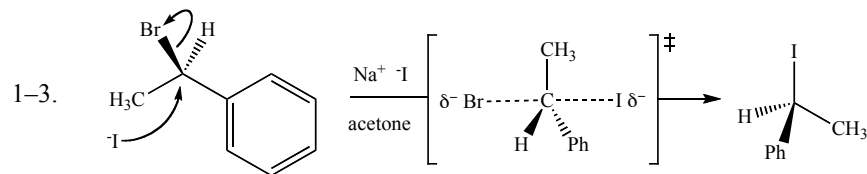


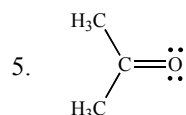
Statistics: High score, average, and low score will be posted on the course web site after exam grading is complete. The exam is ready to be picked up when these numbers are posted.

Some questions have more than one answer, even though only one answer may be listed here.

To see the projected course grade cutoffs, consult the grading scale on the Chemistry 14D course web page.



4. Rate = $k [\text{NaI}] [\text{RBr}]$



6. The C–H and C–C bonds (nonpolar) decrease dielectric constant. The C–O bond (polar) enhances the dielectric constant.

7. DMF Like acetone, DMF is polar and aprotic, the best combination of solvent properties for an S_N2 reaction between a negatively charged nucleophile and uncharged electrophile.

8. (a) Becomes faster. Iodide is a better leaving group than bromide.

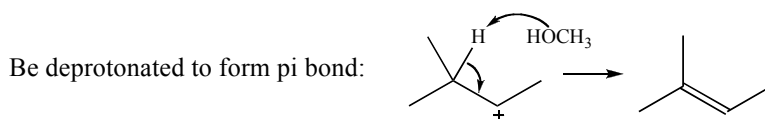
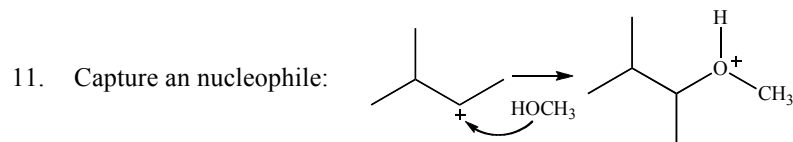
(b) Becomes slower. The carbon bearing the leaving group is changed from secondary to tertiary, causing more steric hindrance, and the S_N2 rate drops to zero. A rate of zero is slower than any other reaction rate.

(c) Becomes faster. Fluoride ion is a better nucleophile than iodide ion in aprotic solvent because of fluoride's smaller atomic radius.

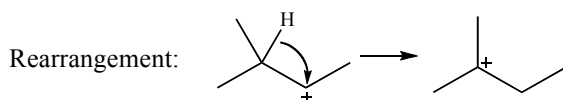
9. Transition state: The highest energy structure between reactants and products for any given mechanism step.

Rate-determining step: The mechanism step with the highest activation energy, and therefore the slowest rate.

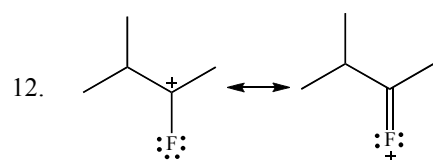
10. Any primary alkyl fluoride is adequate, such as propyl fluoride, $\text{CH}_3\text{CH}_2\text{CH}_2\text{F}$.



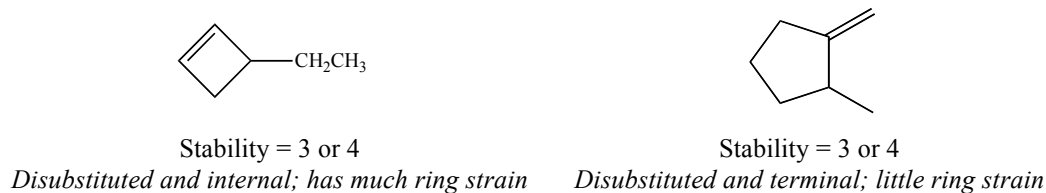
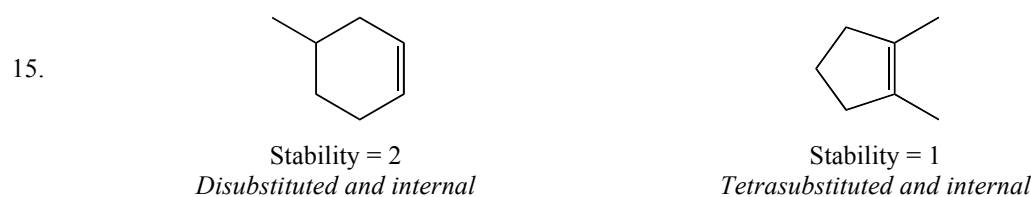
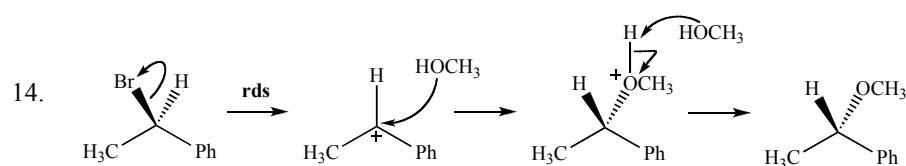
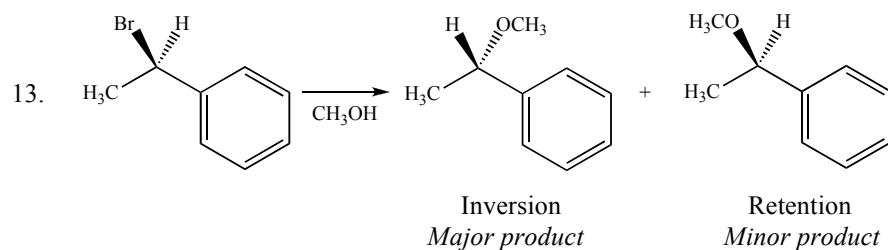
The most stable alkene product is favored.



H shift to give a tertiary carbocation is favored over any other rearrangement in this case.



A fluorine atom has lone pairs, and thus can stabilize an adjacent carbocation by resonance.



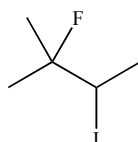
16. (a) Neither A terminal alkene is neither cis or trans.

(b) E The highest priority groups (Cl and F) are on opposite faces of the alkene.

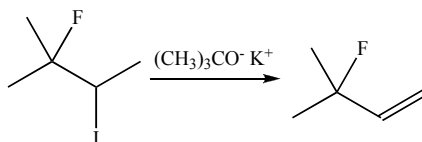
(c) Terminal The pi bond is at the end of the carbon chain.

17. The erroneous words are crossed out and the correct words are in parenthesis. Molecule A is ~~tertiary~~ (secondary) chloride because the carbon bonded to the chlorine atom is also bonded to one OH and two methyl ~~molecules~~ (groups). Molecule A ~~cannot~~ (can) undergo an ~~S_N1~~ (S_N2) reaction because the carbon with the ~~OH~~ (Cl) leaving group ~~is~~ (is not) too sterically hindered.

18. To meet the requirements of the problem, the molecule must have a leaving group in a position that gives only a terminal alkene. Many answers are possible, such as the iodide shown below. Your structure should not be a primary halide, so that the results of the next question are E2 and not S_N2.



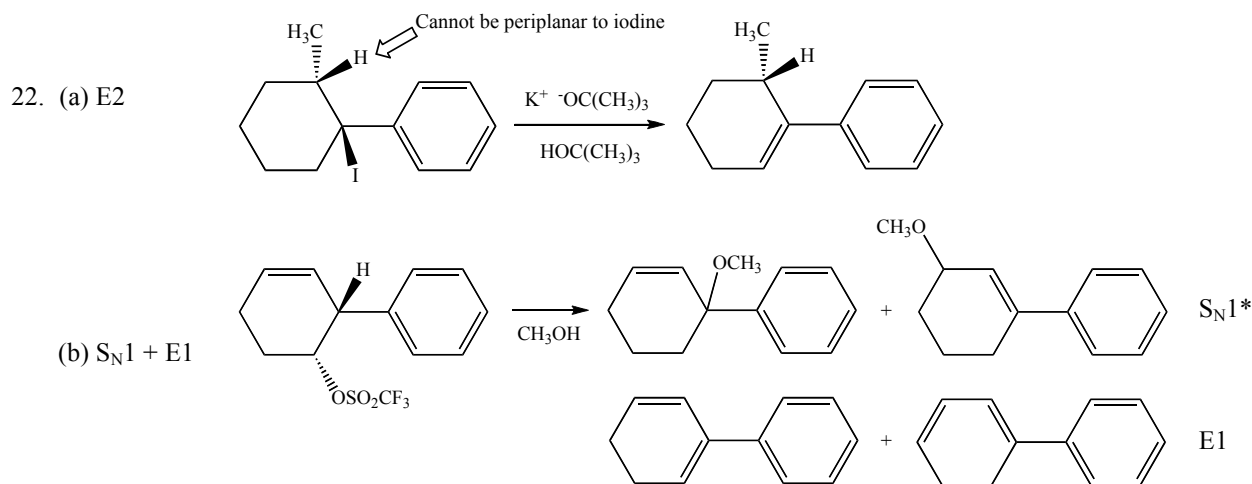
19. Any strong base can be used, such as HO^- , CH_3O^- , $(\text{CH}_3)_3\text{CO}^-$, etc.



20. (a) Methylation occurs at the amine instead of the OH labeled A because oxygen is more electronegative than nitrogen so an alcohol is a poorer nucleophile than an amine.
- (b) Methylation occurs at the amine instead of the OH labeled B because resonance delocalization of the oxygen lone pairs via the benzene ring makes OH group B even less nucleophilic than OH group A.

The proton transfer steps are faster than the nucleophilic substitution steps, so any discussion of acidity or deprotonation rate is irrelevant. The electrophile is SAM (not norepinephrine), and leaving group is SR_2 , not HO^- , so the statement " HO^- is a poor leaving group" is true but irrelevant.

21. (a) Most = H_2O ; least = $\text{CH}_3(\text{CH}_2)_7\text{OH}$
- (b) H_2O and $\text{CH}_3\text{CH}_2\text{OH}$. *We know from lecture that $\text{CH}_3\text{CH}_2\text{OH}$ is on the low end of what we label polar, so the addition of six more carbons is enough to push it into the nonpolar realm.*
- (c) Electrophile *The nucleophile has no charge and so has little interaction with the solvent. The transition state has δ^+ and δ^- charges, so its interactions with polar solvent are small. The electrophile has a full positive formal charge and thus has the strongest interactions with a polar solvent.*
- (d) H_2O *The electrophile has a positive formal charge and thus receives significant stabilization from polar solvent. The transition state has partial charges and receives modest stabilization from polar solvent. Increasing solvent polarity increases electrophile stability more than it increases transition state stability, resulting in largest energy of activation and a lower reaction rate.*



*The $\text{S}_{\text{N}}1$ products are both mixtures of enantiomers.

Carbocation rearrangement ($2^\circ \rightarrow 3^\circ$ with resonance from alkene and phenyl) is very strongly favored.