The Reactions of Alkyl Phosphoramides with Benzene in the Presence of Aluminium Chloride

G. SOSNOVSKY\textsuperscript{1a}, E. H. ZARET\textsuperscript{1b}, and B. BÖHNE

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201 USA

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Phosphoramidates, Trialkyl Phosphoric Triamides, Trialkyl Thiophosphoric Triamides, Friedel-Crafts-Type Reactions, Triethylaminimino Phosphine Oxide

The reactions of dialkyl N-alkyl phosphoramidates (1) with benzene in the presence of aluminium chloride give aralkyls arising from cleavages of the P-O-C and N-C bonds. Analogous reactions of diphenyl N-alkyl phosphoramidates (2) and triamides (4), (RNH)\textsubscript{3}P(X), (X = O, S; R = alkyl) also give aralkyls, and these reactions can also occur from primary amines, only the reaction occurs with almost all phosphoramides derived from secondary amines. In addition not all phosphoramides which undergo N-C cleavage yield alkylation products.

Introduction

We have recently reported the production of aralkyls from the reaction of the corresponding alkyl phosphorus esters\textsuperscript{2-4} and peresters\textsuperscript{3} with benzene in the presence of aluminium chloride.

\[
\begin{align*}
R' & \quad \text{P(O)X} + \text{C}_6\text{H}_4\text{H}_2 + \text{AlCl}_3 \rightarrow \\
\text{R'O} & \quad \text{C}_6\text{H}_4\text{H}_2 + \text{C}_6\text{H}_4\text{R} + \text{C}_6\text{H}_4\text{R} + \text{C}_6\text{H}_4\text{R} + \text{C}_6\text{H}_4\text{R} + \\
\text{X = OR', OH, Cl, OP(O)(OR)(OR'), OOCMe}_3
\end{align*}
\]

These reactions proceed very rapidly and appear to involve an alkyl carbonium ion as would be expected in Friedel-Crafts-type reactions\textsuperscript{4}.

No analogy exists between the reactions of carboxylic acid amides and phosphoric acid amides with aromatic substrates in the presence of a Lewis Acid. Thus, the reactions of carboxylic acid amides under these conditions involve the formation of an acylium ion derived from the amide and give an aromatic ketone, whereas we have shown that the reactions of certain phosphoric acid amides produce alkyl aromatics derived from the cleavage of the N-C bond\textsuperscript{4}. We have investigated the scope of this novel N-C bond cleavage and alkylation reaction, and now report the details of that investigation.

Requests for reprints should be sent to Professor Dr. G. SOSNOVSKY, The University of Wisconsin-Milwaukee, Department of Chemistry, Milwaukee, Wisconsin 53201, USA.
phosphoramidate (3) was obtained, indicating the preservation of the P–N bond.

\[(\text{C}_6\text{H}_5\text{O})_2\text{P(O)}\text{NHR} + \text{C}_6\text{H}_6 + \text{AlCl}_3 \rightarrow \text{C}_6\text{H}_5\text{R} + \text{C}_6\text{H}_4\text{R}_2 + (\text{C}_6\text{H}_5\text{O})_2\text{P(O)}\text{NH}_2\]

The results shown in Table II indicate that extensive N–C bond cleavage occurs even though low yields of aralkyls are obtained. In fact, the yield of 3 is almost always much greater than that of the aralkyls.

Another approach to improve the selectivity of alkylation reactions with phosphorus amides was made by the use of N,N′,N″-trialkyl phosphoric triamides (4, X = O) and N,N′,N″-trialkyl thiophosphoric triamides (4, X = S) as alkylating agents.

### Table I. Reactions of dialkyl N-alkyl phosphoramidates (1) with benzene in the presence of aluminium chloride.

<table>
<thead>
<tr>
<th>R</th>
<th>(RO)₂P(O)NHR'</th>
<th>C₆H₅</th>
<th>AlCl₃</th>
<th>C₆H₆</th>
<th>Products [% yield]</th>
<th>C₆H₅R</th>
<th>C₆H₄R₂</th>
<th>C₆H₃R</th>
<th>Amide Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>cyclo-C₆H₁₁</td>
<td>0.11</td>
<td>0.55</td>
<td>0.33</td>
<td>0.45</td>
<td>33ᵇ</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆H₅</td>
<td>cyclo-C₆H₁₁</td>
<td>0.05</td>
<td>0.28</td>
<td>0.17</td>
<td>0.22</td>
<td>36, 19</td>
<td>32ᶜ</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>C₆H₃</td>
<td>H</td>
<td>0.023</td>
<td>0.21</td>
<td>0.075</td>
<td>0.79</td>
<td>41, 12ᵈ</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-C₃H₇</td>
<td>cyclo-C₆H₁₁</td>
<td>0.05</td>
<td>0.12</td>
<td>0.165</td>
<td>0.22</td>
<td>71, 6</td>
<td>1ᵉ</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>i-C₃H₇</td>
<td>cyclo-C₆H₁₁</td>
<td>0.05</td>
<td>0.12</td>
<td>0.165</td>
<td>0.22</td>
<td>67, 11</td>
<td>5ᶠ</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>i-C₃H₇</td>
<td>cyclo-C₆H₁₁</td>
<td>0.12</td>
<td>0.12</td>
<td>0.165</td>
<td>0.22</td>
<td>56, 14</td>
<td>2.5ˢ</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>C(O)C₆H₅</td>
<td>0.05</td>
<td>0.12</td>
<td>0.165</td>
<td>0.22</td>
<td>67, 7</td>
<td>1⁷ᶜ</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td>(–CH₂)₃</td>
<td>0.025</td>
<td>0.36</td>
<td>0.083</td>
<td>0.11</td>
<td>52, 10</td>
<td>0</td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>

For Table I: 
ᵃ Reactant A added to Reactant B (see Experimental). ᵇ The reaction also produced many unidentified aromatic compounds. ᶜ Plus 7 unidentified products comprising a total of 8 wt percent of the product mixture. ᵈ Reaction mixture stirred at 5 °C for 4 hr. èmes Addition of the amide at 5 °C over 45 min; reaction worked up immediately thereafter. ᶠ Reaction mixture stirred at 5 °C for 4 hr; reaction also produced 1 unidentified component comprising 3 wt percent of the product mixture. ᵍ Reaction mixture stirred at 5 °C for 1 hr; reaction also produced 1 unidentified component comprising 3 wt percent of the product mixture. ʰ Addition of the amide at 40 °C; reaction mixture stirred at 50 °C for 24 hr; reaction also produced 6 unidentified components comprising a total of 2 wt percent of the product mixture. ｉ Addition of the amide at 40 °C, reaction mixture stirred at 50 °C for 24 hr; reaction also produced 6 unidentified components comprising a total of 2 wt percent of the product mixture.

### Table II. Reactions of diphenyl N-alkyl phosphoramidates (2) with benzene in the presence of aluminium chloride.

<table>
<thead>
<tr>
<th>R</th>
<th>(C₆H₅O)₂P(O)NHR'</th>
<th>C₆H₅</th>
<th>AlCl₃</th>
<th>C₆H₆</th>
<th>Products [% yield]</th>
<th>C₆H₅R</th>
<th>C₆H₄R₂</th>
<th>C₆H₃R</th>
<th>Amide Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclo-C₆H₁₁</td>
<td>0.034</td>
<td>0.76</td>
<td>0.11</td>
<td>1.46</td>
<td>60</td>
<td>27</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>cyclo-C₆H₁₁</td>
<td>0.035</td>
<td>0.76</td>
<td>0.1</td>
<td>0.15</td>
<td>8</td>
<td>29ᵇ</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(CH₃)₃</td>
<td>0.03</td>
<td>–</td>
<td>0.1</td>
<td>0.81</td>
<td>55</td>
<td>22</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C₃H₇</td>
<td>0.025</td>
<td>0.56</td>
<td>0.083</td>
<td>0.11</td>
<td>59</td>
<td>45ᵉ</td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>i-C₃H₇</td>
<td>0.025</td>
<td>0.56</td>
<td>0.083</td>
<td>0.11</td>
<td>60</td>
<td>2ᵈ</td>
<td>12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A series of reactions of 4 with benzene in the presence of aluminium chloride, under the same conditions as those employed in the preceding work, produced aralkyls derived from N–C cleavage (Table III) in yields higher than those produced by the reactions of 2.

### Discussion

The reactions of phosphoramides 1, 2, and 4 to produce aralkyls are not general. It appears that in general, N–C bond cleavage occurs only when the amide is derived from a primary amine. Thus,
Table III. Reactions of N,N',N''-trialkyl phosphoric triamides and N,N',N''-trialkyl thiophosphoric triamides with benzene in the presence of aluminium chloride.

<table>
<thead>
<tr>
<th>R</th>
<th>Reactant A&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Reactant B&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Products [% yield]</th>
<th>Amide Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(RNH)&lt;sub&gt;3&lt;/sub&gt;P(X)</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>AlCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>X [mol]</td>
<td>[mol]</td>
<td>[mol]</td>
<td>[mol]</td>
</tr>
<tr>
<td>cyclo-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
<td>O 0.05 1.12</td>
<td>0.25 0.22</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt; (20)</td>
<td>13</td>
</tr>
<tr>
<td>cyclo-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;</td>
<td>S 0.025 1.12</td>
<td>0.25 0.22</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt; (63)</td>
<td>13</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>O 0.2 0.45</td>
<td>0.066 0.09</td>
<td>(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt; (59), (C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt; (5)</td>
<td>13</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>S 0.025 0.56</td>
<td>0.083 0.11</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt; (2)</td>
<td>14</td>
</tr>
<tr>
<td>t-C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;</td>
<td>O 0.01 0.22</td>
<td>0.033 0.34</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt; (63)</td>
<td>14</td>
</tr>
<tr>
<td>t-C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>O 0.01 0.22</td>
<td>0.033 0.22</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;-t (35)</td>
<td>15</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;-CHCH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>O 0.025 0.56</td>
<td>0.033 0.11</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;-CH&lt;sub&gt;2&lt;/sub&gt; (66), 14</td>
<td>16</td>
</tr>
<tr>
<td>sec-C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>O 0.025 0.56</td>
<td>0.033 0.11</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;-sec (37)</td>
<td>16</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reactant A added to Reactant B (see Experimental).

although the reaction of diphenyl N-cyclohexylphosphoramidate (2, R = cyclo-C<sub>6</sub>H<sub>11</sub>) results in a 27% yield of phenylecyclohexane, the reaction of diethyl N,N-di-cyclohexylphosphoramidate produces no phenylecyclohexane. In addition, in the reactions of diphenyl N,N-pentamethylenephosphoramidate<sup>10</sup> (2, R = (CH<sub>2</sub>)<sub>4</sub>) and diphenyl N-diethylphosphoramidate<sup>11</sup>, diphenyl N,N-dimethylphosphoramidate<sup>12</sup>, hexaethylphosphoric triamide<sup>13</sup>, and triis N,N-pentamethylene thiophosphoric triamide, (pi-peridyl)<sub>3</sub>P(S)<sub>3</sub><sup>14</sup>, the starting amides were recovered in yields ranging from 83 to 94%.

In addition to this limitation, there are other factors which severely constrain this reaction as a synthetic route to aralkyls. The reactions of amides derived from low molecular weight n-alkyl amines (C<sub>6</sub> to C<sub>8</sub>) do not, in general, produce aralkyls. Thus reactions of 4 (R = CH<sub>3</sub> 20, n-C<sub>3</sub>H<sub>7</sub> 14, n-C<sub>6</sub>H<sub>9</sub> 14; X = O) do not yield either the expected aralkyl or recovered starting material, and the reaction of 4 (R = n-C<sub>6</sub>H<sub>5</sub> 21; X = S) results in 88–92% yields of the unchanged starting material. Reactions of 2 (R = n-C<sub>6</sub>H<sub>7</sub>, C<sub>6</sub>H<sub>5</sub>)<sup>13</sup> result in recovery of the starting materials in high yield, and the reaction of 2 (R = C<sub>6</sub>H<sub>5</sub>)<sup>12</sup> gives only a 2% yield of ethyl benzene, and 86% of recovered amide; however, the reaction of 2 (R = n-C<sub>6</sub>H<sub>3</sub>)<sup>11</sup> yields 45% of aralkyl.

As has been noted, the yield of diphenyl phosphoramidate (3) provides a measure of the amount of N–C cleavage. Although the N–C cleavage of the amides derived from primary amines seems to be quite general, the concomitant production of the corresponding aralkyl is not. Thus in the cases of 2 (R = (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>CH, cyclo-C<sub>6</sub>H<sub>11</sub>-CH<sub>2</sub>) (Table IV) the hydrocarbons are isolated, whereas the aralkyls are not. These observations do not exclude the formation of the corresponding aralkyls since the hydrocarbons could arise from the disproportionation of the aralkyls.

Although there may be certain cases in which the use of phosphoramides as alkylating agents might be advantageous, the route does not seem to be the method of choice for the preparation of aralkyls. One possible exception, however, is the reaction of N,N',N''-trialkyl phosphoric triamide with benzene in the presence of aluminium chloride to produce

Table IV. Production of hydrocarbons by the reaction of diphenyl N-alkyl phosphoramidates with benzene and aluminium chloride.

<table>
<thead>
<tr>
<th>R</th>
<th>Reactant A&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Reactant B&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Products [% yield]</th>
<th>Hydrocarbon R H</th>
<th>(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;P(O)NH&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;P(O)NHR [mol]</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>AlCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>[mol]</td>
</tr>
<tr>
<td>cyclo-C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;11&lt;/sub&gt;-CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.025 0.56</td>
<td>0.083 0.083</td>
<td>9&lt;sup&gt;b&lt;/sup&gt;</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH</td>
<td>0.01 0.34</td>
<td>0.033 0.34</td>
<td>60</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;CH</td>
<td>0.025 0.56</td>
<td>0.083 0.11</td>
<td>14&lt;sup&gt;c&lt;/sup&gt;</td>
<td>88</td>
<td>88</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reactant A added to Reactant B (see Experimental). <sup>b</sup> Reaction mixture stirred at room temperature for 10 hr; unidentified polymeric products predominated. <sup>c</sup> Reaction mixture stirred at room temperature for 8 days; unidentified polymeric products were also obtained.
after distillation a 44% yield of 1,2-diphenylpropane (5).

\[
\begin{align*}
(CH_2=CHCH_2NH_3)P(O) + C_6H_6 + AlCl_3 &\rightarrow \\
C_6H_5CH_2CH(C_6H_5)CH_3 &\rightarrow \\
5
\end{align*}
\]

The analogous reactions of triallyl phosphate, 
\((CH_2=CHCH_2)P(O),\) and triallyl phosphate, 
\((CH_2=CHCH_2)P(O),\) each produce 5 in 15% yield in addition to several other products including 
\(n\)-propyl benzene. The reaction of 1,2-dichloropropane has been reported to yield 5 as the major product. Under our conditions the reaction produces 5 in 42% yield after distillation.

These observations, coupled with the rearrangement products found in the reactions of \(n\)-propyl and \(n\)-butyl phosphoramides, lend support to the intermediacy of carbonium ions in the reactions of phosphoramides with benzene in the presence of aluminium chloride.

A number of carcinostatic agents contain an aziridine moiety and it appears that this group is a major contributor to the alkylating ability of such agents. The reaction of 6 with benzene and aluminium chloride proceeds readily, even though the amide is not derived from a primary amine, to give a mixture of \(\beta\)-phenethyl amine and its hydrochloride salt. The products are probably formed by the opening of the aziridine ring followed by alkylation of the benzene and subsequent hydrolysis of the intermediate phosphoric triamide (7).

\[
\begin{align*}
(\bigtriangledown N)P(O) + C_6H_6 + AlCl_3 &\rightarrow \\
(C_6H_5CH_2CH_2NH_3)P(O) &\rightarrow \\
C_6H_5CH_2CH(C_6H_5)CH_2NH_2 \cdot HCl &\rightarrow \\
7
\end{align*}
\]

**Experimental**

Benzene was distilled from sodium and was stored over sodium. Pyridine was stored over sodium hydroxide. All other reagents were best commercial grade used without further purification. The phosphoramides, with the exception of those described below, were prepared by the methods given in the tables and in the text. In all cases their physical constants agreed with those reported in the literature.

Gas chromatographic analyses were performed on Varian Aerograph instruments models 1700 and A-90P3 equipped with thermal conductivity detectors. The columns used were 6 ft × 1/4 in. 20% Carbowax 20 M on Chromosorb W and 5 ft × 1/4 in. 3% SE 30 on Varapack. Elemental analyses were performed on a F & M Carbon-Hydrogen-Nitrogen Analyzer, Model 185. All b.p. and m.p. are uncorrected. Unless otherwise noted, materials were concentrated at less than 50 °C on a rotating evaporator at 10–15 Torr.

**Reactions of amides with benzene in the presence of aluminium chloride (Tables I–IV). General procedure**

A solution of the amide in benzene (Reactant A) was added at 5 °C to a well-stirred suspension of aluminium chloride in benzene (Reactant B). The reaction mixture was stirred at 5 °C for 1 hr and then at room temperature for 24 hr and was recooled to 5 °C. Water was added with stirring at 5–10 °C and the stirring was continued at room temperature until all the solids had dissolved. The organic layer was separated; filtered if necessary to remove diphenyl phosphoramidate (3); washed with 10% aqueous hydrochloric acid solution, 10% aqueous sodium bicarbonate solution, and then water; dried (Na_2SO_4); and concentrated by distilling the solvent at atmospheric pressure under nitrogen. The residual oils were distilled when possible and were analyzed by g.l.c.

**Reaction of triethylenimino phosphine oxide (6) with benzene and aluminium chloride**

A suspension of 4.3 g (0.025 mol) 6 in 50 ml benzene was added without cooling to a suspension of 11 g (0.083 mol) aluminium chloride in 10 ml benzene. The temperature rose to 60 °C during the addition. The reaction mixture was stirred at ambient temperature for 18 hr and was then poured onto 100 ml ice. The organic layer was separated and was concentrated by distilling the solvent at atmospheric pressure under nitrogen. The dark residual oil was dissolved in absolute ethanol and filtered to remove a small amount of a dark polymeric material. The filtrate was concentrated and distilled collecting 1.4 g (15%) \(\beta\)-phenethyl amine, b.p. 80 °C (0.2 mm), whose infrared spectrum was exactly superimposable with that of a commercial (Aldrich Chemical Co.) sample. The distillation head contained a white solid which had sublimed during the distillation. This was collected and resublimed at 150 °C (0.2 mm) to yield 0.7 g (6%) \(\beta\)-phenethyl amine hydrochloride, m.p. 210–212 °C [lit. 25, m.p. 217 °C]. An intractable residue, 3 g, was also obtained from the distillation.

**Diphenyl \(N\)-\(n\)-propylphosphoramidate (2, \(R = n-C_3H_7\))**

A solution of 20.2 g (0.2 mol) triethyl amine and 11.8 g (0.2 mol) \(n\)-propyl amine was added at 5 °C to a solution of 46.8 g (0.2 mol) diphenyl phosphite in 500 ml carbon tetrachloride and the resulting mixture was stirred overnight at room temperature. Triethyl amine hydrochloride was removed by
filtration and the filtrate was concentrated. The residual oil was crystallized from Skellysolve B to yield 54.6 g (94%) diphenyl N-n-propylphosphoramide as white needles, m.p. 53–54 °C.

**Analysis for C_{15}H_{18}NO_3P**

Found C 62.12 H 6.22 N 4.97,
Calcd C 61.85 H 6.23 N 4.81.

**Diphenyl N-diphenylmethylphosphoramide**

(2, R = (C_6H_5)eC_6H_5)

A solution of 36.6 g (0.2 mol) diphenylmethyl amine in 50 ml chloroform was added at 3–5 °C to a solution of 26.85 g (0.1 mol) diphenylphosphochloridate in 100 ml chloroform. The reaction mixture was stirred overnight at room temperature and was then filtered. The filtrate was concentrated to yield a white solid, 40 g (98%), m.p. 122–124 °C, which showed one spot to tlc on silica gel using absolute ethanol as eluant and iodine to visualize the spots. A sample (1 g) of the first solid was purified for analysis by chromatography on 25 g neutral alumina using absolute ethanol as the eluant. The product, 0.8 g, was isolated as a white solid, m.p. 108–110 °C.

**Analysis for C_{20}H_{23}NO_3P**

Caled C 72.78 H 5.34 N 3.37,
Found C 72.00 H 5.65 N 3.33.

**Diphenyl N-cyclohexylmethylphosphoramide**

(2, R = cyclo-C_6H_{11}eC_6H_5)

Diphenyl phosphite (23.4 g, 0.1 mol) was added at 0–10 °C to a solution of 70.93 g (0.1 mol) cyclohexylmethyl amine in 200 ml carbon tetrachloride. Then 11.3 g (0.1 mol) cyclohexylmethyl amine was added at 10 °C and the resulting mixture was refluxed for 15 min, cooled to room temperature, and filtered. The filtrate was concentrated and the residual solid was recrystallized from Skellysolve B to yield 18.6 g (92%) diphenyl N-cyclohexylmethylphosphoramide as white needles, m.p. 87.5–88.5 °C.

**Analysis for C_{15}H_{12}NO_3P**

Caled C 66.07 H 7.00 N 4.06,
Found C 65.93 H 7.14 N 3.97.

**N,N',N''-triisopropyl phosphoric triamide**

(4, R = cyclo-C_6H_{11}eC_6H_5)

Pyridine (23.7 g, 0.3 mol) was added at 0–5 °C to a solution of 15.4 g (0.1 mol) phosphorus oxychloride in 200 ml chloroform. The resulting solution was refluxed at 5–10 °C to a solution of 43.9 g (0.6 mol) sec-butyramine in 200 ml chloroform. The resulting mixture was refluxed for 2 hr and stirred overnight at room temperature. The mixture was concentrated, ether was added to the residual oil, and the resultant slurry was filtered. The filtrate was washed with 10% aqueous hydrochloric acid solution (2 × 50 ml), water (3 × 100 ml), and then with 50 ml saturated aqueous sodium chloride solution; dried (MgSO_4); and concentrated to a cloudy white oil, 16.6 g (61%), that gives one spot to tlc on alumina with ethyl acetate as solvent and on silica gel with absolute ethanol as eluant. A sample was purified for analysis by column chromatography on silica gel using absolute alcohol as the eluant.

**Analysis for C_{15}H_{27}N_3O_3P**

Caled C 54.72 H 11.46,
Found C 54.79 H 11.49.

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