Chem 220a

Problem Set 8

Chapter 9

Due: Monday, November 5, 2001

1. The alkyne module in ORGO will give you a good review of some of the fundamental reactions of alkynes.

2. Of the following bases, which ones will deprotonate 1-butyne greater than 90%: C_2H_5ONa, , C_6H_5Li (PhLi, phenyllithium), CH_3NHNa, $NaCH_2SO_2CH_3$, and CH_3Li. Explain the your reasoning. Consult the pKa table.

3. Compare the heats of formation of (Z)-2-butene and (Z)-2-pentene. Do the same for the (E)-isomers. From this information and given the heat of formation of 2-butyne, estimate the heat of formation of 2-pentyne. Compute the heat of hydrogenation of 2-pentyne ---> (Z)-2-pentene ---> n-pentane for each of the steps. Draw a diagram relating the standard states to each of the components. Which reduction is more exothermic, yne --> ene or ene --> ane?

3. When cyclododecyne ($C_{12}H_{20}$) is treated with $NaND_2$ in ND_3, cyclododecyne ($C_{12}D_{20}$) is isolated. Explain and illustrate. See pg. 395.

Sterling Chemistry Laboratory

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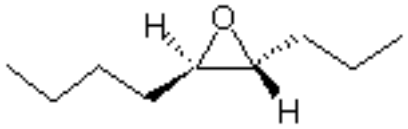
4. Alkyne **A** (C_8H_{14}) reacts with H_2 in the presence of catalyst **B** to give n-octane. [Although **B** may be several things, it is incapable of selective hydrogenation. Pick one.] Treatment of **A** in the presence of catalyst **C** produces **D** (C_8H_{16}). The reaction of compound **D** with reagent **E** produces meso compound **F** ($C_8H_{18}O_2$). What are the reagents and structures of **A**-**F**? Explain and illustrate. How are the stereoisomers of products **D** and **F**, namely, **D'** and **F'**, prepared from **A**? Explain and illustrate.

5. Devise a synthesis of (±)- epoxide **1**. Your source of carbon atoms are 2-butyne, 1-propene, and acetylene. You must use each one once, and only once. All reagents are available to you. [Hint: It is best to work the problem backwards by first thinking abourt how you make **1** from its immediate precursor, etc., etc., until you make the connection. Both 1-propene and 2-butyne cannot be used as is.] Why is your product **1** racemic as opposed to being the 4R, 5R enantiomer shown?



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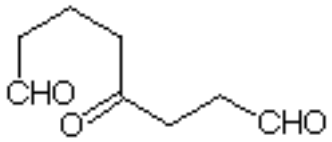
6. When 1,1-dichloropentane is successively heated at 200 ^{o}C with excess KOH, cooled, and poured into water, 2-pentyne is isolated. When the same experiment is conducted with $NaNH_2$ at 150 ^{o}C, 1-pentyne is the product. Illustrate and explain.

7. Two bottles, **A** and **B**, in a laboratory bear only the inscription "pure $C_{10}H_{16}$" on their labels. To determine the structure of the contents of each bottle, a chemist conducts the following experiments. She hydrogenates compound **A** over platinum and obtains **C**, which proves to be identical with an authentic sample of ethylcyclooctane. When **A** is subjected to ozonolysis followed by treatment with dimethyl sulfide, compound **D** is formed. Compound **B** does not react with $NaNH_2$ in NH_3 at the boiling point of ammonia (-33 ^{o}C) but it does undergo reduction with Na/NH_3 to give **E**, $C_{10}H_{18}$. In addition, hydrogenation of **B** over Pt forms n-decane. When she ozonizes **E**, she isolates a C_6 dialdehyde, **F**. From these experiments she is able to determine the structures of **A** and **B** although there is something about **A** that she cannot conclude from her research. Moreover, there was a compound **G** also formed along with **C-F** whose structure she inferred. What were her structures for **A-G**? Explain and illustrate.



Compound **D**

8. When 1-hexyne is heated with KOH at 200 ^{o}C, more 2-hexyne (ΔH_f^{o} = +25.7 kcal/mol) is expected than 3-hexyne (ΔH_f^{o} = +25.2 kcal/mol). Explain.