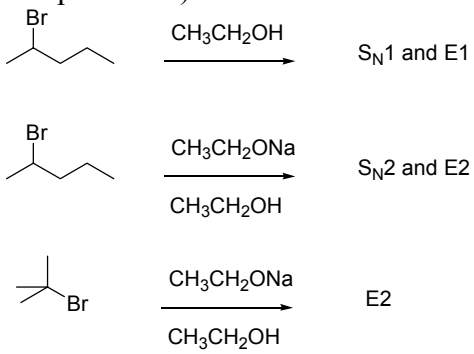
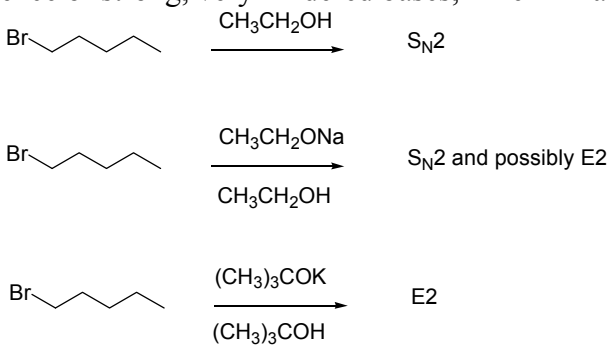
Problem Solving for Substitutions and Eliminations

Use these guidelines to help you decide which reaction will predominate for a given substrate, reagent or solvent. These processes can be best understood by considering the fundamental aspects that control reaction rates, however this set of guidelines may also be useful in many cases.

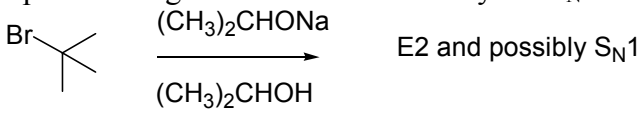
1) **Strong base or strong nucleophile will give second order kinetics (S_N2 or E2).** This is because nucleophilic attack or proton abstraction occurs faster than carbocation formation (the energy pathway is lower for second order processes).



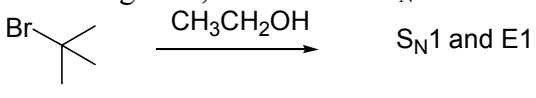
2) **Primary substrates undergo S_N2 reactions.** Primary carbocations are high energy species and are usually not formed unless special conditions are used. Nucleophilic substitution will happen by the S_N2 pathway. In the presence of strong, very hindered bases, E2 eliminations occur.



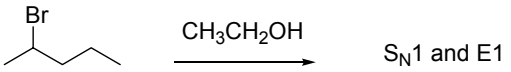
3) **Tertiary substrates undergo E2 reactions in the presence of strong base.** With strong bases, proton abstraction is fast and second order kinetics are observed during the elimination. Unhindered bases that are also nucleophiles will give some substitution by the S_N1 mechanism.

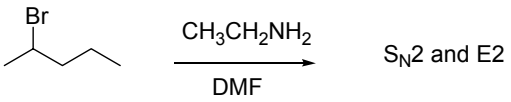


4) **Tertiary substrates undergo first order reactions in the presence of nucleophiles and weak bases.** Tertiary substrates cannot undergo S_N2 displacements. Nucleophilic substitution will happen by the S_N1 reaction only. Depending on reaction conditions, mixtures of S_N1 and E1 products will be obtained. If the nucleophile is a strong base, a mixture of S_N1 and E2 is observed.



5) **Secondary halides can react by first or second order pathways depending on the conditions.** With strong base E2 reactions are noted. With very good nucleophiles S_N2 are observed. With weak base or ionizing solvent (protic solvent) S_N1 and E1 reactions are possible. Mixtures are often obtained.





6) **Bulky strong bases promote elimination.** These compounds are poor nucleophiles and do not easily produce substitution reactions. Nucleophilic substitution works best with good nucleophiles that are weakly basic.