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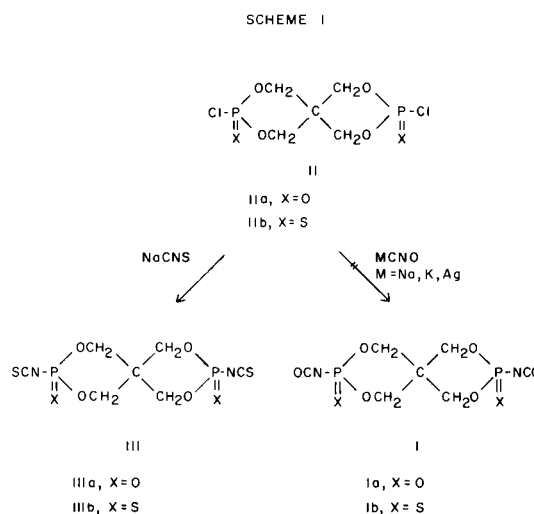
## Synthesis and Reactions of 3,9-Diisocyanates and Diisothiocyanates in the 2,4,8,10-Tetraoxa-3,9-diphosphaspiro[5.5]undecane Series

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The synthesis of several novel phosphorus-containing isocyanates and isothiocyanates is reported. These compounds are spiranes with two six-membered dioxaphosphorinane rings in their respective molecule. The phosphorus-bonded isocyanato and isothiocyanato groups are capable of undergoing addition reactions with active hydrogen atom-containing compounds.

Within the frame work of a broad investigation on 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane structures (1,2) numerous attempts have been made to obtain hitherto unknown bifunctional isocyanates with the NCO groups bonded directly to both phosphorus atoms. These novel compounds are represented by the general structural formula I. While the preparation of isothiocyanates of this type (III) was readily achieved by direct metathetical reaction between the halides IIa (3) or IIb and alkali metal thiocyanate, the synthesis of the corresponding isocyanates was not possible via this method. In order to obtain the pentavalent structures, Ia and Ib, it was necessary to utilize the known trivalent 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (IV) (4). It was observed that this highly reactive, sensitive product could be conveniently purified by vacuum distillation, thus eliminating a previously applied tedious crystallization technique. In the pure state IV dissolved readily in liquid sulfur dioxide. Such a solution was utilized for the reaction with sodium cyanate, because liquid sulfur dioxide is a preferred reaction medium for metathesis with sodium cyanate (5). Thus, the displacement of chloride by  $\text{NCO}^-$  proceeded readily to give the trivalent isocyanate V in high yield. Without prior isolation, V was oxidized directly by means of sulfur trioxide addition to this solution. Although sulfur trioxide has been employed for the conversion of isocyanato phosphines to the corresponding oxides (5), its use in the oxidation of even simple dialkyl isocyanato phosphites has not been reported. By this very convenient procedure the pentavalent bis-isocyanate, Ia, was obtained finally as a crystalline product in a nearly quantitative yield and reasonable purity. This oxidation gave no additional by-products since the sulfur trioxide was readily converted to sulfur dioxide during the reaction. Although it has been reported recently that trivalent phosphorus halides and pseudohalides can be oxidized by sulfur dioxide alone (6) no oxidation of the trivalent isocyanate V occurred in the absence of sulfur trioxide, even on prolonged refluxing in sulfur dioxide solution.

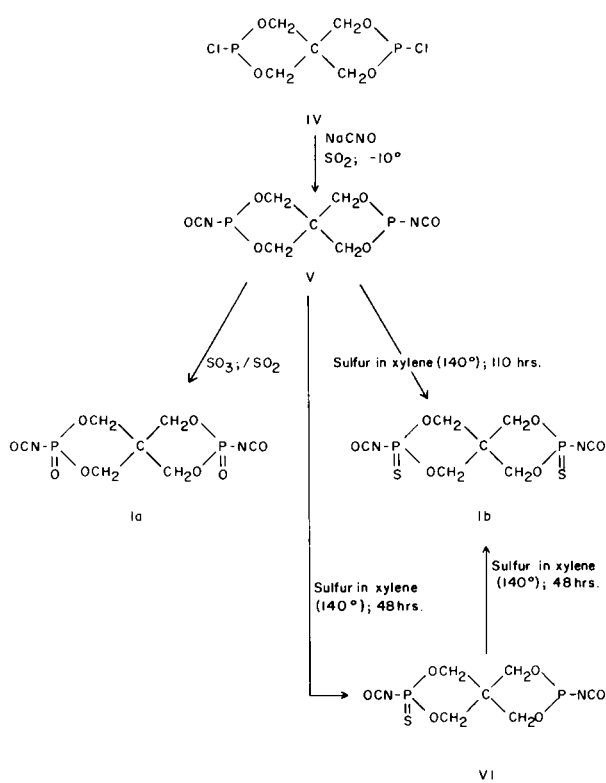
Sulfurization of V to Ib with elemental sulfur was possible by extended refluxing of the components in xylene. When the reaction was terminated too early, the partially sulfurized diisocyanate VI was isolated. The latter, however, could be converted to Ib by further reaction with sulfur in refluxing xylene. Scheme 3 presents two other conceivable methods to obtain structure I. However, both proved unsuccessful. This includes (a) the attempted reaction of phosphoramidates VII with phosgene or oxalyl chloride (7), and (b) the attempted *in situ* reaction of a hypothetical bis-trichlorophosphorane VIII (2,8) at low



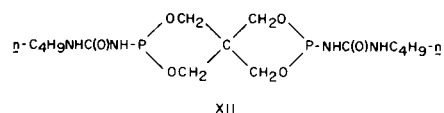
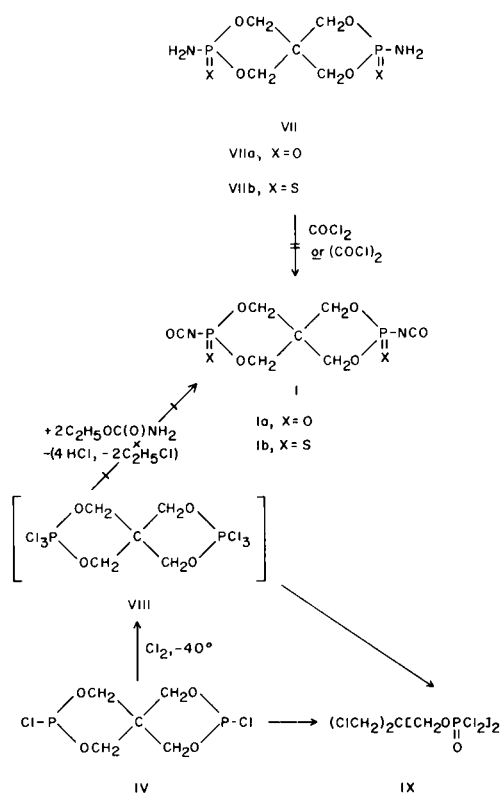
temperature with an alkyl urethane in a Kirsanov-type reaction (9). It was believed that the bis-trichlorophosphorane would not rearrange if chlorination of IV was conducted at  $-40^\circ$ . However conversion to open-chained chloride IX occurred even at this low temperature.

The isocyanates Ia and Ib reacted readily with water to give with carbon dioxide evolution the corresponding crystalline spiro-phosphoramidates VIIa and VIIb in high yield. Unlike the pentavalent compounds Ia and Ib, the

SCHEME 2



SCHEME 3



tervalent compound V proved to be relatively stable toward hydrolysis in cold water (90% recovery after stirring for 15 minutes at 25°), but was degraded completely with cleavage of the rings, by boiling water. The relative hydrolytic and thermal stability of the trivalent isocyanate V makes this compound exceptional in the class of cyclic phosphorus-(III)-pseudohalides. In contrast to the oxidized product Ia, compound V showed also favorable solubility properties permitting recrystallization from organic solvents.

The isocyanates Ia, Ib, and V and the isothiocyanates IIIa and IIIb reacted readily with alcohols and amines yielding the bifunctional ureas and carbamates. The properties of the compounds obtained from Ia, and Ib and IIIb are listed in Tables I and II. All these products were acidic in character due to the P(X)NHC(X) units (X = O or S) present in these structures. The unsubstituted bis-urea Xa (Table I) was titrated as a dibasic acid. Bis-urea Xi (Table I) formed an unusually stable 1:2 diacetone complex which could not be decomposed on heating to 60° *in vacuo*. The phenomenon has been observed with certain other cyclic compounds containing the P=S bond (10). Isocyanate V reacted with two moles of *n*-butylamine to give the P-tervalent bis-urea XII.

## EXPERIMENTAL

Microanalyses were performed by the Analytical Department, Olin Mathieson Chemical Corporation. Infrared spectra were taken on a Perkin-Elmer Infracord. The melting points were taken in a capillary tube and are uncorrected.

3,9-Dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (IV).

Essentially Birum's method (8) has been used for preparing crude IV, however, the material obtained was purified by vacuum distillation, b.p. 128-134°/1.0 mm.; yield of distilled product, 66%, m.p. 124-125°.

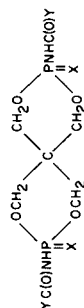
*Anal.* Calcd. for C<sub>5</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>4</sub>P<sub>2</sub>: C, 22.65; H, 3.20; Cl, 26.7; P, 23.4. Found: C, 22.36; H, 3.16; Cl, 26.6; P, 23.1.

3,9-Diisocyanato-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (V).

Distilled IV (26.5 g., 0.1 mole) and sodium cyanate (26.0 g., 0.4 mole) were placed in a 500 ml. round-bottom three-neck flask fitted with a stirrer and a dry-ice condenser fitted with a calcium

TABLE I

## Derivatives of Isocyanates Ia and Ib

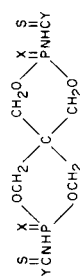


| Y   | X | m.p. (1)<br>°C | % Yield | Recrystn.<br>Solvent    | Formula  | Analyses |      |       |       |      |    |       |       |       |       |       |       |      |
|---|---|----------------|---------|-------------------------|--|----------|------|-------|-------|------|----|-------|-------|-------|-------|-------|-------|------|
|   |   |                |         |                         |  | C        | H    | N     | P     | S    | Cl | C     | H     | N     | P     | S     | Cl    |      |
| Xa NH <sub>2</sub>                                      | O | 257            | 100     | water (3,4)             | C <sub>7</sub> H <sub>14</sub> N <sub>4</sub> O <sub>8</sub> P <sub>2</sub>  | 24.40    | 4.07 | 16.24 | 17.97 |      |    | 23.60 | 4.06  | 15.89 | 17.47 |       |       |      |
| Xb CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> NH   | O | 128-136        | 81      | water (4) or<br>acetone | C <sub>15</sub> H <sub>30</sub> N <sub>4</sub> O <sub>8</sub> P <sub>2</sub>   | 39.47    | 6.58 | 12.28 | 13.60 |      |    | 39.40 | 6.58  | 12.30 | 13.54 |       |       |      |
| Xc C <sub>6</sub> H <sub>5</sub> NH                     | O | 182-185        | 90      | water (3)               | C <sub>19</sub> H <sub>22</sub> N <sub>4</sub> O <sub>8</sub> P <sub>2</sub>   | 45.97    | 4.44 | 11.29 | 12.50 |      |    | 45.94 | 4.48  | 11.29 | 12.40 |       |       |      |
| Xd 3,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH | O | 230-234        | 91      | water (3)               | C <sub>19</sub> H <sub>18</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>8</sub> P <sub>2</sub>                                     | 35.95    | 2.82 | 8.80  | 9.75  |      |    | 22.4  | 35.55 | 3.15  | 8.96  | 10.08 |       | 22.5 |
| Xe  | O | 230-233        | 10(2)   | water,<br>acetone (3)   | C <sub>15</sub> H <sub>20</sub> N <sub>4</sub> O <sub>10</sub> P <sub>2</sub>  | 37.19    | 5.27 | 11.57 | 12.81 |      |    | 36.81 | 5.34  | 11.51 | 12.91 |       |       |      |
| Xf CH <sub>3</sub> O                                    | O | 247-249        | 87      | methanol                | C <sub>9</sub> H <sub>16</sub> N <sub>2</sub> O <sub>10</sub> P <sub>2</sub>   | 28.88    | 4.28 | 7.48  | 16.55 |      |    | 28.55 | 4.62  | 7.22  | 15.93 |       |       |      |
| Xg CH <sub>3</sub> O                                    | S | 218-220        | 98      | methanol                | C <sub>9</sub> H <sub>16</sub> N <sub>2</sub> O <sub>8</sub> P <sub>2</sub> S <sub>2</sub>                                       | 26.60    | 3.92 | 15.27 | 15.76 |      |    | 26.64 | 3.93  | 15.47 | 15.34 |       |       |      |
| Xh NH <sub>2</sub>                                      | S | 203-208        | 98      | water (3)               | C <sub>7</sub> H <sub>14</sub> N <sub>4</sub> O <sub>6</sub> P <sub>2</sub> S <sub>2</sub>                                       | 22.34    | 3.74 | 14.89 | 16.49 |      |    | 22.51 | 4.01  | 15.16 | 16.18 |       | 17.03 |      |
| Xi C <sub>6</sub> H <sub>5</sub> NH                     | S | 200-204        | 99      | acetone                 | C <sub>19</sub> H <sub>22</sub> N <sub>4</sub> O <sub>6</sub> P <sub>2</sub> S <sub>2</sub> ·2C <sub>3</sub> H <sub>6</sub> O(5) | 46.58    | 5.28 | 8.70  | 9.63  | 9.94 |    | 46.75 | 5.43  | 8.50  | 9.82  | 10.13 |       |      |

(1) Since slow decomposition occurred in most cases during the melting point determination these more exact values were obtained in second determinations by use of a Fisher-Johns block preheated to approximately 15° below the melting point. (2) A 100% yield of dimorpholino salt was obtained, loss occurred on reacidification. (3) Purified by dissolving the crude in aqueous sodium hydroxide and acidifying the solution of the disodium salt obtained, thus reprecipitating the compound. After isolation the material was subjected to extraction with hot acetone or methanol. (4) Yields a stable monohydrate. (5) Diacetone complex.

TABLE II

## Derivatives of Isothiocyanate IIIb



| Y                                    | X | m.p. °C    | % Yield | Recrystn. Solvent | Formula   | Calcd. % |       |       | Analyses |       |      | Found % |       |       |
|--------------------------------------|---|------------|---------|-------------------|---|----------|-------|-------|----------|-------|------|---------|-------|-------|
|                                      |   |            |         |                   |   | H        | N     | P     | S        | C     | H    | N       | P     | S     |
| XIa NH <sub>2</sub>                  | S | 173 (dec.) | 98      | acetic acid (1)   | C <sub>7</sub> H <sub>14</sub> N <sub>4</sub> O <sub>4</sub> P <sub>2</sub> S <sub>4</sub>  | 20.58    | 13.72 | 15.17 | 31.40    | 20.24 | 3.19 | 13.82   | 15.04 | 31.27 |
| XIb N(CH <sub>3</sub> ) <sub>2</sub> | S | 166        | 98      | chloroform        | C <sub>11</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> P <sub>2</sub> S <sub>4</sub> | 28.44    | 12.06 | 13.34 | 27.61    | 28.24 | 4.81 | 11.98   | 13.02 | 27.14 |
| XIc                                  | S | 156        | 74      | ethanol           | C <sub>19</sub> H <sub>22</sub> N <sub>4</sub> O <sub>4</sub> P <sub>2</sub> S <sub>4</sub> | 40.71    | 9.99  | 11.05 | 22.88    | 40.39 | 4.29 | 10.01   | 11.02 | 22.65 |

(1) Precipitation from aqueous solution of the diammonium salt first formed during the reaction of IIIb with excess liquid ammonia.

sulfate drying tube. About 300 ml. of sulfur dioxide was condensed into the flask, and the reaction mixture was refluxed for 16 hours. The solution was filtered, the filtrate evaporated and the residual solid distilled *in vacuo* to give 27.0 g. (96%) of V, b.p. 114-117°/0.1 mm. After one recrystallization from 1:1 heptane/benzene mixture, m.p. was 110.5-111°;  $\lambda$  max 4.45  $\mu$  (NCO).

*Anal.* Calcd. for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>: C, 30.22; H, 2.88; N, 10.07; P, 22.30. Found: C, 30.22; H, 3.08; N, 10.19; P, 22.36.

3,9-Bis[3-*n*-butylureido]-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (XII).

Diisocyanate V (1.4 g., 0.05 mole) was dissolved in 15 ml. of benzene and 0.73 g. (0.01 mole) of butylamine in 50 ml. of benzene was added all at once. Benzene was decanted from the gummy precipitate which was washed with methanol and filtered to give 1.8 g. (89%) of product, m.p. 196-200° dec.

*Anal.* Calcd. for C<sub>15</sub>H<sub>30</sub>N<sub>4</sub>O<sub>6</sub>P<sub>2</sub>: C, 42.45; H, 7.08; N, 13.21; P, 14.62. Found: C, 42.34; H, 7.23; N, 13.21; P, 14.18.

3,9-Diisocyanato-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-Dioxide (Ia).

A mixture of 26.5 g. (0.1 mole) of IV and 15.6 g. (0.24 mole) of sodium cyanate was placed in a 500 ml. round-bottom, three-neck flask fitted with a stirrer, a pressure-equalized addition funnel and a dry-ice condenser bearing a calcium sulfate drying tube.

Sulfur dioxide (300 ml.) was condensed into the flask, and the mixture was refluxed for 28 hours. Next 5.6 ml. (0.2 mole) of sulfur trioxide dissolved in 75 ml. of sulfur dioxide was added slowly at -10° over a 1 hour period. This reaction was exothermic. The reaction mixture was stirred for an additional half hour, then the sodium chloride was separated by filtration in a nitrogen atmosphere. The filter cake was washed with 100 ml. of sulfur dioxide and the combined filtrate was allowed to evaporate, leaving 30.0 g. (97%) of Ia, m.p. 190-192° dec. No suitable solvent for crystallization was found. An infrared spectrum showed strong absorption at 4.3  $\mu$  (NCO) and at 7.6  $\mu$  (P=O).

*Anal.* Calcd. for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>8</sub>P<sub>2</sub>: C, 27.10; H, 2.58; N, 9.03; P, 20.00. Found: C, 26.27; H, 2.65; N, 9.19; P, 19.30.

3,9-Diamino-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-Dioxide (VIIa).

## 1. From Ia.

Diisocyanate Ia (3.10 g., 0.01 mole) was placed in a large volume of water and the mixture was stirred until the evolution of carbon dioxide ceased. Evaporation of the water left 2.4 g. (92%) of product which was identified as VIIa, m.p. 303-305° dec. The infrared spectrum was superimposable with that of a sample of VIIa prepared from IIa and ammonia.

## 2. From IIa.

Ammonia was passed through a slurry of 29.7 g. (0.1 mole) of IIa in 250 ml. of chloroform and 20.5 g. (0.2 mole) of triethylamine for 30 minutes. The mixture was stirred for an additional 4 hours and filtered. The solid was washed with cold water, dried *in vacuo* to give 12.8 g. (50%) of VIIa which was recrystallized from water, m.p. 303-305°.

*Anal.* Calcd. for C<sub>5</sub>H<sub>12</sub>N<sub>2</sub>O<sub>6</sub>P<sub>2</sub>: C, 23.22; H, 4.65; N, 10.83; P, 24.00. Found: C, 23.35; H, 4.70; N, 10.63; P, 23.85.

3,9-Diisocyanato-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-Disulfide (Ib).

Diisocyanate V (41.7 g., 0.15 mole) and sulfur (19.2 g., 0.6 mole) were placed in 400 ml. of dry xylene. The reaction mixture, protected from moisture with a calcium sulfate drying tube, was heated, and a clear solution was obtained. This solution was refluxed for 110 hours, then filtered hot to remove a small amount of residue.

On standing the filtrate deposited 44.7 g. (87%) of product, m.p. 176-188°. Two recrystallizations from xylene raised the m.p. to 188-190°;  $\lambda$  max 4.35  $\mu$  (NCO).

*Anal.* Calcd. for  $C_7H_8N_2O_6P_2S_2$ : C, 24.56; H, 2.34; P, 18.13; S, 18.71. Found: C, 25.19; H, 2.48; P, 18.22; S, 18.37.

3,9-Diamino-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-Disulfide (VIIb).

#### 1. From Ib.

Diisocyanate Ib (0.68 g., 0.002 mole) was added to a large excess of water. The mixture was stirred at 50° for 24 hours and then filtered. The filter cake was washed with ether and dried to give 0.57 g. (98%) of product, after one recrystallization from ethanol, m.p. 247-248°.

*Anal.* Calcd. for  $C_5H_{12}N_2O_4P_2S_2$ : C, 20.68; H, 4.17; N, 9.65; P, 21.34; S, 22.07. Found: C, 20.94; H, 4.04; N, 9.43; P, 21.62; S, 21.79.

#### 2. From IIb.

Anhydrous ammonia was passed through a stirred solution of 13.4 g. (0.04 mole) of IIb in 150 ml. of chloroform at 0°. After 1 hour the solution was saturated, the ammonia addition stopped and the mixture filtered. The solid was washed with cold water and dried to give 11.5 g. (99%) of VIIb, m.p. 225-230°, after one recrystallization from ethanol, m.p. 245-247°.

3,9-Diisocyanato-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3-Sulfide (VI).

Diisocyanate V (8.3 g., 0.03 mole) and sulfur (2.24 g., 0.07 mole) were refluxed in 100 ml. of dry xylene for 48 hours. After filtration and cooling, 3.0 g. (30%) of Ib was obtained; m.p. 180-186° after one recrystallization from xylene.

The initial xylene filtrate was reduced by evaporation to about 15 ml. and 200 ml. of heptane was added to precipitate crude VI. After successive washings with carbon disulfide and ether, 6.19 g. (66%) of product was obtained, m.p. 135-138°.

*Anal.* Calcd. for  $C_7H_8N_2O_6P_2S$ : C, 27.10; H, 2.58; N, 9.03; P, 20.00; S, 10.32. Found: C, 27.28; H, 2.69; N, 9.31; P, 20.44; S, 10.47.

#### Conversion of VI to VIIIb.

Monosulfide VI (3.1 g., 0.01 mole) and sulfur (0.64 g., 0.02 mole) were refluxed in dry xylene for 48 hours. The reaction mixture was filtered hot, and the xylene was evaporated. To the resulting solid was added 25 ml. of water, and the reaction mixture was stirred for 24 hours at 50°. The mixture was filtered and the product recrystallized from ethanol to give 2.0 g. (69%) of VIIIb, m.p. 245-247°.

3,9-Bis(isothiocyano)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-Disulfide (IIIb).

Dichloride IIb (13.2 g., 0.04 mole) dissolved in 150 ml. of dry acetonitrile was added to 7.8 g. (0.08 mole) of potassium thiocyanate dissolved in 100 ml. of the same solvent. The initially clear solution was stirred at room temperature for 120 hours and then filtered. The solid was slurried in 100 ml. of cold water, refiltered and dried to give 12.8 g. (85%) of product, which was recrystallized from acetonitrile, m.p. 245-246°;  $\lambda$  max 4.9  $\mu$  (NCS).

*Anal.* Calcd. for  $C_7H_8N_2O_4P_2S_4$ : C, 22.46; H, 2.15; N, 7.50; P, 16.58; S, 34.22. Found: C, 22.76; H, 2.46; N, 7.44; P, 16.71; S, 33.71.

2,4,8,10-Tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide-3,9-dimethylcarbamate (Xg) (Table I).

Diisocyanate Ib (3.42 g., 0.01 mole) was added to 20 ml. of methanol. A slight exotherm occurred, and a white precipitate began to form. The mixture was stirred for 4 hours, cooled to 10° and filtered to give 4.0 g. (98%) of product which was recrystallized from methanol.

3,9-Bis(thioureido)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-Disulfide (XIa) (Table II).

Isothiocyanoate IIIb (3.0 g., 0.008 mole) was added to about 50 g. of condensed ammonia. The solution was stirred and the excess ammonia evaporated within one hour. An aqueous solution of the diammonium salt was acidified by dropwise addition of acetic acid. The white crystals were collected by filtration and vacuum-dried to give 3.2 g. (98%) of product.

3,9-Bis(3-phenylureido)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide (Xc) (Table I).

Diisocyanate Ia (6.2 g., 0.02 mole) was added to 150 ml. of ether containing 30 g. of aniline. The mixture was stirred vigorously for 96 hours and then filtered to give after drying 11.3 g. (96%) of an anilinium complex. The solid was dissolved in dilute sodium hydroxide and reacidified by drop-wise addition of a 10% hydrochloric acid solution. After filtration the solid was washed with warm ethanol and dried to give 9.0 g. of product.

#### Hydrolysis of Diisocyanate V.

Diisocyanate V (5.56 g., 0.02 mole) was added to water (0.72 g., 0.045 mole) in 25 ml. of ethyl acetate. The mixture was stirred for 48 hours, and the precipitate that formed was filtered and dried to give 1.4 g. of powdery solid which softened and became tacky on exposure to air:  $\lambda$  max 3.0  $\mu$  (NH). The solid was placed in a large volume of water and 0.3 g. of pentaerythritol separated, m.p. 258-260°.

Evaporation of the initial ethyl acetate filtrate left 3.0 g. of a tacky solid:  $\lambda$  max 3.0  $\mu$  (NH), 5.8  $\mu$  (C=O). The material also decomposed in water to give 0.4 g. of pentaerythritol, the only isolable product.

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- (11) Note added in proof: We have been notified of the untimely death of Dr. Rudi Rätz on October 27, 1967.

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