

Problem Set Chapter 10 Solutions

January 30, 2013

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

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

You know the molecular formula contains only carbons and hydrogens, so has the general formula: C_xH_y
 $(x * 12.01) + (y * 1.008) = 132$, but there are still a number of different formulas that could add up to a mass of 132. Some of those are listed below:

C_{11}

$C_{10}H_{12}$

C_9H_{24}

C_8H_{36}

Now we can see which of these formulas can translate into feasible chemical structures:

C_{11} isn't going to be good b/c it needs at least some hydrogens

$C_{10}H_{12}$:



Chemical Formula: $C_{10}H_{12}$

C_9H_{24} is an impossible formula. Even with a fully saturated carbon chain, you are still not going to have enough hydrogens in the formula to reach 24:



Chemical Formula: C_9H_{20}

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

Same logic here – First list some formulas:

$C_{13}H_{10}$

$C_{12}H_{22}$

$C_{11}H_{34}$

And try to draw structures that correspond to those formulas:



Chemical Formula: $C_{13}H_{10}$



Chemical Formula: $C_{12}H_{22}$

But $C_{11}H_{34}$ has too many hydrogens to be a feasible molecular formula

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

C_7

C_6H_{12}

C_5H_{24}

The only one of these formulas that will lead to a feasible structure is C_6H_{12} :



Chemical Formula: C_6H_{12}

10.21 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 each molecular ion?

(a) Bromomethane, CH_3Br

Let's figure out the molecular weight for each isotope of bromine:

For ^{79}Br : $(1 \times 12.01) + (3 \times 1.008) + 79 = 94.03$ (at 50.7%)

For ^{81}Br : $(1 \times 12.01) + (3 \times 1.008) + 81 = 96.03$ (at 49.3%)

(b) 1-chlorohexane, $\text{C}_6\text{H}_{13}\text{Cl}$

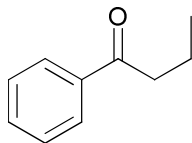
Same strategy here:

For ^{35}Cl : $(6 \times 12.01) + (13 \times 1.008) + 35 = 60.16$ (at 75.8%)

For ^{37}Cl : $(6 \times 12.01) + (13 \times 1.008) + 37 = 62.16$ (at 24.2%)

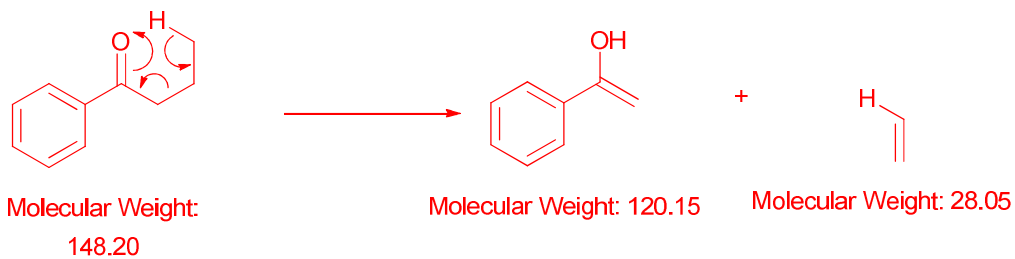
10.25 What fragments might you expect in the mass spectra of the following compounds:

(a)

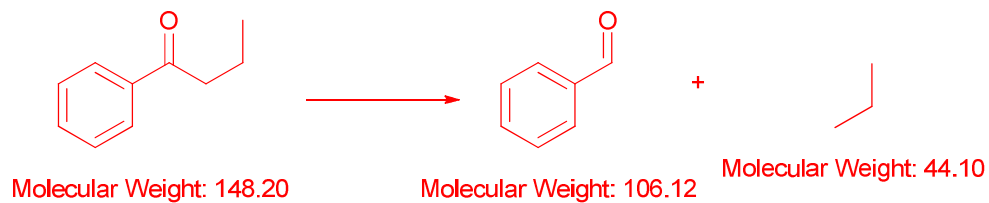


Ketones can either undergo McLafferty rearrangements or alpha cleavage.

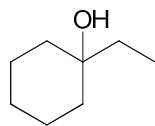
McLafferty rearrangement:



Alpha-cleavage:

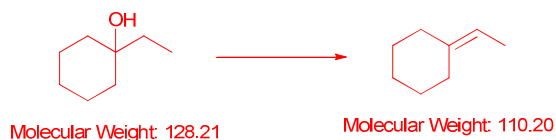


(b)

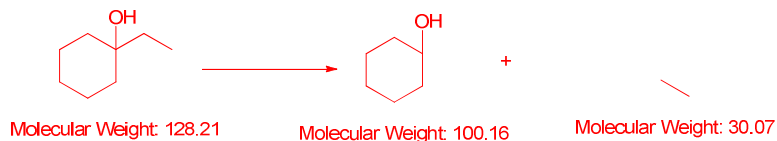


Alcohols can undergo dehydration or alpha-cleavage.

Dehydration:

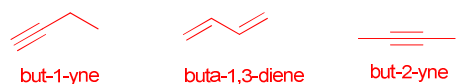


Alpha-cleavage:



10.26 How might you use IR spectroscopy to distinguish among the three isomers but-1-yne, buta-1,3-diene, and but-2-yne?

The structures of each of these isomers are shown below:



To distinguish these by IR spectroscopy, it is helpful to list which bonds are unique to the isomers

But-1-yne: Has an alkyne carbon bound to a hydrogen atom

buta-1,3-diene: Alkene C=C bond, also bond between hydrogen and alkene carbon

but-2-yne: Internal alkyne bond

Finally, I can go to my trusty table on page 381 and find some of these key peaks in the table

but-1-yne: 3300 cm^{-1} (strong); 2100-2260 cm^{-1} (medium)

buta-1,3-diene: 1640-1680 cm^{-1} (medium); 3020-3100 cm^{-1} (medium)

but-2-yne: 2100-2260 cm^{-1} (medium) from the internal alkyne bond, but is likely not to be distinguishable from the terminal alkyne bond. Your best way to distinguish this structure is to look for the absence of an alkyne C-H stretching frequency

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

Identical! Enantiomers have the same properties with the exception of their ability to rotate plane polarized light.

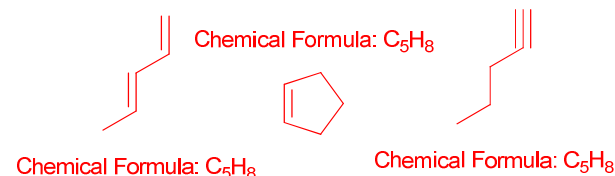
10.28 Would you expect two diastereomers such as meso-2,3-dibromobutane and (2R,3R)-dibromobutane to have identical or different IR spectra? Explain.

Different! The energies of the bonds are slightly different because of the three-dimensional arrangement of the atoms, which translates into different IR spectra.

10.29 Propose structures for compounds that meet the following descriptions:

(a) C_5H_8 , with IR absorptions at 3300 and 2150 cm^{-1}

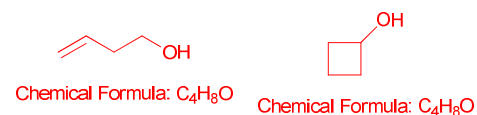
the compound has two degrees of unsaturation (double bonds, rings, etc all count as one degree of unsaturation). I can draw a few structures with this molecular formula:



But the IR absorptions indicate that there is likely an alkyne in the molecule, with absorptions for the C-C triple bond and the bond between the hydrogen and the carbon of the alkyne, which leaves me with structure 3.

(b) $\text{C}_4\text{H}_8\text{O}$, with a strong IR absorption at 3400 cm^{-1}

An oxygen in the compound means that it contains an alcohol, ether, or carbonyl group, but the strong IR absorption at 3400 cm^{-1} means likely an alcohol. I can draw a few structures with this formula that are alcohols:



But the lack of IR absorptions for the alkene makes me think it is most likely the second structure, cyclobutanol.

(c) $\text{C}_4\text{H}_8\text{O}$, with a strong IR absorption at 1715 cm^{-1}

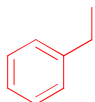
This compound has a carbonyl group, and no other key identifying features. One structure that matches the spectrum is shown below:



Chemical Formula: C₄H₈O

(d) C₈H₁₀, with IR absorptions at 1600 and 1500 cm⁻¹

IR peaks imply an aromatic ring, i.e. the structure shown below:



Chemical Formula: C₈H₁₀

10.31 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.

Spectrum b has a peak around 1600 cm⁻¹ of medium intensity that corresponds to an alkene. Spectrum a has no peaks in that region at all, therefore spectrum b is cyclohexene.

10.42 The following ultraviolet absorption maxima have been measured:

Buta-1,3-diene 217 nm

2-Methylbuta-1,3-diene 220 nm

penta-1,3-diene 223 nm

2,3-dimethylbuta-1,3-diene 226 nm

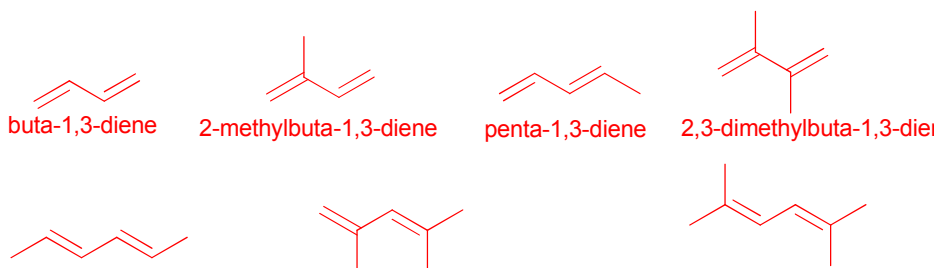
hexa-2,4-diene 227 nm

2,4-dimethylpenta-1,3-diene 232 nm

2,5-dimethylhexa-2,4-diene 240 nm

What conclusion can you draw about the effect of alkyl substitution on UV absorption maxima? Approximately what effect does each added alkyl group have?

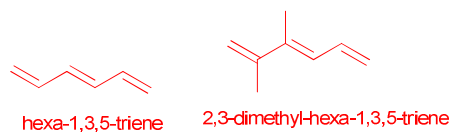
I am going to first draw the structures of each of these compounds



Each alkyl group causes the maximum UV absorption to increase approximately 3 nm.

10.43 Hexa-1,3,5-triene has $\lambda_{\text{max}} = 258$ nm. In light of your answer to Problem 10.42, approximately where would you expect 2,3-dimethylhexa-1,3,5-triene to absorb? Explain.

First I drew the structures of each of these compounds.



Two extra methyl groups means that the maximum wavelength absorption will be at approximately $258 + 6 \text{ nm} = 264 \text{ nm}$

10.50 Benzene has an ultraviolet absorption at $\lambda_{\text{max}} = 204 \text{ nm}$, and p-toluidine has $\lambda_{\text{max}} = 235 \text{ nm}$. How do you account for this difference?

p-toluidine has more conjugation because the nitrogen lone pairs can contribute to the delocalization, which causes the compound to absorb at a longer wavelength maximum.

10.51 Ketones undergo a reduction when treated with sodium borohydride, NaBH_4 . What is the structure of the compound produced by reaction of butan-2-one with NaBH_4 if it has an IR absorption at 3400 cm^{-1} and $M^+ = 74$ in the mass spectrum?

IR at 3400 cm^{-1} means that it is an alcohol, $M^+ = 74$ means a molecular weight of 74 g/mol , both of which are fulfilled in the product shown below:

