Chem 220a

Problem Set 5

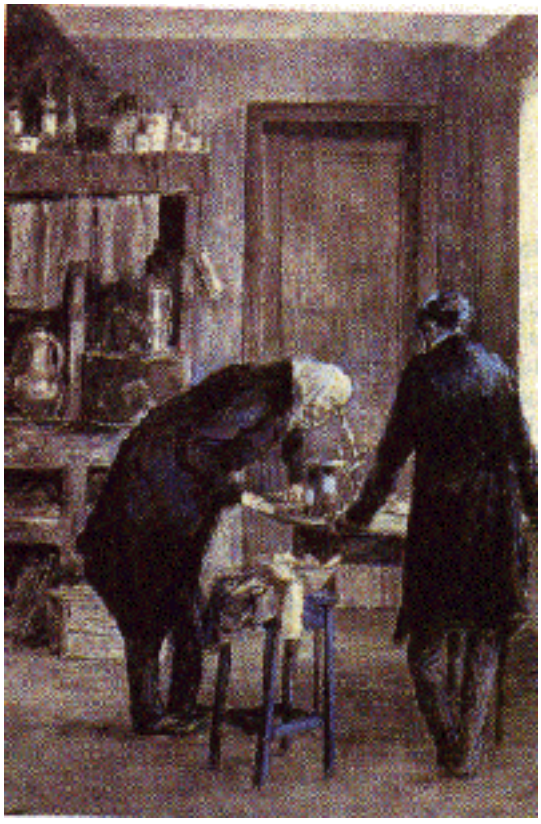
Chapter 6

Due: Monday, October14, 2002

1. Study #2 and #3 in the Alkyl Halide module and #1 in the Ether module in ORGO.

2. When 2-bromo-1,1,1-trideuteriopropane is heated with C_2H_5ONa in ethanol, the major olefin formed is CH_2=$CHCD_3$. Why? What is the structure of the minor olefin?

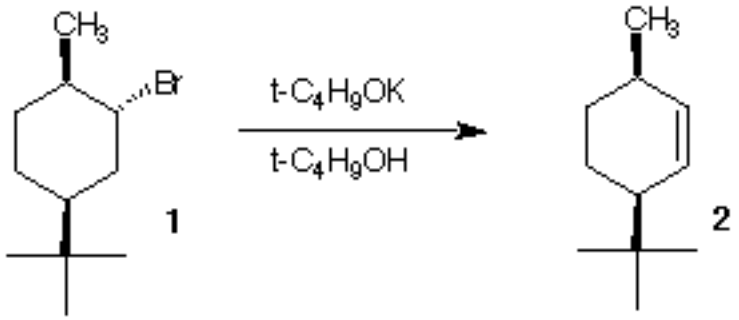
3. Compound **A**, C_7H_{16}, forms three monochloro constitutional isomers (**B**, **C**, and **D**) upon free radical chlorination. Compound **B** readily gives **E**, $C_7H_{16}O$, upon treatment with aqueous NaOH. Compound **C** forms two compounds **F** and **G** (both C_7H_{14}) under the same reaction conditions. Compound **D** reacts readily with water to give **H** ($C_7H_{16}O$) while its reaction with aqueous sodium hydroxide affords a single compound **G**. What are the structures **A**-**H**? Explain. [Hint: How many of the nine heptanes (can you draw them?) form 3 monochloro compounds? The rest of the information reduces the possibilities for **A** to a single compound.]

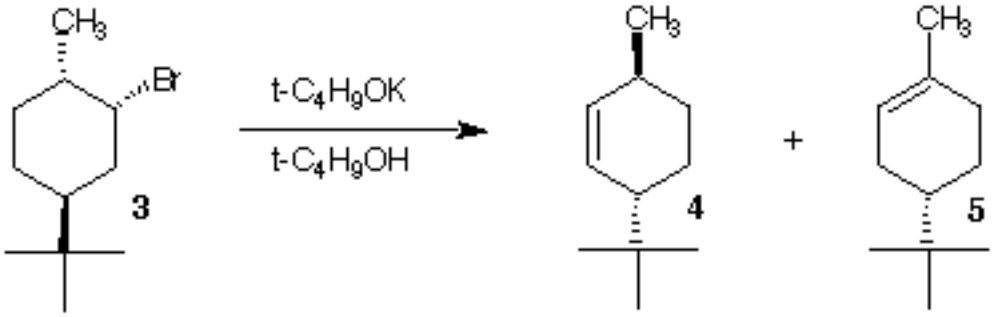


Biot examining Pasteur's tartrate crystals

4. (3R,4R)-4-Bromo-3-methylheptane (**A**) reacts with C_2H_5ONa/C_2H_5OH to form an optically inactive compound **B**. Either enantiomer (**C** and **D**) of the diastereomer of **A**, forms **E** under the same reaction conditions**.** Compound **E** is also optically inactive. Compound **C** reacts with C_2H_5SNa to form a sulfide **F** of the 3R, 4R configuration. Explain and illustrate.

5. A graduate student makes the predictions shown on the right about optically active alkyl bromides **1** and **3** with strong base. Use your knowledge of the conformation of cyclohexanes and E2 elimination reactions to answer the following questions.





a) Would the same prediction apply if **1** and **3** were racemates?

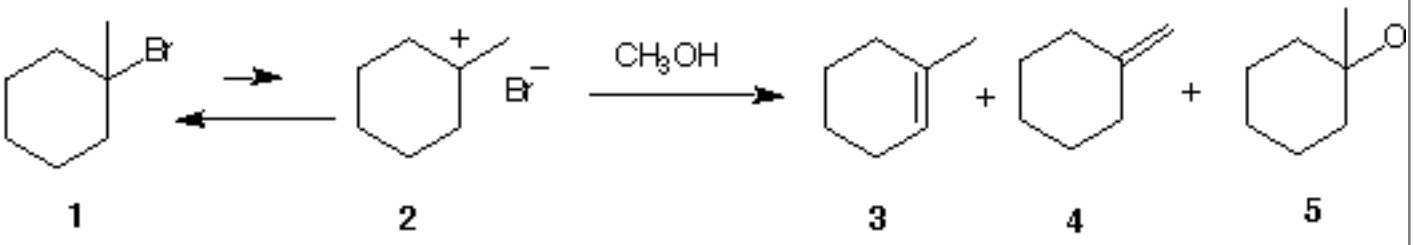
b) Are the alkenes optically active?

c) Why is only alkene **2** predicted in the reaction of bromide **1** while bromide **3** is predicted to afford alkenes **4** and **5**?

d) Is alkene **4** or **5** expected as the major product?

e) What is the relationship between bromides **1** and **3**? Alkenes **2** and **4**? Alkenes **4** and **5**?

6. The solved problem on pg. 279 is reproduced below. Ether 5 is the major prodct of the reaction while alkenes (olefins) 3 and 4 are the minor products of the reaction. Of these two olefins, compound 3 is the major one.



1 2 3 4 5

a) What is the other product of the reaction?

b) What are the mechanisms by which **3**, **4**, and **5** are formed?

c) What if you were told that the ratio **3/4** is not necessarily the same early in the reaction (say 10% of **1** consumed) as it is after the reaction is complete. Respond. [Hint: Look at the arrow under methanol and consider your answer to 5a.]

d) If stoichiometric sodium methoxide were used along with methanol in this experiment, the ratio **3/4** is predicted to be the same during the course of the reaction and ether **5** is not among the products of the reaction. comment.

e) In 5d, is **3** or **4** expected to be the major product? Explain.

f) What mechanism is operative in 5d?

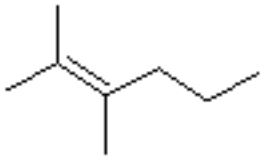
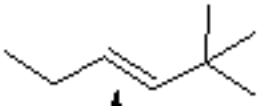
g) What would you expect to happen to the ratio of 5d if the basic conditions of problem 4 were employed instead of CH_3ONa/CH_3OH?

h) Show how ether **5** can be formed by an S_N2 mechanism.

7. Provide reactants or products for the following reactions. Comment and illustrate.

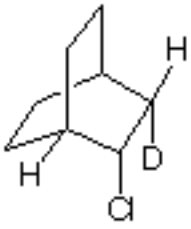
a) (S)-$CH_3CH_2CH_2CDHBr$ $\xrightarrow[C_2H_5SH]{\text{aq. NaOH}}$

b) (R)-3-chloro-3-methylhexane $\xrightarrow{CH_3OH}$

c) $C_8H_{17}Br$ $\xrightarrow{CH_3OH,\ heat}$ (S_N1 products not shown)  + 

CH_3ONa, CH_3OH, heat

d) Ph_3P + 1-bromopropane $\xrightarrow{CH_3OH}$

e) 

$\xrightarrow[C_2H_5OH]{C_2H_5ONa}$