2. Structure and Stability

\[ \Psi_A - 2 \rho_x = D \]

\[ \Psi_B - 2s = C \]

\[ \Psi_A + 2 \rho_x = B \]

\[ \Psi_B + 2s = A \]
9 Kcal/mol
The diagram represents an energy level diagram with the following labels:

- **S\(_1\)**: A state labeled with an 8–10 kcal/mol energy difference above the ground state.
- **T\(_1\)**: Another state.
- **singlet** and **triplet**: States with different multiplicity labels.

The diagram indicates the energy transitions and levels, showing the difference between singlet and triplet states.
alkyl groups such as methyl can help stabilize the **singlet** through a **hyperconjugative interaction** with the empty 2p orbital.

Sterically demanding groups, for example, phenyl, tert-butyl, or adamantyl, should favor the **triplet state** by demanding a wide R-C-R angle.

Atoms with nonbonding electrons that can donate those electrons into the empty 2p orbital of a **singlet** are especially effective at producing ground-state **singlets**. Difluorocarbene, :CF₂:, is a classic example.
Ground States for Typical Carbenes

<table>
<thead>
<tr>
<th>Carbene</th>
<th>Ground State</th>
</tr>
</thead>
<tbody>
<tr>
<td>:CH₂</td>
<td>Triplet</td>
</tr>
<tr>
<td>:CR₂</td>
<td>Singlet or triplet</td>
</tr>
<tr>
<td>HČCOOR</td>
<td>Triplet</td>
</tr>
<tr>
<td>:C(COOR)₂</td>
<td>Triplet</td>
</tr>
<tr>
<td>:C(C₆H₅)₂</td>
<td>Triplet</td>
</tr>
<tr>
<td>:CAr₂</td>
<td>Triplet</td>
</tr>
<tr>
<td>HČC₆H₅</td>
<td>Triplet</td>
</tr>
<tr>
<td>:CX₂ (X=F, Cl, Br, I)</td>
<td>Singlet</td>
</tr>
<tr>
<td>HČX</td>
<td>Singlet</td>
</tr>
<tr>
<td>:C(OR)₂</td>
<td>Singlet</td>
</tr>
<tr>
<td>:C(NR₂)₂</td>
<td>Singlet</td>
</tr>
</tbody>
</table>
In many cases the two reactive intermediates are very close in energy.

<table>
<thead>
<tr>
<th>Carbene</th>
<th>Singlet–Triplet Gap</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>:CH₂</td>
<td>9</td>
<td>Theory</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>Experiment</td>
</tr>
<tr>
<td>:CHCH₃</td>
<td>3–5</td>
<td>Theory</td>
</tr>
<tr>
<td>:C(CH₃)₂</td>
<td>−1.4</td>
<td>Theory</td>
</tr>
<tr>
<td></td>
<td>−1.6</td>
<td>Theory</td>
</tr>
<tr>
<td>HĆC₆H₅</td>
<td>2.5</td>
<td>Theory</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>Experiment</td>
</tr>
<tr>
<td></td>
<td>4.3</td>
<td>Theory</td>
</tr>
<tr>
<td>:CF₂</td>
<td>−57</td>
<td>Experiment</td>
</tr>
</tbody>
</table>

\(^a\) In kcal/mol; positive value indicates triplet ground state.
- Similarly, nitrenes can exist as triplet or singlet.

- Additionally, nitrenes can be protonated to give nitrenium ions that are isoelectronic with carbenes.

\[ \text{singlet} \quad \text{nitrenium ion} \]
In order to establish if these intermediates react as singlet or triplet, Skell and Woodworth proposed a "test" that relied on the stereospecificity of the addition of carbenes and nitrenes to alkenes. 

*JACS 1956, 78, 4496*
3. Generation of carbenes and nitrenes

Carbenes and nitrenes are most commonly formed by α-elimination or fragmentation of appropriate precursors.

Carbenes and Nitrenes are common reactive intermediates in a number of classic reactions:

**Reimer-Thieman reaction:**

\[
\begin{align*}
\text{OH} & \quad \text{H} \quad \text{Cl}_2 \text{C} \quad \text{Cl} \\
\text{KOH} & \quad \xrightarrow{\text{OK}} \quad \text{Cl} \quad \text{Cl} \\
\text{OH} & \quad \text{Cl} \quad \text{Cl} \\
\end{align*}
\]
Bamfords-Stevens reaction:

\[
\begin{align*}
\text{Ts} & \xrightarrow{\text{NaOMe}} \text{N} = \text{N} \cdot \cdot \cdot \\
\text{N} \cdot \cdot \cdot & \xrightarrow{\text{H}} \text{N} \cdot \cdot \cdot \\
\text{N} \cdot \cdot \cdot & \xrightarrow{\text{H}} \text{N} \cdot \cdot \cdot \\
\end{align*}
\]

in aprotic medium: carbene mechanism preferred

Diazirines (for photoaffinity labelling)

\[
\begin{align*}
\text{N}=\text{N} & \xrightarrow{\Delta T \ \text{or} \ \text{hv}} \text{N}=\text{N} \\
\text{R} & \xrightarrow{\text{Protein} \cdot \cdot \cdot} \text{R} \\
\end{align*}
\]
Arylazides (for photoaffinity labelling)

\[
\begin{align*}
&\text{R} &\text{N}_3 &\xrightarrow{\text{hv}} &\text{R} &\text{N}^* \\
&\text{R} &\xrightarrow{\text{Protein-H}} &\text{R} &\text{N}^- &\text{Protein}
\end{align*}
\]

Arndt-Eistert homologization:

\[
\begin{align*}
&\text{O} &\text{N}_2 &\xrightarrow{\text{AgOR}} &\text{O} \\
&\text{O} &\xrightarrow{\text{ROH}} &\text{OR}
\end{align*}
\]

Hoffman-Degradation and Lossen-Schmidt-Reaction

\[
\begin{align*}
&\text{N} &\text{Br} &\xrightarrow{\text{R}} &\text{O} &\text{N}^* \\
&\text{O} &\xrightarrow{\text{ROH}} &\text{N}^- &\text{OR}
\end{align*}
\]
Doering-LaFlamme allene synthesis:

\[ \begin{array}{ccc}
\text{Br} & \text{Br} \\
R & R \\
\text{or} & \\
H & \text{Br} \\
R & R \\
\end{array} \]

\[ \xrightarrow{nBuLi} \]

\[ \text{Li} \]

\[ \text{Br} \]

\[ \xrightarrow{\text{rot.}} \]

\[ R \]

\[ C \]

\[ C=\]

\[ R \]

a **carbenoid**

(*vide infra*)

Corey-Winter olefination:

\[ \begin{array}{ccc}
\text{S} \\
\text{O} & \text{O} \\
R & R \\
\end{array} \]

\[ \xrightarrow{\text{PPh}_3} \]

\[ \text{O} \]

\[ \text{S} \]

\[ \text{PPh}_3 \]

\[ \xrightarrow{\text{rot.}} \]

\[ R \]

\[ R \]

\[ \text{CO}_2 \]

\[ R \]

\[ \equiv \]

\[ R \]