

Chem 225b - Comprehensive Organic Chemistry

Problem Set 6

Chapter 7, Structure and Synthesis of Alkenes

Due: Monday, March 3, 2008

1. Read [Degree \(Elements\) of Unsaturation](#). How many degrees of unsaturation are present in $C_8H_3BrClN_3O_2$? Draw a structure that has the number of degrees of unsaturation you determined and that is necessarily in agreement with the formula.

2. a) Estimate the ΔH_f° of 2-methylpentane from the heat of formation of [2-methylheptane](#). Show work.

b) Estimate the heat of formation of 2-methyl-1-pentene from the heat of hydrogenation of 2-methyl-1-butene, using Table 7-1 (pg. 292, 6th ed.; pg.285, 5th ed.). Show work.

c) Again using Table 7-1, estimate the heat of isomerization of 2-methyl-1-pentene into 2-methyl-2-pentene. Show work.

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** ($C_5H_{11}Cl$) 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 27.0 ± 0.1 kcal/mol heat while **D** liberates 28.5 kcal/mol of heat during hydrogenation. What are the structures **A-D**? 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



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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.

- What are the structures of **A** and **B** ?
- What are the heats of formation of **A** and **B** ?
- What is the difference in strain energy between **A** and **B** ?
- What is the difference in the heat of combustion between **A** and **B** ?
- 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.

