Chemistry 233 Substitution versus Elimination

Introduction

Substitution and elimination reactions are often competing reactions and it is quite common to get a mixture of both substitution and elimination products.

By looking at the substrate and reaction conditions, it is often possible to figure out whether substitution or elimination products will be favored as well as the mechanism (S_N1 , S_N2 , E1, or E2) that leads to the major product.

- a) Look at the nucleophile/base
 - Strong nucleophiles/strong bases favor S_N2 and E2 mechanisms. HO⁻, RO⁻, R₂N⁻
 - Strong nucleophiles, but weak bases favor S_N2 mechanisms. RS⁻, RSH, X⁻
 - Strong bulky bases, but weak nucleophiles favor E2 mechanisms. *t*-BuO⁻, iPr₂N⁻
 - Weak nucleophiles/weak bases favor $S_{\rm N}1$ and E1 mechanisms. $H_2O,\,ROH,\,RNH_2$
- b) Look at the substrate.
 - *Tertiary:* $S_N 1$, E1, E2 In the presence of a strong base, E2 will be the favored pathway.
 - Secondary: S_N1, S_N2, E1, E2 Elimination is typically preferred over substitution unless the reactant is a strong nucleophile, but weak base.
 - *Primary:* $S_N 2$ and E2 only Substitution is typically preferred over elimination unless a strong bulky base is used.
 - Benzylic & Allylic: S_N1, S_N2, E1, E2 Products are highly dependent on the nucleophile/base used. With a strong nucleophile/strong base, as the C-X carbon becomes more sterically hindered, E2 elimination will be preferred over S_N2.
- c) Heating the reaction will result in elimination products favored over substitution products.

See the handout on substitution versus elimination for more information regarding the substrate, base, and nucleophile.

Practice Problems:

Each of these reactions has a short video solutions posted online.

