Silyl-nitrogen compounds:
Part XII – Mode of addition reactions in trisila-phospha-triazene

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Tris(trimethylsilyl)-2-phospha-1-triazene (Me₃Si)₃N-P=N(SiMe₃) (1) reacts with alkyllithium RLi (R = Me, Bu) to form an intermediate amide at low temperature, which rearranges into phosphoranide at room temperature. The intermediate amide reacts with Me₆SnCl to form phosphine, (Me₆Sn)₃P(R)-N(SiMe₃)(SnMe₃) which rearranges slowly at room temperature to form phosphorane (Me₆Sn)₃P(R)(SnMe₃)k(N=NSiMe₃). However, a similar silyl derivative (Me₆Si)₂N-P(R)-N(SiMe₃)k is stable at room temperature and does not migrate intramolecularly into phosphoran.

Tetrakis(trimethylsilyl)-2-phospha-l-tetrazene (Me₆Si)₂N-N(SiMe₃)P=N(SiMe₃)I and pentakis(trimethylsilyl)-3-phospha-2-pentazene (Me₆Si)₂N-N(SiMe₃)-P=N-N(SiMe₃)₂ 24 have been found to be very reactive molecules with respect to oxidative addition as well as addition at P=N. In continuation of these studies, 1,3,3-tris(trimethylsilyl)-2-phospha-l-triazene (Me₆Si)₃N-P=N(SiMe₃) (1) has been reacted with alkyllithium followed by treatment with Me₆ECI (E = Sn, Si) to find out the preference of phospha-triazene towards oxidative addition or addition at P=N.

Materials and Methods

All reactions and measurements were done as reported earlier.

General procedure:

Methylithium (12.0 mmol) solution in diethylether or butyllithium (12.0 mmol) solution in n-hexane was added dropwise to an equivalent solution of 1,3,3-tris(trimethylsilyl)-2-phospha-1-triazene (1) in 25 ml of diethylether at -78°C under constant stirring. The temperature of the reaction mixture was slowly allowed to rise to 0°C. The ³¹P/¹H NMR of the reaction mixture showed a singlet at δ 110.3. An equivalent amount of Me₆ECI (E = Sn, Si) was then added and the reaction mixture allowed to come to room temperature. It was further stirred for 6-8h. Lithium chloride was separated from colourless solution by filtration and the filtrate was evacuated to remove solvent and other volatile impurities. It was then heated in vacuo (to 10⁻³ torr) to obtain colourless liquids: (3a) at 60°C/10⁻³ torr, (3b) at 80°C/10⁻³ torr, (5a) at 55°C/10⁻³ torr, (5b) at 70°C/10⁻³ torr.

A known weight of compound (3) in C₆D₆ was sealed in an evacuated NMR tube which was monitored by ¹H NMR and ³¹P NMR for about four weeks at room temperature. After one week ³¹P NMR of (3a) and (3b) showed higher field peaks at δ -12.6 and -3.5 in addition to their original peaks at δ 67.2 and 74.1 respectively. In two weeks, the intensity of new and old signals was almost same. After a period of four weeks, the signals at δ 67.2 and 74.1 were of very small intensities which indicated the transformation of most of (3) into (4). The compound (3) was also taken in large quantity (10.0 mmol) in an evacuated ampule and kept at room temperature so that it could be gradually changed into compound (4). After two months it was opened, evacuated and distilled in vacuo (10⁻¹ torr) to obtain a colourless liquid (4a) at 65°C/10⁻¹ torr and (4b) at 85°C/10⁻¹ torr.

All the compounds (3-5) are soluble in common organic solvents. Mass spectra of these compounds show low intensity molecular ion peak M⁺. Other prominent fragments corresponding to (M-Me)^⁺.
Results and Discussion

Bis[bis(trimethylsilyl)amino](bromo)phosphine decomposes on warming to provide 1,3,3-tris(trimethylsilyl)-2-phospha-1-triazene (1) as a light green liquid.

\[
\text{(1)}
\]

It is reported that (1) reacts with MeLi to form a probable intermediate iminophosphoranide (A) which on hydrolysis forms a phosphorane (B).

\[
\text{(1)} + \text{MeLi} \rightarrow \text{(A)} \rightarrow \text{(B)}
\]

However, in our earlier investigations on tetrasila-2-phospha-1-tetrazene \(\text{(Me}_3\text{Si})_2\text{N-} \text{N(SiMe}_3\text{)}_2 \text{P=N(SiMe}_3\text{)\text{'}}\), we observed that an intermediate amide is formed at first at low temperatures which then rearranges at higher temperatures to form an iminophosphoranide. Similar results are also expected for studies on trisilaphosphatriazene.

Compound (1) loses its green colour when treated with an equivalent amount of RLi (where R = Me, Bu) at -78°C. This solution is stable up to 0°C. Its \(\text{^1H NMR}\) shows a singlet at \(\delta 110.3\) indicating a phosphorus(III) derivative that is, an intermediate amide (C). However, if this solution is allowed to stay at room temperature and monitored by \(\text{^31P NMR}\) then a new signal appears at 13.2 ppm besides the one at 110.3 ppm. This new signal grows in size with the passage of time and the original signal at 110.3 ppm shows a corresponding decline in size. The signal at 13.2 ppm is attributed to phosphoranide (D).

\[
\text{(1)} \rightarrow \text{(C)} \rightarrow \text{(D)}
\]

A freshly prepared solution of (1) and RLi (R = Me, Bu) at -78°C, when treated with an active halide Me\(_3\)SnCl at 0°C, forms a colourless liquid in a reaction given here

\[
\text{(1)} + \text{RLi} \rightarrow \text{(2)} \rightarrow \text{(3)} \rightarrow \text{(4)}
\]

The \(\text{^1H NMR}\) (Table 1) and \(\text{^29Si NMR}\) (Table 2) values of (3a) support phosphine(III) structure (3). The \(\text{^31P [^1H]}\) NMR spectra in C\(_6\)D\(_6\) of (3a) and (3b) show resonance signals at \(\delta 67.2\) and 74.1 respectively. This range is characteristic of P(III) supportive of structure (3). The \(\text{^119Sn NMR}\) spectra of (3a) and (3b) show a resonance at \(\delta 111.3\) and 105.6 ppm, respectively. This is typical of four-coordinated Sn(IV). Sealed samples of (3a) and (3b) were monitored by \(\text{^31P NMR}\) in C\(_6\)D\(_6\) at room temperature. After a week, new higher field signals at \(\delta -12.6\) and -3.5 looked quite prominent besides the original lower field signals at \(\delta 67.2\) and 74.1. After two weeks, the intensity of new and old signals was almost similar. This shows that (3) transforms slowly into (4). In a few weeks time the transformation is still not complete.

The \(\text{^1H NMR}, \text{^29Si NMR}\) (Tables 1 & 2) and \(\text{^31P NMR}\) of (4a) and (4b) are typical of phosphorane structure (4). The \(\text{^119Sn NMR}\) spectrum of (4) shows a doublet at 0.8 \((\delta 4a)\) or -0.07 ppm \((\delta 4b)\) with \(\text{J}_{\text{SnP}} = 752 \text{ Hz}\). This coupling constant value shows that Me\(_3\)Sn group is directly attached to P in (4).

Similarly, a solution of (1) and RLi at 0°C reacts with Me\(_3\)SiCl to form a colourless liquid (5). The \(\text{^1H NMR}\) (Table 1) and \(\text{^29Si NMR}\) (Table 2) data of (5a) and (5b) in C\(_6\)D\(_6\) support phosphine(III) arrangement (5). The \(\text{^31P [^1H]}\) NMR spectra of (5a) and (5b) show a resonance at \(\delta 105.9\) and 100.3 ppm, respectively. This is characteristic of three-coordinated P(III).
Table 1 — $^1$H NMR data in benzene(n-hexane) in ppm (coupling constant in Hz)

<table>
<thead>
<tr>
<th>Signal group</th>
<th>(3a)</th>
<th>(3b)</th>
<th>(4a)</th>
<th>(4b)</th>
<th>(5a)</th>
<th>(5b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Me}_3\text{Si})_2\text{N-P}$</td>
<td>0.27(0.22)</td>
<td>0.31(0.23)</td>
<td>0.22</td>
<td>0.18</td>
<td>0.33(0.31)</td>
<td>0.41(0.32)</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si}\text{N-P-Sn}$</td>
<td>0.18(0.11)</td>
<td>0.21(0.13)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Sn}\text{N-P-Si}$</td>
<td>0.25(0.20)</td>
<td>0.25(0.22)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si}=\text{N-P-Sn}$</td>
<td>-</td>
<td>0.18</td>
<td>0.27</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Sn}=\text{P-N-Si}$</td>
<td>-</td>
<td>0.27</td>
<td>0.22</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Me}=\text{P}$</td>
<td>1.32</td>
<td>-</td>
<td>1.18</td>
<td>-</td>
<td>1.39</td>
<td>-</td>
</tr>
<tr>
<td>Bu=P</td>
<td>-</td>
<td>-</td>
<td>1.33m</td>
<td>-</td>
<td>1.33m</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Sn satellites at 54 Hz and 52 Hz; m = multiplet

Table 2 — $^{29}$Si NMR data in $\text{C}_6\text{D}_6$ in ppm

<table>
<thead>
<tr>
<th>Signal group</th>
<th>(3a)</th>
<th>(3b)</th>
<th>(4a)</th>
<th>(4b)</th>
<th>(5a)</th>
<th>(5b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{Me}_3\text{Si})_2\text{N-P}$</td>
<td>6.17</td>
<td>5.93</td>
<td>4.86</td>
<td>4.73</td>
<td>7.75</td>
<td>7.65</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Si}\text{N-P-Sn}$</td>
<td>4.69</td>
<td>4.45</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Me}_2\text{Sn}=\text{P}$</td>
<td>-</td>
<td>-</td>
<td>3.12</td>
<td>4.37</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Compound (5) is stable at room temperature and monitoring $^{31}$P NMR over a period of one month did not show any change in $^{31}$P NMR resonance signals. This shows the inability of (5) to undergo any rearrangement at room temperature.

It appears that the stanny1 substituted amide (3) undergoes slow 1,2-intramolecular rearrangement to form an iminophosphorane (4) but silylated amide does not do so. This is attributed to the higher labile nature of trimethylstannyl group and perhaps the easier overlap of outer orbitals of the larger stannyl group with appropriate orbitals of phosphorus leading thereby to easier migration of stannyl group to form more stable phosphorane. This may not happen for trimethylsilyl group perhaps due to its smaller size and lower lability.

Acknowledgement

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References

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