,

Chem 220 -Organic Chemistry

Problem Set 6

Chapter 7, Structure and Synthesis of Alkenes

Due: Monday, October 19, 2009

1. Read Degree (Elements) of Unsaturation. How many degrees of unsaturation are present in $C_{10}H_{12}BrClN_2OS$? 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) **Estimate** the heat of hydrogenation of 3-ethyl-2-pentene using the heat of formation table. Show work.

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

Paul Sabatier
1912 Co-Nobel Prize in Chemistry
Hydrogenation by Metal Catalysis

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

3. a) [2.2.2]-Bicyclooctane forms how many monochloro constitutional isomers upon free radical chlorination? What are their structures?

b) In what ratio are they expected to be formed? Show work.

c) Are they optically active, racemic, or achiral?

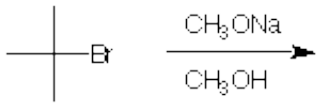
d) How many different alkenes are formed from the monochloro compounds upon treatment with a strong base? Explain and illustrate.

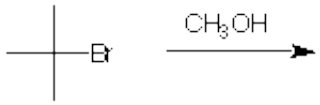
4. Compound **A** ($C_5H_{11}Br$) reacts readily with water to form **B**, $C_5H_{12}O$. Exposure of compound **A** to aq. NaOH gives only **C** (major) and **D** (minor). Hydrogenation of **C** liberates 26.8 ± 0.1 kcal/mol heat while **D** liberates 28.4 ± 0.1 kcal/mol of heat during hydrogenation. Both **C** and **D** form **E** upon hydrogenation. What are the structures **A-E**? Explain.

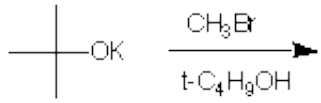
5. a) Determine the heat of hydrogenation of cyclohexene from the heat of formation tables. b) How does this value compare with the heat of hydrogenation of an unstrained cis-disubstituted double bond? c) Given the heat of hydrogenation of cyclopentene (chapter 7) determine the heat of formation of cyclopentene. d) BONUS: Why is the heat of hydrogenation less for cyclopentene than that for cyclohexene? Show all work.

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?

7. Comment critically on the following proposed synthesis of the now banned gasoline additive, methyl tertiary-butyl ether (MTBE). If you believe the reaction will be successful, provide the type of mechanism that is operable and illustrate it with the curved arrow formalism. If you feel that the reaction will not be successful, state the expected product of the reaction and the mechanism by which it is formed. Illustrate with curved arrows. If no reaction takes place, state so and explain why not.

a) 

b) 

c) 

d) $CH_3I + t\text{-}C_4H_9OH \longrightarrow$