EXPERIMENT # 5

NUCLEOPHILIC SUBSTITUTION REACTIONS ($S_N1$ and $S_N2$)

Prelab Answers

1. Which is a better nucleophile in aqueous solution, Br\textsuperscript{−} or Cl\textsuperscript{−}? Why?

   Bromide is the better nucleophile in aqueous solution. Chloride ions solvate (hydrogen bond) more strongly and, in effect, become larger/less reactive than bromide ions and therefore are less effective as nucleophiles. (see Jones pg 291-292)

2. What products form in the $S_N1$ reaction?

   2-bromo-2-methylpropane (tert-butyl bromide) and 2-chloro-2-methylpropane (tert-butyl chloride)

3. In what ratio do you predict they will be formed?

   Although the rate-determining step of an $S_N1$ reaction does not involve the nucleophile, the distribution of products does depend somewhat upon the strength of the nucleophile. Since bromide is a better nucleophile than chloride, one would expect more 2-bromo-2-methylpropane than 2-chloro-2-methylpropane in the product mixture. However, the relative nucleophilicity of bromide vs. chloride does not really give us a good estimate of the product ratio because we are really interested in what the relative transition states look like (see section 8.8 in Jones)

4. What are the products of the $S_N2$ reaction?

   1-bromobutane (n-butyl bromide)
   1-chlorobutane (n-butyl chloride)

5. Do you expect the same ratio of products as in the $S_N1$ reaction? Explain why or why not.

   No. The transition state for an $S_N2$ reaction is very different than an $S_N1$ reaction.

6. Look up the boiling points and densities of all of the organic reactants and products. Densities will help you to determine which layer is the organic layer and which is the aqueous layer in your separatory funnel, and boiling points will help you to determine the order of elution of the products (and any unreacted starting material) from the gas chromatographic column.
<table>
<thead>
<tr>
<th>compound</th>
<th>boiling point, °C</th>
<th>density, g/mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-butanol (n-butyl alcohol)</td>
<td>117-118</td>
<td>0.810</td>
</tr>
<tr>
<td>1-bromobutane (n-butyl bromide)</td>
<td>101.3</td>
<td>1.269</td>
</tr>
<tr>
<td>1-chlorobutane (n-butyl chloride)</td>
<td>78.5</td>
<td>0.881</td>
</tr>
<tr>
<td>2-methyl-2-propanol (tert-butyl alcohol)</td>
<td>82.4 (m.p. = 25.6)</td>
<td>0.781</td>
</tr>
<tr>
<td>2-bromo-2-methylpropane (tert-butyl bromide)</td>
<td>73.3</td>
<td>1.212</td>
</tr>
<tr>
<td>2-chloro-2-methylpropane (tert-butyl chloride)</td>
<td>51.0</td>
<td>0.847</td>
</tr>
</tbody>
</table>

7. Why is it necessary to perform the competing nucleophiles reactions under acidic conditions (Why doesn’t the reaction work with the halide and the unprotonated alcohol?)?

- OH is a poor leaving group. By protonating the alcohol, the leaving group becomes H₂O, a good leaving group. This is required for both Sₙ₁ and Sₙ₂.

8. How many moles of Br⁻ and Cl⁻ are you weighing out for this part of the experiment?

Since they are to make an equimolar mixture of Br⁻ and Cl⁻, calculating the number of moles of one is sufficient.

# moles of Br⁻ = 17.5 g ammonium bromide ÷ 97.96 g/mol = 0.178 moles
# moles of Cl⁻ = 9.5 g ammonium chloride ÷ 53.50 g/mol = 0.178 moles