SUBSTITUTION vs. ELIMINATION

1. The strength of the nucleophile/base determines the order of the reaction.

   If a strong nucleophile or base is present, it will likely force second order kinetics (S_N2 or E2.) A strong nucleophile/base is sufficiently reactive to attack the electrophilic carbon or remove a β-H faster than the molecule can undergo the ionization required for 1st order kinetics (S_N1 or E1).

   If no strong base or nucleophile is present, the fastest reaction will likely be a first order reaction, (S_N1 or E1), as long as polar protic (PP) solvent is present.

2. Primary halides usually undergo the S_N2 reaction, sometimes the E2 reaction.

   Most primary halides cannot undergo first order reactions, since primary carbocations are not formed under normal conditions (exceptions: primary carbocations where resonance delocalization is possible, e.g. benzylic, allylic, and methoxymethyl carbocations). With good nucleophiles, S_N2 substitution is usually observed. With a very strong base present, E2 elimination may also be observed, although this reaction is not as common as S_N2 for primary halides.

   For E2 on a primary, unbranched alkyl halide, use tert-butoxide.

   If the alkyl group on the primary halide is very bulky (it has β-branching), the S_N2 reaction may be slowed enough that more elimination will be observed.

3. Tertiary halides usually undergo the E2 reaction (w/ strong base) or a mixture of E1 and S_N1 (w/ weak base and PP solvent).

   Tertiary halides cannot undergo the S_N2 reaction. A strong base forces 2nd order kinetics, resulting in elimination by the E2 mechanism. In the absence of a strong base, tertiary halides react by first order processes, giving a mixture of S_N1 and E1. The reaction conditions determine the ratio of substitution to elimination, with high temperatures favoring elimination. If the elimination product has three or more R-groups bonded to the alkene, E1 is usually favored.
4. The reactions of secondary alkyl halides are more difficult to predict!

Secondary alkyl halides undergo $S_N1$, $S_N2$, $E1$ and $E2$. Strong nucleophiles that are weak bases will promote the $S_N2$ reaction. Strong nucleophiles that are strong bases will promote the $S_N1/E1$ reaction. The reaction conditions determine the ratio of substitution to elimination in first order reactions, with high temperatures favoring elimination. If the elimination product has three or more $R$-groups bonded to the alkene, $E1$ is usually favored.

And one last thing: Once we cover rearrangements in Chapter 9, watch for rearrangements whenever a carbocation is formed ($S_N1$ and $E1$)!