

Chem 233: Problem Set #7 (on Chapter 7)

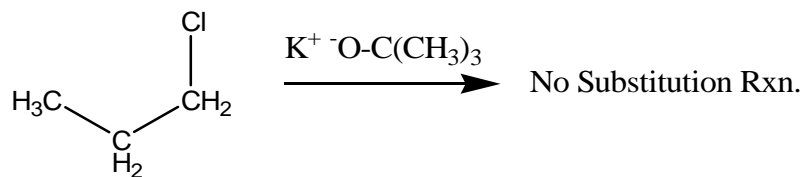
- Specify how each of the following affects the rate of an S_N1 reaction. Does it increase, decrease, or have no effect on the rate of an S_N1 reaction?
 - increase in concentration of nucleophile
 - decrease in nucleophile strength
 - decrease in concentration of alkyl halide
 - increase in strength of halide as a leaving group
 - increase in polarity of solvent
 - change in alkyl halide from 3° to 1°
- 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° to 1°
- 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. $(\text{CH}_3)_2\text{CH-I} + \text{HSCH}_3$
 - $(\text{CH}_3)_2\text{CH-I} + \text{NaSCH}_3$ vs. $(\text{CH}_3)_2\text{CH-I} + \text{NaOCH}_3$
(aprotic solvent) (aprotic solvent)
 - $(\text{CH}_3)_2\text{CH-I} + \text{NaSCH}_3$ vs. $(\text{CH}_3)_2\text{CH-I} + \text{NaOCH}_3$
(protic solvent) (protic solvent)

- G. $(\text{CH}_3)_2\text{CH-I} + \text{NaOCH}_3$ (Ethanol solvent) vs. $(\text{CH}_3)_2\text{CH-I} + \text{NaOCH}_3$ (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. $(\text{CH}_3)_2\text{CH-I} + \text{NaCN}$ ($\text{pK}_\text{A}(\text{HCN})=9.1$) vs. $(\text{CH}_3)_2\text{CH-I} + \text{NaNH}_2$ ($\text{pK}_\text{A}(\text{NH}_3)=36$)

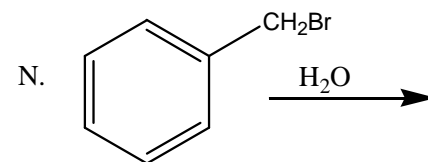
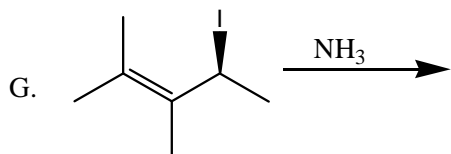
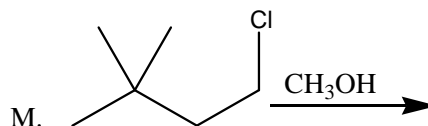
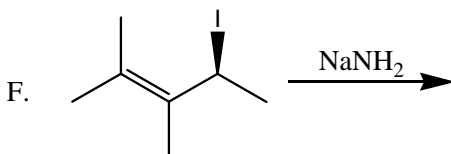
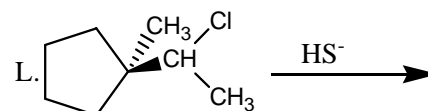
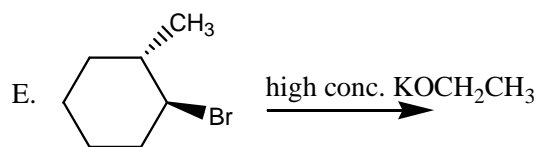
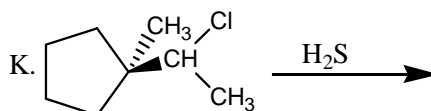
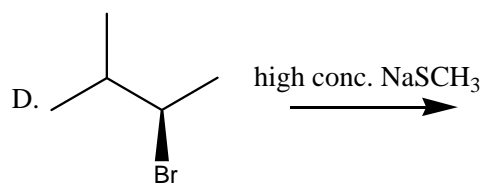
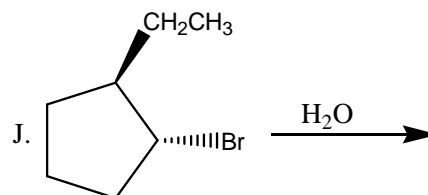
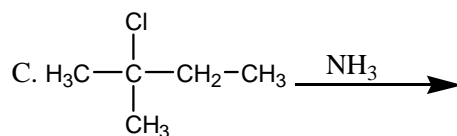
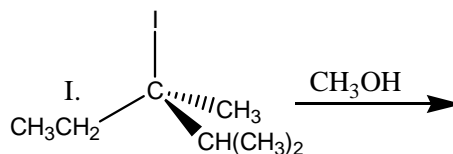
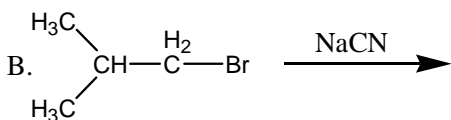
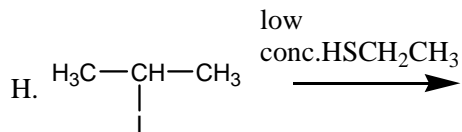
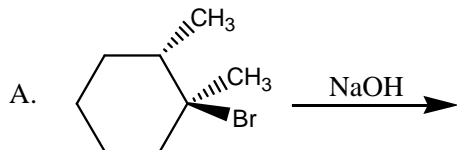
4. Circle which of the following will proceed faster by an $\text{S}_\text{N}1$ reaction mechanism.

- A. $(\text{CH}_3)_3\text{C-Br}$ vs. $(\text{CH}_3)_3\text{CCH}_2\text{-Br}$
- B. chlorocyclopentane + low conc. OH^- vs. chlorocyclopentane + high conc. of OH^-
- C. iodocyclohexane vs. chlorocyclohexane
- D. iodocyclohexane + NH_2^- vs. iodocyclohexane + NH_3
- E. $(\text{CH}_3)_2\text{CH-I} + \text{HSCH}_3$ (polar protic solvent) vs. $(\text{CH}_3)_2\text{CH-I} + \text{HSCH}_3$ (CCl_4 solvent: a non-polar aprotic solvent)

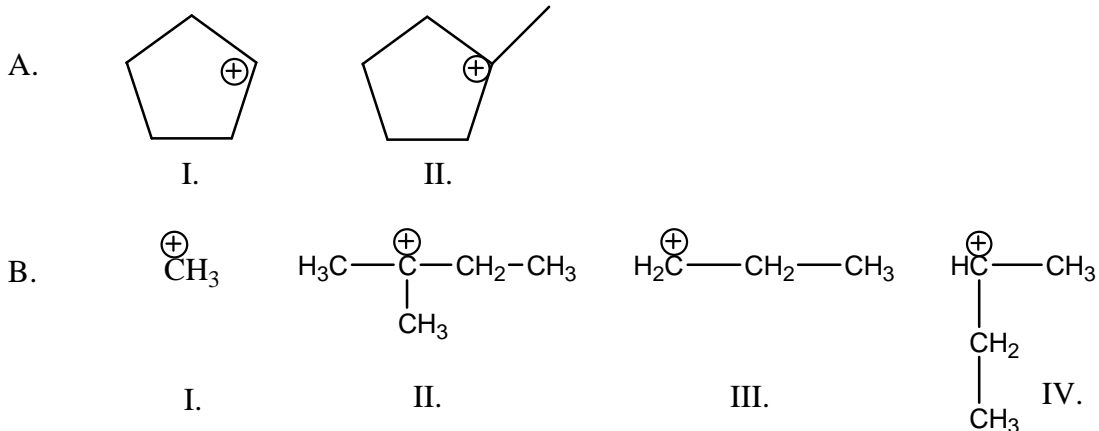
5. Explain why the reaction shown below does not undergo a substitution reaction by either $\text{S}_\text{N}2$ or $\text{S}_\text{N}1$ mechanism.



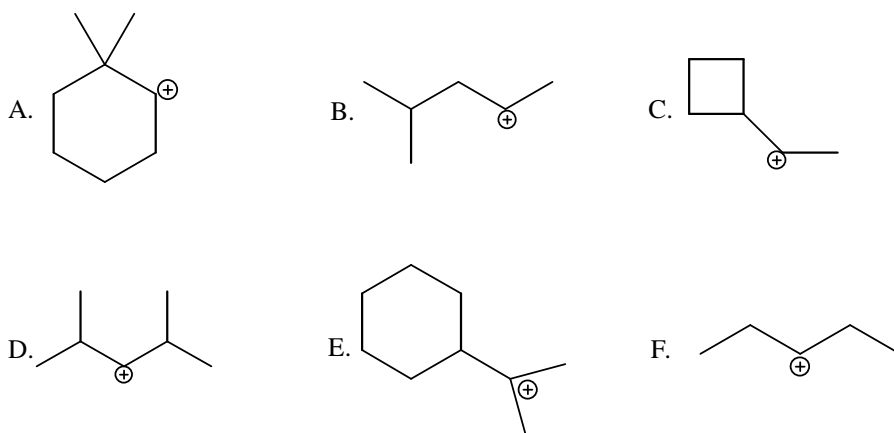
6. Assume the following reactions undergo substitution. Predict the mechanism (S_N1 or S_N2) by which the following reactions occur: 1) give reasons for why the reaction proceeds by the specified mechanism 2) predict the correct products showing stereochemistry where appropriate and then, 3) show the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



7. Place the following carbocations in order of decreasing stability.



8. Which of the following carbocations are likely to rearrange? Show the rearrangement product where applicable.



9. 5-chloro-N-methyl-1-pentanamine can undergo an intramolecular substitution reaction via an S_N2 mechanism when a low concentration of the amine is present. Show the mechanism for this intramolecular substitution reaction.