

palmitate hydrochloride was dissolved in 65% ethyl alcohol containing 4.5% hydrogen chloride, and refluxed for 20 minutes. Upon addition of diethyl ether to the reaction mixture, white crystals separated. The latter were proved to be pyridoxine hydrochloride by means of a mixed melting point determination with authentic pyridoxine hydrochloride.

**2,4,5-Trimethyl-3-palmitoxy pyridine-4 $\alpha$ ,5 $\alpha$ -bis-[pyridinium Bromide] (XI).**—Eight hundred mg. of pyridoxine hydrochloride was dissolved in 20 ml. of 48% hydrobromic acid and refluxed for 10 minutes. The solution was then placed in the refrigerator for 12 hours. The crystals were collected and washed with acetone and with diethyl ether. The dibromo compound, 2-methyl-3-hydroxy-4,5-dibromo-methylpyridine hydrobromide (X), yielded 800 mg., with a m.p. of 225–226° dec.

Seven hundred mg. of the dibromo derivative of pyri-

doxine was suspended in 20 ml. of alcohol-free chloroform and mixed with 570 mg. of palmitoyl chloride. With ice cooling, 3 ml. of dried pyridine was added to the mixture dropwise with strong stirring. The reaction proceeded immediately and the particles of the dibromide disappeared. The clear solution was set aside for 12 hours at room temperature. The solvent was then removed at low temperature *in vacuo* and the sirupy residue dissolved in a small amount of methyl alcohol. Upon cooling in the refrigerator, a precipitate formed, which was immediately removed by filtration and recrystallized from a methanol-acetone-petroleum ether system. Fine needle-like crystals were obtained, which were soluble in water and showed surface activity; yield 1.3 g. (94.2%), m.p. 146.0°. *Anal.* Calcd. for C<sub>34</sub>H<sub>49</sub>O<sub>2</sub>N<sub>3</sub>Br<sub>2</sub>: N, 6.08; Br, 23.12. Found: N, 6.04; Br, 21.98.

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## Organophosphorus Isocyanates

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The preparation and properties of several organophosphorus isocyanates are described.

Organophosphorus isocyanates, a new class of compounds, are available by reaction of phosphonic halides with silver cyanate in inert solvent.<sup>1</sup> The following diisocyanates of this class were prepared and characterized:

Ethylphosphonic	-C <sub>2</sub> H <sub>5</sub> PO(NCO) <sub>2</sub>
Chloromethylphosphonic	-ClCH <sub>2</sub> PO(NCO) <sub>2</sub>
Isopropylphosphonic	-(CH <sub>3</sub> ) <sub>2</sub> CHPO(NCO) <sub>2</sub>
Hexadecylphosphonic	-CH <sub>3</sub> (CH <sub>2</sub> ) <sub>15</sub> PO(NCO) <sub>2</sub>
Benzylphosphonic	-C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> PO(NCO) <sub>2</sub>
Phenylphosphonic	-C <sub>6</sub> H <sub>5</sub> PO(NCO) <sub>2</sub>
Phenylphosphonous	-C <sub>6</sub> H <sub>5</sub> P(NCO) <sub>2</sub>

In general, the appropriate chloride was heated several hours with a small excess of silver cyanate in benzene or acetonitrile. Removal of the silver salts and fractionation of the filtrate afforded the desired phosphonic isocyanate in yields varying from trace to 50%. These compounds are colorless liquids, boiling somewhat higher than the corresponding dichlorides. They polymerize slowly on standing and more rapidly when heated to give hard, glassy polymers. This behavior is in a large measure responsible for the low yields obtained.

Potassium cyanate was used in place of silver cyanate in one preparation of ethylphosphonic diisocyanate. The reaction was considerably slower and a reduced yield of diisocyanate was obtained.

The organophosphorus isocyanates exhibit the characteristic isocyanate reactions. When added to water they liberate carbon dioxide vigorously. Urethans and ureas are obtained from alcohols and amines, respectively. Both these reactions are very rapid at room temperature.

Combustion-resistant polymers were obtained by reaction of ethylphosphonic diisocyanate with hydroquinone, resorcinol, 1,6-hexanediol and *p*-phenylenediamine.

(1) Phosphorus triisocyanate and phosphoryl triisocyanate have been similarly prepared by G. S. Forbes and H. H. Anderson, *This Journal*, **62**, 762 (1940); **64**, 1757 (1942).

## Experimental

**Ethylphosphonic Diisocyanate.**—A suspension of 180 g. of fresh silver cyanate in 1.5 l. of dry benzene was treated with 73.5 g. of ethylphosphonic dichloride and refluxed with stirring for 15 hours. The suspension was filtered and the filtrate concentrated and fractionated to obtain ethylphosphonic diisocyanate, 38.3 g. (48%), b.p. 58–59° (0.70 mm.).

*Anal.* Calcd. for C<sub>4</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>P: C, 30.0; H, 3.15; N, 17.5; P, 19.3. Found: C, 29.8, 29.8; H, 3.19, 3.21; N, 16.8, 16.8; P, 20.1, 18.6.

The bis-methylurethan was prepared by addition of the phosphonic diisocyanate to excess methanol. The resulting solution was evaporated to dryness and the product recrystallized from a mixture of methanol and absolute ether; m.p. 142–144°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>13</sub>N<sub>2</sub>O<sub>5</sub>P: C, 32.1; H, 5.84; N, 12.5. Found: C, 32.6, 32.2, 31.9; H, 5.94, 5.98, 5.86; N, 12.2, 12.4.

The bis-ethylurethan was prepared similarly; m.p. 116–117°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>17</sub>N<sub>2</sub>O<sub>5</sub>P: C, 38.1; H, 6.79; N, 11.1. Found: C, 37.9, 38.1; H, 6.86, 6.86; N, 11.6, 11.4.

The bis-phenylurea was prepared by addition of the diisocyanate to excess aniline. The resulting crude solid was washed thoroughly with 6 *N* hydrochloric acid, water, ethyl alcohol and ether (no solvent was found for recrystallization). The bis-phenylurea had m.p. 204–205°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>19</sub>N<sub>4</sub>O<sub>3</sub>P: C, 55.5; H, 5.53; N, 16.3. Found: C, 55.4, 55.4; H, 5.39, 5.25; N, 16.6, 16.9.

The use of potassium cyanate is illustrated in the following experiment. A suspension of 85 g. of fresh, powdered potassium cyanate and 73.5 g. of ethylphosphonic dichloride in 700 ml. of acetonitrile (distilled over phosphorus pentoxide) was refluxed with stirring for 24 hours. The reaction mixture was filtered and the filtrate concentrated and distilled to give approximately 40 g. of unreacted ethylphosphonic dichloride and 8 g. of ethylphosphonic diisocyanate, b.p. 55–80° (3 mm.).

In some runs there was obtained a fraction boiling at 45–46° (0.75 mm.), intermediate between ethylphosphonic dichloride and ethylphosphonic diisocyanate. This material was tentatively identified as ethylphosphonisocyanatid chloride, C<sub>2</sub>H<sub>5</sub>PO(Cl)NCO. It was converted to the diisocyanate by heating it in benzene with silver cyanate.

**Chloromethylphosphonic Diisocyanate.**—A suspension of 60 g. of silver cyanate in 250 ml. of benzene was dried by refluxing under a continuous water separator. Thirty grams of chloromethylphosphonic dichloride was added to the hot suspension which was then allowed to reflux for one hour and filtered. The filtrate was concentrated and distilled to give approximately 2 g. of material, b.p. 80–82° (0.9 mm.). This material was identified as chloromethylphosphonic diisocyanate by conversion to the usual derivatives. The bis-methylurethan was recrystallized from absolute methanol and ether; m.p. 181–183°.

*Anal.* Calcd. for  $C_5H_{10}ClN_2O_5P$ : C, 24.5; H, 4.12; N, 11.45. Found: C, 24.2, 24.6, 24.4; H, 4.15, 4.09, 4.10; N, 11.3, 11.2.

The bis-phenylurea had m.p. 199–200°.

*Anal.* Calcd. for  $C_{15}H_{16}ClN_4O_5P$ : C, 49.1; H, 4.36; N, 15.3. Found: C, 48.7, 48.8; H, 4.43, 4.35; N, 15.2, 14.9.

**Isopropylphosphonic Diisocyanate.**—A suspension of 60 g. of silver cyanate in 200 ml. of acetonitrile (dried with phosphorus pentoxide) was treated dropwise at 25–50° with 32 g. of isopropylphosphonic dichloride. The mixture was stirred for one hour and filtered. The filtrate was concentrated and distilled to give 6 g. of isopropylphosphonic diisocyanate; b.p. 60–61° (1 mm.), plus a large glassy residue which was non-volatile at 250° and 2 mm. The bis-methylurethan was prepared in the usual manner. After recrystallization from the mixture of methanol and ethyl ether it had m.p. 163–166°.

*Anal.* Calcd. for  $C_7H_{15}N_2O_5P$ : C, 35.3; H, 6.35; N, 11.75. Found: C, 35.4, 35.2; H, 6.42, 6.28; N, 11.3, 11.5.

The bis-phenylurea was prepared from excess aniline. It was washed with water, ethanol and ether to give crystals melting at 192–193°.

*Anal.* Calcd. for  $C_{17}H_{21}N_4O_5P$ : C, 56.7; H, 5.88; N, 15.5. Found: C, 57.4, 57.1; H, 6.06, 5.94; N, 14.7, 14.4.

**Hexadecylphosphonic Diisocyanate.**—A suspension of 68.5 g. of hexadecylphosphonic dichloride and 60 g. of silver cyanate was stirred in 100 ml. of acetonitrile (distilled from phosphorus pentoxide). There was an immediate exothermic reaction. The mixture was stirred for two hours at room temperature and then filtered. The concentrated filtrate was a viscous oil which reacted slowly with water to evolve carbon dioxide.

**Benzylphosphonic Diisocyanate.**—A suspension of 70 g. of silver cyanate in 100 ml. of dry acetonitrile was treated with 47.1 g. of benzylphosphonic dichloride dissolved in 50 ml. of dry benzene. The temperature was controlled between 40 and 50° by means of cooling. After stirring for two hours the reaction mixture was filtered and the filtrate concentrated to a dark oil. The product was distilled to obtain 3 g., b.p. 145° (1–2 mm.). Most of the material in the still-pot suddenly gelled at 200°. The product was converted to the bis-methylurethan in the usual manner. After recrystallization from a mixture of methanol and ether it had m.p. 179–181°.

*Anal.* Calcd. for  $C_{11}H_{15}N_2O_5P$ : C, 46.2; H, 5.28; N, 9.79. Found: C, 45.3, 45.5; H, 5.14, 5.25; N, 10.1, 10.1.

The bis-phenylurea had m.p. 188–193°.

*Anal.* Calcd. for  $C_{21}H_{21}N_4O_5P$ : C, 61.8; H, 5.18; N, 13.7. Found: C, 62.2, 62.4; H, 5.19, 5.16; N, 13.8, 13.9.

**Phenylphosphonic Diisocyanate.**—A mixture of 35 g. of phenylphosphonic dichloride and 60 g. of silver cyanate was allowed to react at 50° for one-half hour in 200 ml. of acetonitrile, distilled from phosphorus pentoxide. The crude product obtained after removal of the silver salts and solvent reacted vigorously with water to evolve carbon dioxide, but polymerized on attempted distillation. The bis-phenylurea derivative had m.p. 192–193°.

**Phenylphosphonous Diisocyanate.**—A suspension of 60 g. of silver cyanate in 100 cc. of dry benzene was treated dropwise with 35.4 g. of phenylphosphonous dichloride. The heat of reaction caused refluxing. The mixture was allowed to reflux for 1.5 hours and the resulting brownish-black precipitate was separated by filtration. The filtrate was concentrated *in vacuo* to an oil which reacted smoothly with water evolving carbon dioxide. This was distilled to obtain the diisocyanate, b.p. 118–122° (3.0 mm.), 5 g. The bis-methylurethan was prepared in the usual manner and crystallized from ether to obtain white needles. After recrystallization from a mixture of methanol and ether the melting point was 161–163°.

*Anal.* Calcd. for  $C_{10}H_{13}N_2O_4P$ : N, 10.9. Found: N, 10.2, 10.7.

The bis-phenylurea had m.p. 175–178°.

*Anal.* Calcd. for  $C_{20}H_{19}N_4O_2P$ : C, 63.4; H, 5.06; N, 14.8. Found: C, 62.2, 63.4, 62.2; H, 5.10, 5.51, 5.28; N, 13.9, 14.0.

**Polymers from Ethylphosphonic Diisocyanate. With *p*-Phenylenediamine.**—Four grams of ethylphosphonic diisocyanate was added to 2.68 g. of *p*-phenylenediamine in a 50-ml. flask equipped with a drying tube. There was an immediate exothermic reaction. After having stood one hour at room temperature the mixture was heated to 90° for 1.5 hours. The product was a crumbly powder insoluble in water, 6 *N* hydrochloric acid, ethyl alcohol and pyridine. It had melting point greater than 300°.

*Anal.* Calcd. for  $(C_{10}H_{13}N_4O_5P)_n$ : N, 20.9. Found: N, 20.8, 20.5.

**With Hydroquinone.**—A mixture of 11.0 g. of hydroquinone and 16.8 g. of ethylphosphonic diisocyanate was heated to 100°. An exothermic reaction took place very quickly. The reaction mixture became homogeneous and fluid and then became very viscous. The reaction was driven to conclusion by heating to 225° at which temperature the polymer was a very viscous fluid. Upon cooling, this was a brittle glass. It was practically incombustible.

**With Resorcinol.**—A solution of 11 g. of resorcinol and 300 ml. of toluene was dried by distillation and treated dropwise with 16.8 g. of ethylphosphonic diisocyanate. After about one-fifth of the isocyanate had been added, an oil separated from the solution. When the addition was complete, the reaction mixture was heated under reflux for one hour and then concentrated *in vacuo* to obtain the polymer. This was a low melting (75°) solid, insoluble in toluene and chloroform and soluble in acetone.

**With 1,6-Hexanediol.**—A mixture of 4 g. of ethylphosphonic diisocyanate plus 2.96 g. of 1,6-hexanediol reacted vigorously. The reaction was driven to completion by heating over a period of two hours to 250°. The resulting product was a white taffy-like polymer insoluble in water and partially soluble in boiling alcohol.

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