Synthesis and thermal stability of silicon-containing esters of phosphorus acids

5.* The relative migration ability of substituents at the silicon atom in the thermal rearrangement of trialkylsilylmethyl diphenyl phosphates

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A number of trialkylsilylmethyl diphenyl phosphates MeRR'SiCH2OP(O)(OPh)2 (1a--e: R = Et (a), Pr (b), CF3CH2CH2 (c, e), Me3SiCH2 (d); R' = Me (a--d), Et (e)) were synthesized and their thermal rearrangement, of the 1,2-shift type, was studied. The rearrangement consists of the migration of an alkyl group from Si atom to the methylene carbon atom and gives the corresponding silyl esters. The rate of the rearrangement was found to increase in the order 1d < 1b < 1a < 1 (R = R' = Me) < 1c corresponding to the enhancement of the total inductive effect (-f) of the substituents at the Si atom. The relative migration ability of the substituents at the Si atom, determined by GC/MS analysis of the disiloxane fraction resulting from hydrolysis of pyrolyzed phosphates 1a--e, increases in the order R = Pr < Et < CF3CH2CH2 < Me << Me3SiCH2, which differs substantially from the order in which the rate of the rearrangement of phosphates 1a--d changes. The electronegativity of the migrating group affects noticeably the relative ability to migrate.

Key words: trialkylsilylmethyl diphenyl phosphates, thermal rearrangement, relative migration ability of substituents.

The ability of various alkyl substituents at the Si atom to migrate in rearrangements of the 1,2-shift type has been studied mainly in relation to rearrangements of trialkyl(chloromethyl)silanes either catalyzed by Lewis acids (mostly AICI3) or caused by fluoride ions. By now, thermally induced rearrangements of the 1,2-shift type have been discovered and studied fairly comprehensively for a large number of silylmethyl esters of oxygen-containing acids of pentavalent phosphorus. However, the relative migration ability (RMA) of substituents at the Si atom has not been studied systematically. It is known that a hydride ion migrates more preferably than a methyl group, and during the thermal rearrangement of dimethylphenylsilylmethyl diphenyl phosphates, the phenyl group migrates. The present study is devoted to the determination of relative migration abilities of alkyl groups in the thermal rearrangement of trialkylsilylmethyl phosphates.

Previously we have shown that on heating above 175 °C, trialkylsilylmethyl diphenyl phosphates undergo rearrangement accompanied by the migration of an alkyl radical R from the Si atom to the methylene C atom to give the corresponding silyl esters.

\[ R_3SiCH_2OP(O)(OPh)_2 \xrightarrow{175 \degree C} R_2SiOP(O)(OPh)_2 \text{CH}_2-R \]

It was found that the rearrangement rate increases in the following sequence of substituents: R = Pr < Et < Me < CF3CH2CH2.

To study the RMA of substituents at the Si atom, we chose a series of dimethylalkylsilylmethyl diphenyl phosphates (1a--d) and compared the rates of migration of the groups R with that of the methyl group. In order to find out whether or not the RMA depends on the nature of the neighboring substituents attached to the Si atom, we also studied the thermolysis of ethyl(methyl)(3,3,3-trifluoropropyl)silylmethyl diphenyl phosphate (1e).

Phosphates 1a--e were synthesized by the previously described procedure (Scheme 1).

The rearrangement of phosphates 1a--d can give two types of silyl esters (5a--d and 6a--d) resulting from the migration of radical R or one of the methyl groups attached to the Si atom, respectively (Scheme 2).

The rearrangement of phosphate 1e can, in principle, give three silyl esters (7--9), the products of migration of the methyl, ethyl, or trifluoropropyl group from the Si atom, respectively (Scheme 3).

In fact, the \(^1H\) NMR spectra of the four pyrolyzates obtained by heating phosphates 1a--d for 5 h at 200 °C, translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 9, pp. 1767--1772, September, 1998.
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Scheme 1

\[
\begin{align*}
2a-e & \xrightarrow{\text{MeRR'SiCH}_2\text{Cl, AcOK}} 3a-e \\
& \xrightarrow{\text{MeRR'SiCH}_2\text{OAc, LiAlH}_4} 4a-e \\
& \xrightarrow{\text{MeRR'SiCH}_2\text{OP(O)(OPh)Cl, } \text{Ph}_2\text{POCl}} 5a-e \\
& \xrightarrow{\text{MeSiOP(O)(OPh)Cl}} 6a-e
\end{align*}
\]

\[R = \text{Et (a), Pr (b), CF}_3\text{CH}_2\text{CH}_2 \text{(c, e), Me}_3\text{SiCH}_2 \text{(d); } R' = \text{Me (a–d), Et (e)}\]

Table 1. Degree of rearrangement (\(\eta\)) of phosphates 1a–e

| Starting compound | R | R' | \(\Sigma \sigma_i\) | \(\eta\) (%)
<table>
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<tbody>
<tr>
<td>1a</td>
<td>Et</td>
<td>Me</td>
<td>0.080</td>
<td>39</td>
</tr>
<tr>
<td>1b</td>
<td>Pr</td>
<td>Me</td>
<td>0.080</td>
<td>37</td>
</tr>
<tr>
<td>1c</td>
<td>CF(_3)CH(_2)CH(_2)</td>
<td>Me</td>
<td>0.007</td>
<td>65</td>
</tr>
<tr>
<td>1d</td>
<td>Me(_3)SiCH(_2)</td>
<td>Me</td>
<td>0.120</td>
<td>30</td>
</tr>
<tr>
<td>1e</td>
<td>CF(_3)CH(_2)CH(_2)</td>
<td>Et</td>
<td>-0.013</td>
<td>63</td>
</tr>
<tr>
<td>Me(_2)SiCH(_2)OP(O)(OPh)Cl</td>
<td>Me</td>
<td>-0.060</td>
<td>58</td>
<td></td>
</tr>
</tbody>
</table>

Note. The \(\Sigma \sigma_i\) values were calculated using the \(\sigma_i\) values reported in the literature.\(^{11}\)

in addition to the signals of the initial compounds, contained two singlets in the region typical of silylmethyl protons in the rearranged silyl esters (8 0.17–0.25). This indicates the formation of two rearranged products. The \(^1\)H NMR spectrum of the pyrolyzate formed from phosphate 1e, together with the signal for the silylmethyl groups of the initial compound, contained two singlets belonging to the methyl groups in silyl esters 8 and 9 (silyl phosphate 7 does not contain Me groups attached to the Si atom).

Scheme 2

\[
\begin{align*}
\text{MeSiCH}_2\text{OP(O)(OPh)Cl} & \xrightarrow{200 ^\circ \text{C}} \text{MeSOOP(O)(OPh)}_2 + \text{MeSiOP(O)(OPh)}_2 \\
& \xrightarrow{R' - \text{CH}_2} \text{CH}_2\text{Me}
\end{align*}
\]

\[1a-d \quad 5a-d \quad 6a-d\]

To determine the yields of the silyl esters resulting from thermolysis of phosphates 1a–e, the pyrolysis products were hydrolyzed. Hydrolysis of the mixture of silyl esters 5a–d and 6a–d gave a ternary mixture of the corresponding isomeric disiloxanes 10–12 (Scheme 4).

Scheme 3

\[
\begin{align*}
\text{Et} & \xrightarrow{\text{MeSiCH}_2\text{OP(O)(OPh)Cl, } \text{200 }^\circ \text{C}} \text{CH}_2\text{Me}
\end{align*}
\]

\[1e \quad 7 \quad 8 \quad 9\]

When phosphates 1a–e were kept at 200 °C for 5 h, one unresolved broad signal with \(\delta = 20\) to -21 from the thermolysis products appeared in the \(^{31}\)P NMR spectra in all cases. The degree of rearrangement was determined from the ratio of the signal areas of the initial phosphate and the resulting silyl esters. The rate of rearrangement of phosphates 1a–e, as in the case of the thermal rearrangement of the trialkylsilylmethyl diphenyl phosphates studied previously,\(^9\) increased with an increase in the total inductive effect \(-/\Sigma \sigma_i\) of the substituents R and R' at the Si atom (Table 1). Thus for compounds 1a–d, the rearrangement rate increases in the order \(R = \text{Me}_3\text{SiCH}_2 < \text{Pr} < \text{Et} < \text{Me} < \text{CF}_3\text{CH}_2\text{CH}_2\).

The relative migration ability of substituent R at the Si atom (\(\theta_R\)) in compounds 1a–d was calculated based on the ratio of the yield of silyl phosphate 5a–d (\(Q_{5a-d}\)) to the yield of the corresponding silyl phosphate 6a–d (\(Q_{6a-d}\)) using Eq. (1) with allowance for the probability coefficient. The RMs of the trifluoropropyl and ethyl groups in relation to the methyl group during thermal rearrangement of phosphate 1e were calculated from Eqs. (2) and (3), respectively.

\[
\begin{align*}
\theta_R &= \frac{Q_{5a-d}}{Q_{6a-d}} \quad (1) \\
\theta_{\text{CF}_3\text{CH}_2\text{CH}_2} &= \frac{Q_8}{Q_7} \quad (2) \\
\theta_{\text{Et}} &= \frac{Q_9}{Q_7} \quad (3)
\end{align*}
\]

To determine the yields of the silyl esters resulting from thermolysis of phosphates 1a–e, the pyrolysis products were hydrolyzed. Hydrolysis of the mixture of silyl esters 5a–d and 6a–d gave a ternary mixture of the corresponding isomeric disiloxanes 10–12 (Scheme 4).

Scheme 4

\[
\begin{align*}
\text{[5a–d + 6a–d]} & \xrightarrow{\text{H}_2\text{O}} \text{Me}_2\text{Si(OH)O-SiMe}_2 + \text{CH}_2\text{R} \cdot \text{CH}_2\text{R}
\end{align*}
\]

\[10a–d \quad 11a–d \quad 12a–d\]

Hydrolysis of the products of thermolysis of phosphate 1e, silyl esters 7–9, gave a six-component mixture consisting of isomeric disiloxanes 13–18 (Scheme 5).

The qualitative and quantitative compositions of the disiloxane fractions of the hydrolysis products were determined by GC/MS analysis. The GC/MS data are presented in Table 2.