

Olin Research Center, Chemicals Division

## 2,4,8,10-Tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide and Some Derived Compounds (I)

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2,4,8,10-Tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (I) has been prepared by the treatment of 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (II) with hydrogen sulfide. The reactions of I with thiocyanates to give esters of 3,9-dimercapto-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (III) and with isocyanates and isothiocyanates to give *P*-carbamoyl and thiocarbamoyl derivatives of I were investigated. I was also found to condense with chloral to produce an  $\alpha$ -hydroxythiophosphonate (XXVIII), but similar reactions with other aldehydes failed to yield analogous products.

In continuation of previous work in our laboratory on the preparation and properties of phosphorus-containing esters of pentaerythritol (2), we have investigated the chemistry of the spiro-bis-phosphorothioite, 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (I).

Simple dialkyl phosphorothioites are conventionally prepared by hydrogen sulfide treatment of a mixture of the corresponding dialkyl phosphorochloridite and a tertiary amine in an appropriate solvent (3). We found, however, that the application of this technique to the known (4) spiro compound, 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (II) yielded a gummy white substance of unknown composition, which appeared to contain little or none of the desired I. It appeared that attack of the tertiary amine on II had caused this, for I could be obtained in 85% yield in the form of a white solid when no amine was present and the reaction was run in *N,N*-dimethylacetamide solution. The stable crystalline product was conveniently isolated by pouring the reaction solution into a large volume of cold water.

It was found to be advantageous to employ unrecrystallized II, prepared by the method of Lucas *et al.* (4), for this reaction, for substantial losses were encountered on recrystallizing II from chloroform, and the exposure of this sensitive compound to atmospheric moisture during the purification produced hydrolysis products which caused a drop in both the yield and purity of I.

Several attempts were made to prepare the disodium salt of I by treatment with ethanolic sodium ethylate and to allow it to react with elemental sulfur to obtain 3,9-dimercapto-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (III). However, cleavage of the dioxaphosphorinane rings occurred with formation of pentaerythritol and *O,O*-diethyl phosphorodithioic acid. The occurrence of the reverse ester interchange was suggested by the fact that heating pentaerythritol and *O,O*-diethyl dithiophosphoric acid gave a nearly quantitative yield

of ethanol. However, the expected III could not be positively identified among the solid products of the reaction.

A number of esters of the acid (III) were prepared from I in yields of 80-95% by the action of alkyl thiocyanates in the presence of catalytic amounts of strong base, a reaction previously described by Schrader (5) for the synthesis of simple phosphorodithioates from dialkyl phosphorothioites. Several esters containing thioether groups in the side chain were prepared. These compounds are listed in Table I.

Two derivatives of esters of the alkylthioalkyl type are also listed in Table I. The water-soluble sulfonium salt (XV) was obtained in 98% yield by treating IX with methyl iodide. Strong heating of this salt resulted in the evolution of methyl iodide and regeneration of IX. The sulfone (XVI) was prepared by permanganate oxidation of VII. Attempts to obtain a sulfoxide of similar structure were unsuccessful since VII failed to react with hydrogen peroxide under mild conditions and gave XVI under more vigorous conditions.

When alkylthioethyl or alkylthiopropyl thiocyanates were allowed to react with I, the colorless phosphorodithioates of Table I were obtained. However, the reaction of I with alkylthiomethyl thiocyanates gave yellow, non-crystalline solids which were found to contain nitrogen. This was shown to be the result of the facile isomerization of thiocyanates of this type into isothiocyanates (6) which reacted with I to give bright yellow thiocarbamoyl derivatives (V, X = S).\* The reaction of simple dialkyl phos-

\*It could be possible that the structures V may have the grouping RNHC(X)-S-P< as a result of the attack of an "SP<" species on the isothiocyanate. Although this possibility cannot be entirely excluded on the basis of presently available evidence, the hydrolytic and oxidative stability of the products suggests that they contain pentavalent phosphorus and possess the structure V. The infrared spectra of all of these compounds (V, X = O, S), the esters of structure IV, the chloral adduct XXVIII and I itself show an absorption near 670 cm<sup>-1</sup>, which we have ascribed to the P=S group. A study of these structures<sup>7</sup> by nuclear magnetic resonance is in progress.

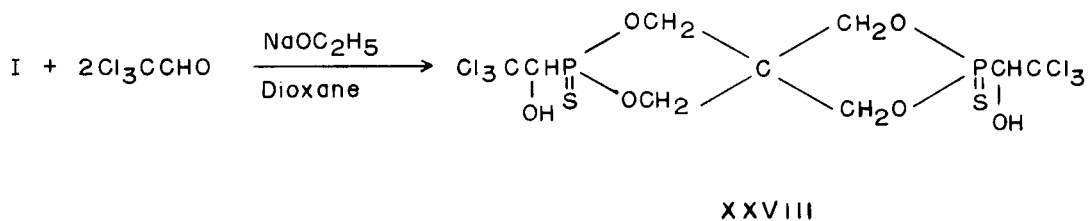
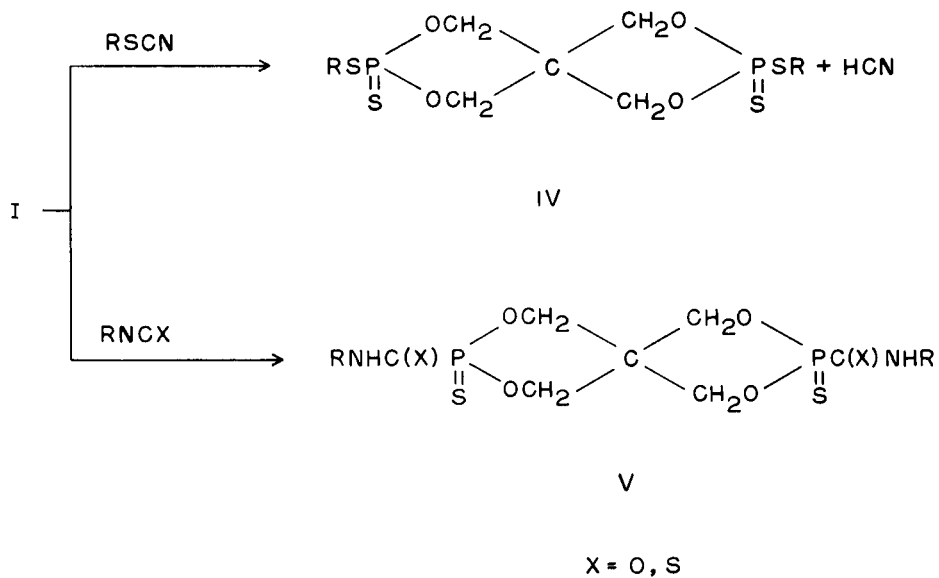
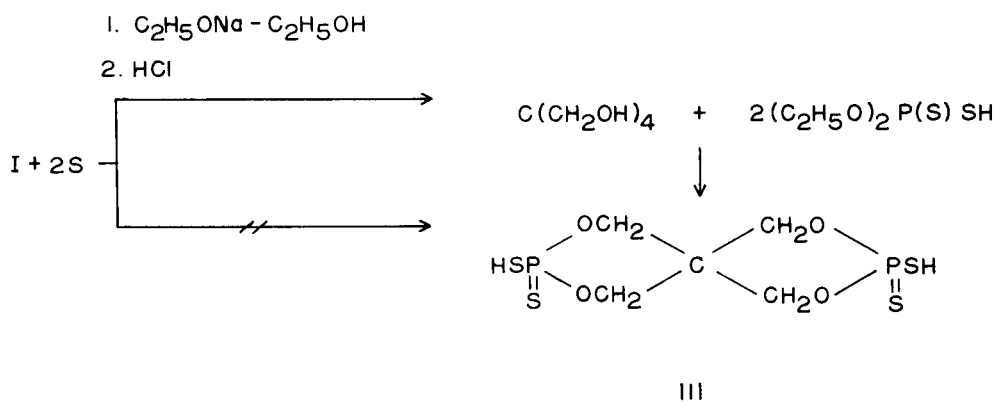
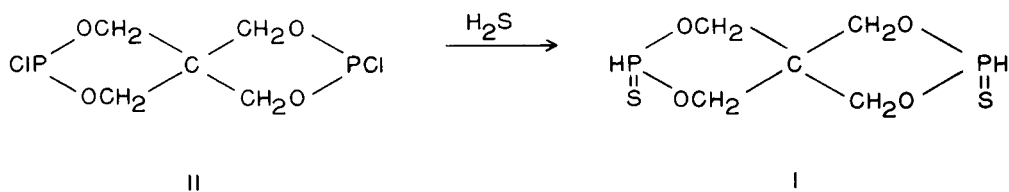


TABLE I

## 3, 9-Bis(Alkylthio)-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5.5]undecane-3, 9-disulfides (IV)

R	Recrystallization Solvent	M. P., °C	Yield, %	Formula	Calcd.			Found		
					C	H	P	C	H	P
VI	$C_2H_5$	158-159	85	$C_9H_{18}O_4P_2S_4$	28.40	4.77	16.28	28.35	4.72	15.85
VII	$CH_3S(CH_2)_2$	187-188	93	$C_{11}H_{22}O_4P_2S_6$	27.95	4.69	13.11	27.98	5.28	12.85
VIII	$C_2H_5S(CH_2)_2$	184-185	87	$C_{13}H_{26}O_4P_2S_6$	31.18	5.23	12.37	31.21	5.26	12.46
IX	$CH_3S(CH_2)_3$	169-170	94	$C_{13}H_{26}O_4P_2S_6$	31.18	5.23	12.37	31.22	5.09	11.96
X	$C_2H_5S(CH_2)_3$	169-170	92	$C_{15}H_{30}O_4P_2S_6$	34.07	5.71	11.72	34.10	5.70	11.72
XI	$C_6H_5S(CH_2)_2$	194-195	84	$C_{21}H_{26}O_4P_2S_6$	42.26	4.39	10.38	42.19	4.35	10.38
XII	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> S(CH <sub>2</sub> ) <sub>2</sub>	208-209	81	$C_{21}H_{24}Cl_2O_4P_2S_6$	37.89	3.63	9.31	37.80	3.66	9.09
XIII	$C_6H_5S(CH_2)_3$	166-167	90	$C_{23}H_{30}O_4P_2S_6$	44.21	4.84	9.91	43.90	4.80	9.88
XIV	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> S(CH <sub>2</sub> ) <sub>3</sub>	152-153	86	$C_{23}H_{28}Cl_2O_4P_2S_6$	39.82	4.07	8.93	39.72	4.01	8.81
XV	$[(CH_2)_3S(CH_2)_3]^+I^-$	163-164 (a)	98	$C_{15}H_{32}I_2O_4P_2S_6$			7.89 (b)			7.87
XVI	$CH_3SO_2(CH_2)_2$	241-242 dec.	75	$C_{14}H_{22}O_8P_2S_6$	24.62	4.13	11.54	24.15	4.16	11.52
XVII	$CH_3SCH_2$	169-170	9	$C_3H_8O_4P_2S_6$	24.31	4.08	13.93	24.57	4.19	13.60

(a) Evolves CH<sub>3</sub>I above 100°. (b) Calcd.: I, 32.3. Found: I, 33.3, (unrecrystallized product).

TABLE II

3, 9-Bis(*N*-substituted carbamoyl/thiocarbamoyl)-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5.5]undecane-3, 9-disulfides (V)

R	X	Recrystallization Solvent	M. P., °C	Yield, %	Formula	Calcd.			Found		
						C	H	N	C	H	N
XVIII	S	Ethanol-Acetone	169-170	64	$C_{14}H_{20}N_2O_4P_2S_6$	26.49	4.04	5.62	12.42	25.95	5.88
XIX	S	Ethanol	145-146	76	$C_{13}H_{24}N_2O_4P_2S_6$	29.64	4.59	5.32	11.76	29.15	5.70
XX	S	Ethanol	186-187	70	$C_{11}H_{20}N_2O_4P_2S_4$	30.40	4.64	6.45	14.26	30.45	6.66
XXI	S	Ethanol	148-149	54	$C_{13}H_{20}N_2O_4P_2S_4$	34.05	4.40	6.11	13.51	34.21	6.40
XXII	O	Acetone	250-251	76	$C_9H_{16}N_2O_6P_2S_2$	28.88	4.31	7.48	16.55	29.15	7.44
XXIII	O	Ethanol	209-210	87	$C_{15}H_{28}N_2O_6P_2S_2$	39.29	6.16	6.11	13.51	39.50	6.18
XXIV	O	Acetone	227-228	65	$C_{19}H_{20}N_2O_6P_2S_2$	45.78	4.04		12.43	46.02	4.15
XXV	<i>p</i> -C <sub>6</sub> H <sub>4</sub> Cl	Acetone	239-240	48	$C_{19}H_{18}Cl_2N_2O_6P_2S_2$	40.22	3.20	4.94	10.92 (a)	40.50	5.12
XXVI	3, 4-C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub>	Ethanol	215-216	50	$C_{19}H_{16}Cl_4N_2O_6P_2S_2$	35.87	2.54		9.74 (b)	35.93	2.24
XXVII	2, 5-C <sub>6</sub> H <sub>3</sub> Cl <sub>2</sub>	Dioxane	252-253	78	$C_{19}H_{16}Cl_4N_2O_6P_2S_2$	35.87	2.54		9.74 (c)	36.37	2.54

(a) Calcd.: Cl, 12.5. Found: Cl, 12.6. (b) Calcd.: Cl, 22.3. Found: Cl, 23.1. (c) Calcd.: Cl, 22.3. Found: Cl, 23.1.

phorothioites with isothiocyanates apparently has not been reported although their reaction with isocyanates has been described (7a, b), as well as the closely related reactions of both isocyanates (8) and isothiocyanates (7b, 9) with dialkyl hydrogen phosphites.

If chloromethyl methyl sulfide was treated with potassium thiocyanate in acetone at low temperature and the resulting crude liquid was allowed to react with I without prior distillation, it was possible to isolate the colorless phosphorodithioate (XVII) in low yield from the pale yellow granular product. The presence of the corresponding thiocarbamoyl compound (XVIII) in the reaction mixture was demonstrated by infrared spectroscopy but the material could not be isolated in a pure state in this experiment. The compound was obtained as bright yellow plates by treating I in dimethylacetamide solution with purified methylthiomethyl isothiocyanate which was prepared by heating the crude product of the potassium thiocyanate reaction to 125° for two hours to complete the isomerization and then distilling the product.

The reaction of I with isothiocyanates occurred slowly in dimethylacetamide solution without the addition of a catalyst. In dioxane, however, there was no apparent reaction in the absence of a basic catalyst. In order to obtain crystalline products, it was necessary to employ carefully purified isothiocyanates. With ethylthiomethyl isothiocyanate, it was necessary to resort to preparative vapor phase chromatography to obtain a sufficiently pure material to give crystalline XIX. In the case of phenylthiomethyl isothiocyanate, a crystalline condensation product with I could not be obtained, although infrared spectroscopy indicated that a substantial amount of the thiocarbamoyl derivative was present. This product resembled those obtained when mixtures known to contain both thiocyanate and isothiocyanate groups were allowed to react with I. There is thus a possibility that the phenylthiomethyl compound exists as an equilibrium mixture of thiocyanate and isothiocyanate, although this was not proven.

Isocyanates reacted with I in the same manner as isothiocyanates, giving *P*-carbamoyl derivatives. These materials were all completely colorless in contrast to the bright yellow thiocarbamoyl compounds. In Table II, the compounds V prepared by the reaction of I with both isocyanates and isothiocyanates are listed.

The treatment of I with anhydrous chloral in the presence of sodium ethylate gave a 50% yield of the  $\alpha$ -hydroxythiophosphonate (XXVIII). However, when similar condensations were attempted with dichloroacetaldehyde and with 2, 4-dichlorobenzaldehyde, complex mixtures of gummy products were obtained. Since simple dialkyl phosphorothioites have been reported to react smoothly with both aldehydes and ketones (10), the failure of I to give the expected  $\alpha$ -hydroxythiophosphonates in these cases may be associated with the instability of the dioxaphosphorinane rings under basic conditions.

Presumably, the condensation of I with chloral is rapid enough to compete successfully with ring-cleavage, while the slower reactions with the other aldehydes permit this side reaction to occur.

#### EXPERIMENTAL

Microanalyses were performed by the Central Analytical Department, Olin Mathieson Chemical Corporation. Infrared spectra were taken on a Perkin-Elmer Infracord. All 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 (II).

The method of Lucas, Mitchell and Skully was employed to prepare II in a yield of 94%. Two recrystallizations from dry chloroform reduced the yield to 31%, m.p. 121-122°. Lit. (4) m.p. 123°.

#### 2, 4, 8, 10-Tetraoxa-3, 9-diphosphaspiro[5. 5]undecane-3, 9-disulfide (I).

The method of Lucas *et al.* (4) was used to prepare I in a yield of 402 g. (92.4%) from 223 g. of pentaerythritol and 454 g. of phosphorus trichloride. The crude product was held for four hours at a pressure of 1 mm. to remove volatile impurities, dissolved in 1 liter of freshly distilled *N,N*-dimethylacetamide (b.p. 165-166°), protected from moisture, cooled by means of an ice bath, stirred vigorously and treated with a rapid stream of hydrogen sulfide for a period of 2.5 hours. The thick, creamy mixture, divided into four approximately equal portions, was poured into cold water (4 x 2 l.). Considerable frothing occurred as a result of the rapid evolution of the excess hydrogen sulfide. A slightly yellow solid was removed by filtration, washed with water (4 x 1 l.) and dried in a shallow pan in a gentle current of warm air for 62 hours. The product weighed 324 g. (82.5%) m.p. = 196-198°. Recrystallization from glacial acetic acid (approx. 16 ml./g. of I) gave a 60% recovery of shining plates, m.p. = 203-204°. A small additional amount, m.p. = 202-204°, could be recovered by adding ether to the acetic acid filtrate.

*Anal.* Calcd. for  $C_5H_{10}O_4P_2S_2$ : C, 23.05; H, 3.87; P, 23.80. Found: C, 23.14, 23.22; H, 3.86, 3.94; P, 23.70, 23.65.

#### Attempted Preparation of 3, 9-Dimercapto-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5. 5]undecane-3, 9-disulfide (III).

Treatment of a suspension of I (2.6 g., 0.01 mole) in dried absolute ethanol (11) (30 ml.) with sodium ethylate (0.02 mole, freshly prepared from 0.46 g. of sodium and 30 ml. of ethanol) caused rapid dissolution of the solid. Powdered sulfur (0.64 g., 0.02 mole) then dissolved readily with spontaneous warming. The yellow reaction solution was allowed to stand two hours at room temperature, cooled in ice and treated with anhydrous hydrogen chloride until precipitation of salt appeared complete. Filtration and vacuum drying of the solid gave 1.12 g. of sodium chloride (calcd. 1.17 g.). The filtrate was evaporated at reduced pressure to a yellow, slightly sticky solid. Extraction of the residue with anhydrous ether left a white, water-soluble solid (1.1 g.), m.p. = 255-260°, unchanged on admixture with authentic pentaerythritol. The addition of petroleum ether (b.p. 30-60°) to the ether filtrate gave a slightly yellow liquid which was isolated by decantation, washed with petroleum ether and dried briefly at a pressure of 25 mm. The liquid weighed 1.2 g. and had an infrared spectrum identical to that of authentic *O,O*-diethyl dithiophosphoric acid. Evaporation of the ether-petroleum ether decantate left a sticky, dark yellow material which was strongly acidic and freely soluble in water. No identifiable compound could be isolated from this residue.

The following  $\omega$ -chloroalkyl alkyl (or aryl) sulfides were prepared by known methods (12, 13, 14) and converted to thiocyanates by treatment with potassium thiocyanate according to the procedure of Kretov and Toropova (15): 2-chloroethyl methyl sulfide, 2-chloroethyl ethyl sulfide, 3-chloropropyl methyl sulfide, 3-chloropropyl ethyl sulfide, 2-chloroethyl phenyl sulfide, 2-chloroethyl-4-chlorophenyl sulfide, 3-chloropropyl phenyl sulfide and 3-chloropropyl-4-chlorophenyl sulfide. Eastman ethyl thiocyanate was used without purification.

#### Formation of Phosphorodithioates from I and Thiocyanates.

A number of spiro-bis-phosphorodithioates were synthesized by treating I in dimethylacetamide solution with two molar quantities of an organic thiocyanate in the presence of a sodium methylate catalyst. All of the products (Table I) were well-characterized crystalline solids. The following example is representative of the technique employed:

#### 3, 9-bis(2-[Methylthio]ethylthio)2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5. 5]undecane-3, 9-disulfide (VII).

To a magnetically stirred solution of 2, 4, 8, 10-tetraoxa-3, 9-diphos-

phosphoro[5.5]undecane-3,9-disulfide (I) (2.6 g., 0.01 mole) and 2-(methylthio)ethyl thiocyanate (2.66 g., 0.02 mole) in *N,N*-dimethylacetamide (20 ml.) contained in a 50 ml. Erlenmeyer flask was added a catalytic amount of sodium methylate powder, and the solution warmed to ca. 50°. Hydrogen cyanide was rapidly evolved and a white crystalline precipitate appeared. The reaction mixture was diluted with dimethylacetamide (10 ml.), stirred for ca. five minutes (by which time the reaction had ceased as evidenced by no further action on addition of sodium methylate and 10 minutes' subsequent stirring), then poured into water (100 ml.) and filtered. The pale yellow precipitate after washing with water (3 x 50 ml.), ethanol (1 x 50 ml.) and drying *in vacuo* over phosphorus pentoxide weighed 4.40 g. (93.6%), m.p. 187-188°. Recrystallization from acetone gave white needles of VII (3.85 g., 81.6%), m.p. 187.5-188.5°.

*Anal.* Calcd. for  $C_{11}H_{22}O_4P_2S_2$ : C, 27.95; H, 4.69; P, 13.11. Found: C, 27.98, 28.25; H, 5.37, 5.28; P, 12.85, 12.75.

3,9-bis( $\gamma$ -[Dimethylsulfonium]propylthio)-2,4,8,10-tetraoxa-3,9-diphosphoro[5.5]undecane-3,9-disulfide diiodide XV.

To a solution of 3,9-bis( $\gamma$ -[methylthio]propylthio)-2,4,8,10-tetraoxa-3,9-diphosphoro[5.5]undecane-3,9-disulfide (IX, 1.25 g., 2.4 mmoles) in *N,N*-dimethylformamide (25 ml.) was added excess methyl iodide (5 ml.). After standing overnight at room temperature, the solution was treated with anhydrous ether and filtered to remove a white precipitate. The solid, after washing with ether and drying *in vacuo*, weighed 1.94 g. (98%), was soluble in water and gave a copious yellow precipitate with aqueous silver nitrate. Upon heating, the product evolved methyl iodide slightly above 100° and melted at 163-164°. A mixture melting point of a resolidified sample with IX (m.p. 169-170°) gave no depression.

*Anal.* Calcd. for  $C_{15}H_{32}I_2O_4P_2S_2$ : I, 32.3; P, 7.89. Found: I, 33.3; P, 7.80, 7.87.

3,9-bis(2-[Methanesulfonyl]ethylthio)-2,4,8,10-tetraoxa-3,9-diphosphoro[5.5]undecane-3,9-disulfide (XVI).

A 250 ml. Erlenmeyer flask was charged with 1.419 g. (3.0 mmoles) of 3,9-bis(2-[methylthio]ethylthio)-2,4,8,10-tetraoxa-3,9-diphosphoro[5.5]undecane-3,9-disulfide (VII). To the solid was added a solution of 1.264 g. of potassium permanganate and 0.2 g. of concentrated sulfuric acid in 150 ml. of water. The flask was stoppered and stirred magnetically at room temperature for 60 hours. The precipitated manganese dioxide was destroyed by the addition of solid sodium bisulfite and a light tan solid was filtered and washed with water and alcohol. The solid was then treated with 50 ml. of hot (100°) *N,N*-dimethylacetamide and filtered to remove a small amount of manganese dioxide. The addition of ethanol to the filtrate gave 1.3 g. of white crystalline material, m.p. 232-234°, dec. Two recrystallizations from mixed ethanol-dimethylformamide raised the melting point to 241-242° dec.

*Anal.* Calcd. for  $C_{11}H_{22}O_8P_2S_2$ : C, 24.62; H, 4.13; P, 11.54. Found: C, 23.96, 24.15; H, 4.16, 4.20; P, 11.52, 11.68.

Methylthiomethyl isothiocyanate, ethylthiomethyl isothiocyanate and a material which was tentatively identified by infrared spectroscopy as a mixture of phenylthiomethyl thiocyanate and isothiocyanate were prepared from the corresponding chloromethyl thioethers by the method of Bohme *et al.* (6). The crude reaction products were held at a temperature of 125° for 2 hours, then distilled to complete the isomerization of thiocyanate to isothiocyanate. Ethylthiomethyl isothiocyanate was further purified by vapor phase chromatography prior to use. Other isothiocyanates and isocyanates used to prepare the thiocarbamoyl and carbamoyl derivatives of I which are listed in Table II were obtained from commercial sources and used without purification. The following examples are representative of all of the reactions.

3,9-bis(Methylthiomethylthio)-2,4,8,10-tetraoxa-3,9-diphosphoro[5.5]undecane-3,9-disulfide (XVII).

A 25 ml. Erlenmeyer flask was charged with 1.30 g. of I and 1.19 g. of the crude liquid product obtained by treating chloromethyl methyl sulfide with potassium thiocyanate in acetone at a temperature of 5-10°. The mixture, dissolved in *N,N*-dimethylacetamide (10 ml.), stirred magnetically with a catalytic amount of sodium methylate, became warm and yellow. After 10 minutes, the solution had cooled and was poured into cold water (100 ml.). A yellow solid, filtered, washed with water, then with ethanol and dried *in vacuo* over phosphorus pentoxide, weighed 2.39 g.; m.p. = 130-165°. Recrystallization from acetone (25 ml.) gave poorly formed pale yellow plates m.p. 169-170°. Four more recrystallizations from acetone were required to produce 0.2 g. (9%) of completely colorless crystals m.p. 169-170°. Evaporation of the acetone filtrates left a non-crystalline yellow solid, which was subsequently identified on the basis of its infrared spectrum as impure 3,9-bis(*N*-[methylthiomethyl]thiocarbamoyl)-2,4,8,10-tetraoxa-3,9-diphosphoro[5.5]undecane-3,9-disulfide (XVIII). The com-

ound could not be obtained in crystalline form in the present experiment.

*Anal.* Calcd. for  $C_9H_{16}O_4P_2S_2$ : C, 24.31; H, 4.08; P, 13.93. Found: C, 24.57, 24.57; H, 4.19, 3.90; P, 13.60, 13.54.

3,9-bis(*N*-[Methylthiomethyl]thiocarbamoyl)-2,4,8,10-tetraoxa-3,9-diphosphoro[5.5]undecane-3,9-disulfide (XVIII).

A solution of 0.595 g. of methylthiomethyl isothiocyanate (b. p. 568-9°) and 0.650 g. of I in 5 ml. of *N,N*-dimethylacetamide was stirred and treated with a very small amount of sodium methylate. The solution immediately became warm and turned deep yellow. When it had cooled, the solution was poured into cold water (75 ml.) and the resulting slightly sticky yellow solid filtered, washed with water, then with ethanol and dried *in vacuo* over phosphorus pentoxide. The granular yellow product weighed 1.2 g., m.p. 164-167°. Two recrystallizations from mixed alcohol-acetone solvent gave 0.8 g. of brilliant yellow platelets, m.p. 169-170°.

*Anal.* Calcd. for  $C_{11}H_{20}N_2O_4P_2S_2$ : C, 26.49; H, 4.04; N, 5.62; P, 12.42. Found: C, 25.95; H, 4.25; N, 5.88; P, 12.31.

Attempted Preparation of 3,9-bis(*N*-[Phenylthiomethyl]thiocarbamoyl)-2,4,8,10-tetraoxa-3,9-diphosphoro[5.5]undecane-3,9-disulfide (XXIX).

Similar treatment of a solution of 0.65 g. of I and 0.9 g. of phenylthiomethyl isothiocyanate (b. p. 120-2; Lit. (6): b. p. 118-120°) in 5 ml. of *N,N*-dimethylacetamide gave 1.5 g. of yellow, granular solid, m.p. 85-89°. The solid was dissolved in boiling methanol and the solution chilled, yielding a granular solid m.p. 90-93°. Three repetitions of this operation failed to yield a crystalline product or to raise the melting point. The infrared spectrum of the product was consistent with the proposed structure XXIX, but the elemental analysis for nitrogen was low.

*Anal.* Calcd. for  $C_{21}H_{24}N_2O_4P_2S_2$ : C, 40.50; H, 3.88; N, 4.50; P, 9.95. Found: C, 40.43; H, 3.81; N, 2.29, 2.28; P, 10.19.

3,9-bis(*N,N*-Butylcarbamoyl)-2,4,8,10-tetraoxa-3,9-diphosphoro[5.5]undecane-3,9-disulfide (XXIII).

To a solution of 5.2 g. of I in *N,N*-dimethylacetamide (40 ml.) was added, in one portion, a solution of 4.4 g. of *n*-butyl isocyanate (Eastman, White Label) in 10 ml. of the same solvent. An immediate reaction occurred and the solution warmed to 50°. After 20 minutes, the solution had cooled to room temperature. A small amount of sodium methylate was added and the solution was stirred for 10 minutes; but there was no evidence of further reaction and the solution was poured into cold water (400 ml.). The white solid precipitate, filtered, washed with water, then with ethanol and dried *in vacuo* over phosphorus pentoxide, weighed 8.7 g. (91%) m.p. 208-209°. Recrystallization from ethanol gave 8.3 g. (87%) of white needles, m.p. 209-210°.

*Anal.* Calcd. for  $C_{18}H_{28}N_2O_8P_2S_2$ : C, 39.29; H, 6.16; N, 6.11; P, 13.51. Found: C, 39.50, 39.57; H, 6.12, 6.18; N, 6.42; P, 13.43.

3,9-bis(2,2,2-Trichloro-1-hydroxyethyl)-2,4,8,10-tetraoxa-3,9-diphosphoro[5.5]undecane-3,9-disulfide (XXVIII).

A suspension of I (2.6 g. 0.01 mole) in dioxane (60 ml., freshly distilled over sodium) was stirred magnetically and treated with anhydrous chloral (3.0 g., 0.02 mole) and 6 drops of a solution of sodium ethylate prepared from sodium (0.5 g.) and absolute ethanol (20 ml.). An exothermic reaction began at once and the suspended solid dissolved within 3 minutes. The yellow solution was allowed to stand at room temperature for 2 hours. The solvent was then evaporated at reduced pressure, leaving 5.4 g. of yellow solid, m.p. 203-205° dec. The solid was dissolved in nitro-benzene at a temperature of 100°. Cooling produced small, slightly off-white crystals which were removed by filtration, washed thoroughly with benzene and dried *in vacuo*. The material weighed 2.8 g. m.p. 216-218°, dec. A small additional quantity m.p. 210-212° dec., was deposited from the filtrate on long standing.

*Anal.* Calcd. for  $C_9H_{12}Cl_6O_8P_2S_2$ : C, 19.47; H, 2.18; Cl, 38.3; P, 11.16. Found: C, 20.08, 20.14; H, 2.17, 2.39; Cl, 37.6, 37.4; P, 11.08, 11.03.

Similar reactions in which dichloroacetaldehyde and 2,4-dichlorobenzaldehyde were substituted for the chloral gave only gummy materials, which could not be positively identified.

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