

## WORKSHOP

### *Alkyl Halides and Tosylates: Mechanism I*

1. a. 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 here:



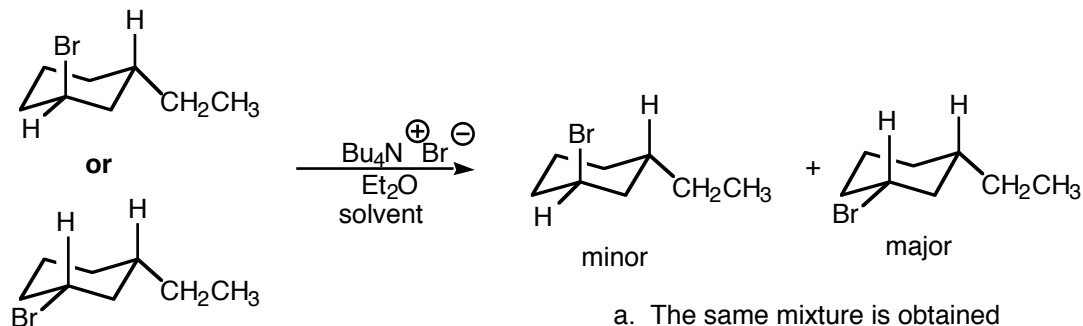
The reactivity order of the following alkyl bromides with NaI/acetone is



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

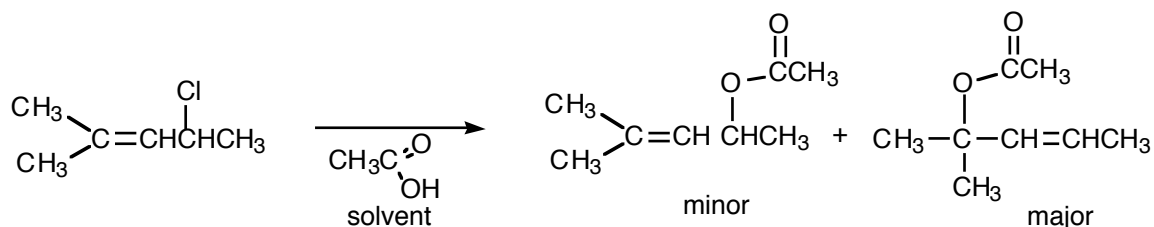
- b. The optical rotation of a solution of (+)-2-bromobutane in diethyl ether does not change with time. However, when tetrabutylammonium bromide is dissolved in this solution, the rotation decreases slowly with time to zero. The NMR spectrum of the solution, however, does not change. Clearly explain what is happening. Construct a graph of the mole fraction of (+)-2-bromobutane and (-)-2-bromobutane as a function of time. Why does the rotation decrease to zero? Why doesn't it become negative?

- c. Explain the following observation.



- a. The same mixture is obtained from either pure starting material.  
 b. The rate of isomerization depends on  $[\text{Bu}_4\text{N}^{\oplus} \text{Br}^{\ominus}]$ .

2. a. When 4-chloro-2-methyl-2-pentene reacts with acetic acid (solvent), two substitution products are formed with the rearranged product predominating as shown here. When small amounts of acetate ion are added to the reaction mixture, no increase in rate is observed. Give a mechanism that accounts for these results. Explain clearly why two products are formed.



- b. Low molecular weight alcohols dissolve in concentrated hydrochloric acid containing  $\text{ZnCl}_2$ . For some alcohols, a reaction takes place to form a new compound that is insoluble in concentrated  $\text{HCl}/\text{ZnCl}_2$ . Thus, a clear solution of the alcohol in the reagent turns cloudy. The rate of formation of this new product varies with structure.



What is the insoluble product? Give a balanced equation for the reaction that occurs. Write a mechanism for formation of the insoluble product. Explain how your mechanism accounts for the relative rates of reaction.

- c. Discuss how the three preceding experiments (above) are related to our general understanding of the mechanism of *unimolecular* nucleophilic substitution reactions.