Evidence for resonance stabilization: enthalpies of hydrogenation

Conservation of energy:

Ethene

\[ \Delta (\Delta H) = 4 \text{ kcal/mol} \]

Ethylene

Energy of delocalization

Conjugation Energy

Resonance Energy
Evidence for resonance stabilization: bond lengths

\[
\begin{align*}
\text{C}_2\text{sp}^2 - \text{C}_2\text{sp}^2 \text{ bond length: } & 1.34 \\
\end{align*}
\]
Consider \((E)-1,3\text{-pentadiene}:\)
Evidence for resonance stabilization: conformational preferences

Just as there is a barrier to rotation about the C₂=C₃ of cis and trans-2-butene, there is a barrier to rotation about the C₂ - C₃ in 1,3-butadiene:

\[ E \text{ kcal/mol} \]

\[ \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\hline
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\hline
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array} \]

\[ s - \text{trans conformation} \quad s - \text{cis conformation} \]

\[ E_k \text{ kcal/mol} \]

\[ \begin{array}{c}
0 \\
90 \\
180
\end{array} \]

\[ C_1 = C_2 - C_3 = C_4 \text{ torsion, degrees} \]

\[ 3.9 \]

\[ 2.8 \]
Synthesis of conjugated dienes:

- Just like alkene synthesis, only twice – *conjugated dienes prefer to form as major products because they are the most thermodynamically stable products*
- Dehydrohalogenation of allylic halides

\[
\begin{align*}
\text{Br} & \quad \xrightarrow{\text{CH}_3\text{CH}_2\text{O}^- \text{ Na}^+ \text{, CH}_3\text{CH}_2\text{OH, } \Delta} \\
& \quad \text{90 %}
\end{align*}
\]

- Isolated dienes form only when it is impossible to form the conjugated isomer
What would the E1 outcome of dehydrobromination of 4-bromo-2,3,3-trimethylhexene be?
Reactions of conjugated dienes:

- Additions of HX

\[
\text{HBr} \quad \text{dark, -80 °C} \quad \text{Br}
\]

\[
\begin{align*}
\text{81 %} & \quad + \\
\text{19 %}
\end{align*}
\]
Reactions of conjugated dienes:

- Additions of HX

\[
\text{\begin{figure}
\begin{align*}
\text{\includegraphics[width=\textwidth]{reaction_diagram.png}}
\end{align*}
\end{figure}}
\]

\[
\text{1,2-addition} \quad \text{1,4-addition}
\]

Markovnikov addition product \quad conjugate addition product
What’s the mechanism?
Looking at the carbocation intermediate more closely: what possible addition products can form?

1,2-addition  
1,3-addition  
1,4-addition

less stable isomer  
ever observed  
more stable isomer
Reactions of conjugated dienes:

- Additions of HX

\[
\text{HBr} \quad \text{Br} \\
\text{dark, -80 °C} \\
\text{81 %} \\
\text{81 %} \\
\]

\[
\text{Br} \\
\text{dark, 45 °C} \\
\text{19 %} \\
\text{19 %} \\
\]

1,2-addition 1,4-addition

major minor

1,2-addition 1,4-addition

minor major
Energy vs reaction coordinate diagram:

\[
\text{Energy vs reaction coordinate diagram:}
\]

\[
\begin{align*}
\text{Br} & \quad \text{Br} \\
+ \quad \text{HBr} & \quad + \quad \text{Br}^{-} \\
\text{conjugate addition} & \quad \text{elimination}
\end{align*}
\]
Energy vs reaction coordinate diagram:

\[ \text{Br} \text{Br} + \text{HBr} \rightarrow \text{Br}^- + \text{Br} \text{Br} \]
Energy vs reaction coordinate diagram:
Energy vs reaction coordinate diagram:

For the second step, $E_{\text{act}} < E_{\text{act}}$ so the rate of 1,2-addition $>$ the rate of 1,4-addition

When the major product that forms is the fastest forming product, a reaction is said to be under rate or kinetic control.
Energy vs reaction coordinate diagram:

For the second step, if the temperature of the reaction is $\geq E_{\text{act reverse}}$, then the 1,2-addition product can equilibrate to the more stable 1,4-addition product.

When the major product that forms is the most stable product, a reaction is said to be under equilibrium, thermodynamic or stability control.
The Alder Rule

diastereoselection is such that endo products predominate:
exo transition state: C=O carbon hoovers over CH$_2$ of 1,3-cyclopentadiene

more stable endo transition state: C=O carbon hoovers over forming C2–C3 C=C of the cyclopentadiene

endo adduct
Consider the ground state electronic configuration of ethene:

\[
\begin{align*}
\text{C-C } & \sigma^* \\
\text{C-H } & \sigma^* \\
\text{C-C } & \pi^* \quad \text{(lumo)} \\
\text{C-C } & \pi \quad \text{(homo)} \\
\text{C-H } & \sigma \\
\text{C-C } & \sigma
\end{align*}
\]
The smallest $\Delta E$ that will promote a bonding electron to an antibonding orbital is:

$$\Delta E = \text{UV-Vis}$$
(with $\lambda = 162$ nm here)
\( \lambda_{\text{max}} = 175 \)

\( \lambda_{\text{max}} = 245 \)

\( \lambda_{\text{max}} = 275 \)

Absorbance

wavelength, nm
Absorbance

\[ \lambda = 280 \text{ nm} \]

A: \( \pi \rightarrow \pi^* \)
\[ A: \pi \to \pi^* \]

\[ B: n \to \pi^* \]
C=O $\pi$ electron transitions

LUMO $\pi^*$

HOMO $n$

HOMO-1 $\pi$
Lawsone in pH 7.2 phosphate buffer

\[ \lambda_{\text{max}} \quad A \]

<table>
<thead>
<tr>
<th>\lambda_{\text{max}}</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td>215</td>
<td>1.52</td>
</tr>
<tr>
<td>265</td>
<td>2.16</td>
</tr>
<tr>
<td>290 (sh)</td>
<td>1.07</td>
</tr>
<tr>
<td>330</td>
<td>0.22</td>
</tr>
<tr>
<td>452</td>
<td>0.27</td>
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