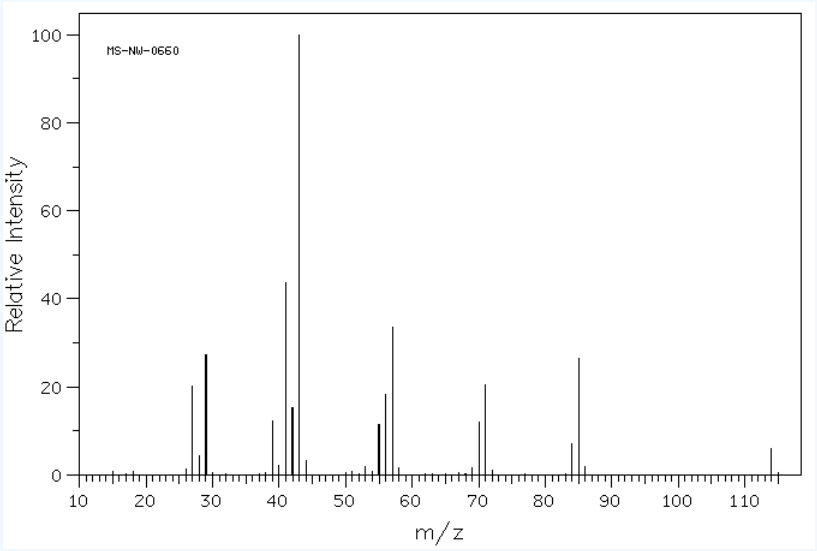
2.8: Mass Spectrometry Problems

Learning Objectives

- Interpret mass spectra

Exercise 2.8.1

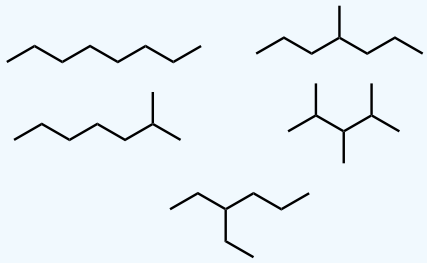
The following figure shows the mass spectrum of a saturated hydrocarbon (containing only carbon and hydrogen with only single bonds between carbons, not double bonds).

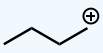


1. Draw five different structures that would have the molecular weight of this compound.
2. Choose three smaller m/z values from the spectrum and draw one structure for each of them. Note that these fragments will not have complete Lewis structures.

Answer

1. Molecular Weight = 114, which cooresponds to a C_8H_{18} hydrocarbon. There is the possibility of 18 isomers, but here are a few isomers:



2. m/z = 57; $[CH_3CH_2CH_2CH_2]^+$ 

m/z = 43; $[CH_3CH_2CH_2]^+$ 

m/z = 29; $[CH_3CH_2]^+$ 

Exercise 2.8.2

Caffeine has a mass of 194.19 amu, determined by mass spectrometry, and contains C, N, H, O. What is a molecular formula for this molecule?

Answer

$C_8H_{10}N_4O_2$

C = 12 × 8 = 96

N = 14 × 4 = 56

H = 1 × 10 = 10

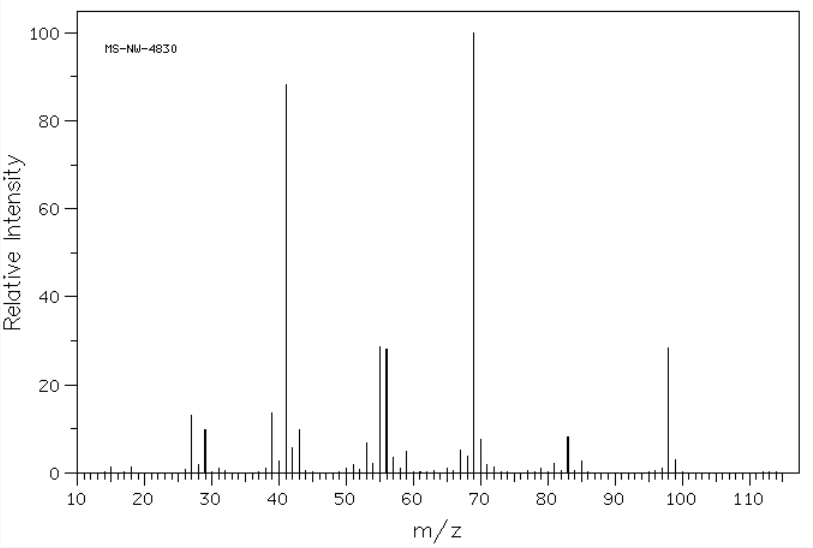
O = 2 × 16 = 32

96+56+10+32 = 194 g/mol

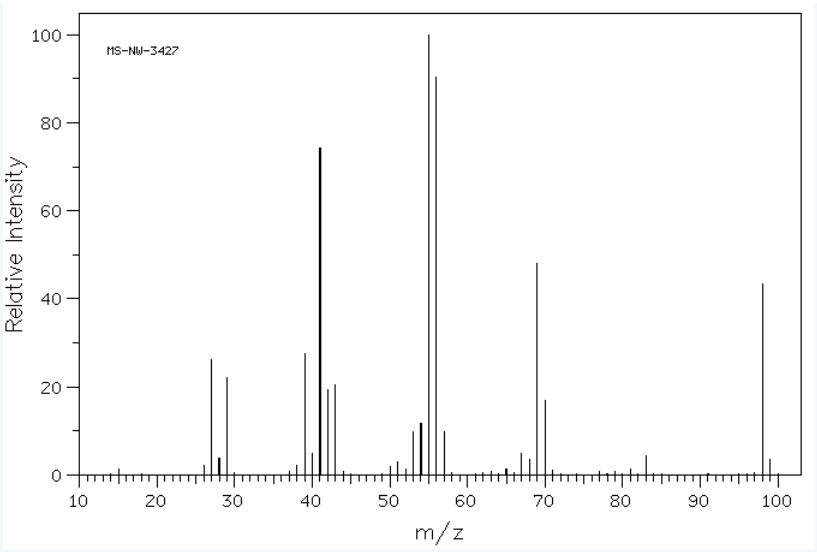
Exercise 2.8.3

The following are the spectra for 2-methyl-2-hexene and 2-heptene, which spectra belongs to the correct molecule. Explain.

A:



B:



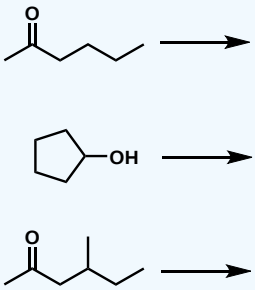
Source: SDBSWeb : http://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, 2 December 2016)

Answer

The (A) spectrum is 2-methyl-2-hexene and the (B) spectrum is 2-heptene. Looking at (A) the peak at 68 *m/z* is the fractioned molecule with just the tri-substituted alkene present. While (B) has a strong peak around the 56 *m/z*, which in this case is the di-substituted alkene left behind from the linear heptene.

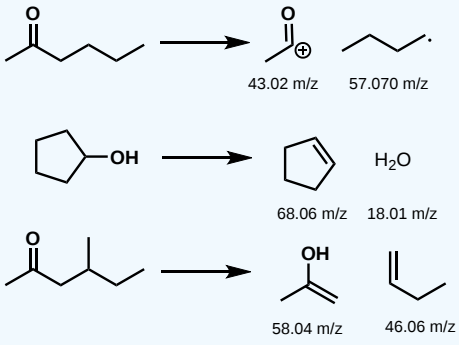
Exercise 2.8.4

What are the masses of all the components in the following fragmentations?



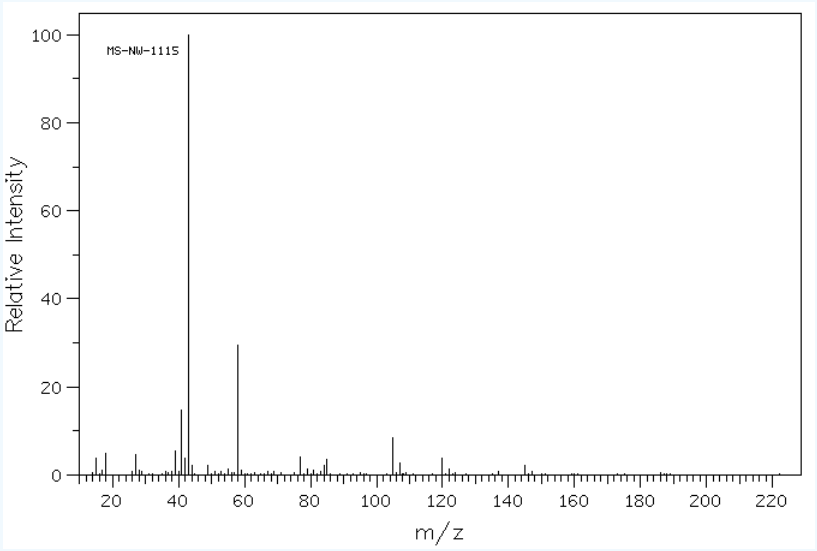
Answer

The first undergoes an alpha cleavage. The second undergoes a dehydration. The final one goes througha McLafferty rearrangement.



Exercise 2.8.5

5-Chloro-2-pentanone has the mass spectrum shown. Which peak represents the M^+? Which is the base peak? Why is there a peak at 122? Explain what the fragment for the base peak would be.



Source: SDBSWeb : https://sdbs.db.aist.go.jp/sdbs/cgi-bin/cre_frame_disp.cgi?sdbsno=10178 (National Institute of Advanced Industrial Science and Technology, 16 August 2022)

Answer

M+ = 120

base peak = 43

The m/z peak at 122 is the M + 2 peak. It occurs because chlorine has two isotopes ^{35}C and ^{37}C in a 3:1 ratio.

The m/z = 43 occurs due to the alpha cleavage. The acylium ion has an m/z of 43. This fragment is particularly stable due to resonance.