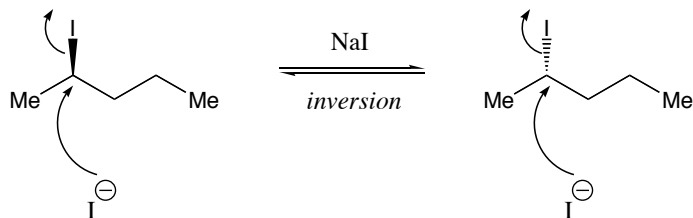


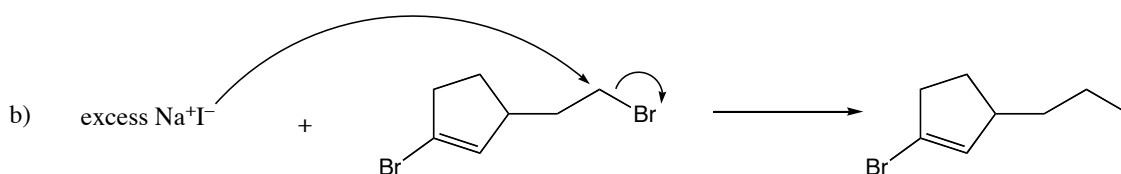
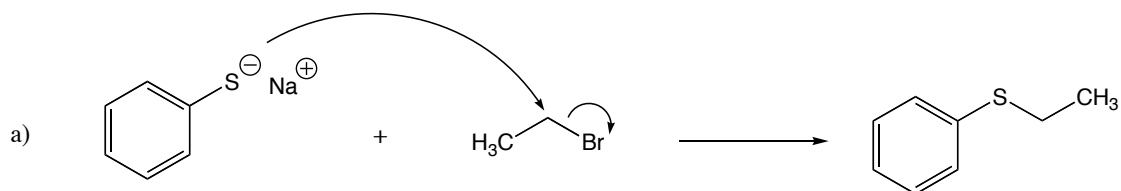
**Problem Set 7a**

Question 1. A student had carefully prepared pure (*R*)-2-iodopentane, but in his/her haste had left the compound in solution overnight. When that student came back in the morning and took an optical rotation, the compound was racemic. It was also discovered that a small amount of sodium iodide was present in the solution. What happened?

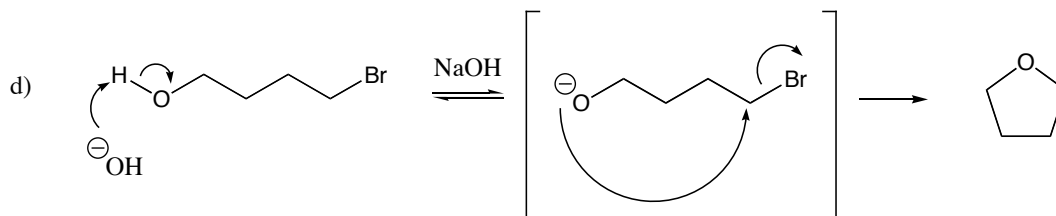
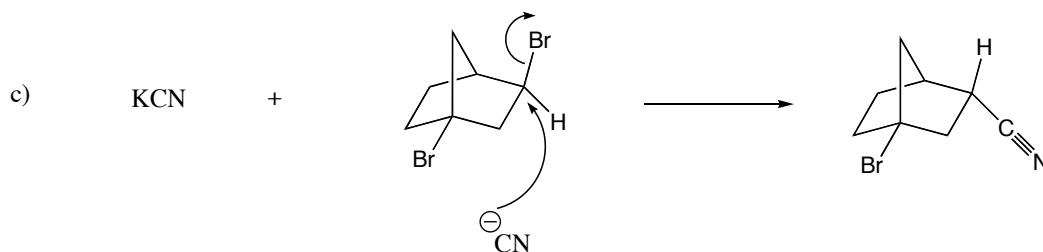
*Racemization was achieved through a reversible  $S_N2$  reaction:*

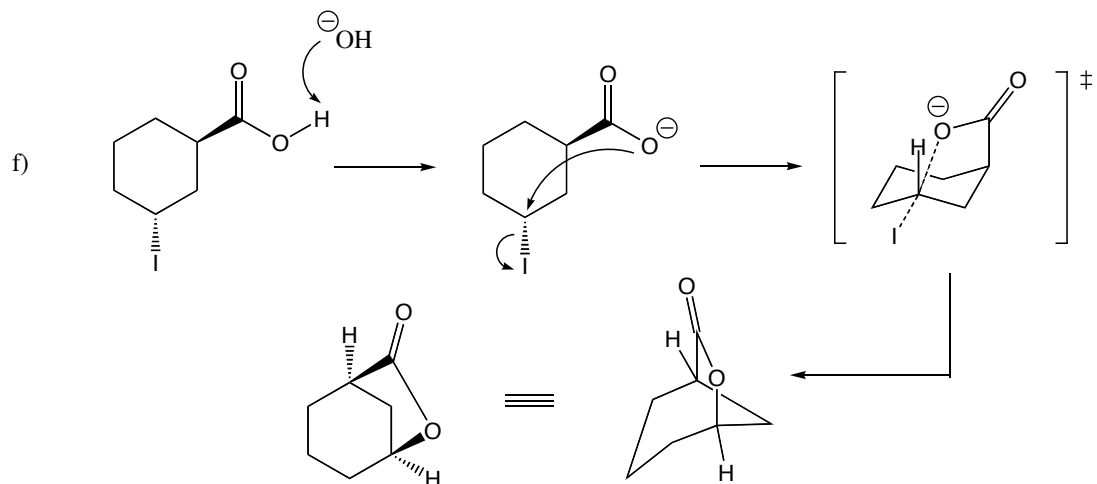
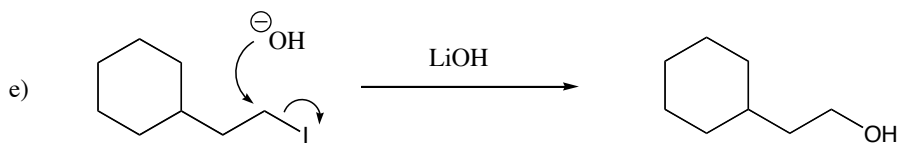


Question 2. For each  $S_N2$  reaction shown below, provide the mechanism (i.e. draw in the curved arrows showing the movement of electrons) and identify the expected major product.

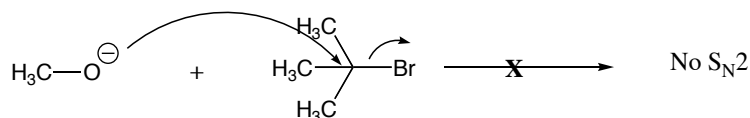
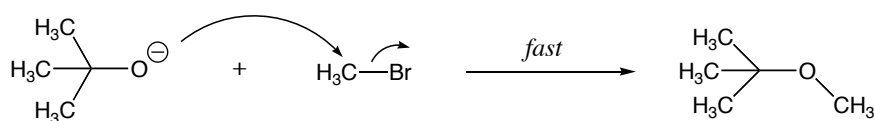
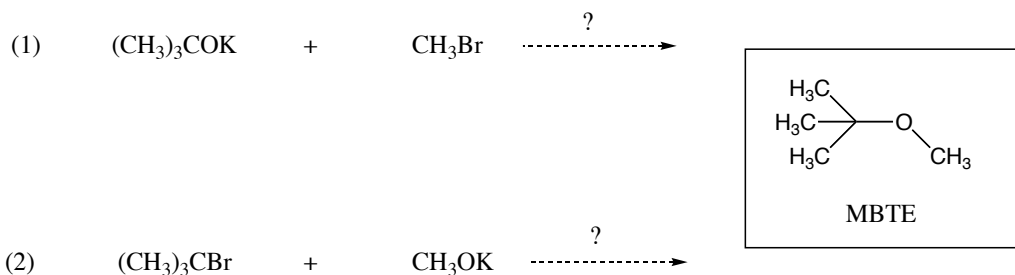


"Backside attack" is not possible (and will never be observed) on an  $sp^2$ -hybridized carbon because:  
 1.  $\sigma^*$  C-LG is shielded by the "in-plane" substituents  
 2. Inversion of configuration is impossible (in the above case it would lead to a trans-olefin in a 5-membered ring!)



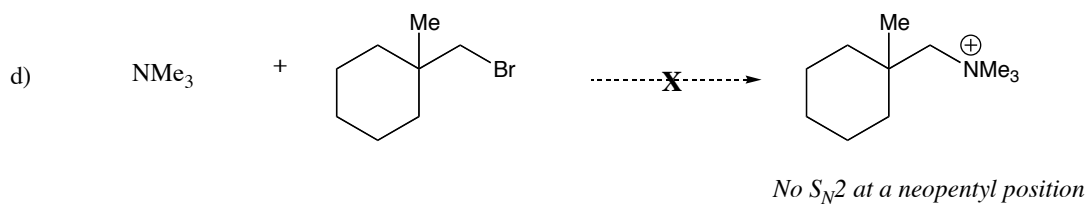
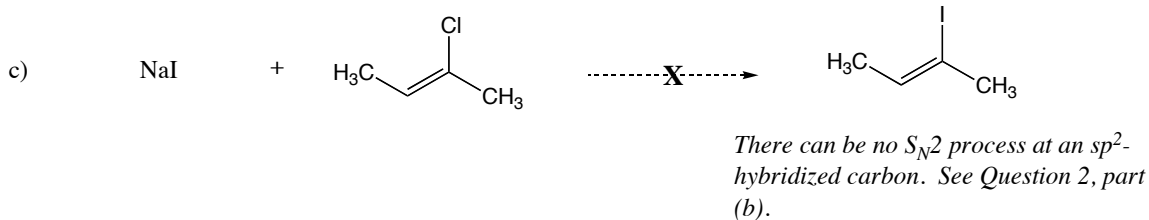
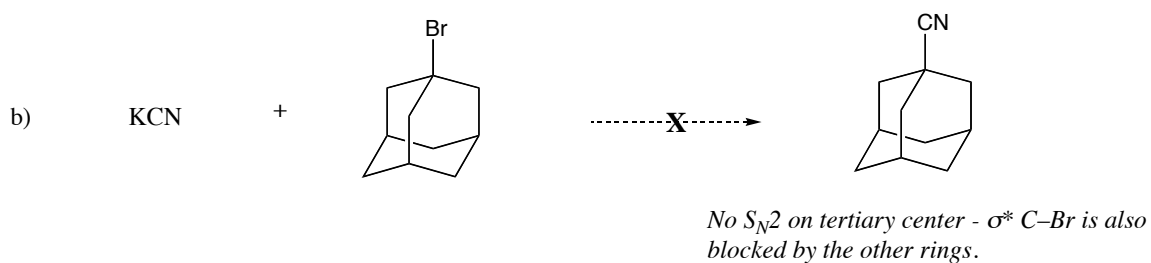
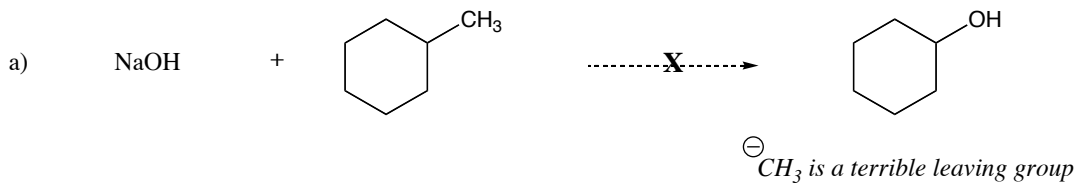


Question 3. Methyl *tert*-butyl ether (MBTE) is a common gasoline additive used to boost octane rating. Below are two reactions that are both attempts to form MBTE. Which reaction will be successful? Which reaction will fail to produce MBTE? Why will it fail?

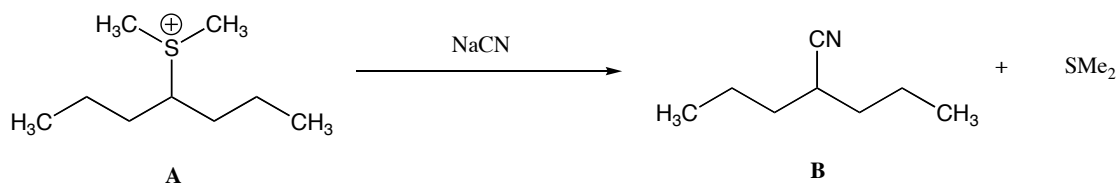


*No S<sub>N</sub>2 on tertiary bromide!*

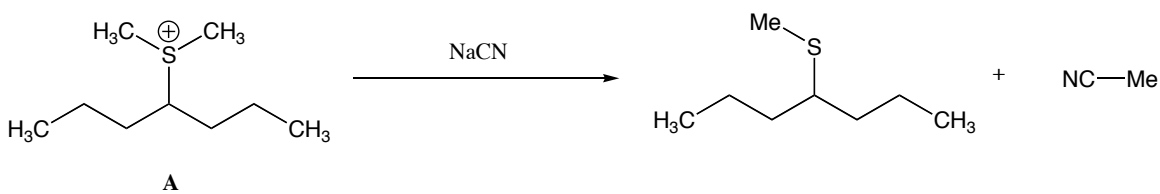
Question 4. Below are a series of reactions that **fail** to give the indicated  $S_N2$  products. Explain why each reaction fails.



Question 5. The reaction below does **not** proceed as written, but an  $S_N2$  reaction does take place. What is the major product formed?

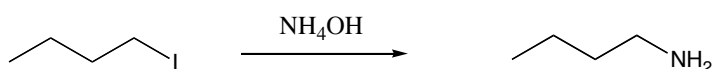
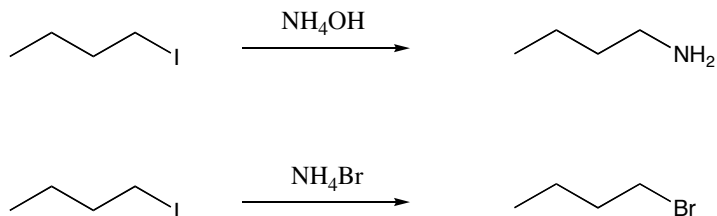


The reaction will proceed as:

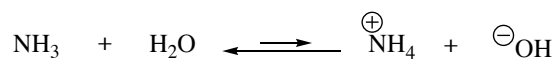


This is an  $S_N2$  reaction, so the displacement will proceed more rapidly at a primary position (either of them) over a secondary position.

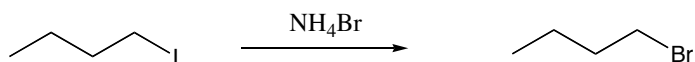
Question 6. Explain the major difference in reactivity between the following pair of reactions. *i.e.*, Why does the ammonia act as the nucleophile in equation 1 (but not hydroxide), yet bromide acts as the nucleophile in equation 2 (but not ammonia).



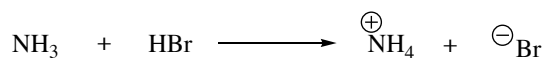
"Ammonium hydroxide" ( $\text{NH}_4\text{OH}$ ) is formed by dissolving ammonia in water:



This is not a favorable equilibrium (favors the left side of the above equation), since  $\text{NH}_3$  is a weaker base than hydroxide ion. Therefore, the concentration of ammonia is much higher than the concentration of hydroxide. Since  $\text{NH}_3$  and  $\text{OH}^-$  have similar nucleophilicities,  $\text{S}_{\text{N}}2$  with  $\text{NH}_3$  as the nucleophile is the major pathway.



A similar equation can be drawn for the formation of ammonium bromide:



This time, the reaction strongly favors products, since  $\text{HBr}$  is a very strong acid. All of the  $\text{NH}_3$  is protonated, and  $\text{Br}^-$  is the sole nucleophile for  $\text{S}_{\text{N}}2$ .

