CHEM1611 Worksheet 6: Addition Reactions

Model 1: Addition to Symmetrical Alkenes and Alkynes

In Worksheet 5, we saw that the double bond of an alkene is made up of one strong σ-bond and one weak π-bond. The process in which this π-bond is broken and two new σ-bonds are formed in its place is called an addition reaction.

![Addition reaction diagram]

The addition reaction usually takes place in two steps. In the first step, an intermediate is formed called a carbocation.

![Carbocation diagram]

Critical thinking questions

1. In this reaction is the alkene acting as an electrophile or a nucleophile?

2. Highlight the bonds that are breaking in one colour, and the newly formed bonds in another.

3. Using the scheme above as a model, determine the outcome of the following reactions:

   (a) 
   
   (b) + H₂ catalytic Pd

   (c)

   (d) + Br₂ (1 equivalent)

   (e) + Br₂ (2 equivalents)
**Model 2: Addition to Unsymmetrical Alkenes and Alkynes**

The alkene used in Model 1 was *symmetrical*: it had the same groups at the two ends of multiple bond.

For *unsymmetrical* alkenes, with different groups at the two ends of the multiple bond, two carbocations may be formed in the first step of the reaction, as illustrated in the scheme opposite.

Because of this, there are two possible products. However, experimentally, one is formed in much greater amount than the other.

**Critical thinking questions**

1. Draw and name the products arising from each of these carbocations.

2. Given that the alkyl groups (CH₃ groups) stabilize carbocations, which carbocation do you expect to be the more stable in the scheme above?

3. Given your answers to Q2, which of the two products you drew in Q1 will be the major product?

*This is Markovnikov’s rule. It states that in an addition to an unsymmetrical alkene, the hydrogen will go predominantly to the end that already has the most hydrogen atoms.*

Another reaction you would have seen is the hydration of alkenes, which is carried out using aqueous sulfuric acid. This is also an addition reaction, but H₂SO₄ is *not* added across the double bond.

4. What is being added across the double bond? (Remember that atoms are added to *both* ends.)

5. What is the role of the H₂SO₄?
Past Exam Paper Questions on this Topic:

- Give the major product from the following reaction. 

  \[ \text{HBr} \quad \text{\begin{tikzpicture}[baseline=(current bounding box.center)]
    \draw[thick,->] (-0.5,0) -- (0.5,0); \end{tikzpicture}} \]

  

  Show the mechanism of the reaction. Make sure you show structural formulas for all relevant intermediate species and the final product, as well as using curly arrows to indicate the movement of electrons \((i.e.\) the breaking and formation of bonds).

  

  Give the structure of the minor product of this reaction and explain why very little of it forms.

  

  Give the names of the major and minor products.

<table>
<thead>
<tr>
<th>Major product:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minor product:</td>
</tr>
</tbody>
</table>
Complete the following table. Make sure you complete the name of the starting material where indicated.

<table>
<thead>
<tr>
<th>STARTING MATERIAL</th>
<th>REAGENTS/ CONDITIONS</th>
<th>CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Cyclohexene" /></td>
<td>HBr / CCl₄ (solvent)</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Cyclopentene" /></td>
<td>HBr / CCl₄ (solvent)</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Propene" /></td>
<td>H₂/Pd</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Cyclohexene" /></td>
<td>HBr / CCl₄ (solvent)</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="Cyclohexene" /></td>
<td>HBr</td>
<td></td>
</tr>
</tbody>
</table>

Consider the following dehydration reaction.

\[
\text{OH} \quad \xrightarrow{\text{conc. } \text{H}_2\text{SO}_4} \quad \text{CH}_2=\text{CH}\text{CH}_2\text{CH}_2\text{CH}_3
\]

Use curly arrows to show the mechanism of this reaction.