(11 mm.), $n^{25}D$ 1.4552; the reported[10] boiling point of triethyl monothiophosphate is 120° (16 mm.). The infrared spectrum shows characteristic peaks at 1018, 1164 and 1254 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{15}O_3PS$: C, 36.35; H, 7.63. Found: C, 36.33; H, 7.81.

When a similar reaction was carried out using equimolar proportions of phosphite and disulfide, the product in the still-pot turned dark before the evolution of diethyl sulfide was complete. Therefore, for preparative purposes, it is desirable to employ one of the reactants in excess or else add an inert solvent so that the boiling point of the reaction mixture does not become too high in the final stages of the reaction.

(10) P. Pishchimuka, *Ber.*, **41**, 3854 (1908); *J. Russ. Phys. Chem. Soc.*, **44**, 1406 (1912).

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Sulfur-containing Pivalic Acid Derivatives. II. Sulfopivalic Acid

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During the past few years sulfocarboxylic acids have been investigated extensively. Suter[3] has discussed in considerable detail the preparation and properties of aliphatic sulfocarboxylic acids. Much of the work has pertained to α-sulfo acids, with lesser effort directed toward the β- and γ-isomers. Nearly all of the lower molecular weight aliphatic sulfo acids have been prepared and characterized. Sulfopivalic acid is an exception. The purpose of this paper is to describe the synthesis and characterization of this compound.

Bromopivalic acid was treated with a large excess of sodium hydrosulfide. When the reaction mixture was at all times protected from the air, moderate yields of mercaptopivalic acid were obtained, but some dithiodipivalic acid was inevitably produced in each case. Oxidation of the mercapto acid with nitric acid gave the sulfo acid, but with considerable decomposition. A better yield of a cleaner product was obtained by treating bromopivalic acid with sodium hydrosulfide then subjecting the reaction mixture to autoxidation conditions in the apparatus depicted in Fig. 1.[4] The dithiodipivalic acid so produced was liberated by acidification and subsequently oxidized with nitric acid to either sulfopivalic acid or to disulfoxydipivalic acid. When the reaction was carried out at 60–70° the former compound was produced exclusively, whereas at 35–45° appreciable yields of the latter were formed. Analysis indicated that the latter compound could be either I or II. Hinsberg[5] and Kloosterziel, *et al.*,[6] prepared and described the so-called thiosulfonates of type I, whereas Toennies

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(2) Texas Eastman Company, Longview, Texas.

(3) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, pp. 141–154.

(4) The authors have used a column of this type for many autoxidation reactions and have found it to be quite satisfactory.

(5) O. Hinsberg, *Ber.*, **41**, 2836 (1908); **42**, 1278 (1909).

(6) H. Kloosterziel, J. S. Boevema and H. J. Backer, *Rec. trav. chim.*, **72**, 612 (1953).

$$\mathrm{HOOCC(CH_3)_2CH_2{-}SO_2{-}S{-}CH_2C(CH_3)_2COOH}$$
I

$$\mathrm{HOOCC(CH_3)_2CH_2{-}SO{-}SO{-}CH_2C(CH_3)_2COOH}$$
II

and Lavine[7] showed that the disulfoxide structure of type II was most probably correct when the substituent groups are the same, as in the present case. The chemistry of disulfoxydipivalic acid will be discussed more fully in a future paper of this series.

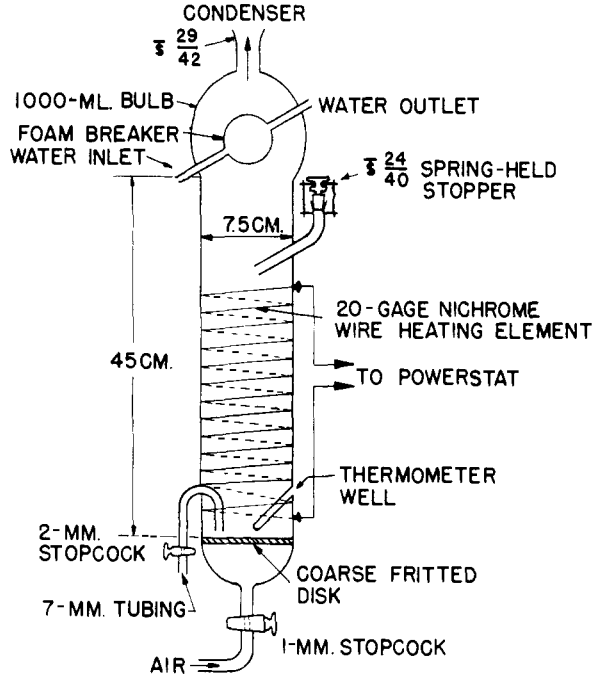

Fig. 1.—Autoxidation apparatus.

Sulfopivalic acid crystallizes with one molecule of water which it loses only under rather drastic conditions. All attempts to prepare chlorosulfonylpivalyl chloride were unsuccessful. Treatment of sulfopivalic acid with thionyl chloride gave excellent yields of the cyclic anhydride. This same anhydride was prepared directly from pivalic acid in poor yields by a method reported by Kharasch, *et al.*[8] These same authors prepared the amide and anilide of 3-sulfopropionic acid from its cyclic anhydride by the reaction with ammonia and aniline, respectively. In the first case, the salt of 3-sulfopropionamide with ammonia was obtained; in the second, the product was the salt of 3-sulfopropionanilide with aniline. In the present work, the salts of sulfopivalamide and sulfopivalo-*p*-toluidide with ammonia and *p*-toluidine, respectively, were obtained from the cyclic anhydride of sulfopivalic acid.

Experimental

Mercaptopivalic Acid.—Sodium hydrosulfide ($NaSH \cdot 2H_2O$, 184 g.) was dissolved in water (1040 ml.). Bromopivalic acid[9] (181 g.) was added in small increments with stirring. The mixture was refluxed in a nitrogen atmosphere for 1 hour then cooled and treated cautiously, while being

(7) G. Toennies and T. J. Lavine, *J. Biol. Chem.*, **113**, 571, 583 (1936).

(8) M. S. Kharasch, T. H. Chao and H. C. Brown, THIS JOURNAL, **62**, 2393 (1940).

(9) J. L. Greene, Jr., and H. J. Hagemeyer, Jr., *ibid.*, **77**, 3016 (1955).

stirred, with 100 g. of concentrated sulfuric acid. The mixture was cooled to 15° and quickly extracted with three 200-ml. portions of ethyl ether. The extract was dried under nitrogen over Drierite and filtered into a distilling flask. Nitrogen was bled slowly into the system while the ether was removed under reduced pressure and the mercaptopivalic acid was distilled; yield 70 g. or 53%, b.p. 101–102° (1 mm.).

Anal. Calcd. for $C_5H_{10}O_2S$: C, 44.72; H, 7.51; S, 23.90. Found: C, 44.44; H, 7.26; S, 23.47.

Dithiodipivalic Acid.—To a stirred solution of sodium hydrosulfide ($NaSH \cdot 2H_2O$, 430 g.) in water (1000 ml.), bromopivalic acid (360 g.) was added in small increments. Upon completion of the addition, more water (1000 ml.) was added and the solution was boiled for 1 hour. The solution was then transferred to the autoxidation column depicted in Fig. 1 and treated with finely dispersed air at a rate of 1000 ml. per minute for 24 hours while the temperature was maintained at 35 ± 2° by external heating when necessary. The clear solution was removed from the column and treated with 200 g. of concentrated sulfuric acid to obtain a white oil which separated and quickly solidified. This solid was collected on a filter, dried at 65°, and dissolved in ethyl alcohol. The solution was filtered to remove elemental sulfur, treated at its boiling point with two-thirds its volume of water and allowed to cool. The crystals of dithiodipivalic acid which separated were dried at 65°; yield 214 g. or 80.5%, m.p. 153–154°.

Anal. Calcd. for $C_{10}H_{18}O_4S_2$: S, 23.05; neut. equiv., 133.2. Found: S, 24.17; neut. equiv., 133.1.

Disulfoxydipivalic Acid.—Dithiodipivalic acid (25 g.) was added to a stirred solution of nitric acid (sp. gr. 1.42, 95 ml.) and water (105 ml.) and allowed to stand overnight at 35–40°. The solution was then placed on a steam-bath to bring about a vigorous reaction with formation of a white precipitate. The product was recrystallized from boiling water; yield 5.6 g. or 20%, m.p. 179–180°.

Anal. Calcd. for $C_{10}H_{18}O_6S_2$: C, 40.30; H, 6.08; S, 21.48; neut. equiv., 149.2. Found: C, 40.57; H, 6.31; S, 21.22; neut. equiv., 149.2.

Dithiodipivalyl Chloride.—Dithiodipivalic acid (50 g.) was refluxed with thionyl chloride (150 g.) for 3 hours. The excess thionyl chloride was removed at reduced pressure, and the dithiodipivalyl chloride was then distilled; yield 35.4 g. or 62%, b.p. 186–187° (7 mm.).

Anal. Calcd. for $C_{10}H_{16}Cl_2O_2S_2$: S, 21.15. Found: S, 20.90.

Diethyl Dithiodipivalate.—This compound, which has a strong onion-like odor, was obtained by the action of dithiodipivalyl chloride on ethyl alcohol; yield 91%, b.p. 178–179° (4 mm.).

Anal. Calcd. for $C_{14}H_{26}O_4S_2$: S, 19.87. Found: S, 19.61.

Dithiodipivalamide and Dithiodipivalo-*p*-toluidide.—Both of these compounds were prepared by a standard procedure.[10] The yield of amide was 82%, m.p. 164–165°.

Anal. Calcd. for $C_{10}H_{20}N_2O_2S_2$: S, 24.25; N, 10.61. Found: S, 24.01; N, 10.37.

The yield of *p*-toluidide was 76%, m.p. 136–137°.

Anal. Calcd. for $C_{24}H_{32}N_2O_2S_2$: S, 14.37; N, 6.28. Found: S, 14.21; N, 6.26.

Sulfopivalic Acid Monohydrate.—Dithiodipivalic acid (100 g.) was added in small increments to a stirred mixture of nitric acid (sp. gr. 1.42, 450 g.) and water (200 g.) at such a rate that the reaction temperature was maintained at 60–70°. The mixture was then heated on a steam-bath for 30 minutes before being allowed to evaporate in a current of air for 16 hours. The residue was distilled under reduced pressure (160 mm.) until the base temperature reached 60°. The residue was concentrated in a vacuum desiccator over sulfuric acid to obtain a slush of crystals which were removed periodically and dried over phosphorus pentoxide at a pressure of 1 mm.; yield 100 g. or 67%, m.p. 107–108°. A sample for analysis was obtained by recrystallization from a mixture of chlorobenzene and ligroin.

(10) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 158.

Anal. Calcd. for $C_5H_{12}O_6S$: S, 16.00; neut. equiv., 100. Found: S, 16.29; neut. equiv., 99.8.

Anhydrous Sulfopivalic Acid.—The acid monohydrate (10 g.) was heated at 118° for 4 hours at a pressure of 1 mm. in a drying apparatus containing phosphorus pentoxide as the desiccant. The gray powder thus produced was dissolved in hot benzene and treated with an equal volume of ligroin. Upon cooling the solution, fine white crystals of the anhydrous acid were deposited; yield 7.5 g. or 82.5%, m.p. 161–162° (sealed tube).

Anal. Calcd. for $C_5H_{10}O_5S$: C, 32.98, H, 5.71; S, 17.69; neut. equiv., 91.1. Found: C, 32.77; H, 5.71; S, 17.60; neut. equiv., 91.1.

Sulfopivalic Acid Cyclic Anhydride. A.—The acid monohydrate (86 g.) was refluxed with thionyl chloride (100 g.) for 8 hours, then the excess of the latter was removed under reduced pressure. Hot benzene (50 ml.) was added to the residue and the solution thereby obtained was poured slowly with stirring into 400 ml. of cold ligroin. The resulting yellow precipitate was collected on a filter, washed with ligroin and redissolved in hot benzene. The solution was then decolorized with carbon. The pure compound was precipitated by dilution of the decolorized solution with twice its volume of ligroin; yield 48.5 g. or 85%, m.p. 62–64°.

Anal. Calcd. for $C_5H_8O_4S$: C, 36.71; H, 4.94; S, 19.53; neut. equiv., 82.1. Found: C, 36.52; H, 5.05; S, 19.30; neut. equiv., 82.0.

B.—Treatment of pivalic acid (51 g.) with sulfuryl chloride by the method of Kharasch[8] gave the cyclic anhydride of sulfopivalic acid; yield 13 g. or 19.7%, m.p. 62–64°.

Ammonium Salt of Sulfopivalamide.—Sulfopivalic acid cyclic anhydride (10 g.) was added to ammonium hydroxide (28%, 150 ml.) at 5°. The resulting clear solution was evaporated to dryness over steam, and the residue was recrystallized from aqueous alcohol. The white, crystalline solid was quite soluble in water and liberated ammonia when it was treated with a cold solution of sodium carbonate.

This product is analogous to that obtained by Kharasch, *et al.*,[8] by the reaction of sulfopropionic cyclic anhydride with ammonia; hence, it is considered to be the ammonium salt of sulfopivalamide. Analyses substantiate this assumption; yield 13.3 g. or 82%, m.p. 187–188°.

Anal. Calcd. for $C_5H_{14}N_2O_4S$: S, 16.18; N, 14.15. Found: S, 16.04; N, 13.98.

***p*-Toluidine Salt of Sulfopivalo-*p*-toluidide.**—Sulfopivalic acid cyclic anhydride (10 g.) in benzene (30 ml.) was added to a solution of *p*-toluidine (20 g.) in benzene (50 ml.). A vigorous reaction took place. The white solid which formed was separated, washed with benzene and recrystallized from aqueous alcohol; yield 21.8 g. or 76%, m.p. 180–182°.

Anal. Calcd. for $C_{19}H_{26}N_2O_5S$: S, 8.46; N, 7.42. Found: S, 8.71; N, 7.70.

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The Schmidt Reaction. IV. Reaction with α-Methyl-α-ethylbutyrophenone

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Unsymmetrical ketones normally undergo the Schmidt reaction to yield one or two N-substituted amides or their hydrolysis products. However, in the case of compounds containing a tertiary alkyl group, abnormal products may arise in any of three ways: cleavage of the tertiary group to form a car-