RATIO OF SEVEN- TO SIX-MEMBERED RING SULFONES IN THE
CYCLIZATION OF A SULFONYL CARBENE

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The ratio of 7- to 6-membered ring intramolecular cyclization
product increases with decreasing solvent polarity in the \((C_6F_5Cu)_4\) catalyzed decomposition of 4 and with increasing temperature in
the uncatalyzed decompositions. Possible explanations are discussed.

To account for the dependence of the ratio of \(\lambda:\xi\) upon solvent polarity
in the thermolysis of biphenyl-2-sulfonyldiazomethane (4) we proposed
a transition state \(\lambda\) in which bond formation between the carbene and the
two ring carbon atoms had proceeded to different extents.\(^1\) We now report
the effect of solvent polarity on the catalyzed low temperature decomposition
of 4 and a striking temperature effect on the \(\lambda:\xi\) ratio from the free
carbene, which shed further light upon the mechanism of the intramolecular
cyclization.

Smooth decomposition of 4 at room temperature was achieved using
catalytic amounts of \((C_6F_5Cu)_4\). Change in the solvent polarity \((CHC_13 -
C_6H_{12})\) has a marked effect upon the \(\lambda:\xi\) ratio. As the weight % of the
non-polar solvent increases from 0 to 100% in the mixture the \(\lambda:\xi\) ratio
changes from 1.6 to 5.8. The total yield \(\lambda + \xi\) remains relatively constant
(53-58%). This is not only a mechanistically, but also a preparatively,
useful observation. No intermolecular insertion into solvent by the carbenoid
intermediate was observed; the ethylene \(\xi\) was obtained, but its formation
was completely suppressed by the addition of piperylene,\(^2\) while the \(\lambda:\xi\)
ratio was unchanged in the presence of piperylene. This confirms that dimer 3 probably arises from the triplet, \(^3\), and supports an unsymmetrical transition state leading to \(^2\).

\[
\begin{align*}
\text{SO}_2\text{CHN}_2 & \rightarrow \text{SO}_2 \quad + \quad \text{SO}_2\text{CH=CHSO}_2\text{Ar} \\
\end{align*}
\]

The triphenylphosphazene (6), mp 173\(^\circ\), was prepared from \(^1\) and \(\text{Ph}_3\text{P}\) and was used as a source \(^5\) of the sulfonylcarbene at temperatures above the normal decomposition temperature of \(^4\). This permitted a study of the variation in the \(\frac{2}{3}\) ratio from \(\frac{3}{3}\) in cyclohexane between 135-180\(^\circ\) (Table). Appreciable amounts of cyclohexane insertion product (\(\frac{7}{7}\)) were obtained as well.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Reaction time (min)</th>
<th>% Yields</th>
<th>(\frac{2}{3})</th>
<th>(\frac{3}{3})</th>
<th>(\frac{7}{7})</th>
<th>(\frac{2+3+7}{\frac{3}{3}})</th>
<th>(\frac{3}{3}:\frac{2}{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>135</td>
<td>600</td>
<td>6.9</td>
<td>31.6</td>
<td>17.0</td>
<td>55.5</td>
<td>2.3</td>
<td>4.6</td>
</tr>
<tr>
<td>150</td>
<td>120</td>
<td>6.1</td>
<td>37.3</td>
<td>16.0</td>
<td>59.4</td>
<td>2.7</td>
<td>6.1</td>
</tr>
<tr>
<td>160</td>
<td>30</td>
<td>5.7</td>
<td>42.4</td>
<td>15.2</td>
<td>63.3</td>
<td>3.2</td>
<td>7.4</td>
</tr>
<tr>
<td>170</td>
<td>20</td>
<td>5.8</td>
<td>45.0</td>
<td>15.8</td>
<td>66.6</td>
<td>3.2</td>
<td>7.7</td>
</tr>
<tr>
<td>180</td>
<td>10</td>
<td>6.0</td>
<td>50.0</td>
<td>15.8</td>
<td>71.8</td>
<td>3.5</td>
<td>8.4</td>
</tr>
</tbody>
</table>
It is clear that, with increasing temperature, the absolute yields of \( \varphi \) and \( \omega \) remain approximately constant but that of \( \chi \) increases appreciably. Alternatively, the relative yield of \( \chi \) may be viewed as going up from 56.9 to 69.6% while those of \( \varphi \) and \( \omega \) go down from 12.4 to 8.4% and 30.6 to 22.0%, respectively. The ratio of seven- to six-membered ring cyclization product almost doubles with a 45° increase in temperature. Both \( \chi \) and \( \omega \) are stable under the reaction conditions and at 180° in the presence of \( \text{Ph}_3\text{P} \). Unlike \( \text{N-sulfonylazepines} \) \( \chi \) does not rearrange thermally to \( \varphi \) at 300° for 1 hr.

Of these, two can be retained for further discussion. The dimer and sulfonate ester \(^1\) are products of triplet carbene reactions. The intermolecular insertion product into cyclohexane \(^7\) and intramolecular cyclization products are singlet carbene (or carbenoid in the catalyzed decompositions) products. To account for the temperature effect one could postulate that two different singlet carbene states are involved: the cyclohexane insertion \( \chi \) and six-membered cyclization \( \omega \) products could arise from an \( S_0 \) state, while the cycloheptatriene \( \varphi \) could arise from an \( S_1 \) carbene (or thermally excited linear \( S_0 \) carbene) via a norcaradiene intermediate. \( S_0 \) carbenes are thought to add via an unsymmetrical transition state to olefinic double bonds; \(^8\) this would be similar to our previously postulated \(^1\) T.S. \( \xi \) which could readily open up to \( \varphi \) via the dipolar \( \sigma \)-complex. On the other hand, \( S_1 \) or linear \( S_0 \) methylene is predicted to add via a symmetric T.S. to ethylene, \(^9\) and such a T.S. would transform smoothly either to the norcaradiene intermediate or directly, in a concerted bond-forming ring-expansion process, to the cycloheptatriene \( \varphi \), a process that would be favoured by entropy considerations. Raising the temperature would increase the population of \( S_1 \) carbene \(^10\) and hence \( \varphi \) relative to \( \omega \). \(^14\)
A simpler explanation would be that \( \xi, \delta, \) and \( \gamma \) all arise from the \( S_0 \) singlet carbene by competing intra- and intermolecular pathways. Formation of \( \gamma \) would be favoured at the higher temperatures, provided \( \xi \) and \( \delta \) were formed irreversibly (\( \xi = \gamma \) does not obtain as shown earlier) from a common norcaradiene intermediate (\( \delta \)), and \( \Delta H^\delta \) is higher that \( \Delta H^\gamma \). This is depicted in the Scheme. Preliminary results\(^1,17\) with the 4'-bromo- and 4'-nitro-derivatives of \( \gamma \) support the above conclusions.

This work was supported by a grant from the National Science Foundation and by a Graduate Council Fellowship (to V. A.). We wish to thank Prof. L. Salem for bringing the possible involvement of an \( S_1 \) carbene to our attention and for subsequent encouraging discussions.

Scheme


4. Gave the correct analytical and spectral data.


6. The lower overall yields of $\mathcal{Q} + \lambda + \pi$ at lower temperatures could be due to a possible competition from phosphorane formation from any solid $\mathcal{P}$. Attempts to isolate such a phosphorane were unsuccessful, however.


10. The $S_1/2$ state of CH$_2$ lies ca. 20 kcal above the $S_0$ state and ca. 10 kcal above the linear $S_2/2$ state and its involvement in the 2062 A photolysis of ketene is suspected. An $S_1$ sulfonyl carbene may be appreciably stabilized relative to the $S_0$ state by the same types of interactions proposed to account for the formation of ar-sulfonyl dicarbanions:

\[
\begin{align*}
\text{Ar} & \rightarrow \text{C} \rightarrow \text{R} \leftrightarrow \text{Ar} - \overset{\equiv \text{C} \rightarrow \text{R}}{\text{Ar}} \\
\text{S} & \rightarrow \text{C} \rightarrow \text{R} \leftrightarrow \text{Ar} - \overset{\equiv \text{C} \rightarrow \text{R}}{\text{Ar}}
\end{align*}
\]

and might make the $S_1$ sulfonyl carbene thermally accessible in solution.


14. An argument against an $S_1$ intermediate could be that one might expect it to be trapped by piperylene in the same way as is the triplet.

15. If such a competitive ring-opening of $\mathcal{P}$ to $\lambda$ and $\pi$ is assumed log ($k_\lambda/k_\pi$) can be plotted vs. $1/T$ to give $\Delta H^\circ = 4.9 \pm 1$ kcal/mole and $\Delta S^\circ = 15 \pm 2$ e.u.


17. R. A. Abramovitch and V. Alexanian, unpublished results.

Received, 20th July, 1974