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REACTION OF SOME CYCLIC PHOSPHORUS CHLORIDES WITH DIMETHYL SULFOXIDE

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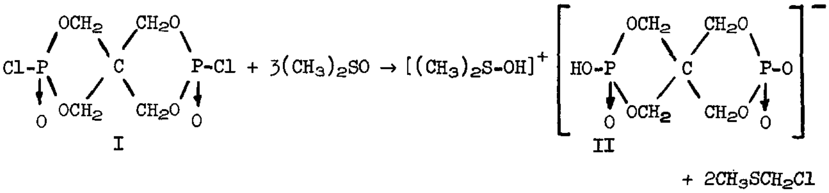
WE have recently prepared pure 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide (I) and have studied some of the chemistry of this reactive bifunctional phosphochloridate.[1] We report here the replacement of chlorine by hydroxyl in anhydrous medium by reaction of I with excess dimethyl sulfoxide. A well defined crystalline intermediate, the hitherto unknown sulfoxonium phosphate (II) was isolated in nearly quantitative yield.


I
II

The structure of II has been elucidated by chemical and spectroscopic methods. Pyrolysis of II gave 3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide, m.p. 314°, a strong acid with two equally ionizable protons. Treatment of either II or the diacid with diazomethane formed the dimethyl ester, m.p. 208°. II was titrated with dimethylamine solution as a monoprotonic strong acid. Infrared measurements performed on II in dimethylformamide showed a strong -OH absorption at 2.95 μ. Since the P-OH group cannot cause this absorption, the structure of the sulfoxonium

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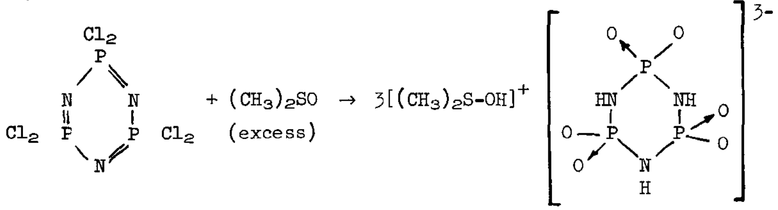
[1] R. Charonnat, J. V. Harispe, M. Harispe, O. Efimovsky, and M. L. Chevillard, Ann. pharm. franç. 10, 666 (1951), reported that the condensation of pentaerythritol and phosphoryl chloride gives an infusible solid, unlike the product obtained in the present work.

cation is probably $[(CH_3)_2S\text{-}OH]^+$ rather than $[HS(CH_3)_2O]^+$.

Methyl chloromethyl sulfide formed during the reaction of I with dimethyl sulfoxide reacted with an excess of the latter to form methyl methanethiolsulfonate. This exemplifies a new mode of formation for methyl alkanethiol sulfonates.

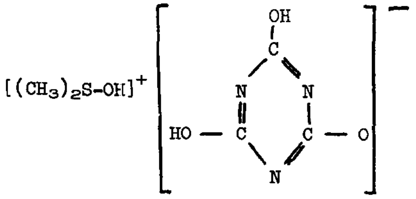
$$CH_3SCH_2Cl + 3(CH_3)_2SO \rightarrow CH_3SO_2SCH_3 + [(CH_3)_3S]^+Cl^- + CH_2O + (CH_3)_2S$$

Similar results were obtained when cyclic trimeric and tetrameric phosphonitrilic chloride were allowed to react with excess dimethyl sulfoxide. The tris(sulfoxonium) salt of trimetaphosphimic acid (IV) was obtained as a water-soluble solid in the case of the trimer, and could be precipitated from aqueous solution by silver ion.



IV

Cyanuric chloride, the carbon analog of $(NPCl_2)_3$, reacted with dimethyl sulfoxide to yield a greasy non-crystallizable water-soluble reaction product and methyl methanethiolsulfonate, $CH_3SO_2SCH_3$, indicating a similar mechanism. A crystallizable sulfoxonium cyanurate (V), m.p. 163-5°, was obtained, however, by an alternative method from excess dimethyl sulfoxide and cyanuric acid.



V

Only brief mention of the experiments performed will be given here, since a detailed account will be published later.

The crude material obtained by heating 2.0 moles of pentaerythritol and 4.3 moles of phosphoryl chloride at 90-100° until evolution of hydrogen chloride had ceased was separated from excess phosphoryl chloride and purified by solvent extraction; recrystallization from glacial acetic acid gave an 80% yield of I, m.p. 233-235°.

Eight grams of dimethyl sulfoxide and 3.0 g. of powdered I reacted exothermally to give a clear colorless solution, which solidified at room temperature. Washing with two 15-ml. portions of dry chloroform resulted in 3.7 g. of product, colorless needles, m.p. 174-176° from absolute ethanol. The compound was free from chlorine; titration and elemental analysis were in agreement with structure II.

The chloroform filtrates from the preceding preparation were distilled at atmospheric pressure and at a bath temperature below 70°. A yellow oil remained, which was distilled at reduced pressure. Dimethyl sulfoxide and water-soluble trimethylsulfonium chloride distilled between 45 to 60° at 0.5 mm., followed by a liquid, b.p. 61° (0.5 mm.), n_D^{22} 1.5039. Analytical results, infrared spectra, and comparison of physical properties with those of an authentic sample indicated that the liquid product obtained was pure methyl methanethiolsulfonate.

Methyl chloromethyl sulfide (4.3 g.) was mixed with 15 g. of anhydrous dimethyl sulfoxide and allowed to stand at room temperature for four hours. By addition of 45 ml. of dry chloroform to the gelatinous mass, solid paraformaldehyde was separated and filtered. The chloroform filtrate yielded 4.5 g. of a yellow oil (dimethyl sulfide, dimethyl sulfoxide, and trace amounts of dimethyl disulfide distilled with the solvent). The oil was distilled at reduced pressure, giving a main fraction, b.p. 61° (0.5 mm.), n_D^{20} 1.5123. The infrared spectrum showed strong $-SO_2-$ group absorption at 7.6 μ and 8.8 μ, and was identical with the spectrum of methyl methanethiolsulfonate obtained as a product during the formation of II initially.

Reaction of Phosphonitrilic Chloride and Dimethyl Sulfoxide. - Trimeric phosphonitrilic chloride (2.0 g., 0.0058 mole) was added to 10 g. (0.13 mole) dimethyl sulfoxide cooled in ice water. A vigorous reaction ensued, causing dimethyl sulfide and formaldehyde to distill and paraformaldehyde to sublime into the receiver. The same procedure as described for the isolation of II was employed and 0.8 g. of a light grey powder, m.p. 130°, with prior softening was obtained (release of dimethyl sulfoxide was observed during melting).

The sulfoxonium salt was soluble in water, and by addition of silver ion, silver trimetaphosphimate was precipitated. Distillation of the chloroform extracts gave a colorless oil, b.p. 63° (0.5 mm.), n_D^{20} 1.5082, which had an infrared spectrum identical in all respects with that of methyl methanethiolsulfonate.

Preparation of Dimethylsulfoxonium Cyanurate. - Cyanuric acid (1.0 g.) was heated in 4.0 g. of dimethyl sulfoxide until solution was effected. Cooling to room temperature caused precipitation of 1.20 g. of dimethylsulfoxonium cyanurate, colorless needles, melting at 163-165°, with loss of dimethyl sulfoxide.