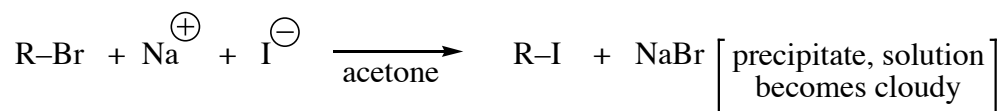
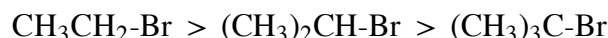


Workshop #7 Nucleophilic Substitution

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 below.

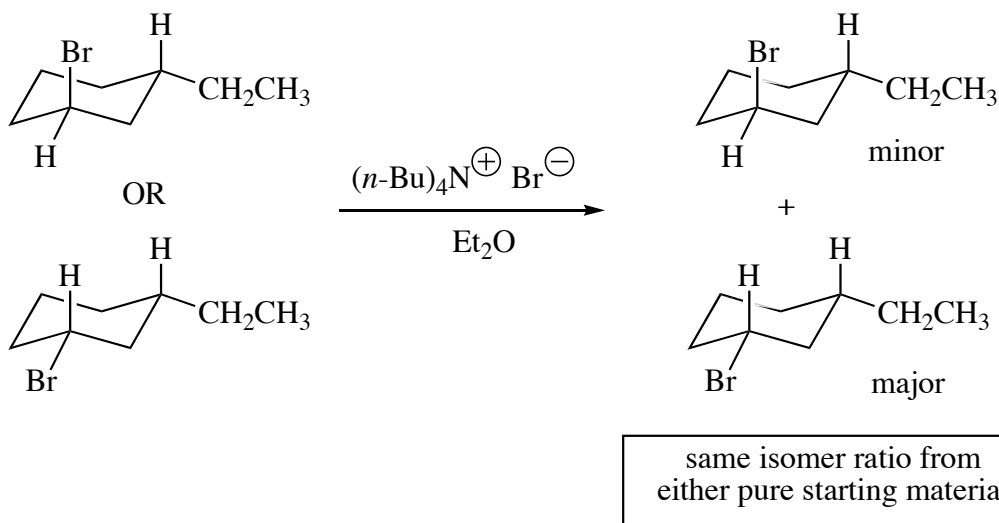


The reactivity order of the following alkyl bromides with NaI/acetone is:



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

- (b) Explain the following observations.

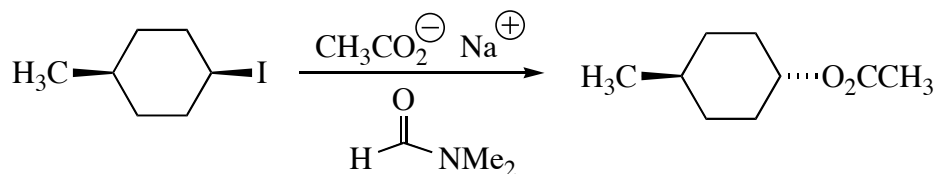
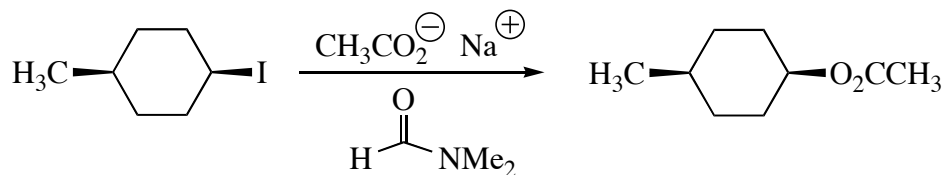


- (c) Discuss how these two experiments described above are related to our general understanding of the mechanism of bimolecular nucleophilic substitution reactions.
2. The optical rotation of a solution of (+)-2-iodooctane in acetone does not change with time. However, when a catalytic amount of sodium iodide is dissolved in this solution, the rotation decreases slowly with time to zero. The ^1H NMR spectrum of the solution, however, does not change.
- (a) Clearly explain what is happening.
- (b) Why does the rotation decrease to zero? Why doesn't it become negative?

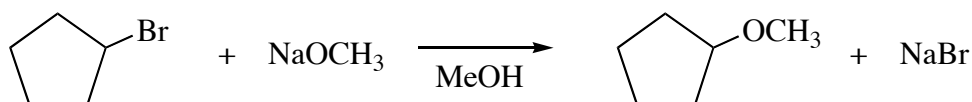
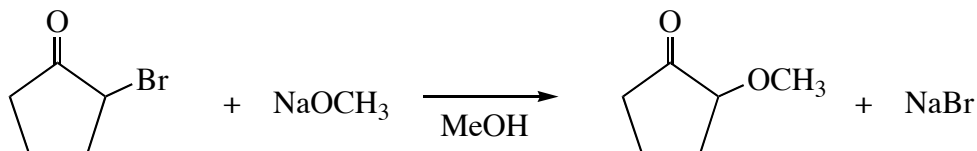
(c) If a *large excess* of radioactive iodide ($^{131}\text{I}^-$) is used and the rate constants for loss of optical activity and for the formation of radioactive 2-iodooctane are measured, one finds that the rate constant for loss of optical activity is *exactly* twice the rate constant for formation of radioactive 2-iodooctane. Clearly explain what this observation requires in terms of the reaction mechanism for the processes that lead to racemization and incorporation of labeled iodide.

3. For each pair of reactions shown below, decide which will occur more rapidly. Explain your answer.

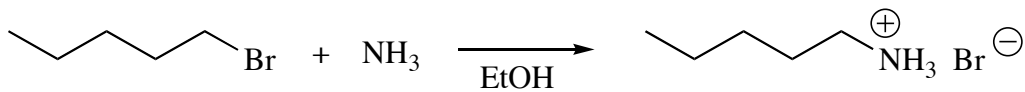
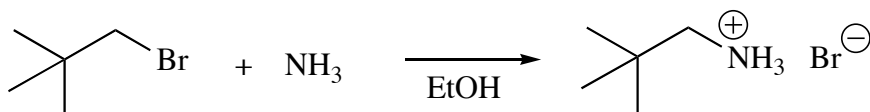
(a)



(b)



(c)



4. The reaction of 1-chlorobutane with NaOH in aqueous ethanol gives **A** ($C_4H_{10}O$) that shows a broad absorption in the IR at 3400 cm^{-1} which was not present in the starting material. When 4-chloro-1-butanol ($ClCH_2CH_2CH_2CH_2OH$) is treated with NaOH in aqueous ethanol, **B** (C_4H_8O) is produced, which does *not* show an IR absorption in the 3400 cm^{-1} region. Propose structures for **A** and **B** and write reaction mechanisms for their formation.