N-(1-Methylpropoxy)phthalimide (4.4 g.) on hydrolysis with hydrobromic acid gave 0.7 g. of a salt (31%), m.p. 128–130° with analysis for hydroxylammonium bromide.

Anal. Calcd. for NH_4OBr: N, 12.15; H, 3.53; Br, 70.13. Found: N, 12.11; H, 3.80; Br, 70.60.

Sodium S-[2-(Phthalimidoöxy)ethyl]thiosulfate.—A mixture of β-(phthalimidoöxy)ethyl bromide Ia ($n = 2$); (25 g., 0.092 mole) and sodium thiosulfate pentahydrate (24 g., 0.096 mole) was refluxed in 50% ethanol (300 ml.) for 3.5 hr. The reaction mixture was evaporated to dryness and the residue extracted twice with boiling absolute ethanol. On cooling the salt (15 g., 50%) was obtained; m.p. 144°. Recrystallization from methanol raised the m.p. to 153–156°.

Anal. Calcd. for $C_{10}H_8NO_6S_2Na$ (325.3): C, 36.92; H, 2.47; N, 4.30; S, 19.71; Na, 7.06. Found: C, 36.72; H, 3.02; N, 4.26; S, 19.68; Na, 6.94.

Some Chemical Reactions of 3,9-Dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-Dioxide

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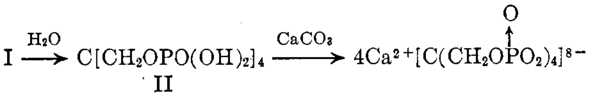
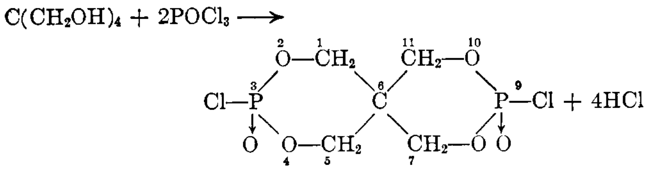
The preparation of pure 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-dioxide and its chemical reactivity are described.

Condensation products of pentaerythritol with phosphoryl chloride have been described.[1,2] With an excess of phosphoryl chloride in the presence of pyridine as an acid acceptor, the open-chain structures I and II were obtained,[1] the latter in the form of its neutral calcium salt. Condensation of pentaerythritol with an excess of more than two moles of phosphoryl chloride in the absence of an acid acceptor apparently led to the difunctional cyclic spiro structure III in contaminated crude form. The analytical data reported for III are incomplete, however, and no reference is made to attempted purification.[2]

$$C(CH_2OH)_4 + 4POCl_3 + \xrightarrow[\text{(excess)}]{C_5H_5N} C(CH_2OPOCl_2)_4 \quad \text{I}$$



$$\text{I} \xrightarrow{H_2O} \underset{\text{II}}{C[CH_2OPO(OH)_2]_4} \xrightarrow{CaCO_3} 4Ca^{2+}[C(CH_2O\overset{\overset{O}{\uparrow}}{P}O_2)_4]^{8-}$$



III

In the present study, we have found that, for the preparation of pure III, a large excess of phosphoryl chloride has to be employed. The crude reaction product finally obtained must be subjected to treatment with several solvents, followed by recrystallization from glacial acetic acid. The compound so obtained, 3,9-dichloro - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro[5.5]-undecane 3,9-dioxide, melted at 233–235°, contrary to a previous report.[2]

Anhydrous dimethylformamide dissolves the phosphospirane in all proportions at room temperature with the formation of clear and colorless solutions. On prolonged standing the solutions remain clear, but become deep yellow after a few hours. Upon careful evaporation at reduced pressure, a yellow-brown glassy material is obtained which possesses the properties of a salt. Structure IV is assigned to this product, which resembles the structure of the so-called Vilsmeier-Haak adducts, since it is soluble in water and contains ionic chlorine.

Such adducts with dimethylformamide are known for highly reactive phosphorus halides, such as phosphoryl chloride[3] and dialkyl phosphorochloridates.[4] The structural formula IV is also supported by the presence of a strong absorption band at approximately 6.0 μ, in its infrared spectrum, indicative of the presence of C=N groups, and the presence of a group of absorptions characteristic of the phosphospirane structure appearing at 10.85–14.60 μ (*cf.* tables of infrared spectra).

A surprising result was obtained when the yellowish solutions of III in dimethylformamide were refluxed in the presence of equimolar amounts of aliphatic compounds containing hydroxyl groups, such as ethylene glycol, 1,4-butanediol, 1,4-hydroxymethylcyclohexane, and 1-octanol. A quantitative amount of the well crystallized acidic dimethylammonium salt (V) separated from the solution after a short heating period. It is apparent that the dimethylammonium cation must have been formed by cleavage of the amide. The relationship of this salt to the hitherto unknown free acid, 3,9-dihydroxy - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro-[5.5]undecane 3,9-dioxide (VI), was demonstrated convincingly by titration of an authentic sample, obtained by direct hydrolysis of III in water at 90°, with one mole of dimethylamine. This titration resulted in a crystalline material, m.p. 263°, identical in all respects with V.

The unexpected reaction of solutions of III in dimethylformamide with aliphatic alcohols will be discussed in detail for the case of 1,4-butanediol. In the absence of solvent, III was converted by the diol into VI. Considerable amounts of tetrahydrofuran, 1,4-dichlorobutane, and 4-chlorobutanol were detected in this reaction. Scheme 1 describes in detail the fate of the phosphorus-containing component in the course of this reaction.

Identification of the diacid VI obtained by the three different routes indicated was made by titration, analysis, and infrared spectrum. The titration curve of VI

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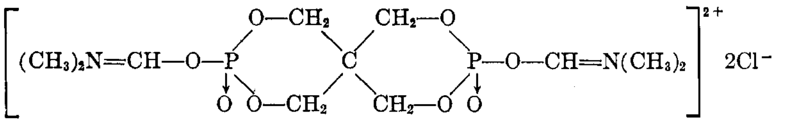
[1] V. Bellavita and O. Tiberi, *Ricerca sci.*, **1952**, 69.

[2] R. Charonnat, J. V. Harispe, M. Harispe, O. Efimovsky, and M. L. Chevillard, *Ann. pharm. franc.*, **10**, 666 (1951).

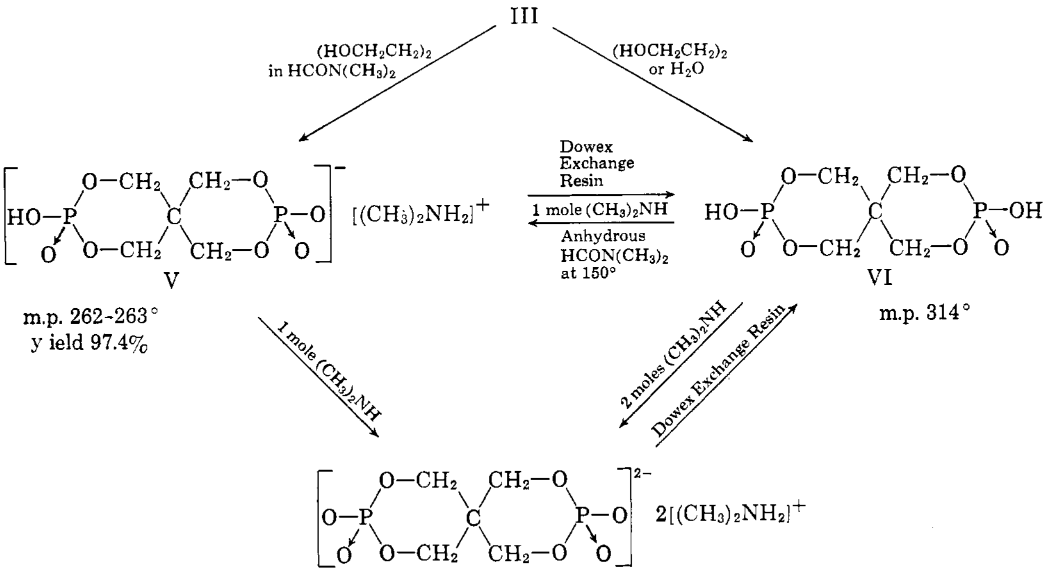
[3] H. Bredereck, R. Gompper, K. Klemm, and H. Rempfer, *Ber.*, **92**, 837 (1959).

[4] F. Cramer and M. Winter, *ibid.*, 989 (1961).



IV

indicates the presence of two strongly acidic hydrogen atoms, both of equal strength. The infrared spectrum shows the broad and shallow P-OH absorption at 2700–2560 cm.$^{-1}$, typical of hydroxyl groups attached to phosphorus[5] (other principal absorptions are listed in Table I). The diacid VI is best prepared from the easily accessible V by ion exchange, since the direct hydrolysis of III produces this compound only in moderate yield. The identity of all samples of VI was proved by mixture melting points and comparison of their infrared spectra.



VII, m.p. 214–215°

SCHEME 1

TABLE I

INFRARED SPECTRUM OF COMPOUND III

Assignment	Absorption peaks, μ
CH stretching	3.5
CH_2 deformation	6.75
CH_2 vibration	6.85
Not assigned	7.20 7.30
P → O	7.70
Not assigned	8.05 8.40 8.70 9.35
C—O—P stretching vibration	9.80
Not assigned; present in all compounds containing the 2,4,8,10-tetraoxa-3,9-diphosphaspiro-[5.5]undecane unit	10.85 11.75 12.90 14.60

The equations given show the conversion of III during the reaction with 1,4-butanediol, but not the fate of the latter. By running the reaction with or without dimethylformamide as a solvent, a low-boiling mobile liquid product was separated and identified by vapor phase chromatography as the 20 to 1 azeotrope of tetrahydrofuran and water, b.p. 68°. Two other liquid products, isolated from the reaction mixture by distillation at reduced pressure, were identified as 1,4-dichlorobutane and as 4-chlorobutanol, also by vapor phase chromatography.

The formation of tetrahydrofuran and water during the reaction of III with 1,4-butanediol can be easily explained by cyclization of the 1,4-diol under the influence of VI, the latter forming during the same reaction. It could be demonstrated that only small amounts of VI were sufficient for the conversion of large amounts of the diol, and that therefore VI is an excellent catalyst for the intramolecular etherification of 1,4-butanediol. Upon heating a sample of pure VI in a large excess of 1,4-butanediol for only a short period and subsequent cooling to room temperature, white leaflets of the empirical formula $C_9H_{20}P_2O_{10}$ separated. This empirical formula is in agreement with a 1:1 complex of VI and 1,4-butanediol. The infrared spectrum (Table II) of this compound shows distinct OH-absorption, but the OH-band is shifted to a higher wave length, indicative of hydrogen-bonded hydroxyl groups. Whereas in the free diacid VI, the P → O absorption appears in a region typical of nonhydrogen-bonded phosphoryl compounds (7.9 μ), this absorption is shifted to 8.2 μ in the adduct, a phenomenon usually observed on hydrogen-bonded P → O groups.[6,7]

Scheme 2 (p. 1610) shows the formation, tentative structures, and thermal behavior of the adduct (VIII) of 1,4-butanediol and VI. Alternatively, only one hydroxyl of 1,4-butanediol might be involved in the hydrogen-bonded complex (VIIIa).

Nuclear magnetic resonance P^{31} measurements conducted on VIII in orthophosphoric acid solution indicated the presence of only one type of phosphorus-atom bonding. In addition, the complete chemical inertness toward phenyl isocyanate supports structure VIII over VIIIa. Upon heating of VIII at 125°, dissociation into the free diacid VI, m.p. 314°, and a mixture of tetrahy-

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(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 259, 262.

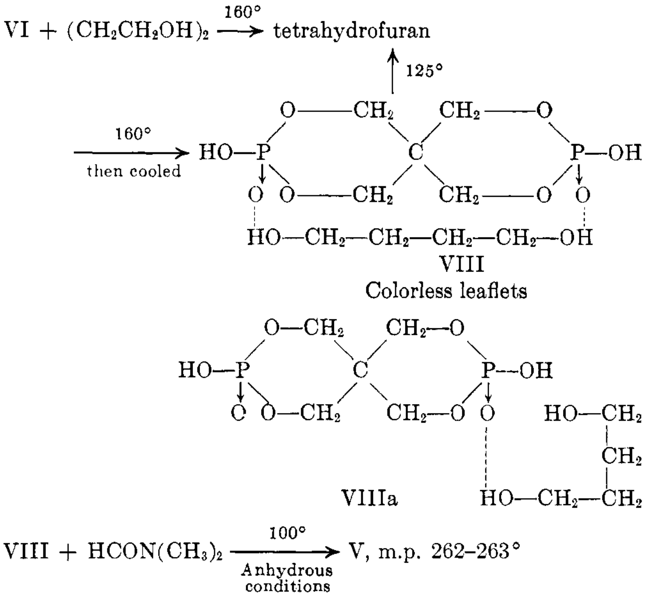
(6) L. F. Audrieth and R. Steinmann, *J. Am. Chem. Soc.*, **63**, 2115 (1941).

(7) K. Niedenzu and J. W. Dawson, *Angew. Chem.*, **72**, 920 (1960).

TABLE II

INFRARED SPECTRA

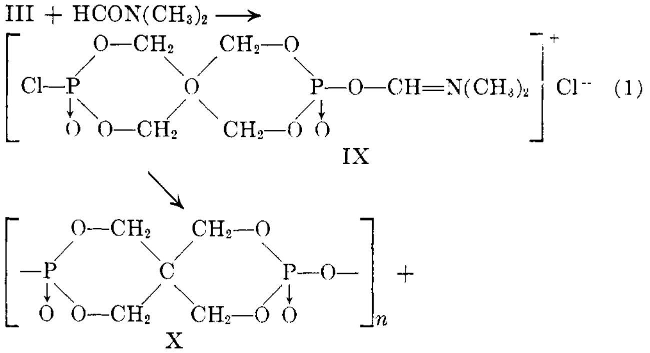
Assignment	—Absorption peaks, μ— Compound VI	Compound VIII
OH, hydrogen-bonded	...	3.15
P—OH	3.5–4.0	3.5–4.0
Not assigned	5.60 6.75	... 6.75
CH_2 deformation	6.80	6.80
Not assigned	7.40	7.30
P → O, not hydrogen-bonded	7.85	...
P → O, hydrogen-bonded	...	8.10
Not assigned	8.35 ... 8.75 9.35	8.32 8.43 8.71 9.30
C—O—P stretching	9.70	9.70
C—O—P stretching	9.90	...
OH deformation	...	10.35
Not assigned; present in all compounds containing the 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane unit	11.00 11.77 12.75 14.50	11.03 11.78 12.88 14.50



SCHEME 2

drofuran and 1,4-butanediol was observed. The latter could be easily detected by reaction with phenyl isocyanate, resulting in the formation of the bis(N-phenylurethane) of 1,4-butanediol, m.p. 183°. It is furthermore of interest that the addition product VIII yielded on heating in anhydrous dimethylformamide at 100° compound V in a very high yield. Since the dimethylammonium cation in V must be derived from the amide, the adduct VIII has a similar ability to cleave anhydrous dimethylformamide, as observed on VI. Compound VIII might rearrange to VIIIa at elevated temperature and the latter might then act as the intermediate necessary to from tetrahydrofuran during heating of VI with excess 1,4-butanediol.

The formation of VI, tetrahydrofuran, 1,4-dichlorobutane, and 4-chlorobutanol by direct interaction of III and 1,4-butanediol can be explained as an attack on phosphorus by the alcohol,[8] with the formation of the bis(4-hydroxybutyl) ester, followed by dealkylation under the influence of hydrogen chloride to yield VI and the 4-hydroxybutyl carbonium ion which can either cyclize to tetrahydrofuran or form the chlorinated products by reaction with hydrogen chloride. From the work reported here and from analogous reactions of other alcohols (among them some which form phosphorus esters with difficulty or not at all),[9] we believe that *in dimethylformamide solution* a Vilsmeier-Haak adduct such as IV or IX forms initially and reacts further as indicated in equations 1–4.



$$[(CH_3)_2N{=}CHCl]^+Cl^- \quad (2)$$
XI

$$XI + HOCH_2CH_2CH_2CH_2OH \longrightarrow (HO)_2CH{-}N(CH_3)_2 + ClCH_2CH_2CH_2CH_2Cl \quad (3)$$
$$\longrightarrow HCON(CH_3)_2 + H_2O$$

$$VI + HCON(CH_3)_2 \longrightarrow V + CO \quad (4)$$

Equation 1 indicates the formation of the Vilsmeier-Haak semi-adduct IX. Its decomposition into a polymeric phosphate with anhydride P–O–P bonds (X) and the amide chloride (XI) is indicated by equation 2. This reaction is analogous to the behavior of the reaction product (XII) of dimethylformamide and phosgene which decomposes easily to the amide chloride XI and carbon dioxide.[10]

$$HCON(CH_3)_2 + COCl_2 \longrightarrow [(CH_3)_2N{=}CHOCOCl]^+Cl^-$$
XII

Amide chlorides of type XI are known to act as powerful chlorinating agents toward aliphatic hydroxyl groups, forming the amide and water (equation 3). The formation of water is essential to the hydrolytic cleavage of the polymer X to the diacid VI. It was demonstrated in an independent experiment that VI is able to cleave dimethylformamide, forming the acidic dimethylammonium salt (V) and carbon monoxide.

The chlorination of the aliphatic hydroxyl groups by the amide chloride XI, as indicated in the over-all equation 3, proceeds *via* an amido ester chloride XIII according to equation 3a.

$$XI + HOCH_2CH_2CH_2CH_2OH \longrightarrow [(CH_3)_2NH{-}CHClOCH_2CH_2CH_2CH_2OH]^+Cl^- \quad (3a)$$
XIII

XIII and the symmetrical analog, $[(CH_3)_2NH{-}CHCl{-}O{-}CH_2CH_2{-}]_2^{2+}\ 2Cl^-$, are extremely unstable compounds which undergo cleavage on warming, yielding the chlorinated hydrocarbon and dimethylformamide. The latter presumably arises through loss of hydrogen chloride by the intermediate formyl dimethylammonium chloride.

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(8) W. Gerrard, W. J. Green, and R. A. Nutkins, *J. Chem. Soc.*, 4076 (1952).

(9) Unpublished work done in this laboratory.

(10) H. Elingsfeld, M. Seefelder, and H. Weidinger, *Angew. Chem.*, **72**, 836 (1960).

Experimental

3,9-Dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-Dioxide (III).—Pentaerythritol, 272.3 g. (2.0 moles; Eastman White Label), and 660 g. of freshly distilled phosphoryl chloride (4.3 moles) were placed in a 3-l. round-bottom flask under reflux, protected from atmospheric moisture. The mixture was heated for 2 hr. at 90°, and held for 20 hr. at 100° until evolution of hydrogen chloride had ceased and the mixture was a colorless hard cake. The product was crushed and returned to the flask, dispersed by addition of 500 g. of phosphoryl chloride, and refluxed for 2 hr. The vigorous evolution of gas which initially occurred had ceased entirely after the 2-hr. period. Most of the excess phosphoryl chloride was recovered by decantation; the rest, by heating to 120° at 10 mm. The crude solid was washed four times with 200-ml. portions of carbon tetrachloride. Before the last washing, the product was collected on a Büchner funnel, dried in air, and crushed to a fine powder. In order to remove a small amount of greasy by-product, one washing with 450 ml. of cold absolute ethanol was necessary, followed by rinsing with ether. The product, a colorless powder, m.p. 229–232° (Fisher-Johns block), was obtained in 80% yield, 478 g. The material was recrystallized from glacial acetic acid as fine needles. The melting point of the dichloride depended on the rate of heating. In order to obtain reproducible melting points, a rate of 6° a minute was applied. After the third recrystallization, the melting point was determined as 233–235°, with no further increase.

Anal. Calcd. for $C_5H_8Cl_2O_6P_2$: C, 20.22; H, 2.72; Cl, 23.88; P, 20.86. Found: C, 20.23, 20.35; H, 2.99, 3.28; Cl, 23.92; P, 20.90, 21.00.

Vilsmeier-Haak Type of Adduct from III and Dimethylformamide.—One gram of III was dissolved in 10 ml. of anhydrous dimethylformamide (DMF). The solution developed a yellow color on standing for several hours at room temperature or upon heating at 100° for 5 min., but no separation occurred. The mixture was refluxed for 20 min. and allowed to stand at room temperature. Excess solvent was distilled after 3 days, leaving 1.2 g. of a yellow-orange glass which was subjected to several ether washings. No recrystallization was possible. The material contained nitrogen, chlorine, and the phosphospirane structure. It possessed salt-like properties, such as water solubility, silver chloride precipitation upon addition of silver ion to the aqueous solution, and hydrogen chloride evolution if brought in contact with cold concentrated sulfuric acid. The possibility of a dimethylamine salt is excluded, since both of the possible salts with dimethylamine were prepared, and they are insoluble in dimethylformamide. Strong infrared absorption at 6.0 μ supported structure IV.

3,9-Dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-Dioxide Monodimethylammonium Salt (V).—Nineteen grams of crude III (0.064 mole) was dissolved in 150 ml. of twice-distilled anhydrous dimethylformamide (b.p. 152–154°, 750 mm.) and 5.75 g. 1,4-butanediol (0.064 mole) was added in one portion. The mixture was refluxed for 40 min.; on cooling to room temperature, 17.5 g. of V precipitated and an additional 1.5 g. was recovered from the filtrate after several days' standing, amounting to 19.0 g. (97.4% yield), m.p. 266°, after recrystallization from 1,4-butanediol (the solvent should not be heated above 130° or slow evolution of dimethylamine occurs).

Anal. Calcd. for $C_7H_{19}NO_8P_2$: C, 27.37; H, 6.23; N, 4.56; P, 20.17. Found: C, 27.58, 28.18; H, 5.71, 5.85; N, 4.50, 4.70; P, 20.10.

From the dimethylformamide filtrate, 2.4 g. of mobile liquid was recovered, b.p. 66°, 750 mm.; it was identified by vapor phase chromatography as a tetrahydrofuran–water mixture.

III (5.94 g., 0.02 mole) was dissolved in 150 ml. of twice-distilled anhydrous dimethylformamide and 2.88 g. of 1,4-bis(hydroxymethyl)cyclohexane (0.02 mole) was added to this solution with shaking until a clear and colorless mixture resulted. After 15 min. of refluxing, 6.0 g. of a crystalline white solid separated, was filtered, and washed twice with acetone. It melted at 264–266°, gave no melting point depression with the product first obtained, and was evidently V (98.4% yield). Dimethylformamide in the filtrate was removed by distillation at 5 mm. (oil-bath temperature finally 130°). A yellowish oil, together with a minor amount of solid material, remained. Ether dissolved the oil and left the solid. After removal of the ether, the oil was subjected to vacuum distillation; b.p. 84–85° (0.08 mm.). Chlorine analysis, vapor phase chromatography, and the ability of the oil to decolorize bromine in carbon tetrachloride solution indicated that it consisted of a mixture of 1,4-bis(chloromethyl)cyclohexane and 1-vinyl-4-chloromethylcyclohexane. In addition, the infrared spectrum did not show any OH-absorption but indicated unsaturation.

Interaction of III and 1,4-Butanediol in the Absence of Dimethylformamide.—III (17.82 g., 0.060 mole) was placed in a 100-ml. round-bottom flask and mixed thoroughly with 5.4 g. of 1,4-butanediol (0.06 mole). The joint of the flask was connected *via* an adapter to a 50-ml. receiver. The system was purged with dry nitrogen. The mixture was heated to 110°, whereupon reaction occurred, with hydrogen chloride elimination; in the ice-cooled receiver, 2 g. of a colorless mobile liquid (n^{25}D 1.4140) collected, identified as a mixture of tetrahydrofuran and water by gas phase chromatography. After 1 hr. at 110°, the temperature was raised to 145° for 3 hr. Application of a 14-mm. pressure at 145° caused fast distillation of 1 g. of an almost colorless oil and formation of residual gray powdery material (16.5 g.). By vapor phase chromatography and infrared analysis, the oil was found to be a mixture of 85% 1,4-butanediol and 15% 4-chlorobutanol. The solid residue, extracted with hot ethanol, gave about 9 g. of an insoluble colorless solid mixture. This mixture was separated by treatment with 50 ml. of cold water, resulting in 4.5 g. of water-insoluble unreacted III and 4.4 g. pure VI, the latter being obtained by evaporation of the water at room temperature. An additional crop of 3.8 g. of VI was obtained by evaporation of the ethanol extract to dryness and treatment of the residue with 30 ml. of acetone, which dissolved the hygroscopic brown glass. The combined fractions of VI weighed 8.3 g. (53.2% yield, 71% conversion), pyramidal crystals, after recrystallization from glacial acetic acid, m.p. 306–307°. Mixture melting point with an authentic sample of VI gave no depression.

Reaction of III and 1,4-Bis(hydroxymethyl)cyclohexane.—An apparatus similar to that just described was charged with 5.94 g. of III (0.020 mole) and 2.88 g. of 1,4-bis(hydroxymethyl)cyclohexane. The reaction started smoothly at 150°, thus making it possible to raise the temperature gradually to 195° where it was kept for 5 hr. Additional 3-hr. heating at 175° at 0.1 mm. gave no distillate, only a crystalline solid. Separation was achieved by two extractions with 20-ml. portions of cold acetone, which left 5.5 g. of solid undissolved. The solid residue was composed chiefly of VI but admixed with a minute amount of a polymeric material. Upon treatment with cold water, VI dissolved completely, but the polymer (m.p. 265–275°) did not. Evaporation of the aqueous solution and recrystallization from glacial acetic acid yielded prismatic crystals, m.p. 306°; a mixture melting point taken with authentic VI showed no depression.

After removal of the solvent from the acetone extract, a chlorine-containing yellow oil remained. Fractional distillation gave 1.5 g. of a colorless liquid fraction, b.p. 82–84° (0.08 mm.), n^{19}D 1.4963. The resemblance to the infrared spectrum of the oil obtained from III and 1,4-bis(hydroxymethyl)cyclohexane in dimethylformamide suggested the formation of a similar product in this experiment, though dimethylformamide was absent.

3,9-Dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-dioxide (VI). a. **By Hydrolysis of III.**—A sample of 3.4 g. of III was suspended in 30 ml. of distilled water and the suspension heated with agitation at 90° for 15 min. During this period, most of the material went into solution with strongly acidic reaction. Evaporation to dryness of the filtered solution at room temperature gave a crystalline residue which was treated first with cold absolute ethanol, followed by one acetone washing. The solvent treatment resulted in 1.7 g. of crystals (57% yield), m.p. 314° after one recrystallization from glacial acetic acid.

Anal. Calcd. for $C_5H_{10}O_8P_2$: P, 23.82%. Found: P, 23.3%.

b. **From V and Dowex Exchange Resin.**—Crude V (2.2 g.) was dissolved in 25 ml. of distilled water and the solution poured over a Dowex-50-W-X-8 column, having a capacity of 1.7 meq./ml. wet resin.

The solution obtained was evaporated at room temperature, resulting in 1.9 g. of VI, m.p. 287°. A second run through the same column gave the same amount of VI, but of higher m.p. (304°). Bipyramidal crystals, m.p. 314°, were obtained after one recrystallization from glacial acetic acid; yield, 98.8%.

Anal. Calcd. for $C_5H_{10}O_8P_2$: C, 23.09; H, 3.88; P, 23.82. Found: C, 23.24, 23.00; H, 3.74, 3.60; P, 23.32.

c. **From V and Hydrochloric Acid.**—To 2 g. of V, 10 ml. of 40% hydrochloric acid was added with external cooling. The solution obtained was evaporated to dryness under reduced pressure at room temperature. From the resulting mixture of crystals, dimethylammonium chloride (m.p. 168–170°) was extracted by hot chloroform. The residue, insoluble in chloroform (VI, 1.6 g., 94%), was recrystallized from glacial acetic acid, yielding crystals, m.p. 308°.

Titration of VI.—a. Conductometric titration of 261.96 mg. of VI with 0.106 *N* aqueous dimethylamine required 18.9 ml. to reach the end point; *i.e.*, 2 meq. of acid were present. Equiv. wt.: 261.96/2 = 131. Calcd. for VI: 130.

The titrated aqueous solution was evaporated to dryness, the solid was dissolved in ethanol, filtered, and reprecipitated by acetone, to yield colorless crystals, m.p. 214–216°. As evidenced by mixture melting point and infrared spectrum, this compound VII was identical with crystals obtained from V and excess dimethylamine. VI (0.5 g.) was dissolved in 10 ml. of 25% aqueous dimethylamine, filtered, and excess acetone was added; a colorless oil separated. The aqueous acetone was decanted, the oil was dissolved in 3 ml. of ethanol and excess acetone was added; the resulting oil crystallized within an hour to a solid, m.p. 214–215°.

b. Titration of 261.96 mg. of VI with 9.45 ml. of 0.106 *N* aqueous dimethylamine solution gave after evaporation colorless crystals, m.p. 261–262°, after one washing with absolute ethanol. Infrared spectrum and mixture melting point determination proved the identity of this material with V, previously obtained from III and 1,4-butanediol in dimethylformamide.

c. Titration of 57.61 mg. of V required 4.65 ml. of 0.0947 *N* sodium hydroxide. Equiv. wt. Calcd.: 130.0. Found: 130.8. A crystalline disodium salt separated upon evaporation of this solution at room temperature.

Hydrogen-Bonded Adduct VIII Obtained from VI and 1,4-Butanediol.—VI (1.0 g.) in a 20-ml. distilling flask was suspended in 4 g. of 1,4-butanediol. When the flask was heated in an oil bath at 160°, a violent reaction occurred, with distillation of 1.8 g. of a tetrahydrofuran–water azeotrope, b.p. 68° (750 mm.). Shiny leaflets separated when the mixture cooled to room temperature. After filtration and drying over phosphoric anhydride, 0.9 g. of a solid was obtained which on heating on a Fisher-Johns plate, partially melted at 125°, resolidified at 185°, and remelted at 314°.

Anal. Calcd. for $C_9H_{20}O_{10}P_2$: C, 30.85; H, 5.73; P, 17.71. Found: C, 30.95, 31.06; H, 5.79, 6.14; P, 16.99.

Equiv. wt.: 39.76 mg. required 2.25 ml. of an aqueous 0.102 *N* dimethylamine solution. Only one inflection was observed. Calcd. for $C_9H_{20}O_{10}P_2$: 175. Found: 175.

Dry distillation of a sample of VIII resulted in elimination of a mixture of tetrahydrofuran and 1,4-butanediol. The latter condensed in the upper cool part of the flask. Reaction with excess phenyl isocyanate resulted in a crystalline material, m.p. 183°, after washing with ether and standing for 2 hr. on a clay plate. Mixture melting point with an authentic sample of the bis-(N-phenyl)urethane of 1,4-butanediol, m.p. 183°, prepared as described in the literature,[11] did not show any depression.

Acidic Ammonium Salt V from VI and Anhydrous Dimethylformamide—A sample of 1.0 g. of VI was dissolved in hot anhydrous dimethylformamide and refluxed for a short period. After standing overnight, 1.1 g. of V, m.p. 264–266°, had separated.

Acidic Ammonium Salt V from VIII and Anhydrous Dimethylformamide.—A sample of 0.5 g. of VIII was heated in 5 ml. of anhydrous dimethylformamide for a short period to reflux temperature and allowed to stand 2 days at room temperature; 0.3 g. of crystals, m.p. 263–265°, separated. Mixture melting point determination with an authentic sample of V did not show any depression.

Dimethylacetamide Salt of VI.—In contrast to dimethylformamide, dimethyl acetamide is not cleaved by VI. Thus, from a solution of 1 g. of VI in 10 ml. of anhydrous dimethylacetamide prepared by gentle heating of the mixture, fine needles started to separate after 3 days' standing. The yield was 0.7 g. Partial melting was observed at 175°, resolidification at 220°, and final melting at 303.5° (apparently the melting point of VI). Nitrogen analysis and infrared spectra supported the assumption of an acidic salt of VI with one mole of dimethylacetamide.

Anal. Calcd. for $C_9H_{18}NO_9P_2$: N, 4.05. Found: N, 4.00.

Polymerization of VI by Anhydride Formation.—This experiment was conducted to demonstrate the possibility of the existence of polymeric X as assumed in the reaction mechanism. The presence of P–O–P linkages in X forecasts hydrolytic sensitivity. The anhydrization was conducted according to the work of Grunze, Dostal, and Thilo[12] on inorganic phosphates.

One gram of VI was suspended in 40 ml. of a 1:1 mixture of glacial acetic acid and acetic anhydride. After the mixture had been allowed to stand overnight at room temperature, no visible change was observed. Refluxing of the mixture for 1.5 hr. resulted in a clear and colorless solution from which no crystals separated upon standing for a period of 3 days. The solution was evaporated to dryness at 85° at 10 mm. The deep brown residue, kept for 2 hr. at 125° at 0.1 mm., gave 0.8 g. of shiny brown material which dissolved in water to form a strongly acid solution. The solid softened at 92–105°, and melted at approximately 150°. Very short fibers could be drawn from this melt.

The infrared spectra were measured by use of the Perkin-Elmer Model 21. The samples were embedded in potassium bromide.

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Reaction of 3,9-Dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-Dioxide with Dimethyl Sulfoxide

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3,9-Dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-dioxide reacts with dimethyl sulfoxide to form a new type of sulfoxonium salt in almost quantitative yield. Methyl chloromethyl sulfide is formed as a by-product during this reaction, and is converted by excess dimethyl sulfoxide into methyl methanethiolsulfonate. The latter reaction exemplifies a new mode of formation for methyl alkanethiolsulfonates.

The preparation of pure 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-dioxide (I) from pentaerythritol and excess phosphoryl chloride has been described in the preceding paper.[1] In the present report, we describe the exothermic reaction of this compound with dimethyl sulfoxide to form a crystalline solid, $C_7H_{16}O_9P_2S$, plus formaldehyde and liquid phosphorus-free materials. The material balance showed that all of the phosphorus was present in the crystalline product, which we believe is the first representative of hitherto unknown sulfoxonium phosphates, for which structure V was elucidated by chemical and

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