Chemistry 2500 (Fall 2017): Assignment #15 – S_N1 and S_N2

1. The following reaction:

 $R_3CBr + NaCN \longrightarrow R_3CCN + NaBr$

can proceed via 2 different pathways (Path A, Path B), each of which are outlined below.

Path A: $R_3CBr \longrightarrow R_3C^+ + Br \xrightarrow{NaCN} R_3CCN + NaBr$ Path B: $R_3CBr \xrightarrow{NaCN} NC^{----}C^{----}Br \longrightarrow R_3CCN + NaBr$

a) Briefly explain why Path A is operative when $R = CH_3$, but Path B is operative when R = H.

b) Which of the two pathways would you expect to require a polar solvent? Why?

2. Which of the following reactions would you expect to react faster? Why?

 $(H_3C)_3CBr + CH_3OH \longrightarrow (H_3C)_3COCH_3$

 $(H_3C)_2CHBr + CH_3OH \longrightarrow (H_3C)_2CHOCH_3$

3. For each of the following compounds rank the expected order of reaction rate for an S_N1 mechanism:

PhCH₂I

4. For each of the following compounds rank the expected order of reaction rate for an $S_N 2$ mechanism:



- 5. *R*-3-bromononane is allowed to stir with *excess* NaI in acetone at room temperature. Additional experiments establish that the rate of the reaction is dependent upon the concentration of both the bromononane and the sodium iodide.
 - a) Write an equation for this reaction.
 - b) What is the expected absolute configuration of the product?
 - c) Suggest a reason why if the product is isolated after 2 hours only one enantiomer is present, but if the mixture is allowed to stir for 48 hours a racemic mixture is obtained.
- 6. Of the following pairs of reactions, which one (if either) is faster. Explain your reasoning. Be sure to indicate which mechanism is operative.











7. The following reaction proceeds via an $S_N 2$ mechanism. Explain why the absolute configuration of both the starting material and product is R.



8. For each of the following compounds rank the expected order of reaction rate for an S_N1 mechanism. No explanation is required. (4 points)



9. Methyl bromomethyl ether (depicted below) is a good substrate for both S_N1 and S_N2 reactions. Why?



10. For the following four compounds, rank the molecules in order of rate of reaction in the $S_N 1$ process. Explain your reasoning.

