Upon acidification of these alkaline extracts mesitoic acid precipitated but no butylnitramine was found.

The organic extracts were dried and concentrated to yield 9.1 g. of a white solid whose infrared spectrum indicated that it was a mixture of an amide and an anhydride. By recrystallization from ligroin there was obtained 3.2 g. (15%) of N-*n*-butylmesitamide, m.p. 83–87° (lit.[14] m.p. 88.5–89°). The melting point was not depressed upon admixture with an authentic sample.

Cyclohexylamine.—The same procedure as that for *n*-butylamine was followed. Again no nitramine could be found in the reaction mixture. By fractional crystallization of the crude amide–anhydride mixture 6.1 g. (25%) of **N-cyclohexylmesitamide** was obtained. Recrystallization from ethanol yielded an analytical sample, m.p. 171–172°.

Anal. Calcd. for $C_{16}H_{23}NO$: C, 78.37; H, 9.39; N, 5.71. Found: C, 77.72; H, 9.17; N, 5.73.

***t*-Butylamine.**—The general procedure employed for *n*-butylamine was used. In this case alkaline extraction of the reaction mixture yielded a mixture of mesitoic acid and *t*-butylnitramine. Distillation of this mixture yielded 2.3 g. (20%) of pure ***t*-butylnitramine**, m.p. 41–42.5° (lit.[15] m.p. 38°).

Reaction of Mesitoyl Nitrate with *n*-Hexyl Alcohol.—The following procedure is typical of those used with alcohols. The mesitoyl nitrate was prepared in exactly the same manner as described above. The ethereal solution of mesitoyl nitrate was cooled to −20° and 10.2 g. (0.1 mole) of *n*-hexyl alcohol was added rapidly. The mixture was stirred for 15 minutes, then poured on ice, made basic and filtered. The filtrate was transferred to a separatory funnel and the organic layer was separated and dried. Removal of the solvent left an oily solid. This material was slurried with silica in methylene chloride to remove any unreacted alcohol. The eluate was concentrated and treated with trifluoroacetic anhydride to remove the mesitoic anhydride. The remainder of the mixture was fractionated to yield 1.8 g. (12%) of ***n*-hexyl nitrate**, b.p. 86–88° (10 mm.), $n^{25}D$ 1.4172 (lit.[16] b.p. 46° (1 mm.), $n^{24.5}D$ 1.4180), and 6.9 g. (28%) *n*-hexyl mesitoate, b.p. 79–80° (0.2 mm.), $n^{20}D$ 1.4927.

Anal. Calcd. for $C_{16}H_{24}O_2$: C, 77.37; H, 9.74. Found: C, 77.72; H, 8.60.

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The Reaction of Triethyl Phosphite with a Dialkyl Disulfide

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Trialkyl phosphites, such as triethyl phosphite, are nucleophilic reagents which react readily with alkyl halides to form the dialkyl esters of the corresponding phosphonic acids (II).[1] This reaction is believed to involve displacement of the halogen substituent by the triethyl phosphite to form a phosphonium compound (I) which, on attack by the halide ion, eliminates ethyl halide to form the phosphonate.

$$P(OEt)_3 + RX \longrightarrow \underset{\text{I}}{[RP^{\oplus}(OEt)_3X^{\ominus}]} \longrightarrow \underset{\text{II}}{RPO(OEt)_2} + EtX$$

Recently it has been found that trialkyl phosphites react with alkyl *p*-toluenesulfonate esters[2] and with quaternary salts of Mannich bases[3] to produce the corresponding phosphonate esters, with bromine to yield dialkyl phosphobromidates[4] and with alkyl sulfenyl chlorides to produce trialkyl monothiophosphate esters.[5] Although the mechanisms of these latter reactions have not been established with certainty, the formation of the observed products in each case is consistent with a mechanism similar to that of the Arbuzov reaction, involving a nucleophilic displacement of the substituent group by the triethyl phosphite moiety coupled with the cleavage of the ethoxy linkage by the displaced anionic species.

If such a mechanism is indeed common to the reaction of trialkyl phosphites with such a variety of substances as alkyl halides, sulfonate esters, Mannich base salts, bromine and sulfenyl halides, it is reasonable to expect that other linkages, which are either polarized or polarizable, might undergo a similar type of reaction with triethyl phosphite, provided the group displaced is capable of cleaving the ethoxy bond. A grouping likely to possess these properties is the disulfide linkage which is known to undergo nucleophilic cleavage with great ease, especially by sulfhydryl anions.[6] Accordingly, the reaction of triethyl phosphite with diethyl disulfide was investigated and found to produce triethyl monothiophosphate (III) and diethyl sulfide (IV) in excellent yield. This phenomenon

$$P(OEt)_3 + EtSSEt \longrightarrow \left[\begin{matrix} EtS^{\ominus} \\ \\ EtS\overset{\oplus}{P}(OEt)_3 \end{matrix}\right] \longrightarrow \underset{\text{III}}{EtSPO(OEt)_2} + \underset{\text{IV}}{EtSEt}$$

provides additional suggestive evidence for a common mechanism of the Arbuzov type in the reaction of trialkyl phosphites with a variety of compounds as well as affording a convenient preparative method for monothiophosphate esters of type III.

Experimental

A mixture of 12.2 g. (0.10 mole) of diethyl disulfide (Eastman Kodak Co.) and 41.5 g. (0.25 mole) of redistilled triethyl phosphite[7] was distilled at atmospheric pressure through a 30-in. Fenske column with take off at such a rate that the distillate temperature remained at 90–92°. In about 10 hours there was collected a practically quantitative yield of diethyl sulfide (IV), b.p. 90°, $n^{25}D$ 1.4401, m.p. of sulfone derivative 70.8–71.2°, reported b.p. 93°,[8] $n^{20}D$ 1.4423,[8] m.p. of sulfone[9] 72°. After removal of the excess triethyl phosphite at reduced pressure, triethyl monothiophosphate (III) was collected at 105–110° (10 mm.), $n^{25}D$ 1.4540; 15.2 g., 77%. Redistillation of this product through the column yielded the analytical sample, b.p. 110°

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(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.

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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

(1) Department of Chemistry, Emory University, Emory University, Ga.

(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.

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(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.

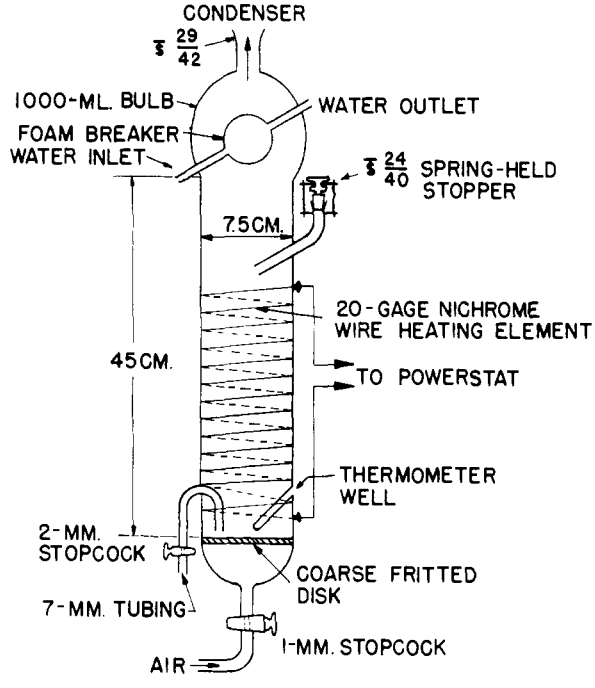

Fig. 1.—Autoxidation apparatus.

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

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