

Chem 220 -Organic Chemistry

Problem Set 6

Chapter 7, Structure and Synthesis of Alkenes

Due: Monday, October 18, 2010

Notice: For those of you who are using the 6th edition of the textbook, you can learn about olefin metathesis by [clicking here](#).

1. Read [Degree \(Elements\) of Unsaturation](#). How many degrees of unsaturation are present in $C_{16}H_{13}ClN_2O$? Draw two structures, one cyclic, the other acyclic, that have the number of degrees of unsaturation you determined and that is necessarily in agreement with the formula.

2. a) Determine the heat of formation of 3-methyl-1-pentene. Use the [heat of formation](#) tables to determine typical heats of hydrogenation for monosubstituted alkenes and to determine the heat of formation of the the reduction product of 3-methyl-1-pentene. Show work.

b) Calculate the heat of hydrogenation of (*E*)- and (*Z*)-3-methyl-2-pentene. Show work.

c) Use a diagram to illustrate that the difference in the heat of hydrogenation of the two geometrical isomers in 2b is equal to the difference in their heats of formation. Which isomer is more stable based upon the heats of formation? Why?

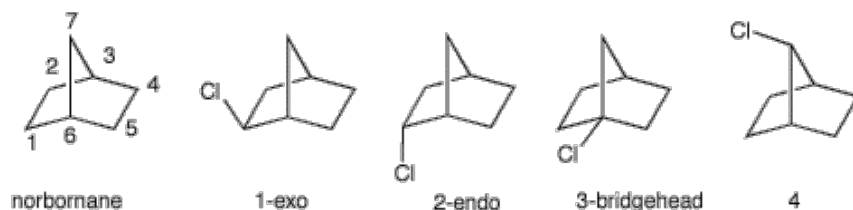
d) There is only one monosubstituted alkene having the carbon skeleton of the (*E*)- and (*Z*)- isomers in 2b. What is its structure? Assuming that $\Delta G^\circ = \Delta H^\circ$, which of the three isomeric alkenes would dominate in an equilibrium mixture? How much heat is liberated in the isomerization of the monosubstituted alkene to the (*E*)-isomer? Show work. Add the monosubstituted alkene to your diagram in 2c and illustrate the heat of isomerization.



[Paul Sabatier](#)

1912 Co-Nobel Prize
in Chemistry
Hydrogenation by
Metal Catalysis

3. a) Using the standard values for the relative reactivity of 1° , 2° and 3° C-H bonds toward free radical chlorination, determine the relative amount of the four possible monochlorides formed from the chlorination of [2.2.1]-bicycloheptane.



b) The experimental result is: **1**, 72%; **2**, 25%; **4**, 3%; **3**, 0%.

Why is no bridgehead isomer formed even though tertiary C-H bonds are highly reactive?

c) There are two types of secondary radicals formed. What is their relative reactivity? [Hints: Measure the $C_2-C_1-C_6$ and the $C_3-C_7-C_6$ bond angles in norbornane on the right in which the radical is formed on the central carbon. How do these values compare with [cyclopentane](#)? The chlorination of cyclobutane is slower than the chlorination of cyclopentane.]

[How to manipulate Jmol structures.](#)

[Larger Version](#)

d) At what point in the radical chain are the endo and exo isomers formed? Why does the exo isomer dominate? Explain and illustrate.

e) Are the four monochlorides optically active, racemic, or achiral?

4. The major product **B** from free radical monobromination of alkane **A** (C_6H_{14}) readily reacts with water to form **C**, $C_6H_{14}O$. Treatment of bromide **B** with KOH in ethanol produces two, and only two, compounds, **D** and **E**. Compound **D** liberates 1.6 kcal/mol more heat upon hydrogenation to **A** than does **E**. What are the structures **A-E**? What is the heat of isomerization of **D** to **E**? Illustrate and explain. [Hint: What are the structures possible for **A**?]

5. In 1968 [Wiberg](#) and Fenoglio determined the heat of combustion of cyclopropene: -485.0 kcal/mol. Determine the heat of hydrogenation of cyclopropene to cyclopropane. Explain and illustrate with a diagram.

6. Two stereoisomers, **A** and **B**, absorb one equivalent of hydrogen upon catalytic hydrogenation to form cyclooctane. Compound **A**, which is capable of resolution, liberates 34.5 kcal/mol of heat while **B** liberates 24.3 kcal/mol of heat.

a) What are the structures of **A** and **B**?

b) What are the heats of formation of **A** and **B**?

c) What is the difference in strain energy between **A** and **B**?

d) What is the difference in the heat of combustion between **A** and **B**?

e) Why is **A** capable of resolution?