Photochemistry of aryl-substituted trigermanes

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(Received December 10th, 1988)

Abstract

The photolysis of phenyl-substituted trigermanes affords digermanes and germlyenes. Trapping experiments, matrix isolation, and laser-photolysis studies indicate that the photoreaction of these compounds involves both the extrusion of germlyenes and the formation of germyl radicals. The mechanism by which the germlyenes are generated is discussed.

The photochemistry of organopolysilanes having a α(Si–Si)/π(C–C) conjugated system has been the subject of considerable interest in synthetic chemistry. However, photochemical studies on the germanium analogue are scarce [1]. We describe herein the first photoreaction of the aryl-substituted trigermanes: (PhMe₃Ge)₃GeMe₂ (1) [2], (Me₃Ge)₃GePhMe (2) [3], and (Me₃Ge)₃GePh₂ (3) [3].

Irradiation of the trigermanes 1–3 in cyclohexane with a 110-W low-pressure Hg arc lamp at room temperature under an argon atmosphere gave the digermanes: (PhMe₃Ge)₂ (33%) for 1, and (Me₃Ge)₂ (25% and 40%) for 2 and 3. In order to detect possible reaction intermediates, cyclohexane solutions of 1–3 and a large excess of 2,3-dimethylbutadiene were similarly irradiated. Digermanes and germacyclopentenes (18–33%) were obtained as the main products. 3-Butenylgermyl derivatives were also detected as minor products (< 5%). Formation of germacyclopentenes suggests the intermediacy of germlyenes [4].

\[
\begin{align*}
R^2_3\text{Ge} & \rightleftharpoons Ge \rightleftharpoons GeR^2_4 \quad \text{or} \quad \lambda \rightarrow (R^2_3\text{Ge})_2 + R^2_3\text{Ge} \\
R^2_3 & \text{Ger} \end{align*}
\]

In the presence of carbon tetrachloride, photolysis of 1–3 in cyclohexane afforded chlorogermanes, chlorodigermanes, and dichlorogermanes, such as for example, PhMe₃GeCl, PhMe₃GeGeMe₃Cl, and PhMeGeCl₂, respectively, together with hexachloroethane. The formation of chlorogermane and chlorodigermane seems to indicate the intermediacy of the germyl and digermyl radicals produced by germanium–germanium bond cleavage of 1–3. This may be further substantiated by
Table 1
The results of photochemical reactions of 1–3

<table>
<thead>
<tr>
<th>Trigermene</th>
<th>Trapping agent</th>
<th>Main products (yield %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{PhMe}_2\text{Ge})_2\text{GeMe}_2) ((1))</td>
<td>none</td>
<td>((\text{PhMe}_2\text{Ge})_2) (33), [GeMe(_2)] (18)</td>
</tr>
<tr>
<td></td>
<td>CCl(_4)</td>
<td>((\text{PhMe}_2\text{Ge})_2) (10), \text{PhMe}_2\text{GeCl} (81), \text{PhMe}_2\text{GeMe}_2\text{GeCl} (52)</td>
</tr>
<tr>
<td>((\text{Me}_3\text{Ge})_2\text{GePhMe}) ((2))</td>
<td>none</td>
<td>((\text{Me}_3\text{Ge})_2) (39), [GePhMe(_2)] (32)</td>
</tr>
<tr>
<td></td>
<td>CCl(_4)</td>
<td>((\text{Me}_3\text{Ge})_2) (9), \text{Me}_3\text{GeCl} ({\text{a}}), \text{Me}_3\text{GePhMeGeCl} (29)</td>
</tr>
<tr>
<td>((\text{Me}_3\text{Ge})_2\text{GePh}_2) ((3))</td>
<td>none</td>
<td>((\text{Me}_3\text{Ge})_2) (46), [GePh(_2)] (22)</td>
</tr>
<tr>
<td></td>
<td>CCl(_4)</td>
<td>((\text{Me}_3\text{Ge})_2) (17), \text{Me}_3\text{GeCl} ({\text{a}}), \text{Me}_3\text{GePh}_2\text{GeCl} (14)</td>
</tr>
</tbody>
</table>

\({\text{a}}\) The yield of \text{Me}_3\text{GeCl} could not be determined. The retention time of \text{Me}_3\text{GeCl} on GLC partially overlapped with that of CCl\(_4\).

The presence of 3-butenylgermyl derivatives in the photo-products detected by means of GC-MS. The formation of dichlorogermane can be rationalized as evidence for interconversion of germynes. The results of the photochemical reactions of 1–3 are summarized in Table 1.

In order to obtain more information on the reaction intermediates and primary photochemical processes, matrix isolation at 77 K and laser-photoysis at 293 K were also carried out. UV irradiation (low pressure Hg arc lamp for 30 min) of 1–3 (10\(^{-4}\) M) in rigid 3-methylpentane (3-MP) at 77 K produced yellow glasses with broad absorption bands at 422 nm for 1, 456 nm for 2, and 462 nm for 3. These bands disappeared upon warming-up. In a glass doped with 2,3-dimethylbutadiene,

Table 2
Rate constants for disappearance of the transients produced by photolysis of 1–3 in cyclohexane

<table>
<thead>
<tr>
<th>Trigermene</th>
<th>(\lambda_{\text{max}}) nm</th>
<th>(k/\epsilon) ({\text{a}})</th>
<th>Rate constant ((M^{-1} s^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Et(_3)SiH</td>
<td>CCl(_4)</td>
</tr>
<tr>
<td>1</td>
<td>320</td>
<td>7.0 \times 10^6</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>420</td>
<td>2.5 \times 10^7</td>
<td>2.4 \times 10^7</td>
</tr>
<tr>
<td>2</td>
<td>320</td>
<td>5.5 \times 10^5</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>440</td>
<td>2.2 \times 10^6</td>
<td>2.2 \times 10^6</td>
</tr>
<tr>
<td>3</td>
<td>330</td>
<td>4.3 \times 10^5</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>3.0 \times 10^6</td>
<td>7.2 \times 10^5</td>
</tr>
</tbody>
</table>

\({\text{a}}\) \(k\) is the rate constant of second-order decay and \(\epsilon\) is the corresponding molar extinction coefficient.
heating yielded the expected trapping products, germacyclopentenes. The yellow species with $\lambda_{\text{max}}$ at 422, 456, and 462 nm, obtained in this study can be assigned to the corresponding germynes on the basis of trapping experiments and from a comparison of the spectral characteristics with those of the germynes previously reported [5–7]. The absorption spectrum of Ph$_2$Ge: generated from 3 is shown in Fig. 1.

Laser-photolysis ($\lambda$ 266 nm, pulse width 5 ns, power 10 mJ per pulse) of 1–3 (10$^{-3}$ M) gave two well-separated transient absorption bands as shown in Fig. 2. The transient at longer wavelength can be assigned to the absorption of a germylene by comparing its spectral and chemical properties with those previously reported [5,8,9]. The transients arising from 1–3 in cyclohexane decayed under second-order kinetics, suggesting the formation of digermenes [1,8]. This is substantiated further by quenching experiments with a germylene trapping agent, 2,3-dimethylbutadiene. The transients from 1–3 in cyclohexane in the presence of large excesses of the diene decayed under first-order kinetics. These transients were quenched with

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**Fig. 1.** Spectral change in absorption of (Me$_3$Ge)$_2$GePh$_2$ (3) during irradiation in 3-methylpentane glass at 77 K.

**Fig. 2.** Transient absorption spectrum at 200 ns after photoexcitation of (Me$_3$Ge)$_2$GePh$_2$ (3) in degassed cyclohexane solution at 293 K.
carbon tetrachloride [5]. However, the transient was not quenched with ethanol [8] and this is consistent with its chemical properties. On the other hand, the transient at shorter wavelength can be assigned to the absorption of the phenyl-substituted digermy radical produced by germanium–germanium bond cleavage of 1–3. The assignment of the transient at shorter wavelength is further substantiated by quenching experiment with carbon tetrachloride. Addition of carbon tetrachloride, an effective germyl radical scavenger [10,11], quenched the transient absorption. The transient absorption of alkyl-substituted germyl radicals is below 300 nm [12].

\[
\begin{align*}
R^2 \quad R^2 \\
R^3 Ge - Ge - GeR^3 + CCl_4 & \longrightarrow R^3 Ge - Ge - Cl + R^3 GeCl \\
R^3 \quad R^2
\end{align*}
\]

The experimentally determined decay constants of these transient species are summarized in Table 2.

Formation of germylene can be accounted by two mechanisms from the results described above. First, germylene might be formed by a simple extrusion process.

\[
\begin{align*}
R^2 \quad R^2 \\
R^3 Ge - Ge - GeR^3 \quad \xrightarrow{hv} \quad [R^2 Ge - GeR^3] & \longrightarrow (R^3 Ge)_2 + R^2 R^3 Ge: \\
R^3 \quad R^3
\end{align*}
\]

Second, germylene might be produced by photodecomposition of digermyl radical generated from germanium–germanium bond cleavage of 1–3.

\[
\begin{align*}
R^2 \quad R^2 \\
R^3 Ge - Ge - GeR^3 \quad \xrightarrow{hv} \quad R^3 Ge - Ge \cdot + GeR^3 \\
R^3 \quad R^3
\end{align*}
\]

To elucidate the mechanism of germylene formation, we carried out the photodecomposition of a digermyl radical by both isolation matrix and laser-photoysis techniques. The phenyltetramethylgermyl radical was photochemically generated from its parent digermene (phenyltetramethylgermane) in 3-MP at 77 K. However, there was no signal of a germylene by successive irradiation of the phenyltetramethylgermyl radical. In a 3-MP glass doped with carbon tetrachloride, heating yielded the expected trapping product, phenyltetramethylchlorodigermane [13].

The laser-photoysis of 1–3 was carried out by two-step excitation. The 308 nm laser-photoysis of the transient at shorter wavelength with a decay time of 1 \( \mu s \) produced by the 266 nm laser-photoysis of 1–3 in cyclohexane was performed. However, there was no change in intensity of either transient because the digermyl radical was at shorter wavelength and the germylene at longer wavelength [13]. Thus, germylenes are not produced via digermyl radicals but may be photo-extruded from the trigermane itself.

Consequently, the photoysis of phenyl-substituted trigermanes involves both the
simple extrusion of germylenes and the formation of germyl and digermyl radicals as shown in Scheme 1.

\[
\begin{align*}
R^2 & \xrightarrow{hP} (R_2'Ge) _2 + R^2R^2Ge: \\
R_3'Ge - Ge - GeR_3 & \rightarrow R^2Ge - Ge^* + \cdot GeR_3 \\
R^3 & 
\end{align*}
\]

Scheme 1

Acknowledgement. We wish to thank Drs. Hisaharu Hayashi and Yoshio Sakaguchi of the Institute for Physical and Chemical Research for providing laser-photoysis apparatus and for helpful discussions. Partial financial support of this research by a Grant-in-Aid from the Ministry of Education, Science, and Culture of Japan is greatly acknowledged.

References

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