

Olin Research Center, Chemicals Division

Preparation and Some Reactions of 3,9-Dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (I)

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3,9-Dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (I), has been synthesized by treating a dimethylacetamide solution of 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (III) with carbon tetrachloride. A number of other known methods for converting dialkyl phosphorothioites to thiophosphorochloridates were also applied to III, but all failed to produce I. Chlorination of either I or III gave an acyclic product, 4,4-bis(chloromethyl)-1,1,7,7-tetrachloro-2,6-dioxa-1,7-diphosphaheptane-1,7-dioxide (IV), in nearly quantitative yield. The same compound was also obtained by the previously known method of chlorinating 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (II). The treatment of pentaerythritol with phosphorus pentachloride gave IV in minor amount along with a 25% yield of 4,4-bis(chloromethyl)-1-chloro-2,6-dioxa-1-phosphacyclohexane-1-oxide (VII). The hydrolysis of I in heated aqueous sodium carbonate gave, after acidification, 3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (VIII). A number of derivatives were prepared by reaction of I with phenoxides and amines. The corresponding thiophosphorofluoridate XI was prepared by treatment of I with potassium fluoride in dioxane.

Previous work in our laboratory showed that the reaction of pentaerythritol with thiophosphoryl chloride gave a bicyclic alcohol, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane-1-sulfide (2), rather than the spiro compound 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (I) which had been expected by analogy to the behavior of pentaerythritol with phosphoryl chloride (3). Since this result made I unobtainable by direct means, we have investigated its preparation by other routes. Surprisingly, in view of the relatively facile reaction of simple dialkylphosphorochloridites with elemental sulfur (4), the known spiro compound 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (II) (5) failed to undergo sulfurization even at temperatures of 170°.

During the course of the present work, a convenient synthesis of the spirophosphorothioite, 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (III) was developed (6) and an attempt was made to convert this to I by treatment with *N*-chlorosuccinimide (7). Although succinimide was formed in this reaction, the other products were an unidentified yellow gum and a chlorine-free white powder, which appeared to be a condensation product of the initially-formed I with unchanged III. When an attempt was made to avoid the formation of this product by adding III in methylene chloride to excess *N*-chlorosuccinimide, only succinimide and a dark yellow gum were formed.

Since diethyl phosphorothioite has been reported (8) to give the corresponding thiophosphorochloridate in high yield upon treatment with elemental chlorine, we attempted the synthesis of I by chlorination of III. However, even at 0° using the calculated amount of

chlorine in carbon tetrachloride, the reaction produced an acyclic product, 4,4-bis(chloromethyl)-1,1,7,7-tetrachloro-2,6-dioxa-1,7-diphosphaheptane-1,7-dioxide (IV). With excess chlorine, the yield of IV was essentially quantitative. The same product was obtained when sulfuryl chloride was employed as a chlorinating agent. Hydrolysis of IV gave the corresponding crystalline tetra-acid V, m.p. 191°, pK_{a1} , 2.60; pK_{a2} , 7.0 (26°, water).

Recently there came to our attention a report that IV could be prepared by chlorination of II (9). We have confirmed that this reaction does yield the same product as the treatment of III with chlorine. We have also found that I reacts rapidly with chlorine, giving IV in 97% yield, and postulated that IV is produced in all of these reactions by the rearrangement of the common intermediate VI. However, we have not been able to isolate this material.

The treatment of pentaerythritol with phosphorus pentachloride produced IV as a minor product, as evidenced by the isolation of approximately 5% of the tetra-acid (V) after hydrolysis of a portion of the crude reaction mixture. The only other product of this reaction which could be positively identified was the known (10) cyclic chloride (VII), which could be distilled from the mixture in a yield of 25%. The distillate crystallized readily and melted at 86° after recrystallization from carbon tetrachloride. Hydrolysis of VII gave the corresponding acid VIIa, m.p. 148°, identical with 2,2-bis(chloromethyl)-1-hydroxy-2,6-dioxa-1-phosphacyclohexane-1-oxide (m.p. 145-148°) synthesized previously by A. M. Meston (11). The reaction of dialkyl hydrogen phosphite with carbon tetrachloride in the presence of triethylamine to yield a phosphorochloridate and chloroform was first described by Atherton, Open-

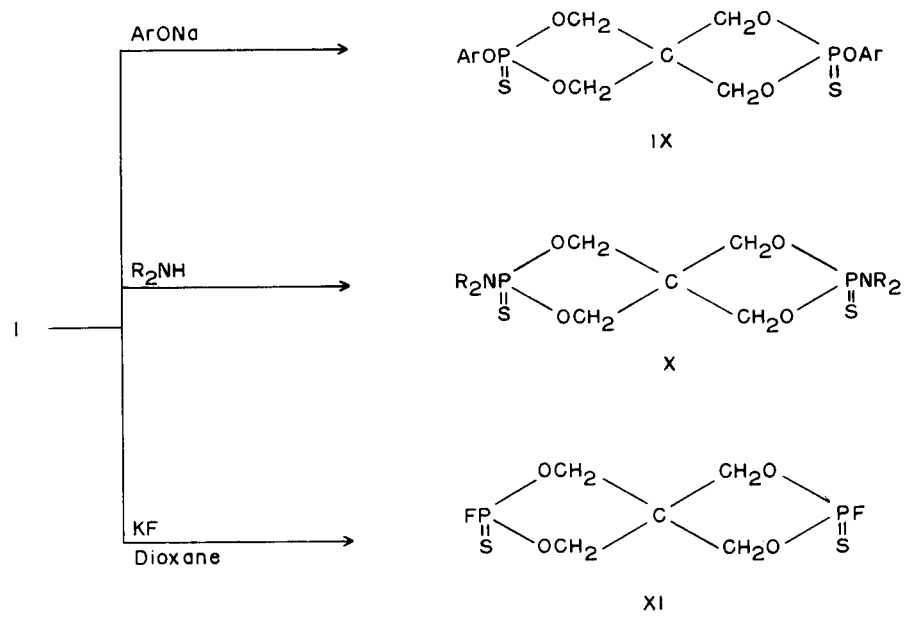
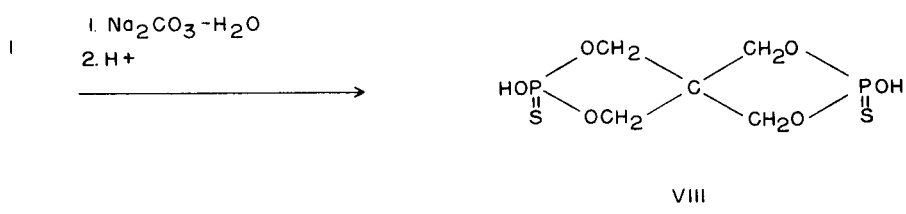
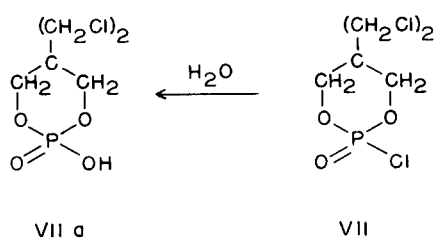
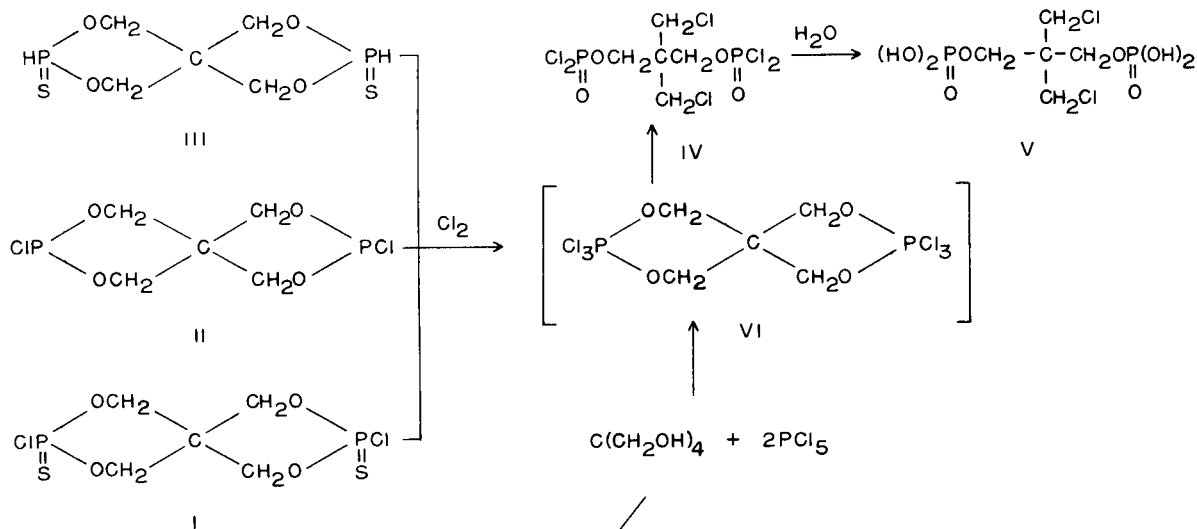
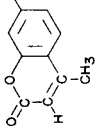
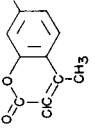
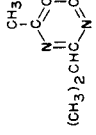
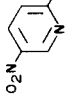
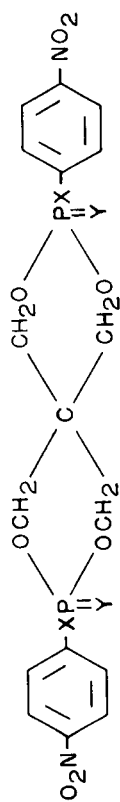


TABLE I
3, 9-Bis(Aryloxy)-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5, 5]undecane-3, 9-disulfides (IX)

Ar	Recrystn. Solvent	M.P., °C	Yield, %	Formula	Calcd., %			Found, %				
					C	H	P	C	H	P		
<i>p</i> -CH ₃ SC ₆ H ₄	Ethanol- acetone	207-208	44	C ₁₉ H ₂₂ O ₈ P ₂ S ₄	42.53	4.13	11.54	23.91 (S)	42.52	4.10	11.46	23.63 (S)
3, 4-C ₆ H ₃ -CH ₃ SC ₆ H ₃ C ₆ Cl ₅	Acetone Not re- crystallized	231-232 >325	63 98	C ₂₁ H ₂ O ₈ P ₂ S ₄ C ₁₇ H ₆ Cl ₁₀ O ₈ P ₂ S ₂	44.67 25.88	4.64 1.02	10.97 7.85	22.72 (S) 44.9 (Cl)	44.50 26.24	4.27 1.24	11.33 7.71	22.71 (S) 44.7 (Cl)
2, 4, 5-Cl ₃ C ₆ H ₂ 2, 4-ClFC ₆ H ₃	Toluene Ethanol- acetone	242-243 202-203	75 65	C ₁₇ H ₁₂ Cl ₆ O ₈ P ₂ S ₂ C ₁₇ H ₁₄ Cl ₂ F ₂ O ₈ P ₂ S ₂	31.36 37.17	1.86 2.57	9.51 11.23	32.7 (Cl) 6.92 (F)	31.82 38.12 (a)	1.84 2.57	9.53 11.25	32.0 (Cl) 6.46 (F)
2, 4-Cl ₂ C ₆ H ₃	Ethanol- acetone	204-205	83	C ₁₇ H ₁₄ Cl ₄ O ₈ P ₂ S ₂	35.06	2.42	10.64	24.4 (Cl)	35.23	2.29	10.66	24.4 (Cl)
<i>p</i> -BrC ₆ H ₄	Ethanol- acetone	217-218	80	C ₁₇ H ₁₂ Br ₂ O ₈ P ₂ S ₂	33.90	2.68	10.29	26.5 (Br)	33.90	2.57	10.10	26.6 (Br)
2, 6-Br ₂ -4-NO ₂ C ₆ H ₂ 2, 6-Cl ₂ -4-NO ₂ C ₆ H ₂	Ethanol- DMF	>320 >320 dec.	70 86	C ₁₇ H ₁₂ Br ₂ N ₂ O ₁₀ P ₂ S ₂ C ₁₇ H ₁₂ Cl ₂ N ₂ O ₁₀ P ₂ S ₂	24.02 30.37	1.42 1.80	7.29 9.22	37.6 (Br) 21.1 (Cl)	24.32 31.24 (a)	1.70 1.93	7.14 9.10	37.2 (Br) 20.6 (Cl)
2-Cl-6-NO ₂ C ₆ H ₃ 4-Cl-2-NO ₂ C ₆ H ₃	Ethanol- acetone	254-255 203-205	82 92	C ₁₇ H ₁₄ Cl ₂ N ₂ O ₁₀ P ₂ S ₂ C ₁₇ H ₁₄ Cl ₂ N ₂ O ₁₀ P ₂ S ₂	33.34 33.84	2.34 2.34	10.27 10.27	4.64 (N) 4.64 (N)	33.84 34.16	2.28 2.30	10.25 10.27	4.83 (N) 4.79 (N)
2-Cl-4-NO ₂ C ₆ H ₃ 3-Cl-4-NO ₂ C ₆ H ₃	Ethanol- acetone	238-239 198-199	88 70	C ₁₇ H ₁₄ Cl ₂ N ₂ O ₁₀ P ₂ S ₂ C ₁₇ H ₁₄ Cl ₂ N ₂ O ₁₀ P ₂ S ₂	33.84 33.84	2.34 2.34	10.27 10.27	4.64 (N) 4.64 (N)	33.89 34.01	2.33 2.28	10.07 10.09	4.81 (N) 4.90 (N)
	o-Dichloro- benzene	260-261 dec.	81	C ₂₅ H ₂₀ O ₁₀ P ₂ S ₂	49.34	3.64	10.18	10.54 (S)	49.02	3.51	10.09	10.52 (S)
	Ethanol- DMF	308-309 dec.	76	C ₂₅ H ₂₀ Cl ₂ O ₁₀ P ₂ S ₂	44.32	2.98	9.14	10.5 (Cl)	44.52	3.09	8.88	10.7 (Cl)
	Petroleum Ether (65-110°)	120-122 dec.	85	C ₂₁ H ₃₀ N ₄ O ₈ P ₂ S ₂	44.99	5.39	11.05	10.00 (N)	43.67 (a)	5.25	11.36	9.10 (N) (a)
	Ethanol- acetone	226-227 dec.	45	C ₁₅ H ₁₄ N ₄ O ₁₀ P ₂ S ₂	33.58	2.63	11.55	10.45 (N)	33.54	2.60	11.47	10.41 (N)

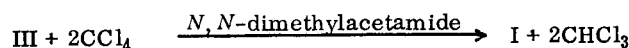
(a) Repeated recrystallizations did not improve these values.

TABLE II
3, 9-Bis(*p*-Nitrophenyloxy/thio)-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5. 5]undecane-3, 9-dioxide/disulfides



X	Y	Recrystallization Solvent	M. P., °C	Yield, %	Formula	Calcd., %				Found, %			
						C	H	N	P	C	H	N	P
O	S	Ethanol-acetone	243-244	80	C ₁₇ H ₁₆ N ₂ O ₁₀ P ₂ S ₂	38.20	3.02	5.24	11.29	38.65	3.02	5.43	11.45
O	O	Ethanol-acetone	228-229	70	C ₁₇ H ₁₆ N ₂ O ₁₂ P ₂	40.65	3.21	5.58	12.33	40.58	3.19	5.61	12.34
S	O	Not Recrystallized	223-225 dec.	40	C ₁₇ H ₁₆ N ₂ O ₁₀ P ₂ S ₂	38.20	3.02	5.24	11.59	37.07	3.05	4.70	12.53
S	S	Not Recrystallized	dec. > 260	50	C ₁₇ H ₁₆ N ₂ O ₈ P ₂ S ₄	36.04	2.85	4.95	10.93	34.32	2.86	4.80	10.49

shaw and Todd (12). The mechanism of this transformation has been discussed by Steinberg (13). Lorenz and Schrader (14) later applied a similar reaction to the preparation of thiophosphorochloridates from phosphorothioites. We found that III suspended in carbon tetrachloride failed to react even at reflux when treated with triethylamine, apparently because of its lack of solubility. However, when carbon tetrachloride was added to a solution of III in *N,N*-dimethylacetamide, a vigorous reaction occurred in the absence of added base. Chilling the reaction solution gave crystalline I in the form of a dimethylacetamide complex. Since I was quite resistant to hydrolysis, the complete removal of solvent could be effected by washing the product with water. A single crystallization from glacial acetic acid gave pure I, m.p. 192-193°, in a yield of 75%.



Heating I for several hours on the steam bath with a solution of sodium carbonate in aqueous dioxane gave, after acidification, the crystalline acid VIII, m.p. 125° dec., *p*K_a, 1.95 (23°), in a yield of 50%.

The preparation of a number of esters of VIII was accomplished by treating the new phosphorus halide (I) in dimethylacetamide solution with alkali metal salts of phenols and heterocyclic hydroxyl compounds. The new compounds IX prepared by this means are listed in Table I.

The reaction product of I and sodium *p*-nitrophenoxide (IX, Ar = *p*-NO₂C₆H₄) was of particular interest because of its structural resemblance to "Parathion". Compound I, and its oxygen analog, 3, 9-dichloro-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5. 5]undecane-3, 9-dioxide (3), were allowed to react with salts of both *p*-nitrophenol and *p*-nitrothiophenol to yield the compounds listed in Table II, which represent all the possible combinations of phosphorus-bonded oxygen and sulfur. No recrystallization solvent could be found for either of the products derived from *p*-nitrothiophenol, and they were purified by extraction with boiling acetone. Satisfactory elemental analysis could not be obtained for either of these compounds, although their infrared spectra were consistent with the proposed structures.

The reaction of I with aziridine in the presence of triethylamine gave 3,9-bis(1-aziridinyl)-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5. 5]undecane-3, 9-disulfide (X, R₂ = (CH₂)₂), identical in physical properties to material previously obtained by treatment of the corresponding spiro-phosphoramidite with elemental sulfur (15). The expected products (X, R = CH₃, and XI) were obtained in high yield when I was treated with dimethylamine or potassium fluoride. The thiophosphorofluoridate XI was converted into the acid VIII by refluxing for three hours in aqueous dioxane.

EXPERIMENTAL

Microanalyses and infrared spectra determinations were performed by the Central Analytical Department, Olin Mathieson Chemical Corporation. Infrared spectra were recorded on a Perkin-Elmer Infracord. With the exception of one, 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-3,9-disulfide (I).

To a solution of 50 g. of 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (III) (6) in 350 ml. of anhydrous *N,N*-dimethylacetamide, stirred and cooled to 5° by means of an ice bath, was added 100 ml. of carbon tetrachloride in one portion. The temperature rose immediately to 11°, then slowly to 43° before falling again.

When the solution had cooled to 3°, a white crystalline solid precipitated. The mixture was allowed to warm to room temperature, causing the solid to dissolve, and to stand for two hours. The solution was then chilled in the freezer and the white crystalline precipitate filtered and dried overnight in vacuum. The dried solid weighed 65 g. and melted over the range 90-115°. Its infrared spectrum showed a very strong carbonyl absorption at 6.1 μ , which was attributed to dimethylacetamide. Stirring the crystalline product with 500 ml. of cold water, filtering and drying gave 52 g. (80%) of white powder, which melted at 189-192°. Its infrared spectrum showed no carbonyl absorption. Recrystallization from glacial acetic acid produced 46.8 g. of shining white platelets m.p. 192-193°.

The filtrate of the reaction solution was warmed *in vacuo* to remove chloroform and excess carbon tetrachloride. The residual dimethylacetamide was poured into water to give, after drying, 8 g. of yellow solid, m.p. 160-166°. Four recrystallizations of this material from glacial acetic acid were required to produce 1.2 g. of reasonably pure product, m.p. 189-191°.

Anal. Calcd. for $C_5H_6Cl_2O_4P_2S_2$: C, 18.24; H, 2.45; Cl, 21.6; P, 18.81; S, 19.49. Found: C, 18.25, 18.05; H, 2.49, 2.51; Cl, 21.8, 21.8; P, 18.90, 18.60; S, 19.47.

3,9-Dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-disulfide (VIII).

To a solution of 2.2 g. of sodium carbonate in 30 ml. of water was added 3.3 g. of I. Dioxane was added dropwise until the crystals of I became thoroughly wetted by the solution. After two hours heating on the steam bath, all but a trace of solid had dissolved. The solution was cooled, filtered, acidified with dilute hydrochloric acid and evaporated to a white solid. Attempts to extract the organic material with alcohol and with acetone were unsuccessful. The solid was then dissolved in 50 ml. of distilled water and passed through a cation exchange column (Dowex 50W-X-8, acid form). The effluent was evaporated at reduced pressure to a slightly yellow solid, which was dried *in vacuo* over sodium hydroxide. The material was dissolved in anhydrous ether; and the solution was filtered to remove a slight haze. Petroleum ether (b.p. 30-60°) was added until the solution became slightly turbid. Chilling produced a colorless oil, which crystallized after standing two days at -5°. The solid melted at 119-123°, with decomposition and weighed 1.7 g. Another recrystallization from mixed ether/petroleum ether (b.p. 30-60°) gave 1.45 g. of white crystals melting at 125-128°, with decomposition. The material was extremely hygroscopic, strongly acidic and freely soluble in water. After fusion with sodium, it gave a positive sulfide and negative chloride test.

Anal. Calcd. for $C_5H_{10}O_6P_2S_2$: C, 20.55; H, 3.45; P, 21.20; S, 21.95. Found: C, 20.14, 20.11; H, 3.65, 3.67; P, 20.63, 20.33; S, 21.12. pK_a 1.95 (23°, water).

A sample which was allowed to equilibrate with moist air for 48 hours, gave an analysis close to that calculated for a dihydrate.

Anal. Calcd. for $C_5H_{10}O_6P_2S_2 \cdot 2H_2O$: P, 18.87. Found: P, 18.48, 18.37.

Attempted Preparation of I, Method A.

An intimate mixture of 0.132 g. (0.5 mmole) of II (5) and 0.032 g. (1.0 mmole) of powdered sulfur was heated under dry nitrogen. A clear, yellow melt was obtained at a bath temperature of 115°. The melt was heated to 170° and held at that temperature for 30 minutes. Cooling produced a yellow solid melting at 110-112°. (A mixture of II and sulfur placed in a melting point bath preheated to 110° melted at 112-113°.) Most of the solid gradually dissolved in cold water forming a strongly acidic solution. The insoluble yellow residue, 0.03 g., melted at 113-114°, unchanged on admixture with sulfur.

Attempted Preparation of I, Method B.

To a suspension of 2.6 g. of III in 50 ml. of dry chloroform was added dropwise, with stirring, a solution of 2.67 g. of *N*-chloro-

succinimide in 50 ml. of methylene chloride. The mixture became warm and the solid appeared to be dissolving. However, when about half of the *N*-chlorosuccinimide solution had been added, a sudden precipitation of fine, white solid occurred. The remaining solution was added and the mixture was stirred for one hour at room temperature. The solid was then removed by filtration, washed with methylene chloride, dried and found to weigh 1.1 g. It decomposed without melting above 250°. Its infrared spectrum showed only absorptions attributable to CH, P-O-C and P = S groups. The solid gave a negative test for chloride following fusion with sodium and also gave a negative Beilstein test. Evaporation of the filtrate of the reaction mixture left 4.1 g. of sticky yellow solid. Extraction of this with carbon tetrachloride left 1.2 g. of succinimide melting at 124-125°, unchanged on admixture with authentic material. The carbon tetrachloride-soluble material was a yellow gum, which could not be identified.

This experiment was repeated in an inverse fashion, a solution of 0.8 g. of III in methylene chloride being added to 3.3 g. of *N*-chlorosuccinimide in the same solvent. In this case, only succinimide and yellow gum were produced.

4,4-Bis(chloromethyl)-1,1,7,7-tetrachloro-2,6-dioxo-1,7-diphosphaspiroheptane-1,7-dioxide (IV) Method A.

A suspension of 1.2 g. of III in 35 ml. of carbon tetrachloride was cooled in an ice bath and treated with a rapid stream of chlorine. The solid dissolved forming a clear yellow solution. Excess chlorine was displaced by a stream of dry nitrogen. The solution was allowed to stand overnight at room temperature, filtered to remove a slight turbidity and evaporated to 1.9 g. of a colorless oil. Distillation was not attempted, but the oil was kept for 30 minutes at 65°/10 mm. prior to analysis, n_D^{20} 1.5092.

Anal. Calcd. for $C_5H_6Cl_4O_4P_2$: C, 14.76; H, 1.98; Cl, 34.9 (ionizable); Cl, 52.3 (total); P, 15.23. Found: C, 15.05, 14.98; H, 2.05, 2.01; Cl, 35.4 (ionizable); Cl, 50.5, 50.7 (total); P, 14.63, 14.75.

Hydrolysis of IV to 4,4-bis(chloromethyl)-1,1,7,7-tetrahydroxy-2,6-dioxo-1,7-diphosphaspiroheptane-1,7-dioxide (V).

One gram of IV was treated with 10 ml. of water at 25°. After a short period, hydrolysis proceeded exothermically with complete dissolution of the oil. Evaporation gave a colorless oil which crystallized on standing in vacuum over phosphorus pentoxide. The crystals, 0.82 g. (100%) were washed with cold ethyl acetate to remove a minor amount of tacky by-product and were then found to melt at 191°. An aqueous solution of the solid gave no precipitate with silver nitrate, but did give a positive Beilstein test.

Anal. Calcd. for $C_5H_{12}Cl_2O_6P_2$: C, 18.00; H, 3.63; Cl, 21.29; P, 18.60; S, 0.00. Found: C, 17.52; H, 3.91; Cl, 20.92; P, 18.70; S, 0.00.

Neut. equiv.: Calcd.: 83.3. Found: 82.3; pK_{a1} , 2.60; pK_{a2} , 7.0 (26°, with water).

Compound IV, Method B.

A suspension of 1.0 g. of I in 15 ml. of carbon tetrachloride was cooled in ice and treated with a slow stream of chlorine. The solid dissolved forming a clear orange solution. Excess chlorine was displaced with dry nitrogen and the solution was evaporated to a colorless oil. After being held for 2 hours at 0.5 mm., the oil weighed 1.2 g. (97%). Its infrared spectrum was identical to that of the product obtained in Method A. Hydrolysis yielded a crystalline acid, m.p. 190-191°, unchanged on admixture with V previously obtained.

Compound IV, Method C.

This is essentially the method of G. H. Birum (9). A mixture of 54.5 g. (0.4 mole) of pentaerythritol and 137.5 g. (1 mole) of phosphorus trichloride was heated to 80° over a period of 3 hours and held at that temperature until hydrogen chloride evolution ceased (2.5 hours) and the mixture had become solid. The product was held at 80°/20 mm. for two hours to remove excess phosphorus trichloride. The solid was then crushed under 200 ml. of carbon tetrachloride. The mixture was cooled in ice, stirred vigorously, and treated with chlorine at such a rate that the internal temperature remained at 25-30°. After 2 hours all the solid had dissolved and the color of chlorine persisted in the solution. Excess chlorine was displaced with nitrogen and the solution was evaporated at reduced pressure. After the residual oil had been held for 2 hours at 0.5 mm., there was obtained 153 g. (94%) of a nearly colorless oil with an infrared spectrum identical to that of IV previously prepared. Hydrolysis of a portion of the product gave V, m.p. 190-192°, unchanged on admixture with an authentic sample.

Compound IV, Method D.

A mixture of 16.1 g. of pentaerythritol, 49.2 g. of phosphorus pentachloride and 200 ml. of tetrachloroethane was stirred and heated

rapidly to 70° then to 145° over a period of 3 hours, at which point hydrogen chloride evolution had ceased and only a small amount of yellow solid remained undissolved. The mixture was cooled, filtered, and the filtrate evaporated at reduced pressure to 38.5 g. (80%) of yellow oil. A 4.7 g. sample of the oil was stirred for 1 hour with 75 ml. of ice-water. A strongly acidic solution was decanted from 3.4 g. of white, gummy material and evaporated at reduced pressure to 0.7 g. of colorless oil. Extraction of the oil with cold ethyl acetate left a small amount of oily residue which crystallized when scratched. The material was dried on a porous clay plate in vacuum over phosphorus pentoxide. There was obtained 0.2 g. of white solid melting at 188-190°, unchanged on admixture with authentic V. Its infrared spectrum was identical to that of V previously prepared. Distillation of 5.2 g. of original reaction product gave 4,4-bis(chloromethyl)-1-chloro-2,6-dioxo-1-phosphacyclohexane-1-oxide (VII), (1.3 g.) b.p. 155-161°/0.2 mm., m.p. 86-88° unchanged on recrystallization from carbon tetrachloride, (lit. (10) m.p. 85°).

Anal. Calcd. for $C_6H_8Cl_2O_3P$: C, 23.68; H, 3.16; Cl, 14.0 (ionizable). Cl, 41.96 (total); P, 12.22. Found: C, 23.27, 23.19; H, 3.20, 3.21; Cl, 12.8 (ionizable); Cl, 42.5 (total); P, 11.91, 12.10.

A portion of the solid was dissolved in aqueous acetone and allowed to stand at room temperature for 24 hours. Evaporation of the solvent and extraction of the residue with refluxing ether gave a crystalline, water soluble acid which melted at 148°. No increase of the melting point was observed after one recrystallization from benzene. However, the VIIa-crystals separating from this solvent contained always 0.5 mole of benzene. The latter was removed by two hours heating *in vacuo* at 80°.

The following phenols were obtained from commercial sources and converted, without prior purification, into their alkali metal salts by treatment with an ethanolic solution of sodium or potassium hydroxide followed by evaporation of the solvent or by filtration in the cases where the phenoxides were insoluble: *p*-methylmercaptophenol, pentachlorophenol, 2,4,5-trichlorophenol, 2-chloro-4-fluorophenol, 2,4-dichlorophenol, *p*-bromophenol, 2,6-dibromo-4-nitrophenol, 2,6-dichloro-4-nitrophenol, 2-chloro-6-nitrophenol, 4-chloro-2-nitrophenol, 2-chloro-4-nitrophenol, *p*-nitrophenol and 2-hydroxy-5-nitropyridine.

The following compounds were synthesized by known methods and converted to their salts: 3-methyl-4-methylmercaptophenol (16), 3-chloro-4-nitrophenol (17) (we were not able to obtain this compound by the method of Ungnade (18)), 4-nitrothiophenol (19), 4-methyl-7-hydroxycoumarin (20), 3-chloro-4-methyl-7-hydroxycoumarin (21), and 2-isopropyl-4-methyl-6-hydroxypyrimidine (22).

3, 9-bis(Aryloxy)-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5.5]undecane-3, 9-disulfides (IX).

The following example is representative of the methods used to prepare the compounds listed in Table I and also the related materials given in Table II.

3, 9-bis(4-Methylmercaptophenoxy)-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5.5]undecane-3, 9-disulfide (IX, Ar = *p*-CH₃SC₆H₄).

To a stirred solution of 5 g. (0.015 mole) of I in 35 ml. of *N,N*-dimethylacetamide was added, in one portion, a solution of 5.3 g. (0.033 mole) of sodium 4-methylmercaptophenoxide in 50 ml. of the same solvent. The mixture was stirred 5 hours at room temperature, then filtered to remove precipitated salt. The salt was washed with dimethylacetamide, then with anhydrous ether and dried. It weighed 1.7 g. (Calcd. 1.76 g.). The dimethylacetamide filtrate was poured into 600 ml. of cold water. The fine, white solid so obtained was found, after filtration, washing with water, then with cold ethanol and drying, to weigh 5.8 g. (72% yield) and to melt at 194-197°. After recrystallization from a mixture of ethanol and acetone, the solid weighed 3.5 g. (44%) and melted at 207-208°.

Anal. Calcd. for $C_{19}H_{22}O_4P_2S_4$: C, 42.53; H, 4.13; P, 11.54; S, 23.91. Found: C, 42.52, 42.71; H, 4.10, 4.05; P, 11.36, 11.46; S, 23.63, 23.49.

3, 9-bis(1-Aziridiny)-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5.5]undecane-3, 9-disulfide (X, R₂ = (CH₂)₂).

A solution of 6.6 g. of I and 4.0 g. of triethyl amine in 100 ml. of chloroform, stirred vigorously and cooled by means of an ice bath, was treated dropwise with a solution of 1.7 g. of aziridine in 10 ml. of chloroform. After completion of the addition, the slightly hazy solution was stirred for 30 minutes at 0°, then allowed to warm to room temperature. The solvent was evaporated at reduced pressure; and the solid residue was extracted with water until the extracts gave no precipitate with silver nitrate. The dried solid weighed 6.7 g. and melted at 217-220°, followed by immediate polymerization, when lightly pressed between cover glasses on a Fisher-Johns melting point block, which had been pre-heated to 215°. Recrystallization from a 50-50 mixture of acetone and ethanol gave 5.6 g. (82% yield)

of white needles melting at 220-222°, with polymerization (block pre-heated to 218°).

Anal. Calcd. for $C_9H_{16}N_2O_4P_2S_2$: C, 31.57; H, 4.71; N, 8.18; P, 18.10; S, 18.74. Found: C, 31.46, 31.27; H, 4.71, 4.51; N, 8.06, 8.18; P, 17.89, 17.95; S, 18.64, 18.65.

This compound had previously been prepared in our laboratory in a yield of 45% by the treatment of 3,9-bis(1-aziridiny)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane with flowers of sulfur (15). The physical properties and analysis of the product were the same as those described above.

3, 9-Bis(dimethylamino)-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5.5]undecane-3, 9-disulfide (X, R = CH₃).

A solution of 3.3 g. of I in 50 ml. of chloroform, rapidly stirred and cooled by means of an ice bath, was treated with a stream of anhydrous dimethylamine. After a few minutes, a fine white precipitate appeared in the yellow solution. When the solution became basic, the gas was shut off and the mixture allowed to warm to room temperature. The solid, removed by filtration, washed thrice with chloroform and dried, weighed 2.5 g. and melted at 260-262°. Evaporation of the filtrate, thorough extraction of the residue with water and drying gave 0.8 g. of solid with the same melting point. Recrystallization of the product from a mixture of dioxane and ethanol produced 2.3 g. melting at 260-261°.

Anal. Calcd. for $C_9H_{20}N_2O_4P_2S_2$: C, 31.21; H, 5.82; N, 8.09; P, 17.89. Found: C, 31.30, 31.47; H, 5.83, 5.82; N, 8.24, 8.42; P, 17.52, 17.52.

3, 9-Difluoro-2, 4, 8, 10-tetraoxa-3, 9-diphosphaspiro[5.5]undecane-3, 9-disulfide (XI).

A 250 ml. Monel metal flask fitted with a stainless steel stirrer, copper condenser and calcium chloride drying tube was charged with 6.6 g. (0.02 mole) of I, 100 ml. of dioxane (freshly distilled over sodium) and 13 g. of powdered potassium fluoride (Baker and Adamson, anhydrous) which had been dried overnight at 100° in a vacuum oven. The mixture was stirred and heated to 105 ± 5° by means of an oil bath for a period of 16 hours. The mixture was cooled, filtered and the salts washed with dioxane. The dried solids weighed 13.2 g. (Calcd. 13.3) and gave a very strong chloride test. The dioxane filtrate was evaporated at reduced pressure to a yellow solid. This was washed several times with water and dried *in vacuo*. It weighed 5.9 g. (100%), and sintered at 170-172° with evolution of hydrogen fluoride (capillary became etched) and melted at 180-181°. Its mixture melting point with I was 160°. After fusion with sodium, the product gave a very weak chloride test. Two recrystallizations from glacial acetic acid (3 ml. of solvent per gram of compound) gave 2.7 g. of white crystals sintering at 173-174°, with hydrogen fluoride-evolution, melting at 182-183°. The recrystallized product contained no chlorine.

Anal. Calcd. for $C_9H_8F_2O_4P_2S_2$: C, 20.27; H, 2.72; F, 12.83; P, 20.91. Found: C, 20.25, 20.29; H, 2.86, 2.85; F, 13.2, 13.2; P, 20.78, 20.89.

A small sample of XI was refluxed for 3 hours in 50% aqueous dioxane. The solvent was then evaporated at reduced pressure and the residue dried overnight in vacuum over phosphorus pentoxide. Recrystallization from ether-petroleum ether (30-60°) gave a hygroscopic acid melting at 125-127° dec. Its mixed melting point with authentic XIII showed no depression.

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