Lecture 8: Nucleophilic Substitution - $S_N1$ Part 2

Discussion Section Problems Solutions

1. General comments: When deciding if a substitution reaction proceeds by the $S_N1$ or $S_N2$ mechanism, consider $S_N2$ first as this reaction pathway does not involve a carbocation and is generally less energetically expensive than $S_N1$.

(a) $S_N2$ analysis: The carbon bearing the leaving group is tertiary, so this reaction cannot proceed by the $S_N2$ mechanism.

$S_N1$ analysis:

- Leaving group: Chloride ion is a moderate leaving group.
- Carbocation: The carbocation is tertiary with resonance, and therefore sufficiently stable to participate in an $S_N1$ reaction.
- Polar solvent: The solvent is a three-carbon alcohol, which is less polar than ethanol. We estimate the solvent to be of moderate to low polarity.

**Conclusion:** This is a reasonable $S_N1$ reaction, but may be sluggish because of low solvent polarity and moderate leaving group.

(b) $S_N2$ analysis:

- Leaving group: Chloride ion is a moderate leaving group.

*The electrophile is allyl chloride, $H_2C=CHCH_2Cl$. There is no convention that the electrophile (or any reactant) must be written in a particular spot. For example, the electrophile might be above, below, or to the left of the reaction arrow. In most cases the solvent is written below the arrow, but this is not a guarantee.*

- Nucleophile: An alkoxide (RO$^-$) is a good nucleophile, due to the small atomic radius of oxygen as well as the negative charge.
- Not tertiary: The carbon accepting the nucleophile is primary.
• Solvent: When the nucleophile has a negative formal charge and the electrophile is neutral, the reaction rate increases as solvent polarity decreases. DMF is a moderately polar, aprotic solvent, which favors this S_N2 reaction.

Conclusion: This is a reasonable S_N2 reaction, so for this question we need not consider S_N1.

Mechanism:

(c) S_N2 analysis:

• Leaving group: Chloride ion is a moderate leaving group.

• Nucleophile: Trimethylamine is a moderate nucleophile (EN N = 3.0 and nitrogen is small).

• Not tertiary: The reaction takes places at a secondary carbon.

• Solvent: When the reactants are uncharged and the transition states bears $\delta^-$ and $\delta^+$ charges, the best solvent is polar. CH_3OH is polar ($\varepsilon = 33$). CH_3OH is protic, which reduces nucleophilicity, but does not prevent it.

Conclusion: This is a reasonable S_N2 reaction, so for this question we need not consider S_N1.

Mechanism: