Worksheet – Nucleophilic Addition and Substitution

A variety of reagents can add across the C=C of alkenes, H-X, H-OH, Br-Br and H-H. When the non-symmetric species (H-X and H-OH) add, Markovnikov’s rule can be used to predict the major and minor products, based on the stability of the intermediate carbocations. Reagents, like H-OH and H-OR (alcohols) can add across the C=O bond of aldehydes and ketones. The acid catalyzed mechanism is very similar to the addition to alkenes, but in these reactions, the H always adds to the O and the nucleophile (:OH or :OR) adds to the carbon.

1. Write the mechanism for the hydration of 2-methylpropene:

   \[
   \begin{align*}
   \text{CH}_2=\text{CHCH}_3 + \text{H}_2\text{O} & \quad \text{H}^+ \\
   \text{CH\_2\_OH} & \quad \text{CH\_3\_OH}
   \end{align*}
   \]

   The π electrons in the C=O double bond can be used in the same way. Because of the polarity of the C=O bonds, the H⁺ will add to the O and the O-H or O-R will add to the carbon.

2. Write the mechanism for the addition of water to 2-propanone:

   \[
   \begin{align*}
   \text{CH}_2=\text{CHO} + \text{H}_2\text{O} & \quad \text{H}^+ \\
   \text{CH\_2\_OH} & \quad \text{CH\_2\_CO\_OH}
   \end{align*}
   \]

   This product is called a “diol” or “hydrate” and is unstable. The same reaction can take place between an aldehyde and water.
3. Write the mechanism for the addition of ethanol to propanone:

\[
\text{\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{CH}_2\text{OH}} \xrightarrow{H^+} \quad \text{\text{CH}_3\text{CO}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{OH}}
\]

This product, also unstable, is called a hemi-ketal (ketone + alcohol). The same reaction takes place between an aldehyde and an alcohol forming a hemi-acetal. There are no more \(\pi\) electrons, so no further addition products are possible.

However, a second equivalent of alcohol can react with the hemi-acetals and hemi-ketals in a **nucleophilic substitution** reaction. The –OH on the hemi-ketal is replaced by the –OR group from the alcohol. The other product is water. This is also called a **condensation reaction**.

4. Fill in the curved arrows and formal charges and products in the nucleophilic substitution reaction shown below, the product of problem 3 reacts with another equivalent of ethanol.

\[
\text{H}^+ \quad \text{OH} \quad \rightarrow \quad \text{H} \quad \text{OH} \\
\text{step 1} \\
\text{H} \quad \text{OH} \quad \rightarrow \quad \text{H} \quad \text{OH} \\
\text{step 2} \\
\text{H} \quad \text{OH} \quad \rightarrow \quad \text{H} \quad \text{OH} \\
\text{step 3} \\
\text{H} \quad \text{OH} \quad \rightarrow \quad \text{H}^+ \\
\text{step 4}
\]
5. Categorize the compounds shown below and identify the **reactants** that produced them.

a. 

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_3
\]

b. 

\[
\text{O} \quad \text{O} \quad \text{O}
\]

c. 

\[
\text{O} \quad \text{O} \quad \text{O}
\]

d. 

\[
\text{CH}_3\text{C(OH)}\text{CH}_2\text{OH}
\]

6. Draw the product of the reaction of 3-heptanone and two equivalents of 2-propanol.