

Chem 225b

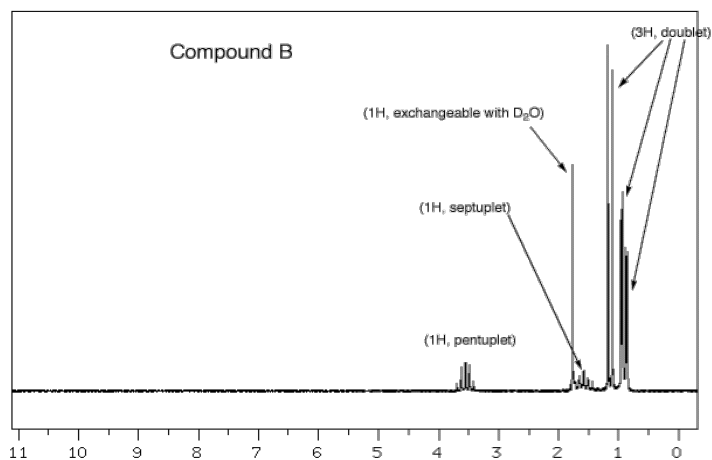
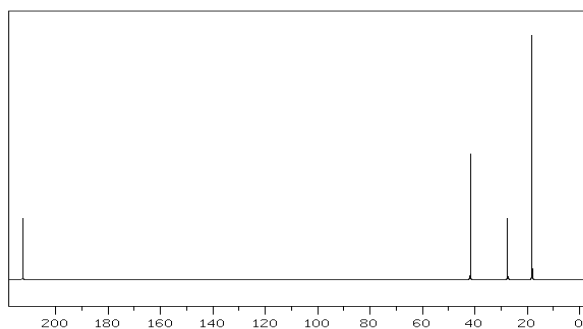
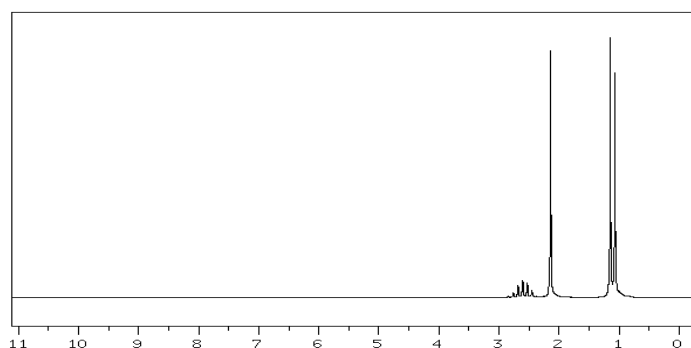
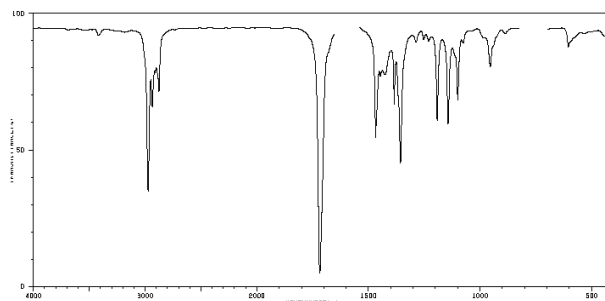
Comprehensive Organic Chemistry

Problem Set 10

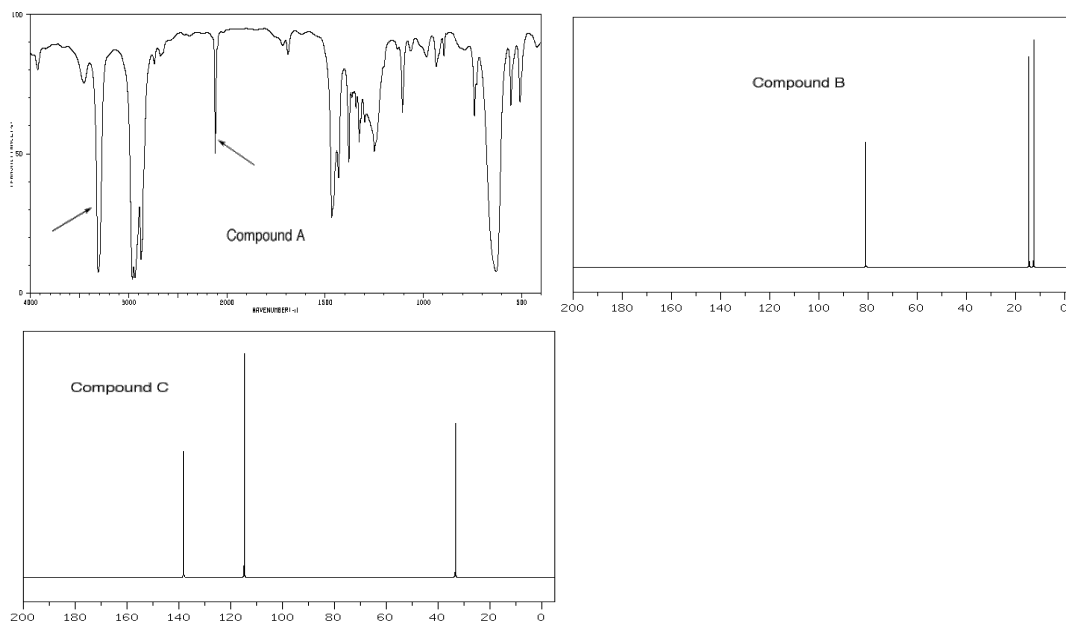
Chapter 11

Due: Monday, April 24, 2006

1. Compound **A**, three spectra of which are shown on the right, is converted to compound **B** with LiAlH_4 . Compound **B** reacts with tosyl chloride/pyridine to form **C**, which upon exposure to EtONa/EtOH , affords compound **D** (major) and compound **E** (minor). Hydrogenation of **D** and **E** both produce compound **F**. Compound **E** liberates 30.0 kcal/mol of heat while compound **D** is exothermic by 26.8 kcal/mol. What are the structures **A-F**? Explain how you interpreted the spectra and determined the structures. What is the difference in the heat of formation of **D** and **E**? [Click on spectra for larger versions.](#)



2. Three isomers **A**, **B** and **C** (C_6H_{10}) have IR and ^{13}C spectra displayed below. All three undergo hydrogenation to produce the same alkane **D** (C_6H_{14}). Heat liberated upon hydrogenation (kcal/mol): **A**: -69.1; **B**: -65.1; **C**: -60.3. What are the structures **A-D**? Explain your reasoning. Help is [here](#). [Click on spectra for larger versions.](#)



3. In the E_2 elimination of 2-bromo-2-methylbutane with NaOMe/HOMe, the ration of Zaitsev/Hofmann product is 70/30. when KO-t-Bu/HO-t-Bu is employed, the ratio is 27/73.

- Calculate the selectivity for each type of hydrogen in each experiment.
- Why is the the ratio different even though the energy of the two products does not change.
- How much heat is liberated in the hydrogenation of each isomer? Construct a standard state diagram to illustrate the thermochemistry.

4a) Using the [Heat of Formation](#) tables, determine the heat of hydrogenation of (Z)-2-butene.

b) Repeat part a) for (Z)-cyclohexene.

c) Knowing that cyclohexane is strain free (how do you know this from its ΔH_f° ?), what can be said about strain in (Z)-cyclohexene.

d) If cycloheptane and (Z)-cycloheptene were strain free, what would be there respective heats of formation? What would be the heat of hydrogenation?

e) The ΔH_f° for cycloheptane is -28.2 kcal/mol and the ΔH_f° for (Z)-cycloheptene is -1.8 kcal/mol. What is the heat of hydrogenation of (Z)-cycloheptene?

f) Draw a standard state diagram illustrating the three hydrogenations b), d) and e). Your diagram should confirm that the 7-membered ring compounds are less stable than the strain free 7-membered ring compounds. Which 7-membered ring, (Z)-cycloheptene or cycloheptane, is more responsible for the smaller heat of hydrogenation relative to the 6-membered compounds. Illustrate and explain.

g) (E)-Cycloheptene has never been isolated (put in a bottle) but it has been detected as an intermediate in reactions. Its ΔH_f° has been calculated as +18.7 kcal/mol. What is its heat of isomerization to (Z)-cycloheptene? Show work.

h) What is its calculated heat of hydrogenation?