REACTION OF AMIDES OF ACIDS OF TRIVALENT PHOSPHORUS WITH 3-THIETHANOL

B.A. Arbuzov and O.N. Nuretdinova

It is known [1, 2] that aliphatic thtyranes react with certain compounds of trivalent phosphorus according to the scheme:

\[
\begin{align*}
S + R_3P & \rightarrow S + R_3PS \\
\end{align*}
\]

With tertiary phosphines, the reaction proceeds rapidly at room temperature. Little heating is required when phosphites are used. Such reactions are also known for oxides of olefins [3]. Compounds of the thiethane series also react with compounds of trivalent phosphorus [4]. Thus, when triphenylphosphine or triethyl phosphite were heated with chlorothiethane at the temperature 140° (in boiling xylene) for 70 h, triphenylphosphine sulfide and triethyl thiophosphate were obtained with yields of 93 and 66%, respectively [4]:

\[
\begin{align*}
\text{CH}_2 \quad \text{S} + \text{R}_3\text{P} & \rightarrow \text{R}_3\text{PS} + \text{CH}_2=\text{CH}+\text{CH}_2\text{Cl} \\
\text{R} &= \text{C}_6\text{H}_5\text{O}, \text{C}_6\text{H}_5
\end{align*}
\]

Under the same conditions, 3-thiethanol reacts more slowly. To obtain 34% triphenylphosphine sulfide it was necessary to boil 3-thiethanol and triphenylphosphine in xylene for 115 h [4]. Embarking upon a study of the reaction of certain amides of acids of trivalent phosphorus with 3-thiethanol, glycidol, and thioglycidol, we assumed that the reaction with these alcohols may proceed in two directions.

1. The formation of compounds of pentavalent phosphorus according to the schemes:

\[
\begin{align*}
\text{HOCH}_2\text{CH} & \rightarrow \text{PNR}_2 \rightarrow \text{PNR}_3 \\
\text{HOCH}_2\text{CH} & \rightarrow \text{PNR}_2 \rightarrow \text{PNR}_3 \\
\text{X} &= \text{O}, \text{S}
\end{align*}
\]

2. The production of 3-thiethanyl, glycidyl, and thioglycidyl esters of acids of trivalent phosphorus:

\[
\begin{align*}
\text{HOCH}_2\text{CH} & \rightarrow \text{S} + \text{R}_3\text{NP} \rightarrow \text{CH}_2\text{CH} \rightarrow \text{CH}_2\text{OP} \\
\text{R} &= \text{C}_6\text{H}_5\text{O}; \text{R}^* \text{a} - \text{(C}_6\text{H}_5\text{H})\text{N}; \text{b} - \text{(C}_6\text{H}_5\text{H})\text{N}; \text{c} - \text{C}_6\text{H}_5; \text{d} - \text{CH}_3\text{O}; \text{e} - \text{C}_6\text{H}_5\text{H}; \text{f} - \text{C}_6\text{H}_5\text{O}, \text{C}_6\text{H}_5\text{O}; \\
\text{HOCH}_2\text{CH} & \rightarrow \text{CH}_2\text{CH} \rightarrow \text{CH}_2\text{OP} \\
\text{X} &= \text{O}, \text{S}; \text{R} &= \text{C}_6\text{H}_5\text{O}; \text{R}^* \text{a} - \text{(C}_6\text{H}_5\text{H})\text{N}; \text{b} - \text{CH}_3\text{O}, \text{(C}_6\text{H}_5\text{H})\text{N}
\end{align*}
\]
### TABLE 1. 3-Thiethyl and Glycidyl Esters of Acids of Trivalent Phosphorus

<table>
<thead>
<tr>
<th>Formula of compound</th>
<th>Sp. °C (p, mm Hg)</th>
<th>$d^2_4$</th>
<th>$n_D$</th>
<th>Found, %</th>
<th>Calculated, %</th>
<th>Found, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>P</td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>($C_6H_5)NPOCHCH₀₂</td>
<td>99—99,8 (0,5)</td>
<td>1,0220</td>
<td>1,4970</td>
<td>11,67</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>($C_6H_5)NPOCHCH₀₂</td>
<td>98—100 (0,06)</td>
<td>1,1464</td>
<td>1,5600</td>
<td>12,57</td>
<td>54,59</td>
<td>6,40</td>
</tr>
<tr>
<td>($C_6H_5)NPOCHCH₀₂</td>
<td>58—59 (0,06)</td>
<td>1,1094</td>
<td>1,4770</td>
<td>14,20</td>
<td>40,23</td>
<td>7,22</td>
</tr>
<tr>
<td>($C_6H_5)NPOCHCH₀₂</td>
<td>165—175 (0,07 with dec.)</td>
<td>1,1803</td>
<td>1,6208</td>
<td>11,48</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>($C_6H_5)NPOCHCH₀₂</td>
<td>105 (0,07)</td>
<td>1,0910</td>
<td>1,5600</td>
<td>11,43</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>($C_6H_5)NPOCHCH₀₂</td>
<td>68—71 (0,07)</td>
<td>1,0816</td>
<td>1,4970</td>
<td>13,54</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>($C_6H_5)NPOCHCH₀₂</td>
<td>92—93 (0,5)</td>
<td>0,9838</td>
<td>1,4699</td>
<td>11,94</td>
<td>52,91</td>
<td>10,50</td>
</tr>
<tr>
<td>($C_6H_5)NPOCHCH₀₂</td>
<td>68,5 (0,08)</td>
<td>1,0530</td>
<td>1,4570</td>
<td>15,07</td>
<td>--</td>
<td>6,78</td>
</tr>
</tbody>
</table>