Chem 220a

Problem Set 6

Chapter 7

Due: Monday, October 17, 2005

Do problems 2-4 in the Alkyl Halide module in ORGO. They need not appear on your homework.

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1. Read Degrees (Elements) of Unsaturation here and/or here. How many degrees of unsaturation are present in $C_6H_8Br_2ClN_3O_2S$?

a) Draw a structure that has the number of degrees of unsaturation you determined and that is necessarily in agreement with the formula.

b) Comment on the formula $C_9H_{20}BrCl_2NO_2$.

c) The compound $C_7H_xBrCl_2N_2O_2P$ satisfies all the valences of its atoms. Is "x" odd or even? Explain.

2a) 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^o?), what can be said about strain in (*Z*)-cyclohexene.

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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^o for cycloheptane is -28.2 kcal/mol and the ΔH_f^o 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^o 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?

3. Hydrocarbon **A** (ΔH_f^o = -45.3 kcal/mol) gives three compounds upon free radical chlorination: Compounds **B** and **C** are achiral and (±)-**D** is not. Exposure of **B** to aq. NaOH gives principally

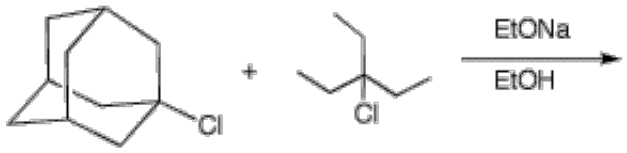
product **E** (C = 72.41%, H = 13.79%) and little **F**. Compound **C** reacts readily with excess water to form **G** and some **H**. On the other hand, treatment of **C** with aqueous NaOH affords only **H** and no **G**. Treatment of compound **D** with the hindered base t-C_4H_9OK gives both **H** and **F**. Catalytic hydrogenation of **F** gives **A** with the liberation of 30.0 kcal/mol of heat. The heat of hydrogenation of **H** is -25.5 kcal/mol.

a) What are the structures **A-H**? Explain.

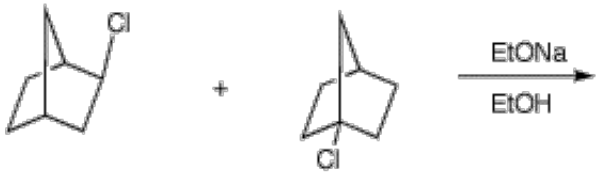
b) What is the ΔH_f^o of **H**? Show work.

4. In all of the following reactions, a limited amount of reagent is employed. In parts a) and b), which of the starting reactants disappears faster. Explain. In c) and d), what is the structure of the product and how and why is it formed. Use curved arrow mechanisms where applicable.

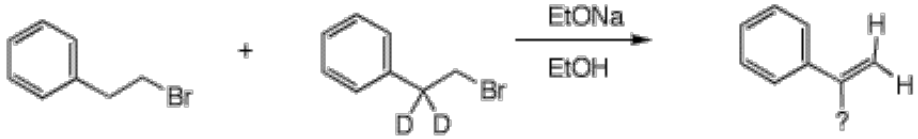
a)



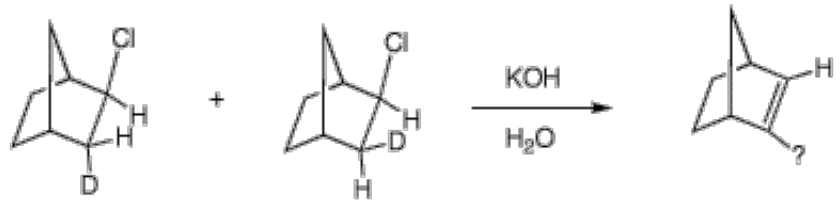
b)



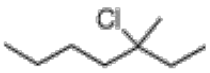
c)

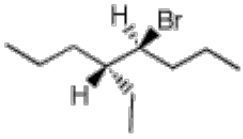


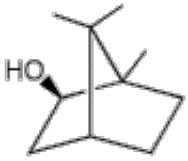
d)

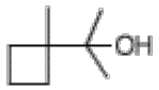


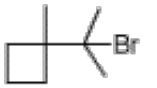
5. In each of the following questions, provide the missing structure with a mechanism for its formation. In cases where a product is provided, show a mechanism for its formation. Pay attention to optical activity and stereochemistry.

a) (R)-  CH_3OH → **A**

b)  CH_3ONa / CH_3OH → **A**

c)  opt. act. H_2SO_4 →  opt. act.

d)  H_2SO_4 → 

 hot water → **A**