

### Chem 233: Problem Set #11 (on Chapter 11)

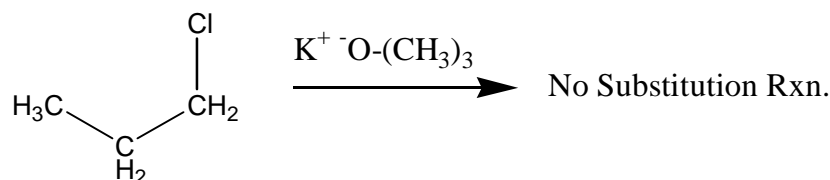
- Specify how each of the following affects the rate of an  $S_N1$  reaction. Does it increase, decrease, or have no effect on the rate of an  $S_N1$  reaction?
  - increase in concentration of nucleophile
  - decrease in nucleophile strength
  - decrease in concentration of alkyl halide
  - increase in strength of halide as a leaving group
  - increase in polarity of solvent
  - change in alkyl halide from 3 $^\circ$  to 1 $^\circ$
- Specify how each of the following affects the rate of an  $S_N2$  reaction. Does it increase, decrease, or have no effect on the rate of an  $S_N2$  reaction?
  - increase in concentration of nucleophile
  - decrease in nucleophile strength
  - decrease in concentration of alkyl halide
  - increase in strength of halide as a leaving group
  - change in polarity of solvent from aprotic to protic
  - change in alkyl halide from 3 $^\circ$  to 1 $^\circ$
- Circle which of the following will proceed faster by an  $S_N2$  reaction mechanism.
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Br}$  vs.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-F}$
  - $(\text{CH}_3)_2\text{CH-I}$  vs.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-I}$
  - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-Cl}$  vs.  $(\text{CH}_3)_2\text{CHCH}_2\text{-Cl}$
  - $(\text{CH}_3)_2\text{CH-I} + \text{NaSCH}_3$  vs.  $(\text{CH}_3)_2\text{CH-I} + \text{HSCH}_3$
  - $(\text{CH}_3)_2\text{CH-I} + \text{NaSCH}_3$   
(aprotic solvent) vs.  $(\text{CH}_3)_2\text{CH-I} + \text{NaOCH}_3$   
(aprotic solvent)

- F.  $(\text{CH}_3)_2\text{CH-I} + \text{NaSCH}_3$  vs.  $(\text{CH}_3)_2\text{CH-I} + \text{NaOCH}_3$   
 (protic solvent) (protic solvent)
- G.  $(\text{CH}_3)_2\text{CH-I} + \text{NaOCH}_3$  vs.  $(\text{CH}_3)_2\text{CH-I} + \text{NaOCH}_3$   
 (Ethanol solvent) (DMSO solvent)
- H.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Br} + \text{OH}^-$  vs.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Br} + \text{F}^-$
- I.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Br} + \text{high conc. F}^-$  vs.  $\text{CH}_3\text{CH}_2\text{CH}_2\text{-Br} + \text{low conc. F}^-$
- J.  $(\text{CH}_3)_2\text{CH-I} + \text{NaCN}$  vs.  $(\text{CH}_3)_2\text{CH-I} + \text{NaNH}_2$   
 $\text{pK}_A(\text{HCN})=9.1$   $\text{pK}_A(\text{NH}_3)=36$

4. Circle which of the following will proceed faster by an  $\text{S}_\text{N}1$  reaction mechanism.

- A.  $(\text{CH}_3)_3\text{C-Br}$  vs.  $(\text{CH}_3)_3\text{CCH}_2\text{-Br}$
- B. chlorocyclopentane + low conc.  $\text{OH}^-$  vs. chlorocyclopentane + high conc. of  $\text{OH}^-$
- C. iodocyclohexane vs. chlorocyclohexane
- D. iodocyclohexane +  $\text{NH}_2^-$  vs. iodocyclohexane +  $\text{NH}_3$
- E.  $(\text{CH}_3)_2\text{CH-I} + \text{HSCH}_3$  vs.  $(\text{CH}_3)_2\text{CH-I} + \text{HSCH}_3$   
 (polar protic solvent) (CCl<sub>4</sub> solvent: a non-polar aprotic solvent)

5. Explain why the reaction shown below does not undergo a substitution reaction by either  $\text{S}_\text{N}2$  or  $\text{S}_\text{N}1$  mechanism.



6. Assume the following reactions undergo substitution. Predict the mechanism ( $S_N1$  or  $S_N2$ ) by which the following reactions occur: 1) give reasons for why the reaction proceeds by the specified mechanism 2) predict the correct products showing stereochemistry where appropriate and then, 3) show the step-by-step mechanism.

