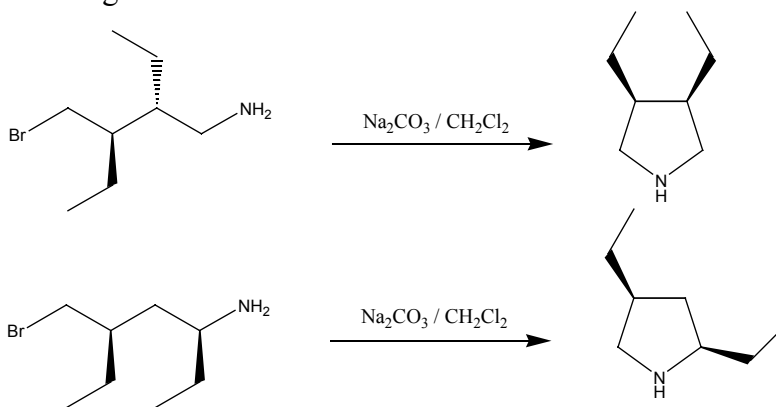


Organic Chemistry - CHEM 231A

Problem Set #2

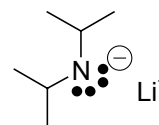
Due FRIDAY, October 11, 2002 @ 5:00 p.m. (delayed because of technical difficulties)

- 1a. Draw the pertinent conformers for the C3-C4 bond of 3,4-dimethylhexane. Label each conformer with an appropriate designation in order to differentiate the conformational interactions.
- 1b. Consider the following two reactions:

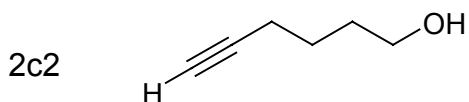
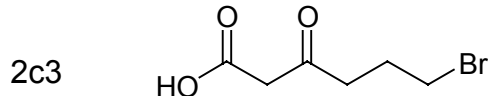
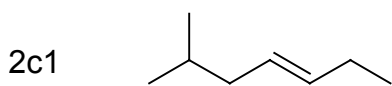


- 1b1. What kind of reaction is occurring? What is the mechanism for the reaction?
- 1b2. Why are Na_2CO_3 and CH_2Cl_2 in the reaction, since they apparently play no role in the reaction?
- 1b3. When observing the two reactions, it is noted that the first reaction is significantly slower than the second reaction. Explain.
- 1b4. Draw an energy diagram that represents your explanation for the difference between the two reactions.

2. Consider the following molecule, lithium diisopropyl amine (LDA):



- 2a. LDA has a pK_b of 35. What does this mean? Explain how we explain this number in terms of the reactivity of LDA.
- 2b. LDA is considered to be non-nucleophilic. Does this contradict the answer to 2a? Explain. Why might it not be nucleophilic (consider the relationship between structure and function of this molecule)?
- 2c. Consider the reaction of LDA with each of the following molecules. For each molecule:
- Predict the probable product
 - If the molecule acts as an acid, identify the pK_a of the acidic part.
 - If the reaction is an acid/base reaction, predict the direction the equilibrium will lie and provide an overall reaction equilibrium constant.

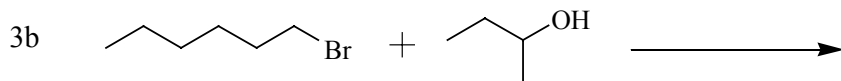


- 2d. Consider the molecule from question 2c3. If two mole equivalents of LDA are used, a second reaction results in the formation of a product with the formula $C_6H_7O_3Li$. What is the structure of this product? Write a mechanism that accounts for the formation of this product. Why would 2 equivalents be needed for this reaction to occur?

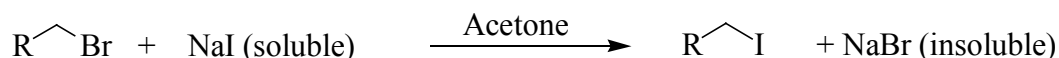
3. Consider the following reaction.

For each reaction:

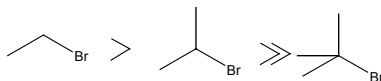
1. Identify the nucleophile, electrophile, acid and/or base (more than one may exist).
2. Predict the possible product(s) for the reaction.
3. Explain whether the reaction is likely to occur or not.
4. If the reaction is not likely, explain and suggest how one might change the reactants to facilitate a better reaction.



- 4a. Iodide ion is a good nucleophile and sodium iodide is quite soluble in acetone. On the other hand, sodium chloride and sodium bromide have low solubilities in acetone. As a result, the reaction of alkyl bromides and alkyl chlorides with NaI/acetone can serve as a *simple* test reaction as indicated below.



The reactivity order of the following alkyl bromides with NaI/acetone is:



Write a mechanism for this reaction. Explain how your mechanism accounts for the observed reactivity order. (It will help to build molecular models.)

- 4b. The optical rotation of a solution of (+)-2-bromobutane in diethyl ether does not change with time. However, when tetrabutylammonium bromide is dissolved in this solution, the rotation decreases slowly with time to zero. The NMR spectrum of the solution, however, does not change. Clearly explain what is happening. Why does the rotation decrease to zero? Why doesn't it become negative? (see chapter 5 for optical rotation information)
- 4c. Discuss how these two experiments are related to our general understanding of the mechanism of bimolecular nucleophilic substitution reactions.