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 $C_{12}H_7N_2O_8P$: 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.

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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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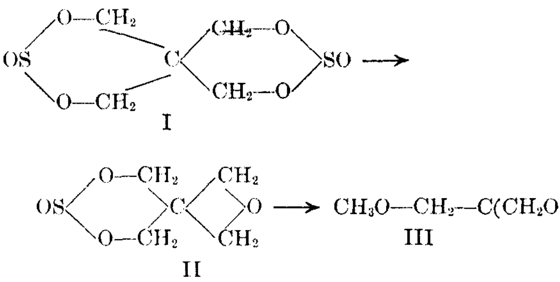
The pyrolysis of the cyclic sulfites of pentaerythritol, 1,3-propanediol, 2,2-dimethyl-1,3-propanediol, and 2-hydroxymethyl-2-methyl-1,3-propanediol was studied at various temperatures. The disulfite of pentaerythritol gave 2,4,8-trioxa-3-thiaspiro[5,3]nonane-3-oxide. The sulfite of 2,2-dimethyl-1,3-propanediol 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.



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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).

The structure of this compound (II) was demonstrated by its conversion with methanol and sulfuric acid to pentaerythritol monomethyl ether (III). The pyrolysis was followed by measuring the evolution of sulfur dioxide and gave the best yield when only about 25% of the theoretical amount of sulfur dioxide was evolved. Heating beyond this point produced mainly polymeric materials. No dioxaspiroheptane was produced.

The sulfite of 2,2-dimethyl-1,3-propanediol was stable up to temperatures of 500°. The corresponding derivative of 2-hydroxymethyl-2-methyl-1,3-propanediol was stable at 450°. At 600–625° a small amount of a compound analyzing approximately for methallyl alcohol was obtained but the amount was too small to investigate further. No attempt was made to identify the formaldehyde which was probably also formed in this reaction. This behavior is markedly different from that reported for the cyclic carbonate[5] in which 3-hydroxymethyl-3-methyloxetane was produced by heating at 180–200°.

Pyrolysis of the sulfite of 1,3-propanediol at 230° gave sulfur dioxide and tars and no oxetane. The same reaction at 300° using a tube packed with glass wool gave a small amount of a polymer derived from formaldehyde. No attempt was made to collect the ethylene which was probably formed in this decomposition.

The course of the decomposition for the sulfites of 1,3-propanediol and 2-hydroxymethyl-2-methyl-1,3-propanediol follows that observed for the sulfite of 2,2-bis(chloromethyl)-1,3-propanediol[4] and probably goes by the mechanism suggested for the latter compound. The possibility that an oxetane is formed as an intermediate cannot be completely excluded since trimethylene oxide is reported to decompose at 420–460° in a similar way into formaldehyde and ethylene.[6]

EXPERIMENTAL[7]

Pyrolysis of pentaerythrityl disulfite(2,4,8,10-tetraoxa-3,9-dithia[5,5]undecane-3,9-dioxide (I). Pentaerythrityl disulfite (I) (45.6 g.) was heated at 260–270° until 2 l. of sulfur dioxide was evolved. The resulting liquid was cooled, triturated with methanol (50 ml.) in order to precipitate the unchanged disulfite (22 g.). Filtration of the solid was followed by evaporation of the methanol. The oil obtained, when crystallized from methylene chloride and petroleum ether (60–70°), gave more of the disulfite (3.25 g.). Removal of the solvent followed by extraction with cyclohexane gave 2,4,8-trioxa-3-thiaspiro[5,3]nonane-3-oxide (II) (8.0 g.) melting at 65–66°. Crystallization from cyclohexane followed by several sublimations at 60° (1 mm.) gave a sample melting at 74–75°.

Anal. Calcd. for $C_5H_8O_4S$: C, 36.61; H, 4.87. Found: C, 36.23; H, 4.75.

Continuing the heating beyond this point usually gave polymeric products from which only a small amount of 2,4,8-trioxa-3-thiaspiro[5,3]nonane-3-oxide (II) was isolated. No 2,6-dioxaspiro[3,3]heptane was produced in the pyrolysis.

Reaction of 2,4,8-trioxa-3-thiaspiro[5,3]nonane-3-oxide (II) *with methanol and sulfuric acid.* 2,4,8-Trioxa-3-thiaspiro-[5,3]nonane-3-oxide (II) (4.1 g.) in methanol (50 ml.) was treated with 3 drops of concentrated sulfuric acid and allowed to stand for 24 hr. at room temperature. The solution was refluxed for 2 hr. and then neutralized with solid sodium carbonate. Removal of the methanol gave an oil which upon crystallization from a mixture of chloroform and ethyl acetate gave pentaerythritol monomethyl ether (III) (1.35 g.) melting at 63–67°. One recrystallization from chloroform gave a sample melting at 70–73° which did not depress the melting point of an authentic sample.[9] The infrared spectra of the two samples were identical. A mixture with 2,4,8-trioxa-3-thiaspiro[5,3]nonane-3-oxide (II) melted at 58–65°.

Pyrolysis of trimethylene sulfite (*1,3,2-dioxathiane-2-oxide*). Pyrolysis of trimethylene sulfite[10] at 230° gave sulfur dioxide and tar but no trimethylene oxide. The same reaction using a glass tube at 300° packed with glass wool and 50 g. of the sulfite gave in addition to the tars a solid (4 g.) melting at 155°. The product was insoluble in acetone, dimethylformamide, and acetonitrile and melted after this treatment at 157–158°.

Anal. Calcd. for $(CH_2O)_x$: C, 40.00; H, 6.66. Found: C, 40.30; H, 6.66.

The infrared spectra for this compound resembled that of paraformaldehyde.

Pyrolysis of 5,5-dimethyl-1,3,2-dioxanthiane-2-oxide. This sulfite[11] was stable at 230° and was practically completely recovered unchanged when dropped on barium oxide at 350° and aluminum oxide at 400–500°.

5-Methyl-5-hydroxymethyl-1,3,2-dioxathiane-2-oxide. A mixture of 2-methyl-2-hydroxymethyl-1,3-propanediol (240 g.) suspended in 200 ml. of methylene chloride was treated slowly with thionyl chloride (236 g.) with stirring at 0–10°. After the addition the solution was allowed to stand at 25° for 48 hr. Removal of the solvent gave a liquid which boiled at 118° (3 mm.); yield 296 g.; n_D^{24} 1.4786; d_4^{25} 1.498.

Anal. Calcd. for $C_5H_{10}O_4S$: C, 36.13; H, 6.04. Found: C, 35.77; H, 5.94.

Passing this sulfite (40 g.) at 450° using nitrogen as a diluent through a glass tube packed with glass helices gave only unchanged sulfite. Using 600–625° a small amount of liquid (4 g.) boiling at 118° at atmospheric pressure and analyzing for approximately methallyl alcohol was formed. The literature[12] reports a value of 114°.

Anal. Calcd. for C_4H_8O: C, 66.7; H, 11.1. Found: C, 65.2; H, 11.24.

This fraction was not studied further.

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(5) D. B. Pattison, *J. Am. Chem. Soc.*, **79**, 3455 (1957).

(6) D. A. Bittker and W. D. Walters, *J. Am. Chem. Soc.*, **77**, 1429 (1955).

(7) Melting points and boiling points are not corrected.

(8) L. Orthner, *Ber.*, **61B**, 116 (1928).

(9) S. Wawzonek and D. A. Rees, *J. Am. Chem. Soc.*, **70**, 2433 (1948).

(10) P. B. D. de la Mare, W. Klyne, D. J. Miller, J. G. Pritchard, and D. Watson, *J. Chem. Soc.*, 1813 (1956).

(11) D. G. Markees and A. Burger, *J. Am. Chem. Soc.*, **71**, 2031 (1949).

(12) Z. A. Pogorshelski, *J. Russ. Chem. Soc.*, **36**, 1129 (1904).