[CONTRIBUTION FROM THE VENEREAL DISEASE EXPERIMENTAL LABORATORY, COMMUNICABLE DISEASE CENTER, U. S. PUBLIC HEALTH SERVICE, SCHOOL OF PUBLIC HEALTH, UNIVERSITY OF NORTH CAROLINA]

Preparation and Ultraviolet Absorption Spectra of Some Derivatives of Phosphafluorinic Acid[1]

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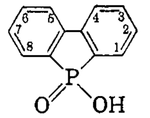
The Busch reaction, which involves the formation of carbon-carbon bonds through the reduction of aryl or alkyl halides, was used to prepare 3,6-dimethyl- and 2,7-dimethylphosphafluorinic acid. Three other derivatives were prepared by the nitration of phosphafluorinic acid, the reduction of 2,7-dinitrophosphafluorinic acid, and the oxidation of 3,6-dimethylphosphafluorinic acid. The ultraviolet absorption spectra of these compounds exhibit the intensity characteristic of the phosphafluorinic acid ring system. Hydrogenation of phosphafluorinic acid over rhodium-on-alumina yielded a dodecahydro derivative which showed no absorption in the ultraviolet.

Only five phosphinic acids have been reported in which the phosphorus atom is a member of a ring system. The first compound of this type was phenphosphazinic acid,[2] the heterocyclic ring of which contains nitrogen as well as phosphorus. More recently Kosolapoff[3] has used the Grignard reaction to prepare cyclopentamethylene-, cyclotetramethylene-, and cyclotrimethylenephosphinic acids, and we[4] have reported the synthesis of phosphafluorinic acid (I) by means of the Busch reaction.[5] The present paper is concerned with the preparation and properties of several derivatives of phosphafluorinic acid.



I

3,6-Dimethylphosphafluorinic acid was readily prepared from bis(2-bromo-4-tolyl)phosphinic acid[6] under the same conditions used for preparing phosphafluorinic acid itself. As indicated in Table I, the spectrum of the 3,6-dimethyl derivative exhibits the intensity and fine structure characteristic of the spectrum of the parent compound. There is a slight bathochromic shift such as one usually observes for alkyl substituted aromatic systems.[7] The spectrum of di-*p*-tolylphosphinic acid (which is formed as a by-product in the preparation of 3,6-dimethylphosphafluorinic acid) is included in Table I for comparison with the phosphafluorinic acid derivatives.

Application of the Busch reaction to bis(2-chloro-5-tolyl)phosphinic acid was not successful under the conditions used with the *o*-bromo derivatives. Even after a reaction period of eleven days, only 60% of the chlorine was split from the ring, and the ultraviolet absorption spectrum of the reaction mixture indicated that little or none of the desired phosphafluorinic acid derivative was present. However, when the amount of palladium used was doubled and the concentration of potassium hydroxide was increased from 1.25*N* to 3*N*, over 90% of the chlorine was cleaved from the ring in six days; and a small yield of 2,7-dimethylphosphafluorinic acid was obtained from the reaction mixture. As might be expected, the spectrum of this compound is similar to that of the 3,6-dimethyl derivative. The main product of the reduction was di-*m*-tolylphosphinic acid, the spectrum of which is also given in Table I.

3,6-Dicarboxyphosphafluorinic acid was prepared from the 3,6-dimethylphosphafluorinic acid by means of the pyridine-permanganate oxidation procedure recently used by Morgan and Herr[8] for preparing carboxylic acids containing the phosphine oxide group. The spectrum of 3,6-dicarboxyphosphafluorinic acid is devoid of fine structure and includes a low intensity long wave length band. Diminished fine structure is often produced by carboxy groups in polynuclear hydrocarbons.[9] It is seen also that the spectrum of

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(1) The nomenclature and numbering system employed in this paper are in accord with the usage of F. G. Mann, *The Heterocyclic Derivatives of Phosphorus, Arsenic, Antimony, Bismuth, and Silicon*, Interscience Publishers, Inc., New York, 1950.

(2) P. G. Sergeev and D. G. Kudryashov, *Zhur. Obshcheĭ Khim.*, **8**, 266 (1938).

(3) (a) G. M. Kosolapoff, *J. Am. Chem. Soc.*, **77**, 6658 (1955); (b) G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 3739 (1957).

(4) L. D. Freedman and G. O. Doak, *J. Org. Chem.*, **21**, 238 (1956).

(5) The formation of carbon-carbon bonds by the reaction of an alkyl or aryl halide with palladium-on-calcium carbonate and a reducing agent has been thoroughly investigated by M. Busch and his coworkers; *cf.* M. Busch and W. Weber, *J. prakt. Chem.*, **146**, 1 (1936). In the present paper this reaction is termed the "Busch reaction."

(6) The preparation of bis(2-bromo-4-tolyl)phosphinic acid was described in ref. 18, but was erroneously called "(2-Br-5-$CH_3C_6H_3)_2PO_2H$."

(7) B. Pullman and A. Pullman, *Les Theories Electroniques de la Chimie Organique*, Masson & Cie, Paris, 1952, p. 515.

(8) P. W. Morgan and B. C. Herr, *J. Am. Chem. Soc.*, **74**, 4526 (1952).

(9) R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley & Sons, Inc., New York, 1951, p. 20.

TABLE I

Ultraviolet Absorption Maxima[a]

Compound	λ_{max}, mμ	ϵ_{max}
Phosphafluorinic acid[b]	226	26,200
	232.5	30,200
	239.5	27,500
	278	10,100
	289.5	8,370
	320	1,060
3,6-Dimethylphosphafluorinic acid	232	32,900
	237.5	38,800
	244.5	31,900
	282	7,180
	293	5,920
	324[c]	656
Di-*p*-tolylphosphinic acid	231	19,000
	263	993
2,7-Dimethylphosphafluorinic acid	227	28,800
	235	31,200
	241.5	28,600
	283	15,400
	295	14,600
	331	1,170
Di-*m*-tolylphosphinic acid	226.5	12,900
	270	1,880
	277	1,620
3,6-Dicarboxyphosphafluorinic acid	249	70,000
	336	626
Bis(*p*-carboxyphenyl)phosphinic acid	246.5	27,900
	277	3,290
2,7-Dinitroarsafluorinic acid[d]	255.5	10,600
	325	21,200
2,7-Dinitrophosphafluorinic acid	261.5	11,600
	326	21,400
	335	20,900
2,7-Diaminophosphafluorinic acid	223.5	30,800
	229.5	35,200
	236.5	33,700
	276.5	11,800
	288	10,200
Bis(*m*-aminophenyl)phosphinic acid[e]	221	14,600
	260[c]	784
	264	885
	271	784
Diphenylphosphinic acid[f]	224	13,100
	259.5	956
	265	1,200
	271.5	917
Phosphanilic acid[e]	257	528
	262.5	544
	268.5	431
Phenylphosphonic acid[f]	258	391
	263.5	524
	270	432

[a] Spectra of amino-substituted compounds were determined in 0.1*N* hydrochloric acid solution. Ethyl alcohol (95%) was used as the solvent for all other compounds. [b] The spectrum of this compound is described in ref. 4, but the low intensity peak at 320 mμ was not previously noted. [c] Shoulder. [d] Prepared as described in ref. 10. [e] Prepared as described by G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 753 (1952). [f] Taken from H. H. Jaffé and L. D. Freedman, *J. Am. Chem. Soc.*, **74**, 1069 (1952).

the phosphafluorinic acid derivative is similar to, but more intense than, its non-heterocyclic analog, bis(*p*-carboxyphenyl)phosphinic acid.

Nitration of phosphafluorinic acid to give a dinitro derivative was accomplished by a procedure very similar to that described by Feitelson and Petrow[10] for the dinitration of arsafluorinic acid. The structure of the dinitro derivative of phosphafluorinic acid was not established unequivocally, but it almost certainly is the 2,7-derivative by analogy with the results obtained in the nitration of arsafluorinic acid. It is seen in Table I that the spectrum of the dinitrophosphafluorinic acid is quite like the spectrum of 2,7-dinitroarsafluorinic acid. Reduction of the dinitrophosphafluorinic acid with Raney nickel and hydrogen yielded diaminophosphafluorinic acid; by contrast, the reduction of 2,7-dinitroarsafluorinic acid with Raney nickel yields benzidine.[10] The spectrum of diaminophosphafluorinic acid in 0.1*N* hydrochloric acid solution resembles the spectrum of phosphafluorinic acid itself. It has often been observed that the ammonio (NH_3^+) group has little effect on ultraviolet absorption.[11] As shown in Table I, the spectrum of bis(*m*-aminophenyl)phosphinic acid in acid solution is remarkably similar to the spectrum of diphenylphosphinic acid; and the spectrum of phosphanilic (*p*-aminophenylphosphonic) acid in acid solution is almost identical with the spectrum of phenylphosphonic acid.

An attempt was made to prepare 2,7-diaminophosphafluorinic acid by the Busch reaction on bis(2-bromo-5-aminophenyl)phosphinic acid. The theoretical amount of bromine was cleaved from the ring, and the spectrum of the reaction mixture indicated that the phosphafluorinic acid ring system had been formed. However, the crude product contained only 5.79% nitrogen (theoretical nitrogen is 11.38%); and the properties of this material did not become constant even after repeated reprecipitations from alkaline solution. We have been unable to isolate any pure compound from the reaction mixture.

Hydrogenation of phosphafluorinic acid over rhodium-on-alumina[12] yielded a phosphinic acid which exhibited no ultraviolet absorption. This compound was shown not to be dicyclohexylphosphinic acid[12] and is therefore, presumably, a dodecahydrophosphafluorinic acid. No attempt was made to investigate the stereochemistry of this compound.

EXPERIMENTAL[13]

3,6-Dimethylphosphafluorinic acid. Bis(2-bromo-4-tolyl)-phosphinic acid[6] (10.1 g.) was treated with palladium-on-

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(10) B. N. Feitelson and V. Petrow, *J. Chem. Soc.*, 2279 (1951).

(11) See, for example, L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.*, **69**, 2714 (1947).

(12) L. D. Freedman, G. O. Doak, and E. L. Petit, *J. Am. Chem. Soc.*, **77**, 4262 (1955).

(13) Melting points under 300° were taken as previously described; *cf.* ref. 15a. M.p.'s over 300° were determined in capillary tubes on a copper block and are uncorrected. Phosphorus was determined by the method of B. C. Stanley, S. H. Vannier, L. D. Freedman, and G. O. Doak, *Anal. Chem.*, **27**, 474 (1955).

calcium carbonate and methanolic potassium hydroxide by the same procedure previously used for converting bis(*o*-bromophenyl)phosphinic acid to phosphafluorinic acid.[4] The solid obtained upon acidification of the reaction mixture was dissolved in 65 ml. of hot 4% sodium hydroxide soluton. When the solution was cooled, the sodium salt of 3,6-dimethylphosphafluorinic acid crystallized. This salt was removed by filtration and washed with 20 ml. of 5% sodium hydroxide solution. In order to obtain the free phosphinic acid, the sodium salt was dissolved in 75 ml. of hot water, and the solution was filtered from a trace of undissolved material; acidification of the filtrate yielded 3.5 g., 57%, of pure 3,6-dimethylphosphafluorinic acid, m.p. 303–305°. Recrystallization of the acid from 95% ethanol did not appreciably change the analysis, m.p., or ultraviolet absorption.

Anal. Calcd. for $C_{14}H_{13}O_2P$: P, 12.68; neut. equiv., 244.2. Found: P, 12.61; neut. equiv., 240.4.

When the alkaline filtrate from the sodium salt of 3,6-dimethylphosphafluorinic acid was acidified to Congo red, a sticky precipitate was obtained which was dried and recrystallized from ether to yield 0.7 g. of di-*p*-tolylphosphinic acid, m.p. 133.5–135.5° (lit.[14] 131–132°). The identity of this material was confirmed by analysis, by ultraviolet absorption, and by mixed m.p. with an authentic sample of di-*p*-tolylphosphinic acid, the synthesis of which is described below.

p-Tolylphosphonic acid and di-p-tolylphosphinic acid. Dry *p*-toluenediazonium fluoborate was suspended in isopropyl acetate and treated with phosphorus tribromide and cuprous bromide; these conditions have been shown to increase the yield of phosphinic acid.[15] After the reaction was steam distilled, the residual liquid in the distilling flask was transferred to a beaker and cooled. The phosphinic acid, which separated out of the solution, was removed by filtration and dissolved in sodium carbonate solution. The alkaline solution was treated with charcoal, filtered, and the acid reprecipitated by the addition of hydrochloric acid. After recrystallization from ether, the yield of di-*p*-tolylphosphinic acid was 11%; m.p. 132–135°.

The usual treatment of the original filtrate from the crude phosphinic acid resulted in the isolation of *p*-tolylphosphonic acid, which was purified by procedure A as previously described.[15a] The yield was 20%; m.p. 192–194.5° (lit.[15a] 198–199°).

2-Chloro-5-tolylphosphonic acid and bis(2-chloro-5-tolyl)-phosphinic acid. 2-Chloro-5-methylaniline (Eastman P7406) was purified by distillation and then converted to the corresponding diazonium fluoborate by the method designated by Roe as II A.[16] The dried diazonium salt was suspended in isopropyl acetate and treated with phosphorus trichloride and cuprous bromide.[15] After the steam distillation, the residual liquid in the distilling flask was filtered hot. The crude phosphinic acid, which remained on the filter paper, was washed several times with hot water and then purified by reprecipitation from 2% sodium hydroxide solution and subsequent recrystallization from aqueous alcohol. The yield of pure bis(2-chloro-5-tolyl)phosphinic acid was 9%; m.p. 235–237.5°.

Anal. Calcd. for $C_{14}H_{13}Cl_2O_2P$: Cl, 22.50; P, 9.83; neut. equiv., 315.1. Found: Cl, 22.37; P, 9.50; neut. equiv., 308.7.

The original filtrate from the crude phosphinic acid was evaporated on the steam bath to incipient crystallization, cooled, and filtered. The resulting crude phosphonic acid was dissolved in an excess of 5% sodium hydroxide solution, and, after the solution was treated with charcoal, was reprecipitated by the addition of hydrochloric acid. The precipitate obtained was recrystallized from 6*N* hydrochloric acid. The yield was 36%; m.p. 185–190°.

Anal. Calcd. for $C_7H_8ClO_3P \cdot H_2O$: P, 13.79, neut. equiv., 112.3; H_2O, 8.02. Found: P, 13.80, neut. equiv., 112.5; wt. loss at 120°, 7.80.

When phosphorus tribromide was used in place of phosphorus trichloride in the above reaction, the yield of phosphinic acid was increased to 14% while the yield of phosphonic acid decreased to 23%.

2,7-Dimethylphosphafluorinic acid. Bis(2-chloro-5-tolyl)-phosphinic acid (7.90 g.) was dissolved in a mixture of 80 ml. of 3.0*N* aqueous potassium hydroxide and 90 ml. of methanol and heated under reflux with 6.0 g. of 2% palladium-on-calcium carbonate for 6 days. The mixture of phosphinic acids was isolated from the reaction mixture by the procedure previously described[4] and then dissolved in 35 ml. of hot 5% sodium hydroxide solution. When this solution was cooled, the sodium salt of 2,7-dimethylphosphafluorinic acid crystallized. The salt was removed by filtration and washed with 10 ml. of 5% sodium hydroxide solution. A second crop of the sodium salt was obtained by evaporating the combined filtrate and washings to 25 ml., cooling to room temperature, and washing the resulting crystals with 10 ml. of 5% sodium hydroxide solution. Both crops of sodium salt were combined and converted to the free phosphinic acid by the same procedure used for the 3,6-isomer. The yield was 0.34 g., 5.5%, m.p. 320–323°. Recrystallization of the acid from 95% ethanol changed the m.p. to 325–328° but did not affect the analysis or ultraviolet absorption.

Anal. Calcd. for $C_{14}H_{13}O_2P$: P, 12.68; neut. equiv., 244.2. Found: P, 12.53; neut. equiv., 241.2.

When the alkaline filtrate from the second crop of sodium 2,7-dimethylphosphafluorinate was acidified to Congo red, a sticky precipitate was obtained which was recrystallized from aqueous acetone to yield 1.9 g. of slightly impure di-*m*-tolyl-phosphinic acid, m.p. 165–167.5°. The ultraviolet absorption of this material was identical with that of authentic di-*m*-tolylphosphinic acid, the synthesis of which is described below.

m-Tolylphosphonic acid and di-m-tolylphosphinic acid. Dry *m*-toluenediazonium fluoborate[17] was suspended in isopropyl acetate and treated with phosphorus tribromide and cuprous bromide in the usual manner.[15] The phosphinic acid was isolated from the reaction mixture by the procedure described above for the *p*-isomer and was then recrystallized from aqueous acetone. The yield of pure di-*m*-tolylphosphinic acid was 8.5%, m.p. 173.5–175° (lit.[17a] 166–168°).

Anal. Calcd. for $C_{14}H_{15}O_2P$: P, 12.58; neut. equiv., 246.2. Found: P, 12.25; neut. equiv., 242.8.

The original filtrate from the crude phosphonic acid was extracted with ether (three 25-ml. portions for preparations on a 0.1-mole scale), the ethereal extracts were combined, and the ether was removed by evaporation. The oily residue was dissolved in an excess of 10% sodium carbonate solution and treated with charcoal. On acidifying the decolorized solution, *m*-tolylphosphonic acid separated as an oil. The mixture was then extracted with ether (three 25-ml. portions for preparations on a 0.1-mole scale); evaporation of the combined ethereal extracts yielded a white solid which was recrystallized from a mixture of benzene and chloroform. The yield of pure *m*-tolylphosphonic acid was 16%; m.p. 121–122.5° (lit.[17] 121°).

3,6-Dicarboxyphosphafluorinic acid. 3,6-Dimethylphosphafluorinic acid (2.20 g.), dissolved in a mixture of 15 ml. of pyridine and 15 ml. of water, was treated with 25 g. of potassium permanganate according to the procedure of Morgan and Herr.[8] After steam distillation to remove pyridine, the

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[14] G. M. Kosolapoff, *J. Am. Chem. Soc.*, **71**, 369 (1949).

[15] (a) G. O. Doak and L. D. Freedman, *J. Am. Chem. Soc.*, **73**, 5658 (1951); (b) **75**, 683 (1953).

[16] A. Roe in *Org. Reactions*, V, 204 (1949).

[17] E. C. Ashby and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **75**, 4903 (1953).

[17a] J. M. Denham and R. K. Ingham, *J. Org. Chem.* **23**, 1298 (1958). This paper appeared subsequent to the completion of our work.

reaction mixture was filtered, decolorized with charcoal, and then added slowly, with good stirring, to 100 ml. of 10% hydrochloric acid. The precipitated phosphinic acid was removed by filtration and recrystallized from aqueous acetone. The yield was 1.21 g. (44%); m.p. >300°.

Anal. Calcd. for $C_{14}H_9O_6P$: P, 10.18; neut. equiv., 101.4. Found: P, 9.97; neut. equiv., 101.6.

Bis(p-carboxyphenyl)phosphinic acid. Di-*p*-tolylphosphinic acid (2.46 g.) was oxidized with 25 g. of potassium permanganate by the procedure described above. The yield of bis(*p*-carboxyphenyl)phosphinic acid, after recrystallization from aqueous acetone, was 2.39 g. (78%) m.p. > 300°.

Anal. Calcd. for $C_{14}H_{11}O_6P$: P, 10.12, neut. equiv., 102.1. Found: P, 10.11, neut. equiv., 102.1.

2,7-Dinitrophosphafluorinic acid. Phosphafluorinic acid was nitrated by the procedure used for the arsenic analog.[10] The yield of dinitrophosphafluorinic acid was 93%, decomposition point above 260°. The sample used for analysis and for determination of the ultraviolet absorption spectrum was recrystallized from a mixture of 95% ethanol and acetone.

Anal. Calcd. for $C_{12}H_7N_2O_6P$: N, 9.15, P, 10.12. Found: N, 9.05, P, 9.95.

2,7-Diaminophosphafluorinic acid. 2,7-Dinitrophosphafluorinic acid (1.90 g.) was dissolved in a mixture of 150 ml. of 0.2% sodium hydroxide solution and 100 ml. of 95% ethanol, and the *p*H adjusted to 6.9 with acetic acid. Reduction was effected with Raney nickel and hydrogen at 30 lb. pressure. After the catalyst was removed, the solution was acidified to *p*H 4.0 with acetic acid whereupon 2,7-diaminophosphafluorinic acid separated from solution. The yield was 0.96 g. (63%), m.p. > 300°.

Anal. Calcd. for $C_{12}H_{11}N_2O_2P$: N, 11.38, P, 12.58. Found: N, 11.32; P, 12.42.

Bis(2-bromo-5-aminophenyl)phosphinic acid. Bis(2-bromo-5-nitrophenyl)phosphinic acid[18] (4.66 g.), dissolved in a mixture of 150 ml. of 0.3% sodium hydroxide and 75 ml. of 95% ethanol, was reduced by the method described above. The *p*H of the solution before reduction should be 6.9. Some bromine was split from the ring at this *p*H; however, the amount of splitting increased at higher *p*H's. The reduction product was purified by reprecipitation from alkaline solution. The yield was 2.16 g. (53%), decomposition point about 300°.

Anal. Calcd. for $C_{12}H_{11}Br_2N_2O_2P$: Br, 39.36; N, 6.90; P, 7.63. Found: Br, 39.25; N, 6.90; P, 7.53.

Dodecahydrophosphafluorinic acid. Phosphafluorinic acid (1.0 g.) was dissolved in 125 ml. of absolute ethanol and shaken for 4 hr. at 50° with 3.0 g. of rhodium-on-alumina and hydrogen at an initial gage pressure of 50 lb. After the catalyst was removed, the filtrate was evaporated to dryness on a boiling water bath. The residue, which consisted of a colorless oil, was dissolved in warm aqueous alcohol. On cooling, 0.16 g. (15%) of white crystals, m.p. 153–154.5°, separated from solution. Mixed m.p. with dicyclohexylphosphinic acid was 78–82°.

Anal. Calcd. for $C_{12}H_{21}O_2P$: C, 63.14; H, 9.27; P, 13.57. Found: C, 62.87; H, 9.22; P, 13.36.

The mother liquors gave an oily material, which presumably consists of a mixture of stereoisomers. We have been unable to obtain any additional crystalline material from this mixture.

CHAPEL HILL, N. C.

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[18] L. D. Freedman, H. Tauber, G. O. Doak, and H. J. Magnuson, *J. Am. Chem. Soc.*, **75**, 1379 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

Pyrolysis of Cyclic Sulfites of 1,3-Glycols

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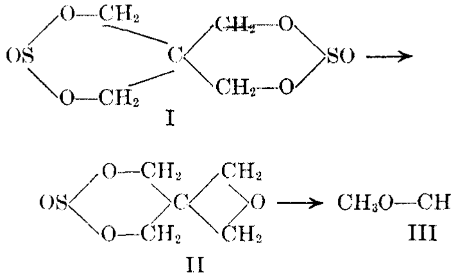
The pyrolysis of the cyclic sulfites of pentaerythritol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, and 2-hydroxymethyl-2-methyl-1,3-propanediol was studied at various temperatures. The disulfite of pentaerythritol gave 2,4,8-trioxa-3-thiaspiro[5,3]nonane-3-oxide. The sulfite of 2,2-dimethyl-1,3-propanediol was stable at 500°. The corresponding derivatives of 2-hydroxymethyl-2-methyl-1,3-propanediol and 1,3-propanediol gave no oxetanes.

The pyrolysis of cyclic sulfites of glycols has been of interest since the first report[2] that 2,3-butylene oxide was formed from the sulfite of 2,3-butylene glycol. Extension of the reaction to other 1,2-glycols, however, has been found to yield only aldehydes or ketones.[3]

In the 1,3-glycol series the pyrolysis has been carried out only for the cyclic sulfite of 2,2-bis-(chloromethyl)-1,3-propanediol.[4] No oxetane was formed but decomposition occurred to 3-chloro-2-chloromethyl-1-propene, sulfur dioxide, and formaldehyde.

In the present work the pyrolysis of the cyclic sulfites of pentaerythritol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, and 2-hydroxymethyl-2-methyl-1,3-propanediol was studied under various conditions in an attempt to prepare oxetanes. The reaction was successful only for the disulfite of pentaerythritol (I); 2,4,8-trioxa-3-thiaspiro-[5,3]-nonane-3-oxide (II) was formed.


I

II

CH₃O—CH₂—C(CH₂OH)₃ III

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[1] Abstracted in part from the Ph.D. Thesis of J. T. Loft, August 1959.

[2] L. Denivelle, *Compt. rend.*, **208**, 1024 (1939).

[3] C. C. Price and G. Berti, *J. Am. Chem. Soc.*, **76**, 1211 (1954).

[4] A. S. Matlack and D. S. Breslow, *J. Org. Chem.*, **22**, 1723 (1957).