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2,2,4,4,6,6-Hexaphenylcyclotriphosphazatriene, Diphenylphosphinothioic Amide, 1,1,3,3,5,5-Hexaphenyl-1-methylaminotriphosphazene-5-sulphide, P,P-Diphenyl-N-dimethylphosphinothioic Amide


The thermal condensation of some phenylphosphinothioic diamides [1] and some diphenylphosphinothioic amides [2] have been described. Trippett showed that the thermolysis of N,N'-dibenzylphosphonothioic diamides gave cyclodiphosphazanes [3], which were identified by proton NMR spectra. The possibility of geometrical isomerism was discussed. The thermolysis depends on the nature and on the reaction conditions. We now wish to report the thermal decomposition of P,P-diphenyl-N-benzylphosphinothioic amide (1a) and P,P-diphenyl-N-methylphosphinothioic amide (1b).

Thermolysis of P,P-diphenyl-N-benzylphosphinothioic amide gave, in a stream of nitrogen at 310 °C for 1/4 h, hexaphenylycyclotriphosphazatriene (2) and diphenylphosphinothioic amide (3).

The thermolysis of P,P-diphenyl-N-methylphosphinothioic amide was carried out under an atmosphere of nitrogen a 300–310 °C for 1/4 h, 1,1,3,3,5,5-Hexaphenyl-1-methylaminotriphosphazene-5-sulphide (4), P,P-diphenyl-N,N-dimethylphosphinothioic amide (5) and the methyl ester of diphenylphosphinodithioic amide (6) were separated by means of thin-layer-chromatography (TLC) using a silica-gel column with benzene as eluent.

In proton NMR of organophosphorus compounds, phosphorus spin-spin couples with hydrogen on the carbon-nitrogen atom to the phosphorus with $J_{PH} = 14.5$ Hz. The $^1$H NMR spectrum of 4 (in CDCl$_3$, TMS as internal standard) exhibits two doublets at $\tau = 7.55$ (P–NCH$_3$) and 7.45 (P–NH). On exchange of the N–H proton with D$_2$O only one doublet for the methyl group remains at $\tau = 7.55$ ($J_{PH} = 14.5$ Hz). The P–N stretching vibration in the group P–NH$_2$ occurs near 800 cm$^{-1}$. The P–N–C group has two fairly well defined stretching vibrations: one near 1100–1300 cm$^{-1}$, the other near 850 cm$^{-1}$ and they are assigned as “C–N stretching” and “P–N stretching” [4] respectively. The P–N stretching vibration occurs mostly in the region 1100–1300 cm$^{-1}$. Bellamy [5] has noted that the P–S stretching frequency as a variable band in the region 600–750 cm$^{-1}$, Chittenden and Thomas [6] have suggested that many organophosphorus compounds containing the P=S group show two characteristic bands: one in the region 570–700 cm$^{-1}$, the other in the region 685–865 cm$^{-1}$.

Experimental

Chromatography of the crude decomposition product of P,P-diphenyl-N-benzyl-phosphinothioic amide gave the compounds 2 and 3 on silica-gel (TLC) with methylene chloride-diethyl ether as eluent. 2. Colourless crystals of 2,2,4,4,6,6-hexaphenylycyclotriphosphazatriene, which was crystallized from methylene chloride and diethyl ether (m.p. 230–232 °C). The mass spectrum showed the molecular peak at $m/e$ 596 (C$_{36}$H$_{30}$N$_3$P$_3$). Proton NMR spectrum was obtained by dissolution of the compound...
Table I. Analytical data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C</th>
<th>H</th>
<th>Found (Caled.) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C₆H₅)₂P(:S)NHCH₂C₆H₅ (1a)</td>
<td>70.32(70.05)</td>
<td>5.58(5.6)</td>
<td>4.16(4.3)</td>
</tr>
<tr>
<td>(C₆H₅)₂P(:S)NHCH₃ (1b)</td>
<td>62.42(63.10)</td>
<td>5.85(5.7)</td>
<td>6.35(5.7)</td>
</tr>
<tr>
<td>(C₆H₅)₂P(N₃)₂ (2)</td>
<td>62.42(63.10)</td>
<td>5.85(5.7)</td>
<td>6.35(5.7)</td>
</tr>
<tr>
<td>(C₆H₅)₂P(:S)NH₂ (3)</td>
<td>61.72(62.0)</td>
<td>5.14(6.0)</td>
<td>5.88(6.0)</td>
</tr>
<tr>
<td>(C₆H₅)₆P(:S)CH₃ (4)</td>
<td>69.64(68.82)</td>
<td>5.3 (5.3)</td>
<td>6.55(6.51)</td>
</tr>
<tr>
<td>(C₆H₅)₂P(:S)N(CH₃)₂ (5)</td>
<td>64.25(64.5)</td>
<td>6.11(6.15)</td>
<td>5.22(5.38)</td>
</tr>
<tr>
<td>(C₆H₅)₂P(:S)SCH₃ (6)</td>
<td>59.5(59.1)</td>
<td>4.94(4.90)</td>
<td>12.01(11.74)</td>
</tr>
</tbody>
</table>

in CDCl₃ at $\tau = 2.26$ (m, 30H, P-C₆H₅). IR (KBr): 1440 cm⁻¹ (P-C₆H₅), 1190 cm⁻¹ (P=N); 720 cm⁻¹ (P-N).

3. Diphenylphosphinothioic amide was crystallized from methylene chloride-diethyl ether (m.p. 100–102 °C). The mass spectrum showed the molecular peak at m/e 233 (C₁₂H₁₂NPS). Proton NMR spectrum was obtained (CDCl₃) at $\tau = 2.97$ (m, 10H, P-C₆H₅) and 6.8 (2H, P-NH₂). IR (KBr): 3300 cm⁻¹ (NH); 1435 cm⁻¹ (P-C₆H₅); 1240 cm⁻¹ (P-N) and 860-605 cm⁻¹ (P=S).

4. 1,1,3,3,5,5-Hexaphenyldimethylaminotriphosphazene-5-sulphide was crystallized from benzene-petroleum ether (60–80 °C) (m.p. 166–168 °C). The mass spectrum showed the molecular peak at m/e 646 (C₃₇H₃₄N₃P₃S). Proton NMR spectrum showed (CDCl₃) two doublets at $\tau = 7.55$ (d, 3H, P-NCH₃; $J_{PH} = 14.5$ Hz) and 2.41 (m, 30H, P-C₆H₅). IR (KBr): 3300 cm⁻¹ (NH); 3025 cm⁻¹ (CH₃); 1440 cm⁻¹ (P-C₆H₅); 1240 cm⁻¹ (P=N) and 860-605 cm⁻¹ (P=S).

5. P,P-diphenyl-N,N-dimethylphosphinothioic amide was crystallized from benzene-petroleum ether (40–60 °C) (m.p. 83–84 °C). Mass spectrum m/e 261 (C₁₄H₁₇NPS). Proton NMR spectrum showed (CDCl₃) at $\tau = 7.5$ (d, 6H, P-NCH₃; $J_{PH} = 14.5$ Hz) and 2.26 (m, 10H, P-C₆H₅). IR (KBr): 2915 cm⁻¹ (NH); 1435 cm⁻¹ (P-C₆H₅); 725-715 cm⁻¹ (P-N) and 655 cm⁻¹ (P=S).

6. The methyl ester of diphenylphosphinodithioic amide was crystallized from benzene-petroleum ether (60–80 °C) (m.p. 100–102 °C). The mass spectrum showed the molecular peak at m/e 264 (C₁₃H₁₃PS₂). Proton NMR spectrum showed (CDCl₃) a doublet at $\tau = 7.75$ (d, 3H, PSCH₃; $J_{PH} = 14.8$ Hz) and a multiplet at 2.34 (m, 10H, P-C₆H₅). IR (KBr): 3025 cm⁻¹ (NH); 1435 cm⁻¹ (P-C₆H₅) and 655 cm⁻¹ (P=S).