- **Spectroscopy** is the study of the interaction between _______ and ________.
- The difference in energy (ΔE) between vibrational energy levels is determined by the nature of the bond. If a photon of light possesses exactly this amount of energy, the bond can absorb the photon to promote a __________________ **excitation**.
- IR spectroscopy can be used to identify which ______________________ are present in a compound.
- The location of each signal in an IR spectrum is reported in terms of a frequency-related unit called _________________.
- The wavenumber of each signal is determined primarily by bond __________ and the __________ of the atoms sharing the bond.
- The intensity of a signal is dependent on the ______________ of the bond giving rise to the signal.
- _________________ C=C bonds do not produce signals.
- Primary amines exhibit two signals resulting from ___________ **stretching** and _____________ **stretching**.
- **Mass spectrometry** is used to determine the ____________________ and _________________________ of a compound.
- **Electron impact ionization** (**EI**) involves bombarding the compound with high energy _______________, generating a radical cation that is symbolized by $(M)^{+\bullet}$ and is called the **molecular ion**, or the __________ **ion**.
- Only the molecular ion and the cationic fragments are deflected, and they are then separated by their ____________________ (*m/z*).
- The tallest peak in a mass spectrum is assigned a relative value of 100% and is called the __________ **peak**.
- The relative heights of the $(M)^{+\bullet}$ peak and the $(M+1)^{+\bullet}$ peak indicates the number of ___________________.
- A signal at M-15 indicates the loss of a _________ group; a signal at M-29 indicates the loss of an _________ group.
- ______________ alkanes have a molecular formula of the form C_nH_{2n+2}.
- Each double bond and each ring represents one **degree of** _______________.

Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 15. The answers appear in the section entitled *SkillBuilder Review*.

15.1 Analyzing an IR Spectrum

STEP 1 - *LOOK FOR _____________ BONDS BETWEEN 1600 AND 1850* ***GUIDELINES:*** *C=O BONDS PRODUCE ________ SIGNALS* *C=C BONDS GENERALLY PRODUCE ______ SIGNALS. SYMMETRICAL C=C BONDS DO NOT APPEAR AT ALL*	***STEP 2 -*** *LOOK FOR ___________ BONDS BETWEEN 2100 AND 2300* ***GUIDELINES:*** *___________________ TRIPLE BONDS DO NOT PRODUCE SIGNALS*	***STEP 3 -*** *LOOK FOR _________ BONDS BETWEEN 2750 AND 4000* ***GUIDELINES:*** *DRAW A LINE AT 3000, AND LOOK FOR _________ OR ____________ C-H BONDS TO THE LEFT OF THE LINE* *THE SHAPE OF AN O-H SIGNAL IS AFFECTED BY ______________________ (DUE TO H-BONDING)* *PRIMARY AMINES EXHIBIT TWO N-H SIGNALS (____________ AND ___________ STRETCHING)*

15.2 Distinguishing Two Compounds Using IR Spectroscopy

STEP 1 - *WORK METHODICALLY THROUGH THE EXPECTED _______________________ OF EACH COMPOUND*	***STEP 2 -*** *DETERMINE IF ANY __________ WILL BE PRESENT FOR ONE COMPOUND BUT ABSENT FOR THE OTHER*	***STEP 3 -*** *FOR EACH EXPECTED SIGNAL, COMPARE FOR ANY POSSIBLE DIFFERENCES IN _____________, ________________, OR ________________.*

15.3 Using the Relative Abundance of the $(M+1)^{+\bullet}$ Peak to Propose a Molecular Formula

STEP 1 - *FILL IN THE BOXES BELOW TO COMPLETE THE FORMULA THAT CAN BE USED TO DETERMINE THE NUMBER OF CARBON ATOMS IN A COMPOUND USING MASS SPECTROMETRY:* $\dfrac{\left(\dfrac{\text{abundance of } \boxed{\quad\quad} \text{ Peak}}{\text{abundance of } \boxed{\quad\quad} \text{ Peak}}\right) \times 100\%}{1.1\ \%}$	***STEP 2 -*** *ANALYZE THE MASS OF THE MOLECULAR ION TO DETERMINE IF ANY _________________ ARE PRESENT.*

15.4 Calculating HDI

STEP 1 - *REWRITE THE MOLECULAR FORMULA "AS IF" THE COMPOUND HAD NO ELEMENTS OTHER THAN C AND H, USING THE FOLLOWING RULES:* *- ADD ONE H FOR EACH ______________* *- IGNORE ALL ______________ ATOMS* *- SUBTRACT ONE H FOR EACH _______________*	***STEP 2 -*** *DETERMINE WHETHER ANY H'S ARE MISSING. EVERY TWO H'S REPRESENTS ONE DEGREE OF UNSATURATION:* $C_4H_9Cl \longrightarrow$ *HDI = _____* $C_4H_8O \longrightarrow$ *HDI = _____* $C_4H_9N \longrightarrow$ *HDI = _____*

Solutions

15.1.

Increasing wavenumber
$\longleftarrow$

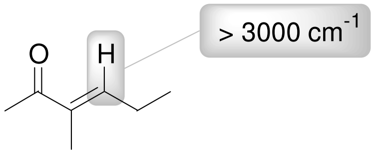
a) C−H C≡C C=C

Increasing wavenumber
$\longleftarrow$

b) C−H C−C

15.2.

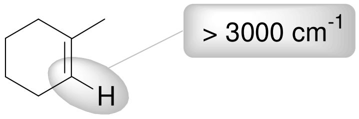
a)



b) No

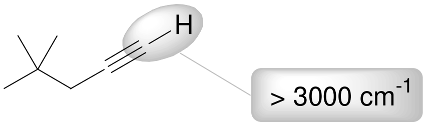
c) No

d)



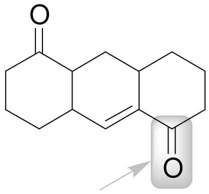
e) No

f)



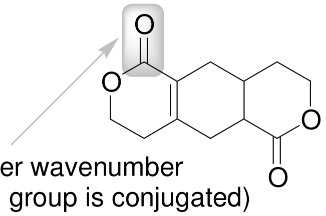
15.3.

a)



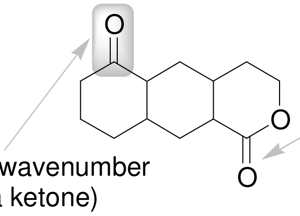
lower wavenumber
(carbonyl group is conjugated)

b)



lower wavenumber
(carbonyl group is conjugated)

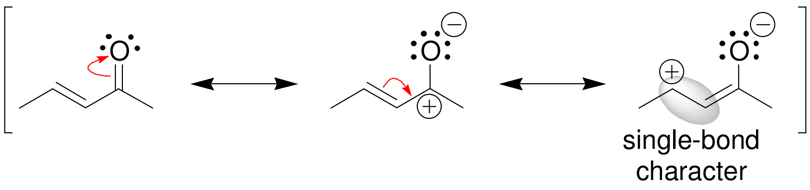
c)



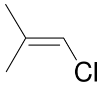
higher wavenumber
(an ester)

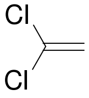
lower wavenumber
(a ketone)

15.4. The C=C bond in the conjugated compound produces a signal at lower wavenumber because it has some single bond character, as seen in the third resonance structure below:

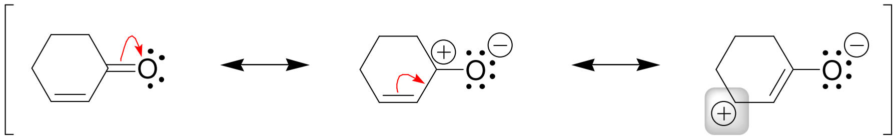


15.5.

a)  The presence of the Cl will cause the C=C bond in this compound to have a larger dipole moment than the C=C bond in the other compound.

b)  The C=C bond in this compound will have a larger dipole moment than the C=C bond in the other compound.

15.6. The C=C bond in 2-cyclohexenone has a large dipole moment, as can be rationalized with the third resonance structure below:



15.7. The vinylic C-H bond should produce a signal above 3000 cm^{-1}.

15.8. The narrow signal is produced by the O-H stretching in the absence of hydrogen bonding effect. The broad signal is produced by O-H stretching when hydrogen bonding is present. Hydrogen bonding effectively lowers the bond strength of the O-H bonds, because each hydrogen atom is slightly pulled away from the oxygen to which it is connected. A longer bond length (albeit temporary) corresponds with a weaker bond, which corresponds with a lower wavenumber.

15.9.

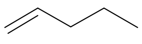
a) ROH b) neither c) RCO_2H d) neither e) ROH f) RCO_2H

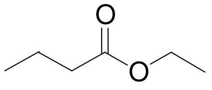
15.10.

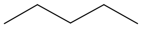
a) ketone b) RCO_2H c) R_2NH d) RNH_2 e) ROH f) ketone

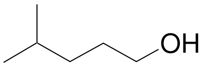
15.11. The C_{sp^3}—H bonds can stretch symmetrically, asymmetrically, or in a variety of ways with respect to each other. Each one of these possible stretching modes is associated with a different wavenumber of absorption.

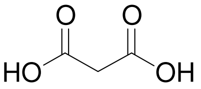
15.12.

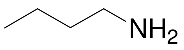
a) 

b) 

c) 

d) 

e) 

f) 

15.13.

1) The O-H bond of the carboxylic acid moiety (expected to be 2200 - 3600 cm^{-1})
2) The vinylic C-H bond (expected to be ~ 3100 cm^{-1})
3) All other C-H bonds (expected to be <3000 cm^{-1})
4) The C=O bond of the carboxylic acid moiety (expected to be ~ 1720 cm^{-1})
5) The C=C bond (expected to be ~ 1650 cm^{-1})

15.14.

a) The starting material is an alcohol and is expected to produce a typical signal for an O-H stretch –a broad signal between 3200 - 3600 cm^{-1}. In contrast, the product is a carboxylic acid and is expected to produce an even broader O-H signal (2200 - 3600 cm^{-1}) as a result of more extensive hydrogen bonding. Alternatively, the product can be differentiated from the starting material by looking for a signal at around 1720 cm^{-1}. The product has a C=O bond and should exhibit this signal. The starting material lacks a C=O bond and will not show a signal at 1720 cm^{-1}.

b) The starting material is secondary amine and is expected to produce a typical signal for an N-H stretch at around 3400 cm^{-1}. In contrast, the product is a tertiary amine and is not expected to produce a signal above 3000 cm^{-1}.

c) The starting material is an unsymmetrical alkyne and is expected to produce a signal at around 2200 cm^{-1}. In contrast, the product is an unsymmetrical alkene and is expected to produce a signal at around 1600 cm^{-1}. Also, the product has vinylic C-H bonds that are absent in the starting material. The product is expected to have a signal at around 3100 cm^{-1}, and the starting material will have no signal in that region.

d) The C≡C bond in the starting material and the C=C bond in the product are both symmetrical and will not produce signals. However the product has vinylic C-H bonds that are absent in the starting material. The product is expected to have a signal at around 3100 cm^{-1}, and the starting material will have no signal in that region.

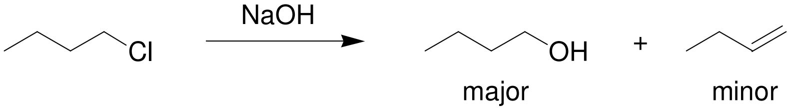
e) The starting material will have two signals in the double-bond region: one for the C=O bond and one for the C=C bond. The product only has one signal in the double-bond region. It only has the signal for the C=O bond, which is now at higher wavenumber because it is no longer in conjugation.

15.15. The starting material has a cyano group (C≡N) and is expected to produce a signal at around 2200 cm^{-1}. In contrast, the product is a carboxylic acid and is expected to produce a broad signal from 2200 – 3600 cm^{-1}, as well as a signal at 1720 cm^{-1} for the C=O bond.

15.16. The C≡C bond in the starting material (1-butyne) is unsymmetrical and produces a signal at 2200 cm^{-1}, corresponding with the C≡C stretch. In contrast, the C≡C bond in the product (3-hexyne) is symmetrical and does not produce a signal at 2200 cm^{-1}.

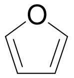
15.17. The starting material should have a C=O signal at 1720 cm^{-1}, while the product should have an O-H signal at 3200 – 3600 cm^{-1}.

15.18. 1-chlorobutane is primary substrate. When treated with sodium hydroxide, substitution is expected to dominate over elimination (see Chapter 8), but both products are expected to be obtained:

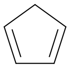


The substitution product is an alcohol and should have a broad signal from 3200 – 3600 cm^{-1}. The elimination product is an unsymmetrical alkene and is expected to give a C=C signal at approximately 1650 cm^{-1}, as well as a vinylic C-H signal at 3100 cm^{-1}.

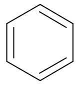
15.19.



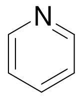
a) m/z = 68



m/z = 66



b) m/z = 78



m/z = 79

15.20.
a) This compound does not have any nitrogen atoms. According to the nitrogen rule, this compound should have an even molecular weight (*m/z* = 86).
b) This compound does not have any nitrogen atoms. According to the nitrogen rule, this compound should have an even molecular weight (*m/z* = 100).
c) This compound has one nitrogen atom. According to the nitrogen rule, this compound should have an odd molecular weight (*m/z* = 101).
d) This compound has two nitrogen atoms. According to the nitrogen rule, this compound should have an even molecular weight (*m/z* = 102).

15.21.
a) There must be four carbon atoms, and the molecular weight must be 72. The molecular formula could be C_4H_8O.

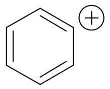
b) There must be four carbon atoms, and the molecular weight must be 68. The molecular formula could be C_4H_4O.

c) There must be four carbon atoms, and the molecular weight must be 54. The molecular formula could be C_4H_6.

d) There must be seven carbon atoms, and the molecular weight must be 96. The molecular formula could be C_7H_{12}.

15.22. Each nitrogen atom in the molecular formula of a compound should contribute 0.37% to the $(M+1)^{+\bullet}$ peak. Three nitrogen atoms therefore contribute the same amount (1.1%) as one carbon atom. A compound with molecular formula $C_8H_{11}N_3$ should have an $(M+1)^{+\bullet}$ peak that is 9.9% as tall as the molecular ion peak. If the molecular ion peak is 24% of the base peak, then the $(M+1)^{+\bullet}$ peak must be 2.4% of the base peak.

15.23.
a) This fragment is M – 79, which is formed by loss of a Br. So the fragment does not contain Br.

b) 

15.24.

a) There is not a significant (M+2)$^{+\bullet}$ peak, so neither bromine nor chlorine are present.

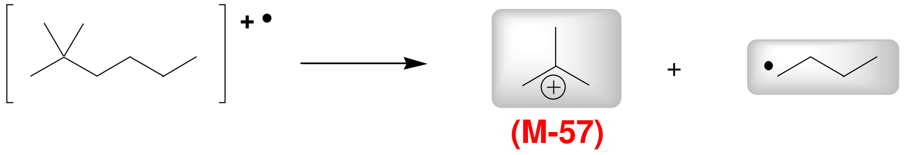
b) There is not a significant (M+2)$^{+\bullet}$ peak, so neither bromine nor chlorine are present.

c) The (M+2)$^{+\bullet}$ peak is approximately equivalent in height to the molecular ion peak, indicating the presence of a bromine atom.

d) The (M+2)$^{+\bullet}$ peak is approximately one-third as tall as the molecular ion peak, indicating the presence of a chlorine atom.

15.25.

a)

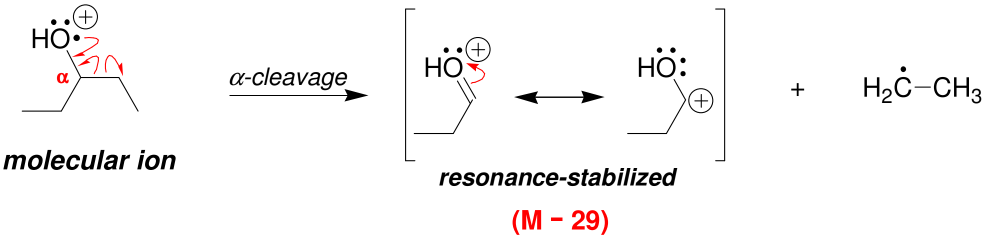


b) This carbocation is tertiary, and its formation is favored over the other possible secondary and primary carbocations.

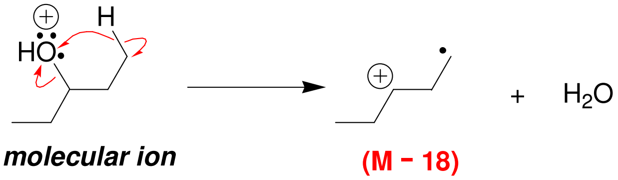
c) They readily fragment to produce tertiary carbocations.

d) M-15 corresponds with loss of a methyl group. Indeed, loss of methyl group would also produce a tertiary carbocation, but at the expense of forming a methyl radical. That pathway is less favorable.

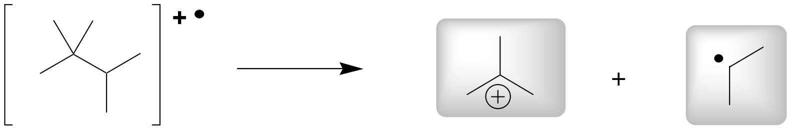
15.26. A fragment at M-29 should result from α cleavage:



and a fragment at M-18 should result from dehydration:



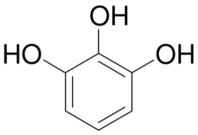
15.27. The fragment at M-43 is expected to be the base peak because it corresponds with formation of a tertiary carbocation:

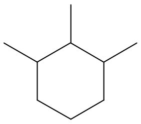


(M-43)

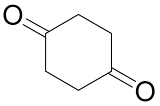
15.28. In the first spectrum, the base peak appears at M-29, signifying the loss of an ethyl group. This spectrum is likely the mass spectrum of ethylcyclohexane. The second spectrum has a base peak at M-15, signifying the loss of a methyl group. The second spectrum is likely the mass spectrum of 1,1-dimethylcyclohexane.

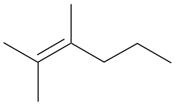
15.29.





a) *m/z* = 126.0315   *m/z* = 126.1404





b) *m/z* = 112.0522   *m/z* = 112.1248

15.30.

a) The first compound should have a very broad signal between 3200 and 3600 cm^{-1}, corresponding with O-H stretching. The second compound will not have such a signal.

b) The first compound should have a pair of strong signals around 1720 cm^{-1}, corresponding with symmetric and asymmetric stretching of the C=O bonds. In contrast, the second compound will have a weak signal at around 1650cm^{-1}, corresponding to the C=C bond.

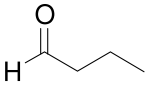
15.31.

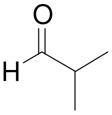
a) 2   b) 1   c) 2   d) 1   e) 1

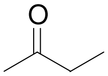
f) 1   g) 4   h) 0   i) 1   j) 0

15.32. Both $C_3H_5ClO_2$ and C_3H_6 have one degree of unsaturation.

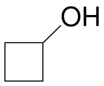
15.33. The compound has one degree and unsaturation, which is a C=O bond:. The following are all of the possible structures that have molecular formula C_4H_8O and contain a C=O bond:

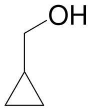


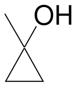


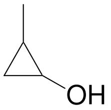


15.34. The compound must have one degree of unsaturation. The broad signal between 3200-3600 cm^{-1} indicates an OH group, and the absence of signals between 1600 and 1850 cm^{-1} indicates the absence of a double bond (either a C=O bond or an unsymmetrical C=C bond). This implies the presence of a ring (to achieve one degree of unsaturation). Below are possible structures:







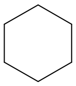
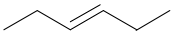


(Four possible stereoisomers)

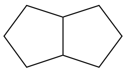
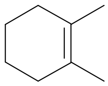
15.35. A signal at 2200cm^{-1} signifies the presence of a C≡C bond. There are only two possible constitutional isomers: 1-butyne or 2-butyne. The latter is symmetrical and would not produce a signal at 2200cm^{-1}. The compound must be 1-butyne.

15.36. The compound has exactly one degree of unsaturation, which means that it must contain either one ring or one double bond.

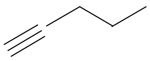
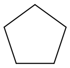
15.37.

a) HDI = 1 HDI = 1

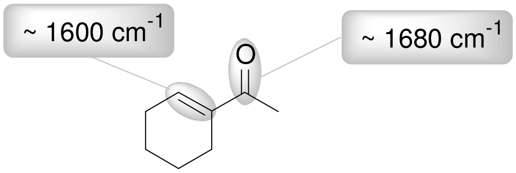
b) HDI = 2 HDI = 2

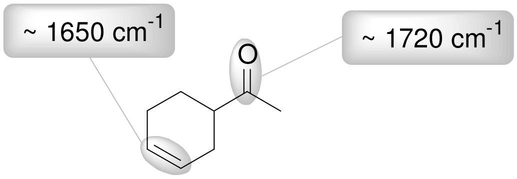
c) HDI = 2 HDI = 1

15.38.

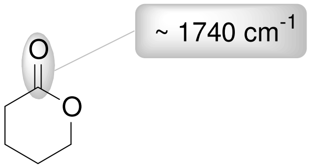
a)



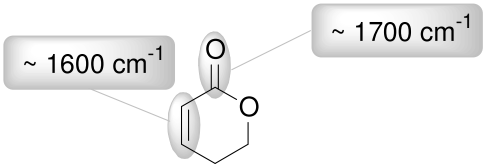
b)



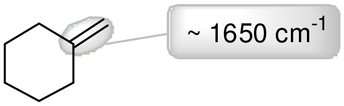
c)



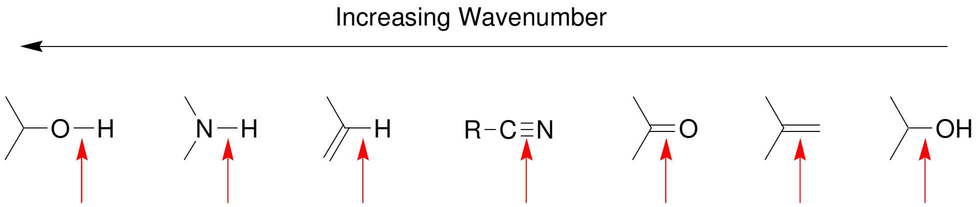
d)



e)



15.39.



15.40.

a) The C=N bond and the C=O bond should each produce a signal in the double bond region, 1600 - 1850 cm^{-1}

b) The C=C bond should produce a signal in the double bond region, 1600 - 1850 cm^{-1}

c) The C=C bond and the C=O bond should each produce a signal in the double bond region, 1600 - 1850 cm^{-1}, In addition, the two C≡C bonds should produce two signals around 2200 cm^{-1}, and the C*sp*-H bond should produce a signal around 3300 cm^{-1}.
d) The C=O bond should produce a signal in the double bond region, 1720 cm^{-1}, and the O-H of the carboxylic acid moiety should produce a very broad signal from 2200 – 3600 cm^{-1}.

15.41.
a) The reactant should have signals at 1650 cm^{-1} and 3100 cm^{-1}, while the product should not have either signals.

b) The reactant should have a broad signal from 3200 - 3600 cm^{-1}, while the product should lack this signal and instead should have a signal at ~ 1720 cm^{-1}.

c) The C=O bond of an ester should appear at higher wavenumber (~1740 cm^{-1}) than the C=O bond of a ketone (~1720 cm^{-1}).

d) The reactant should have signals at 1650 cm^{-1} and 3100 cm^{-1}, while the products should both have a signal at ~ 1720 cm^{-1}.

e) The reactant should not have signals at 1650 cm^{-1} or 3100 cm^{-1}, while the product should have such signals.

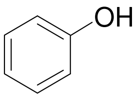
15.42.
a) a C=O signal at ~ 1720 cm^{-1}
b) a C=O signal at ~ 1680 cm^{-1} (conjugated) and a C=C signal at ~ 1600 cm^{-1} (conjugated) and a Csp^2-H signal at 3100 cm^{-1}.
c) a C=O signal at ~ 1720 cm^{-1} and a C=C signal at ~ 1650 cm^{-1} and a Csp^2-H signal at 3100 cm^{-1}.
d) a C=C signal at ~ 1650 cm^{-1} and an O-H signal at ~ 3200 – 3600 cm^{-1} and a Csp^2-H signal at 3100 cm^{-1}.
e) a C=O signal at ~ 1720 cm^{-1} and an O-H signal at ~ 2200 – 3600 cm^{-1}
f) a C=O signal at ~ 1720 cm^{-1} and an O-H signal at ~ 3200 – 3600 cm^{-1}

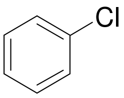
15.43.
a) C_7H_8 (*m/z* = 92) b) C_6H_6O (*m/z* = 94) c) $C_6H_{10}O$ (*m/z* = 98)
d) C_6H_8O (*m/z* = 96) e) $C_6H_{15}N$ (*m/z* = 101)

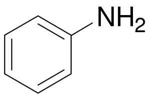
15.44. $C_5H_{10}O$

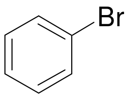
15.45. There are nine carbon atoms in the compound (10 / 1.1).

15.46.

a) 

b) 

c) 

d) 

15.47.

a) an OH group and double bonds.

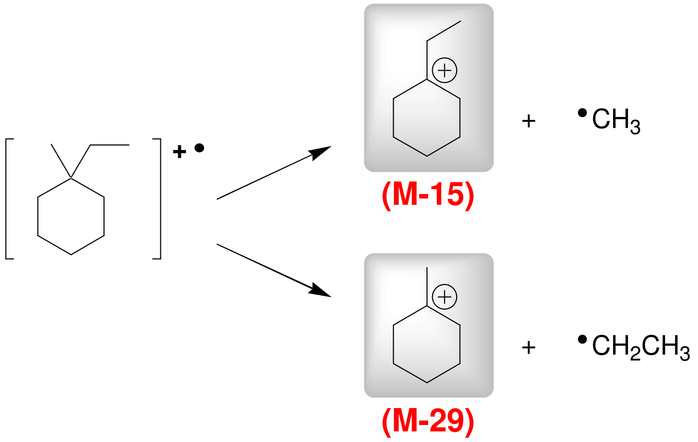
b) $\dfrac{3.9\ \%}{27.2\ \%} \times 100\% = 14.3\%$

$$\# \text{ of C} = \frac{14.3\ \%}{1.1\ \%} = 13$$

c) $C_{13}H_{24}O$ has thirteen carbon atoms and two degrees of unsaturation, consistent with the information that there are two double bonds.

15.48.
a) Both compounds are C_6H_{12}
b) Both compounds have an HDI of 1.
c) No, both compounds have exactly six carbon atoms and twelve hydrogen atoms, so they should have the same *m/z* even with high resolution mass spectrometry.
d) The IR spectrum of the alkene would have a signal at ~ 1650 cm^{-1} for the C=C bond and another signal at ~ 3100 cm^{-1} for the vinylic C-H bond. The IR spectrum of cyclohexane lacks both of these signals.

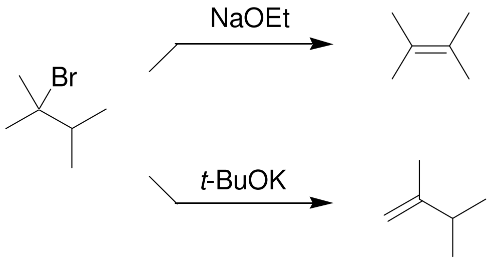
15.49. The signal at *m/z* = 111 is (M-15) which corresponds with loss of a methyl group. The signal at *m/z* = 97 is (M-29) which corresponds with loss of an ethyl group. Both fragmentations lead to a tertiary carbocation:



15.50.

a) No, because this fragment does not contain the bromine atom.
b) Yes, because this fragment still contains the bromine atom.
c) Yes, because this fragment still contains the bromine atom.

15.51. The more substituted alkene will not produce a signal at 1650 cm^{-1} nor will it produce a signal at 3100 cm^{-1}. The less substituted alkene will display both signals in its IR spectrum:

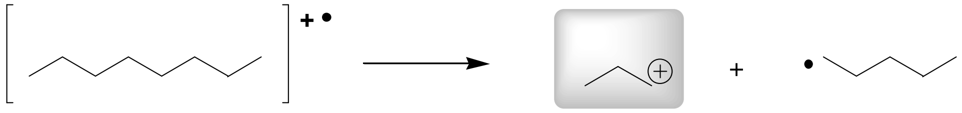


15.52.

a) C_5H_6
b) C_4H_6O

15.53.

a) the molecular ion peak appears at *m/z*= 114
b) the base peak appears at *m/z*= 43
c)

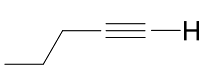


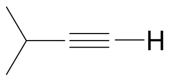
(M-71)
m/z = 43

15.54.

a) 2 b) 2 c) 2 d) 36 e) 4
f) 4 g) 5 h) 1 i) 4 j) 1

15.55



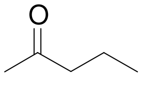


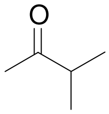
15.56. Limonene has three degrees of unsaturation and is comprised of only carbon and hydrogen atoms. The molecular weight is 136, so the molecular formula of limonene must be $C_{10}H_{16}$.

15.57. The IR spectrum of *trans*-3-hexene is expected to have a signal at 3100 cm^{-1} as a result of the vinylic C-H stretch. In contrast, 2,3-dimethyl-2-butene lacks a vinylic C-H group and does not exhibit that signal.

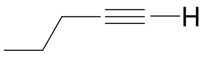
15.58. The compound exhibits intramolecular hydrogen bonding even in dilute solutions.

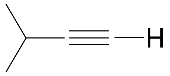
15.59. The IR spetrum indicates that the compound is a ketone. The mass spectrum indicates a molecular weight of 86. The base peak is at M-43, indicating the loss of a propyl group. The compound likely has a three carbon chain (either a propyl group or isopropyl group) on one side of the ketone:



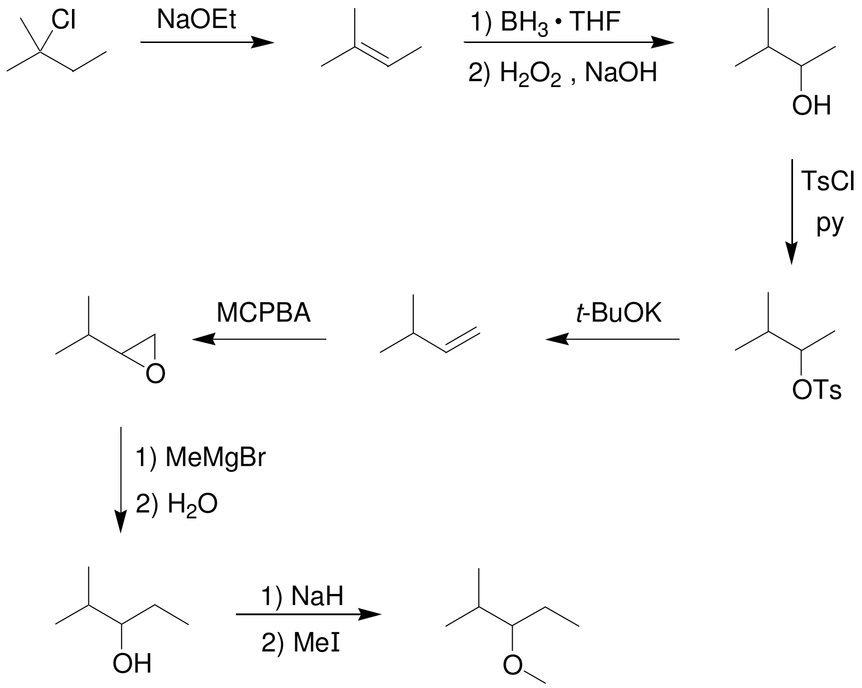


15.60. The IR spectrum indicates the presence of a triple bond as well as a C-H bond indicating that the triple bond is terminal. The mass spectrum indicates a molecular weight of 68. The following two structures are consistent with these data:



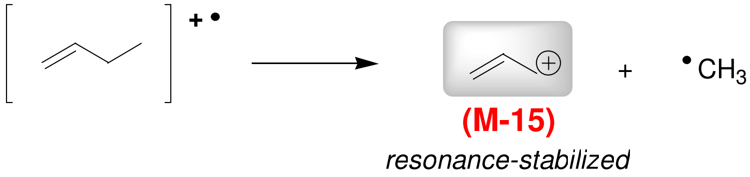


15.61.

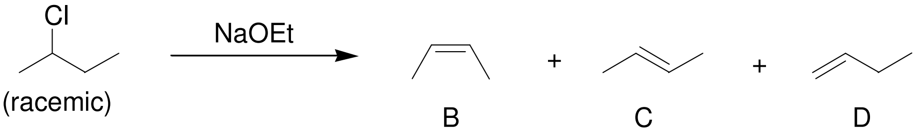


a) Compound F is an alcohol and its IR spectrum will exhibit a broad signal between 3200 and 3600 cm^{-1}. Compound G is an ether and its IR spectrum will not exhibit the same signal.
b) Compound D is an alkene and its IR spectrum will exhibit a signal at approximately 1650 cm^{-1} (for the C=C bond), as well as a signal at 3100 cm^{-1} (for vinylic C-H stretching). Compound E is an epoxide and its IR spectrum will not have these two signals.
c) IR spectroscopy would not be helpful to distinguish these two compounds because they are both alcohols. Mass spectrometry could be used to differentiate these two compounds because they have different molecular weights.
d) No, they both have the same molecular formula, although a trained expert might be able to distinguish these compounds based on their fragmentation patterns.

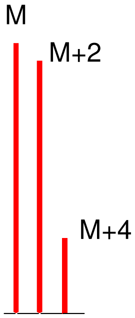
15.62. 1-butene can lose a methyl group to form a resonance stabilized carbocation



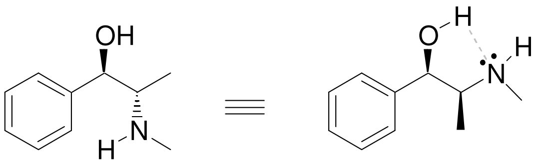
15.63. Yes, compound D is an unsymmetrical alkene:



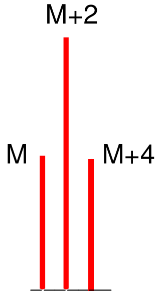
15.64.



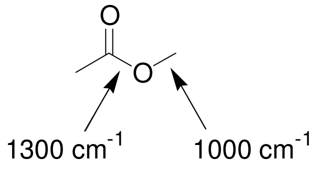
15.65. The OH group in ephedrine can engage in intramolecular hydrogen bonding, even in dilute solutions.



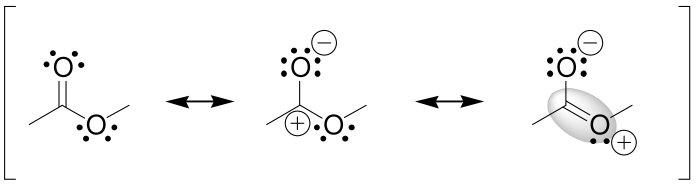
15.66.



15.67.



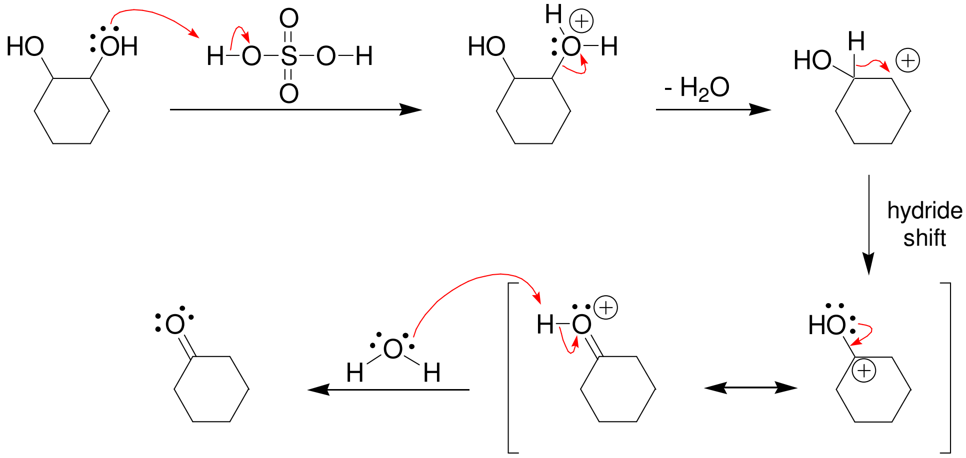
Explanation #1) One of the C-O bonds of the ester has some double bond character, as can be seen in the third resonance structure below:



This C-O bond is a stronger bond than the other C-O single bond, which does not have any double bond character. As a result, the stronger C-O bond (highlighted above) appears at higher wavenumber.

Explanation #2) The C-O bond at 1300 cm^{-1} involves an sp^2 hybridized carbon atom, rather than an sp^3 hybridized carbon atom. The former has more *s*-character and holds its electrons closer to the positively charged nucleus. A C_{sp2}—O bond is therefore stronger than a C_{sp3}—O bond.

15.68.



15.69.