Electrophilic Addition Reactions of Dienes

1. Stability and Structure
   1. Compare the following diene isomers:
      \[ \text{Diene Isomers} \]
      
      a. Which has the lowest $-\Delta H_{\text{rxn}}$ with 2 equivalents of H\textsubscript{2} with Pd/C?
      b. Which has the highest $-\Delta H_{\text{rxn}}$ with 2 equivalents of H\textsubscript{2} with Pd/C?
      c. Which is the most stable?

2. Which of the following diene isomers is the most stable:
   \[ \text{Diene Isomers} \]

2. Electrophilic Addition
   Dienes form products of 1,2- and 1,4-addition in hydrohalogenation and hydration reactions:
   \[ \text{Dienen} + \text{HBr} \rightarrow \text{1,2-Addition} + \text{1,4-Addition} \]
   The mechanism involves a resonance stabilized carbocation.

   Addition of Br\textsuperscript{−} to either carbocation affords the respective product. Under low temperatures the bromide ion moves slower and will react with the nearer cation faster (1,2-addition). This is called a 'kinetic' product. At higher temperatures the high mobility of Br\textsuperscript{−} will give both 1,2- and 1,4-products with a greater amount of the more stable 1,4-product (alkene is more substituted). This is called the ‘thermodynamic’ product.
1. Give the products for the following reactions; propose a mechanism to explain the formation of each:

(a) \( \text{HCl} \rightarrow ? \)

(b) \( \text{HCl} \rightarrow ? \)

(c) \( \text{HCl} \rightarrow ? \)

(d) \( \text{HBr} \rightarrow ? \)

(e) \( \text{HBr} \rightarrow ? \)

(f) \( \text{HBr} \rightarrow ? \)

2. Determine whether the process is kinetic or thermodynamic and predict the product(s).

(a) \( \text{HBr} \rightarrow ? \) at 40°C

(b) \( \text{HCl} \rightarrow ? \) at 0°C

(c) \( \text{HBr} \rightarrow ? \) at 0°C

3. Consider the following. When 1,4-dimethylcyclohepta-1,3-diene is treated with HBr at elevated temperature, the 1,2-product predominates rather than the 1,4-product. Provide a hypothesis for this observation.

\[ \text{1,4-dimethylcyclohepta-1,3-diene} \xrightarrow{\text{HBr}} \text{1,2-product} \]

**KEY**

1. **Stability and Structure**

   1. a. Most stable alkene has smallest \( -\Delta H_{\text{rxn}} \)

   b. Least stable has highest \( -\Delta H_{\text{rxn}} \)

   c. Which is the most stable? Answer from a.

2. Which of the following diene isomers is the most stable:
2. Electrophilic Addition

1.

a)

![Chemical structures and reactions involving electrophilic addition.](image)

b)
c) 

\[ \text{[chemical structure]} \quad \xrightarrow{\text{H}_2} \quad \text{[chemical structure]} \]

\[ \text{[chemical structure]} \quad \xrightarrow{\text{Br}_2} \quad \text{[chemical structure]} \]

\[
\begin{align*}
\text{[chemical structure]} & \quad \text{(racemic)} \\
+ & \quad \text{[chemical structure]} \quad \text{(racemic)}
\end{align*}
\]

d) 

\[ \text{[chemical structure]} \quad \xrightarrow{\text{H}^+} \quad \text{[chemical structure]} \]

\[ \text{[chemical structure]} \quad \xrightarrow{\text{Br}_2} \quad \text{[chemical structure]} \]

\[
\begin{align*}
\text{[chemical structure]} & \quad \text{(racemic)} \\
& \quad \text{(racemic)} \\
& \quad \text{(racemic)} \\
& \quad \text{(racemic)}
\end{align*}
\]
2.

a) \[
\text{HBr} \quad 40^\circ C \\
\text{major} + \text{minor}
\]

b) \[
\text{HCl} \quad 0^\circ C \\
\text{major} + \text{minor}
\]

c) \[
\text{HBr} \quad 0^\circ C \\
\text{major} + \text{minor}
\]
3. Explain: Always remember why a product is favored, don’t just memorize a class of answers. The reason 1,4 is favored in most cases is that it is the most substituted alkene. In this case the 1,2-product is more substituted than the one from 1,4-addition.