tals, 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.

Acknowledgment.—The analytical work was carried out by the Olin Central Analytical Laboratories, Dr. Sidney Siggia, Director, whose assistance and advice are gratefully acknowledged. The authors are also grateful to Dr. H. Agahigian, W. W. Harple, H. G. Nadeau, and Dr. R. Rittner and their co-workers for performing instrumental and microanalytical work.

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[11] J. Hamonet, *Bull. soc. chim. France*, [3] **33**, 525 (1905).

[12] T. Grunze, K. Dostal, and E. Thilo, *Z. anorg. allgem. Chem.*, **302**, 221 (1959).

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

RUDI RÄTZ AND ORVILLE J. SWEETING

Packaging Division, Film Operations, Olin Mathieson Chemical Corporation, New Haven, Connecticut

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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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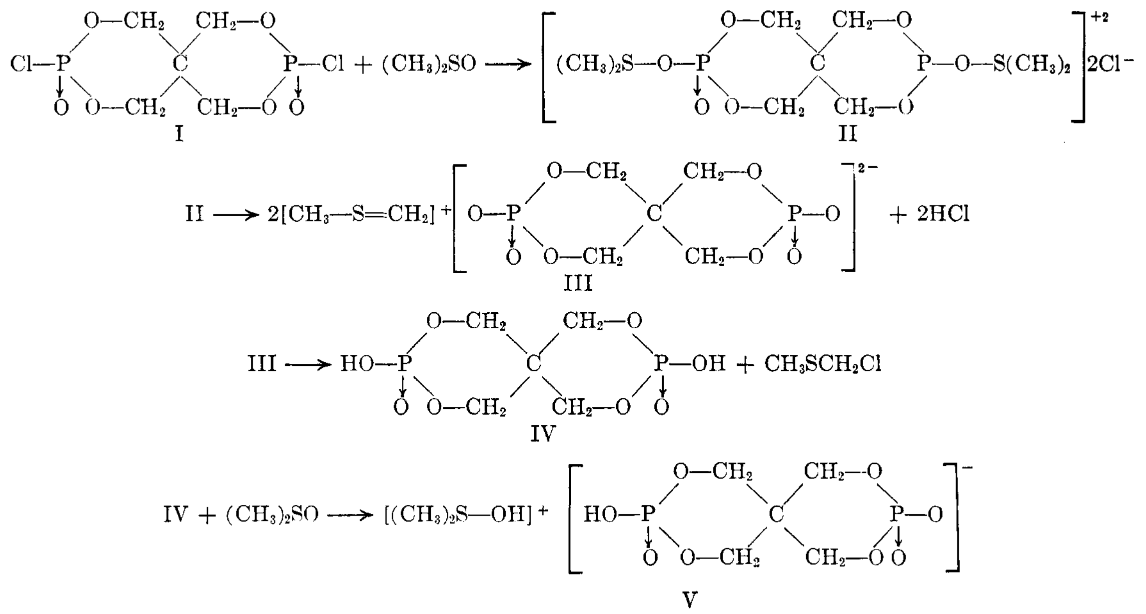
[1] R. Rätz and O. J. Sweeting, *J. Org. Chem.*, **28**, 1608 (1963).



spectroscopic means. We find no previous report of the isolation and identification of defined reaction products deriving from reactions of phosphorus halides with dimethyl sulfoxide.

The probable steps in the formation of V are as indicated above.

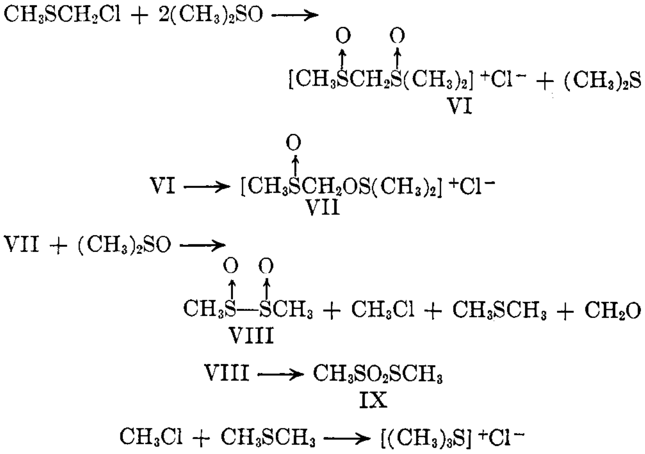
It is postulated that the unstable intermediate II is first formed; by loss of a proton from a methyl group, another unisolated intermediate III forms, with a methylenesulfonium cation associated at either end. Action of the hydrogen chloride present results in formation of the free acid IV and methyl chloromethyl sulfide. IV formed the sulfoxonium salt V in the presence of excess dimethyl sulfoxide, but methyl chloromethyl sulfide could not be separated. Rather, methyl methanethiolsulfonate (IX) was isolated.

The validity of the proposed route from dimethyl sulfoxide to V *via* IV is supported by the fact that a solution of an independently prepared authentic sample of IV in dimethyl sulfoxide, upon cooling, deposited the same acidic sulfoxonium salt V. The existence of methyl chloromethyl sulfide as an intermediate in the formation of the isolated by-product methyl methanethiolsulfonate (IX) was supported by treating authentic methyl chloromethyl sulfide, synthesized according to known procedures,[2-4] with excess dimethyl sulfoxide. The products isolated were IX, paraformaldehyde, and an oily chlorine-containing material, probably trimethylsulfonium chloride,[5] which could not be freed entirely from admixed dimethyl sulfoxide.

Thus the over-all reaction appears to be

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

It was demonstrated that the first step in the reaction of methyl chloromethyl sulfide and dimethyl sulfoxide is probably the formation of an oxidized form of a salt-like addition compound of equimolecular amounts of both reactants with the tentative structure VI, indicated in the following possible scheme of reactions,



$$CH_3SCH_2Cl + 2(CH_3)_2SO \longrightarrow [CH_3\overset{O}{\overset{\uparrow}{S}}CH_2\overset{O}{\overset{\uparrow}{S}}(CH_3)_2]^+Cl^- + (CH_3)_2S$$

VI

$$VI \longrightarrow [CH_3\overset{O}{\overset{\uparrow}{S}}CH_2OS(CH_3)_2]^+Cl^-$$

VII

$$VII + (CH_3)_2SO \longrightarrow CH_3\overset{O}{\overset{\uparrow}{S}}-\overset{O}{\overset{\uparrow}{S}}CH_3 + CH_3Cl + CH_3SCH_3 + CH_2O$$

VIII

$$VIII \longrightarrow CH_3SO_2SCH_3$$

IX

$$CH_3Cl + CH_3SCH_3 \longrightarrow [(CH_3)_3S]^+Cl^-$$

which accounts for all of the isolated products (VII and VIII are hypothetical).

Compound VI showed a powerful absorption peak at 8 μ which is indicative of the presence of S→O groupings in sulfoxonium salts, R_3SO^+.[6] Detection by vapor phase chromatography of considerable amounts of dimethyl sulfide supports the view that dimethyl sulfoxide had acted as an oxidizing agent before or after the combination of dimethyl sulfoxide with methyl chloromethyl sulfide. We assume that, after rearrangement of VI into VII, the latter degrades under the influence of excess dimethyl sulfoxide to form dimethyl disulfoxide (VIII), which rearranges to form the thiolsulfonate (IX).

By infrared and nuclear magnetic resonance spectra, complete elemental analysis, and comparison with physical data in the literature,[7] the formation of IX from methyl chloromethyl sulfide and dimethyl sulfoxide was well established. The strong absorption bands formed at 7.6 μ and 8.8 μ are typical of the sulfonyl grouping; the absence of S→O absorption in the 9.0–10.0-μ region excludes structure VIII. The possible participation of dimethyl disulfide as an intermediate in the conversion of methyl chloromethyl sulfide into IX is unlikely, since it was found that dimethyl sulfoxide cannot oxidize dimethyl disulfide to IX, a result giving further support to the route illustrated.

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[2] H. Böhme, *Ber.*, **69**, 1610 (1936); **70**, 379 (1937).

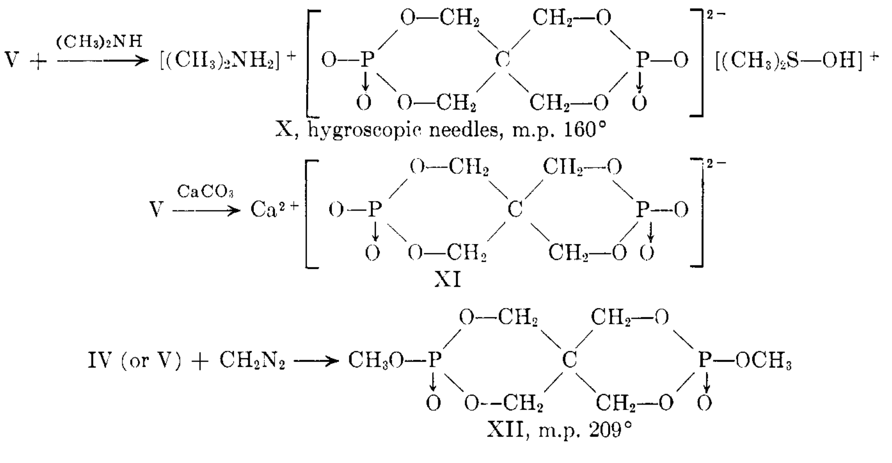
[3] L. A. Walter, L. H. Goodson, and R. J. Fosbinder, *J. Am. Chem. Soc.*, **67**, 655 (1945).

[4] W. E. Truce, G. H. Birum, and E. T. McBee, *ibid.*, **74**, 3594 (1952).

[5] H. Blättler, *Monatsh.*, **40**, 417 (1920).

[6] R. Kuhn and H. Trischmann, *Ann.*, **611**, 117 (1948).

[7] H. J. Backer, *Rev. trav. chim.*, **69**, 1127 (1950).



X, hygroscopic needles, m.p. 160°

XI

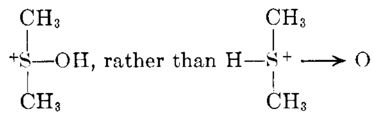
XII, m.p. 209°

In the past, esters of alkanethiolsulfonic acids have been prepared mainly by oxidation of disulfides with dilute nitric acid[8] or peracetic acid,[9] by alkylation of alkali alkanethiolsulfonates,[10] or by oxidation of methanesulfenyl chloride with concentrated nitric acid.[11] The synthesis of alkyl alkanethiolsulfonates by interaction of alkyl α-haloalkylsulfides with dimethyl sulfoxide is an entirely new route to this class of compounds.

The novel and unexpected reaction between an α-chloromethyl thioether and dimethyl sulfoxide was extended to ethyl chloromethyl sulfide. An almost quantitative yield of methyl ethanethiolsulfonate, $CH_3CH_2SO_2SCH_3$, instead of $CH_3CH_2SO_2SCH_2CH_3$, gave further support to the above route and proved that the —SCH_3 group in IX and in its ethyl homolog, $C_2H_5SO_2SCH_3$, must arise from dimethyl sulfoxide.

Chemical reactions performed on V showed that this compound is an acidic sulfoxonium salt of IV. Simple heating of V resulted in dimethyl sulfoxide and small amounts of dimethyl sulfide as volatile materials, and the diacid IV remained as a distillation residue. Compound V can be precisely titrated with dimethylamine solution as a monobasic acid resulting in compound X. Heating of an aqueous solution of V with excess calcium carbonate replaces the sulfoxonium cation, with the formation of the calcium salt XI. Diazomethane reacts with V in the same way as with IV, to form the dimethyl ester XII. These transformations are shown above.

Infrared measurements performed on V in dimethylformamide showed a very distinct OH absorption at 2.95 μ. Since the P—OH group in V cannot cause this absorption and the presence of moisture was discounted by the absence of any band at 6.1 μ, the structure of the sulfoxonium cation of V can be assumed to be



$$(CH_3)_2\overset{+}{S}{-}OH, \text{ rather than } H{-}\overset{+}{S}(CH_3)_2 \longrightarrow O$$

Experimental

Reaction of 3,9-Dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-Dioxide (I) and Dimethyl Sulfoxide.—Eight grams of dimethyl sulfoxide, b.p. 74° (10 mm.), was charged into an upright 7.5 × 1 in. tube, 3.0 g. of finely ground I was added, and the tube was connected by a U-tube to a side-arm test-tube receiver immersed in a beaker filled with powdered Dry Ice. After a brief interval, an exothermic reaction occurred which it was necessary to moderate by cooling the reaction tube frequently with ice–water. A clear colorless solution resulted which finally solidified. The receiver contained a few droplets of condensed formaldehyde. The solid residue was washed twice with 15-ml. portions of dry chloroform (previously dried over anhydrous potassium carbonate) and filtered. The chloroform filtrates (A) were combined and studied (see following text).

The dry solid weighed 3.7 g., most of it soluble in water (some insoluble material was identified by conventional methods as paraformaldehyde). Upon recrystallization from absolute ethanol, small colorless needles, m.p. 174–176°, were obtained. The compound was chlorine-free; titration and elementary analysis are in agreement with structure V.

Anal. Calcd. for $C_7H_{16}P_2SO_9$: C, 24.92; H, 4.73; P, 18.32; S, 9.47. Found: C, 24.82; H, 4.91; P, 18.65; S, 9.18.

Equiv. Wt. Calcd.: 169. Found: 168. A 31.74-mg. sample required 2.97 ml. of 0.0636 *N* aqueous dimethylamine to titrate to a phenolphthalein end point. The titrated solution was evaporated at room temperature and kept for a short time over phosphorus pentoxide. A crystalline, extremely hygroscopic salt (X), m.p. 160°, remained.

Infrared Spectrum of V.—The infrared spectrum of the sulfoxium salt V was determined in anhydrous dimethylformamide by use of the Perkin-Elmer Model 21 with carefully purified dimethylformamide in the reference beam. A cell 0.1 mm. thick was used. A strong OH-absorption was found at 2.95 μ. The presence of water was discounted by the absence of a strong absorption at 6.1 μ. Because of hydrogen bonding, the P–OH group cannot be related to this absorption. The nonhydrogen-bonded P O absorption appeared at 7.80 μ and the C–O–P absorption at 9.70 μ. As observed in other compounds of this type, absorptions occurred at 11.3–11.9 μ and at 13.0 μ. In all phosphorus acids examined, broad shallow absorptions appear in the range of 2700–2560 cm.$^{-1}$, instead of in the normal region.[12]

Examination of Filtrates (A).—The solvent was removed by distillation at atmospheric pressure and at a bath temperature not exceeding 70°. A yellow oil (5.2 g.) remained, which was distilled from a 25-ml. Claisen flask at reduced pressure. About 2 g. distilled at 45 to 60° (0.5 mm.), apparently a mixture of dimethyl sulfoxide and a distillable, water-soluble compound, probably trimethylsulfonium chloride (this compound is known to be stable up to 100°[5]). Addition of a drop of this mixture to cold concentrated sulfuric acid liberated copious amounts of hydrogen chloride, indicating the presence of ionic chlorine.

Following this forerun, a 2-g. fraction distilled at 61° at 0.5 mm. (bath temperature 75°), which had a refractive index, n^{22}D 1.5039, and was chlorine-free after redistillation. Analytical results, infrared spectra, and comparison of physical properties with those of an authentic sample of methyl methanethiolsulfonate, prepared as described later, indicated this product to be mainly IX.

Anal. Calcd. for $C_2H_6S_2O_2$: C, 19.05; H, 4.76; S, 50.80. Found: C, 20.36; 20.38; H, 6.23, 6.08; S, 49.06.

The infrared spectrum exhibited strong absorptions at 8.85 and 7.60 μ, characteristic of the sulfone grouping. Absence of an absorption in the 9.1 to 10.0-μ region eliminated from consideration the structure $(CH_3SO)_2$.

Preparation of Methyl Methanethiolsulfonate (IX) from Methyl Chloromethyl Sulfide and Dimethyl Sulfoxide.—Methyl chloromethyl sulfide was prepared from 12.2 g. of paraformaldehyde suspended in 25 g. of methanethiol essentially according to the procedure of Böhme.[7] The flask, equipped with reflux condenser and gas inlet tube, was immersed in ice–salt and a slow stream of hydrogen chloride was introduced. After 4 hr., a clear viscous solution was obtained. After addition of 30 g. of anhydrous cal-

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[8] R. Otto, *Ann.*, **145**, 317 (1868); *Ber.*, **13**, 1282 (1880); **15**, 121 (1882).

[9] L. D. Small, J. H. Bailey, and C. J. Cavallito, *J. Am. Chem. Soc.*, **71**, 3565 (1949).

[10] M. A. Belous and I. Ya. Postovskii, *Zh. Obshch. Khim.* (*J. Gen. Chem.*), **20**, 1701 (1950) [*Chem. Abstr.*, **45**, 239 (1951)].

[11] H. Brintzinger and M. Langheck, *Ber.*, **86**, 557 (1953).

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

cium chloride the mixture was allowed to stand overnight. The upper layer was distilled at atmospheric pressure, yielding 11 g., b.p. 112–114° (769 mm.), n^{20}_{D} 1.4923.

(a) **Reaction of Excess Dimethyl Sulfoxide with Methyl Chloromethyl Sulfide.**—Four and three-tenths grams of methyl chloromethyl sulfide was mixed with 15 g. of anhydrous dimethyl sulfoxide and allowed to stand at room temperature. After 4 hr., a gelatinous mass had been formed and no further visible change took place overnight. By consecutive additions of three 15-ml. portions of dry chloroform, solid paraformaldehyde was separated which after filtration was obtained tack-free by one additional acetone washing. The dry product weighed 1.4 g. (calcd., 1.34 g.). The combined chloroform extracts were carefully evaporated at 10 mm. (maximum bath temperature 37°) to yield 4.5 g. of a yellow oil. The chloroform distillate possessed a repugnant odor. Vapor phase chromatographic analysis detected dimethyl sulfide, dimethyl sulfoxide, and trace amounts of dimethyl disulfide. The yellow oil gave in water a strong chloride reaction with silver nitrate; strong evolution of hydrogen chloride was observed when a droplet was mixed with cold concentrated sulfuric acid. The oil was distilled at reduced pressure to give, after a chlorine-containing forerun, a main fraction distilling at 61° (0.5 mm.), n^{20}_{D} 1.5123. The colorless, water-insoluble oil was free from chlorine after redistillation. The infrared spectrum showed strong $-SO_2-$ group absorption at 7.60 μ and 8.85 μ, and was nearly identical with the spectrum of material obtained as a by-product during the formation of V initially. Analysis by vapor phase chromatography indicated a purity of at least 98%.

Anal. Calcd. for $C_2H_6S_2O_2$: C, 19.05; H, 4.76; S, 50.80. Found: C, 19.12, 19.03; H, 4.84, 4.87; S, 50.79.

(b) **Reaction of Dimethyl Sulfoxide and Methyl Chloromethyl Sulfide in 1:1 Mole Ratios.**—Anhydrous dimethyl sulfoxide (0.625 g.) was mixed with 0.7724 g. of methyl chloromethyl sulfide and allowed to stand for 3 days at room temperature. After 2 hr., the mixture had become light yellow, and, after 3 days, the flask contents was a pasty mixture of a solid and a heavy oil. Separation of the solid was effected by adding 5-ml. portions of dry ether, which dissolved the oil and converted the solid gradually into a powder. Two washings with 10-ml. portions of dry acetone gave 0.4 g. of a solid, free from oily contamination. Attempted recrystallization of this sensitive deliquescent material was unsuccessful. It was first believed that purification could be achieved by dissolving the crystals in cold water, followed by careful evaporation at room temperature. Beautiful crystals appeared, but only on the upper part of the porcelain dish, while the main portion remained tacky, even after prolonged standing over phosphorus pentoxide. The crude material melted between 72 and 74° with decomposition. A sample evolved hydrogen chloride when brought into contact with cold concentrated sulfuric acid. The infrared spectrum showed a strong $S \rightarrow O$ absorption at 8.15 μ. All of these observations are consistent with the assigned structure VI.

Excess dimethyl sulfoxide converted the crystals at room temperature into an oil and paraformaldehyde. Three-tenths gram of the material was dispersed in 10 ml. of anhydrous dimethyl sulfoxide and allowed to stand 24 hr. Dry chloroform was added, which left the paraformaldehyde undissolved. From the filtrate, the chloroform and excess dimethyl sulfoxide were removed by distillation, and the small amount of residual oil was distilled at reduced pressure. The amount of distillate was sufficient only for refractive index (n^{20}_{D} 1.5100) and infrared spectrum. Both indicated that this oil was IX.

Attempted Oxidation of Dimethyl Disulfide by Dimethyl Sulfoxide.—Dimethyl disulfide (4.71 g., 0.050 mole) was dissolved in 15.6 g. (0.20 mole) of anhydrous dimethyl sulfoxide, and the mixture was allowed to stand at room temperature for 3 days. Distillation separated the mixture into two fractions: (1) 3.5 g., b.p. 42° (1.6 mm.), n^{20}_{D} 1.5261 (n^{20}_{D} 1.5282 for purified authentic CH_3SSCH_3); (2) 14.0 g., b.p. 49° (1.6 mm.), n^{20}_{D} 1.4802 [n^{20}_{D} 1.4783 for purified authentic $CH_3S(O)CH_3$]. Neither a higher boiling third fraction, nor a distillation residue was obtained, thus indicating that no IX was formed.

Thermal Decomposition of V.—A sample of 0.2812 g. of V in a 10-ml. distillation flask with bent side arm leading into a receiver cooled with Dry Ice was heated to 190° (oil-bath temperature); distillation of a liquid was observed. Pressure was reduced to 0.01 mm. for a short period. The gray solid residue, weighing 0.2 g. after recrystallization from glacial acetic acid, obtained as bipyramidal crystals, melted at 295–297°. Though the melting point is some 10° low,[1] the material appeared to be 3,9-dihydroxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane 3,9-dioxide.

The distilled liquid was found by vapor phase chromatography to consist mainly of dimethyl sulfoxide admixed with some dimethyl sulfide.

Reaction of V with Calcium Carbonate.—A sample of 0.5 g. of V was dissolved in 6 ml. of distilled water, excess calcium carbonate (Mallinckrodt analytical reagent) was added to this solution until no more carbon dioxide was evolved, unchanged calcium carbonate was removed by filtration, and to the clear filtrate excess ethanol was added. Separation of a microcrystalline, colorless calcium salt (XI) (0.4 g.) occurred, which did not melt below 315°.

3,9-Dimethoxy-1,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]-undecane 3,9-dioxide (XII) was prepared by action of diazomethane on both IV and V.

(a) **From IV and Diazomethane.** A solution of 100 ml. of ether containing 2 g. of diazomethane was placed in a 250-ml. round-bottomed flask, and 2 g. of recrystallized finely divided IV was added in five equal portions at 10-min. intervals. A vigorous evolution of nitrogen occurred after each addition. After 12 hr., gas evolution had ceased and, by filtration, 2.1 g. of the solid ester (XII) was recovered. After recrystallization from absolute ethanol, colorless plates, m.p. 208°, soluble with neutral reaction in water, were obtained.

Anal. Calcd. for $C_7H_{14}O_8P_2$: C, 29.18; H, 4.86; P, 21.55. Found: C, 29.10, 29.30; H, 5.01, 5.15; P, 21.50, 21.20.

(b) **From V and Diazomethane.**—In similar manner 0.5 g. of V was added in three portions to 50 ml. of ether containing 1.0 g. of diazomethane. The yield of ether-insoluble ester was 0.44 g. Recrystallization as before gave small needles, m.p. 208°, which gave no depression by mixture melting point with the product of method a.

As further confirmation of the correctness of the reactions forming methyl methanethiolsulfonate, the ethanethiol analog was prepared by the following method.

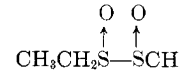
Ethyl chloromethyl sulfide was prepared similarly by treating 24.2 g. of paraformaldehyde with 50.0 g. of ethanethiol to yield 38.5 g. of the desired sulfide, b.p. 127–129° (750 mm.), n^{20}_{D} 1.4892.

Methyl ethanethiolsulfonate was prepared from 6.2 g. of double-distilled ethyl chloromethyl sulfide and 16 g. of anhydrous dimethyl sulfoxide. The mixture stood overnight, forming a gel, which was broken by treating with three 20-ml. portions of dry chloroform. A solid, 1.6 g., identified as paraformaldehyde (95.4%) was separated. The combined chloroform extracts gave a yellow oil when evaporated at 39° at 10 mm. Fractional distillation resulted in three fractions: (1) 3.0 g., b.p. 69–76° (0.7 mm.) n^{20}_{D} 1.5100, soluble in water, immediate silver chloride precipitate with silver ion, hydrogen chloride evolution with cold concentrated sulfuric acid; (2) 2.1 g., b.p. 76° (0.7 mm.), n^{20}_{D} 1.4960, sparingly soluble in water, contained only traces of chlorine; (3) 3.0 g., b.p. 78° (0.7 mm.), n^{20}_{D} 1.5021, insoluble in water, free of chlorine. Fraction 3 was subjected to two redistillations; each time a small forerun was discarded. After the second redistillation the liquid has a refractive index, n^{20}_{D} 1.5037.

Anal. Calcd. for $C_3H_8S_2O_2$: C, 25.68; H, 5.71; S, 45.74. Found: C, 26.25, H, 6.14, S, 45.50.

The analytical results are in satisfactory agreement with methyl ethanethiolsulfonate, $C_2H_5SO_2SCH_3$, or its isomer, ethyl methanethiolsulfonate, $CH_3SO_2SC_2H_5$. The infrared spectrum is very similar to that of IX, but shows some $S \rightarrow O$ absorption in the 1040-cm.$^{-1}$ region, probably as a result of slight contamination by dimethyl sulfoxide.

Nuclear magnetic resonance spectra indicated a methyl group attached to a methylene group, and that the methylene group is attached to an electronegative species. This result strongly favors the methyl ethanethiolsulfonate structure, $CH_3CH_2SO_2$-SCH_3, but does not eliminate completely the possibility of the isomeric structure $CH_3SO_2SCH_2CH_3$. One unexplained peak was attributed to some sulfoxide, possibly the following isomer



$$CH_3CH_2\overset{\overset{\displaystyle O}{\uparrow}}{S}-\overset{\overset{\displaystyle O}{\uparrow}}{S}CH_3$$

or traces of dimethyl sulfoxide.

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The Dehydrobromination of 3-Methoxy-17α-bromoestra-1,3,5(10)-trien-16-one

WILLIAM F. JOHNS

Division of Chemical Research, G. D. Searle and Company, Chicago 80, Illinois

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The title reaction is effected with a variety of reagents, leading in part to the formation of 3-methoxyestra-1,3,5(10),14-tetraen-16-one.

Although two different synthetic routes to the C-17α bromides of 16-ketoandrostanes[1] and estratrienes[2] have been described in the literature, few of the reactions of these compounds have been described. To explore the chemical reactivity of this α-halo ketone system as well as the biological activity of resulting products, several transformations of the 17-bromo ketone **1a** were investigated.

One of the initial phases of this problem involved production of 17β-halo steroids by displacement reactions. Accordingly, the bromo ketone **1a** was treated with lithium chloride in dimethylformamide. To effect complete reaction, as measured by the absence of bromine in the product, extended treatment at 100° was necessary. This can be contrasted to the analogous displacement in the 16α-bromo ketone **10** in which case the reaction is complete within a few hours at room temperature.[2] This large difference in reaction rates affords a measure of the relative steric accessibility of the bromine atoms in these two electronically similar systems.

The major product, isolable by direct crystallization, was an unsaturated ketone, $C_{19}H_{22}O_2$, (λ_{max} 5.89 μ and λ_{max} 231 mμ), initially assigned the structure **3**. This product was thought to have been formed by the elimination of the C-17α bromine atom with a simultaneous retropinacolic rearrangement. Due to the *trans* diaxial arrangement of the bromine atom and carbon atoms 13, 17, and 18, this reaction would be expected to occur with fair ease.[3,4] That the assigned structure was incorrect became clear on inspection of its n.m.r. spectrum: the absorption of the methyl group, although shifted, showed that the group was still tertiary and not attached to a carbon–carbon double bond; further, a single vinyl proton showed clearly. The structure **2** was then postulated as best fitting this data. Additional evidence for this structure was obtained by hydrogenation of the unsaturated ketone, a reaction which occurred rapidly. The product, the cyclopentanone **5** (λ_{max} 5.75 μ), showed a molecular rotatory dispersion curve typical of *cis*-hydrindanones; its n.m.r. spectrum was seen to have a tertiary methyl group (72 c.p.s.), but no vinyl proton. A preliminary infrared comparison indicated the unsaturated ketone **2** to correspond to the racemic isomer B of this structure prepared by Wilds and Doban by total synthesis.[5] A more complete infrared comparison of the saturated ketone **5** with their racemic *trans–syn–cis* isomer of that structure confirmed the identity.

A second compound obtained from the lithium chloride reaction was isolated after chromatography. Its analysis and spectrum showed clearly that it was the 17β-chloro ketone **4b**. A comparison with a sample prepared by epimerization[2] of the 17α-chloro ketone **1b** proved the structure of this product.

The unsaturated ketone **2** had also been isolated in earlier epimerization studies of the 17α-bromo ketone **1a**. The acid-catalyzed epimerization of this compound is a very slow reaction, successful conversion requiring prolonged treatment in boiling acetic acid containing toluenesulfonic acid.[2] When ethanolic sulfuric acid was used, an anomalous change in the rotation was seen. Instead of the levorotatory shift expected of the 17α to β isomerization, a marked dextrorotatory change was observed. Analysis of the product by chromatography showed that this phenomenon was due to the competitive formation of ketone **2**, a process precluding measurement of the 17α–β equilibrium ratio here. It is interesting to note that no dehydrohalogenation (to yield ketone **2**) was seen when toluenesulfonic acid–acetic acid was used.

Further work was undertaken to define better the conditions necessary to produce ketone **2** and also to determine the feasibility of producing ketone **3**. To this end a more normal type of elimination reaction was tried, that using collidine. Again the reaction of the 17α-bromo ketone **1a** required much more vigorous conditions than did the 16-bromo-17-ketoandrostane.[6] The product from a sixteen-hour reflux in collidine contained both 17α- and 17β-bromo ketones (**1a, 4a**) as well as the unsaturated ketone **2**. After the reaction had proceeded for forty hours, no 17α-bromo compound remained. The major product was the unsaturated ketone **2**. Also found were smaller amounts of the 17β-bromo ketone **4a** and the reduction product, 3-methoxyestratrien-16-one (C-14α isomer of **5**). No trace of the isomer **3** was seen despite careful chromatographic inspection.

The reaction of the 17α-bromide with sodium methoxide was expected *a priori* to effect epimerization of the bromide[1,2] and, secondly, to produce the hydroxy ketal

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(1) (a) J. Fajkos and J. Joska, *Collection Czech. Chem. Commun.*, **26**, 1118 (1961); (b) J. Fajkos, J. Joska, and F. Sorm, *ibid.*, **27**, 64 (1962); (c) J. Fishman, *J. Org. Chem.*, **27**, 1745 (1962).

(2) G. P. Mueller and W. F. Johns, *ibid.*, **26**, 2405 (1961).

(3) D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

(4) See W. F. Johns, *J. Org. Chem.*, **26**, 4583 (1961), for references to and the description of similar rearrangements in the steroidal D-ring.

(5) We wish to thank Prof. Alfred Wilds for making possible this comparison; see Robert C. Doban, Ph.D. thesis, University of Wisconsin, 1952; A. L. Wilds and T. L. Johnson, *J. Am. Chem. Soc.*, **70**, 1166 (1948); Donald W. Stoutamire, Ph.D. thesis, University of Wisconsin, 1957.

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