

335. *Organophosphorus Compounds of Sulphur and Selenium. Part XV.* Reactions of Organic Thiosulphonates with Trialkyl Phosphites and Dialkyl Phosphites.*

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Reaction of trialkyl phosphites, $(RO)_3P$, with alkyl esters of aliphatic and aromatic thiosulphonic acids, $R'S\cdot SO_2R''$ led to formation of *OOS*-trialkyl phosphorothiolates and esters of sulphinic acids, in high yields. Reaction of trialkyl phosphites with aryl esters of aromatic thiosulphonic acids took, however, a different course, involving primarily reduction of the thiosulphonates to disulphides. Reaction of sodium dialkyl phosphites, $(RO)_2P\cdot ONa$, with thiosulphonates gave phosphorothiolates and sodium sulphinates. *S*-Alkyl sodium thiosulphates (Bunte salts), $RS\cdot SO_3Na$, failed to react with trialkyl phosphites; with sodium dialkyl phosphites, however, they gave phosphorothiolates in low yield.

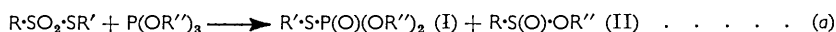
ELECTROPHILIC attack on esters of tervalent phosphorus acids by compounds exhibiting sulphenyl activity offers interesting possibilities of synthesizing organic phosphorothioates and their derivatives. This type of reaction was recently studied in this laboratory,

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sulphenyl activity of various organic thiocyanates¹ and disulphides^{2,3} being demonstrated in reactions with trialkyl phosphites and dialkyl phosphites. It seemed of interest to extend our studies on organic thiosulphonates and S-alkyl sodium thiosulphates (Bunte salts).

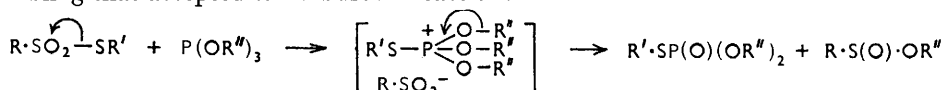
(1) *Reactions of Thiosulphonates with Trialkyl Phosphites*.—Two structures may be considered for the esters of thiosulphonic acids—a disulphoxide, $R\cdot SO\cdot SO\cdot R'$, and a thiosulphonate type, $RS\cdot SO_2R'$, of which the latter shows better agreement with experimental evidence.^{4,5,6} Thiosulphonates exhibit some interesting chemical properties. Foss⁴ includes them in compounds with sulphenyl activity, on the grounds of their ability to split off cations RS^+ in reactions with nucleophilic reagents, such as cyanides, mercaptides,^{7,8,9} and compounds with active methylene groups.⁵ On the other hand, thiosulphonates may be considered as mixed pseudohalogens (interhalogenoids), owing to the pseudohalogen character of both the sulphonyl¹⁰ and the alkylthio-radicals.⁴

We have found that alkyl, but not aryl, esters of aliphatic and aromatic thiosulphonic acids react readily with trialkyl phosphites, forming *OOS*-trialkyl phosphorothiolates (I) and alkyl esters (II) of aliphatic or aromatic sulphinic acids:



The reactions were carried out without solvent, and the temperature of the slightly exothermic process was kept at 20–30°. The products were isolated by distillation *in vacuo*. The yield of either ranged between 80 and 90%. Where unambiguous identification of *OOS*-trialkyl phosphorothiolates by comparison with known compounds was impracticable, degradation by oxidative chlorination¹¹ was the method of choice. The resulting alkanesulphonyl chlorides were converted into readily characterizable *p*-toluidides. To identify alkyl sulphinates (II), we used controlled alkaline hydrolysis to sulphinic acids, which were formed in almost quantitative yield. Sulphinic acids were recognized after being converted into corresponding sulphones by condensation with 1-chloro-2,4-dinitrobenzene. Some difficulties were experienced when boiling points of reaction products precluded isolation by distillation. Compositions of the mixtures were then calculated from refractive indexes and analytical data, and from some additional degradation experiments, according to the following procedure: the mixture was oxidized and then hydrolyzed, and the resulting sodium benzenesulphonate converted into benzenesulphonyl chloride and identified as anilide. The reaction of ethyl *n*-butanethiosulphonate with triethyl phosphite gave in addition to ethyl *n*-butanesulphinic acid, as the main product, the isomeric butyl ethyl sulphone. Thiosulphonic esters failed to react with triaryl phosphites even at 180°.

For the reactions described we propose a mechanism involving heterolysis of the sulphur-sulphur bond and formation of a quasi-phosphonium complex, analogous to that suggested for reactions of trialkyl phosphites with thiocyanates¹ and disulphides,² and resembling that accepted for Arbusov's reaction:¹²



¹ Michalski and Wiczorkowski, *Bull. Acad. polon. Sci.*, Cl. III, 1956, **4**, 279; *Roczniki Chem.*, 1959, **33**, 105.

² Michalski and Wiczorkowski, *Bull. Acad. polon. Sci.*, Cl. III, 1957, **5**, 917.

³ Michalski, Wiczorkowski, Wasiak, and Pliszka, *Roczniki Chem.*, 1959, **33**, 247.

⁴ Foss, *Acta Chem. Scand.*, 1947, **1**, 307.

⁵ Brooker and Smiles, *J.*, 1926, 1726.

⁶ Cymerman and Willis, *J.*, 1951, 1332.

⁷ Smiles and Gibson, *J.*, 1924, **125**, 176.

⁸ Otto and Rössing, *Ber.*, 1887, **20**, 2079.

⁹ Footner and Smiles, *J.*, 1925, **127**, 2887.

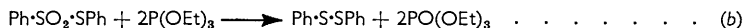
¹⁰ Horner and Nickel, *Annalen*, 1955, **597**, 20.

¹¹ Stirling, *J.*, 1957, 3597.

¹² Kukhtin and Pudovik, *Uspekhi Khim.*, 1959, **28**, 96.

Although isomerization of the sulphinate cannot be fully excluded, side-formation in one case of sulphone results probably from the mesomeric nature of the sulphinic anion which is capable of forming *O*- and *S*-derivatives.¹³

Reaction between triethyl phosphite and phenyl benzenethiosulphonate was more complicated than the analogous reactions discussed above. The process appears to involve three parallel reactions: the reaction of thiosulphonate with triethyl phosphite yielding ethyl benzenesulphinate and *OO*-diethyl *S*-phenyl phosphorothiolate (scheme *a*), the reduction of thiosulphonate by triethyl phosphite to diphenyl disulphide with formation of triethyl phosphate (scheme *b*), and a third reaction, involving disulphide, referred to further below:

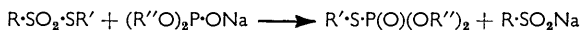


One mol. of thiosulphonate, reacting with 2 mol. of triethyl phosphite, gave a mixture containing triethyl phosphate, ethyl benzenesulphinate, *OO*-diethyl *S*-phenyl phosphorothiolate, and a small amount of diphenyl disulphide. The disulphide disappeared when more triethyl phosphite was added. When triethyl phosphite and thiosulphonate were used in equimolar proportion, or the latter was used in excess, diphenyl disulphide and triethyl phosphate were the main products. It may be concluded that the reaction of thiosulphonate (*a*) and also reduction (*b*) are more rapid than the reaction of triethyl phosphite with diphenyl disulphide:¹⁴



Similar reduction of compounds possessing a sulphonyl group by triethyl phosphite has been recently demonstrated by Hoffman *et al.*¹⁵ for benzenesulphonyl chloride.

(2) *Reactions of Thiosulphonic Esters with Sodium Dialkyl Phosphites.*—We have also demonstrated reactions of esters of aliphatic and aromatic thiosulphonic acids with sodium dialkyl phosphites. Although dialkyl phosphites are only slightly nucleophilic, their sodium derivatives are much more so and were expected to react with esters of thiosulphonic acids in a similar manner to reaction with disulphides³ and thiocyanates.¹⁶ This was found to be the case; esters of aliphatic and aromatic thiosulphonic acids react readily with sodium dialkyl phosphites:



OO-Dialkyl *S*-alkyl(aryl) phosphorothiolates and sodium salts of sulphinic acids were formed in high yields (70—90%). The phosphorothiolates were identified as in the previous section. The sodium sulphinates were condensed with 1-chloro-2,4-dinitrobenzene and recognized as corresponding sulphones.

(3) *Reactions of S-Alkyl Sodium Thiosulphates with Trialkyl Phosphites and Dialkyl Phosphites.*—*S*-Alkyl sodium thiosulphates (Bunte salts) are known also to exhibit sulphenyl activity in reactions with cyanides and mercaptides;¹⁷ however, their reactivity with regard to nucleophilic reagents, due to the presence of a negative charge in the molecule, may be expected to be considerably decreased. Bunte salts failed to react with trialkyl phosphites, when sodium diethyl phosphite was used as nucleophilic reagent formation of *OOS*-triethyl phosphorothiolate in *ca.* 10% yield was observed:



EXPERIMENTAL

Materials.—Ethyl *n*-butanethiosulphonate, b. p. 86—87°/0.4 mm., n_D^{20} 1.4866, was prepared according to Boldyrev and Litkovits,¹⁸ and so was ethyl benzenethiosulphonate, b. p. 83—85°/0.01 mm., n_D^{20} 1.5724.

¹³ Gilman, "Organic Chemistry," Wiley, New York, 1947, Vol. I, 916.

¹⁴ Poshkus and Herweh, *J. Amer. Chem. Soc.*, 1957, **79**, 4245.

¹⁵ Hoffman, Moore, and Kagan, *ibid.*, 1956, **78**, 6413.

¹⁶ Schrader, U.S.P. 2,640,847; *Chem. Abs.*, 1954, **48**, 5206.

¹⁷ Bunte, *Ber.*, 1874, **7**, 646.

¹⁸ Boldyrev and Litkovits, *Zhur. obshchei Khim.*, 1956, **16**, 3360.

Phenyl benzenethiosulphonate was prepared by a modified Hinsberg method:¹⁹ diphenyl disulphide, hydrogen peroxide in 30% excess, and glacial acetic acid were heated with stirring to 80° on a water-bath. The temperature then rose spontaneously and a violent reaction occurred, which made intensive cooling necessary. The mixture was diluted with a large volume of water, and extracted with benzene. The solvent was removed under reduced pressure, and the crude product separated from ethanol in white crystals, m. p. 39—40° (yield 50%).

S-Ethyl sodium thiosulphate was prepared by Bunte's method.¹⁷

Reaction of Ethyl n-Butanethiosulphonate with Tributyl Phosphite.—Ethyl butanethiosulphonate (27.3 g., 0.15 mole) was treated with the tri-n-butyl phosphite (37.5 g., 0.15 mole) and the temperature of the slightly exothermic reaction was kept at 20—25°. The products were fractionated by distillation *in vacuo* and afforded n-butyl n-butanethiosulphinate (24.0 g., 90%), b. p. 52—54°/0.2 mm., n_D^{25} 1.4444 (Found: C, 53.1; H, 9.9. Calc. for $C_8H_{18}O_2S$: C, 53.9; H, 10.2%), and *OO*-di-n-butyl S-ethyl phosphorothiolate (33.7 g., 89%), b. p. 87—89°/0.3 mm., 157—158°/14 mm., n_D^{25} 1.4524 (Found: P, 11.9. Calc. for $C_{10}H_{23}O_3PS$: P, 12.2%). Michalski and Wieczorkowski¹ reported b. p. 156—158°/14 mm., n_D^{25} 1.4523, for the latter. In order to confirm the structure of the phosphorothiolate, the product was treated with chlorine in water,¹¹ yielding ethanesulphonyl chloride, b. p. 66°/14 mm., n_D^{25} 1.4509 (lit.,²⁰ b. p. 172—175°, n_D^{20} 1.4518), which was transformed into ethanesulphon-*p*-toluidide, m. p. and mixed m. p. 79—80°. In order to confirm the structure of the sulphonic ester it was hydrolysed in 1.4*N*-aqueous alcoholic sodium hydroxide, and the resulting sodium butanesulphinate was condensed with 1-chloro-2,4-dinitrobenzene, which afforded n-butyl 2,4-dinitrophenyl sulphone, m. p. and mixed m. p. 91—92°.

Reaction of Ethyl n-Butanethiosulphonate with Triethyl Phosphite.—Ethyl butanethiosulphonate (36.4 g., 0.2 mole) was treated with triethyl phosphite (33.2 g., 0.2 mole) under conditions identical with those of the preceding experiment. Fractional distillation of the product gave three fractions, of which the lowest-boiling (13.6 g.) was identified as an azeotropic mixture of 83% of ethyl butanesulphinate and 17% of *OOS*-triethyl phosphorothiolate, b. p. 80—83°/11 mm., n_D^{20} 1.4385. The second fraction (16.2 g.) proved to be pure *OOS*-triethyl phosphorothiolate, b. p. 115°/12 mm., n_D^{20} 1.4572 (Found: C, 36.5; H, 7.7; P, 15.6. Calc. for $C_6H_{15}O_3PS$: C, 36.4; H, 7.6; P, 15.6%). Michalski and Wieczorkowski² reported b. p. 112°/11 mm., n_D^{20} 1.4570. The composition of the azeotropic mixture being taken into account, yields of ethyl ester of n-butanethiosulphonic acid and of *OOS*-triethyl phosphorothiolate were 67 and 89%, respectively. The highest-boiling fraction (2.1 g.), which solidified, was recrystallised from ethanol and proved to be n-butyl ethyl sulphone (yield 9%), m. p. and mixed m. p. 49—50°. The structure of the ester of butanesulphonic acid was confirmed by the methods referred to in the preceding experiment.

Reaction of Ethyl Benzenethiosulphonate with Triethyl Phosphite.—Ethyl benzenethiosulphonate (20.3 g., 0.1 mole) was treated with triethyl phosphite (16.6 g., 0.1 mole) at 20—25° (cooling with cold water), and the products were fractionated *in vacuo*. Two fractions were obtained: (i) b. p. 121°/14 mm., n_D^{20} 1.4695; (ii) b. p. 127°/16 mm., n_D^{20} 1.5030. Fraction (i) contained 84% of *OOS*-triethyl phosphorothiolate and 16% of ethyl benzenesulphinate (Found: C, 39.9; H, 7.5; P, 13.6. Calc. for the mixture: C, 39.6; H, 7.4; P, 13.1%). The structures of the products were confirmed as follows: fraction (i) was treated with chlorine in aqueous medium, yielding ethanesulphonyl chloride, which was transformed into ethanesulphon-*p*-toluidide, m. p. and mixed m. p. 78°. Fraction (ii), containing 59% of the ethyl benzenesulphinate and 41% of *OOS*-triethyl phosphorothiolate, was hydrolysed by the theoretical amount of aqueous-alcoholic sodium hydroxide, and the resulting sodium benzenesulphinate was condensed with 1-chloro-2,4-dinitrobenzene, yielding 2,4-dinitrodiphenyl sulphone, m. p. and mixed m. p. 158°. From the compositions of fractions (i) and (ii), overall yields of *OOS*-triethyl phosphorothiolate and ethyl benzenesulphinate were 98 and 74%, respectively.

Reaction of Ethyl Benzenethiosulphonate with Tri-n-butyl Phosphite.—The benzenethiosulphonate (30.5 g., 0.15 mole) was treated with the phosphite (37.5 g., 0.15 mole) as in a previous experiment. Distillation gave a constant-boiling mixture, b. p. 95—96°/0.4 mm., n_D^{20} 1.4848. The structure of the resulting n-butyl benzenesulphinate was confirmed as follows:

¹⁹ Hinsberg, *Ber.*, 1908, **41**, 2836.

²⁰ Lee and Dougherty, *J. Org. Chem.*, 1940, **5**, 83.

(i) a sample was hydrolysed by aqueous-alcoholic sodium hydroxide, giving sodium benzenesulphonate, which was converted into 2,4-dinitrodiphenyl sulphone, m. p. and mixed m. p. 158°; (ii) a sample was dissolved in acetone and treated with potassium permanganate, yielding *n*-butyl benzenesulphonate (b. p. 78°/0.01 mm., n_D^{20} 1.4774). The product was then hydrolysed by the above alkaline solution, and the solid product, after crystallisation from ethanol, was heated at 170° with phosphorus oxychloride and gave benzenesulphonyl chloride, b. p. 117°/10 mm., n_D^{20} 1.5518 (lit.,²¹ b. p. 120°/10 mm., n_D^{23} 1.5505); this was converted into the anilide, m. p. and mixed m. p. 108°. The structure of *OO*-di-*n*-butyl *S*-ethyl phosphorothiolate was confirmed as in previous experiments, *i.e.*, by chlorination and conversion of ethanesulphonyl chloride (b. p. 70°/15 mm., n_D^{25} 1.4563) into the corresponding *p*-toluidide, m. p. and mixed m. p. 79°.

Attempted Reaction of Ethyl n-Butanethiosulphonate with Triphenyl Phosphite.—The thiosulphonate (18.2 g., 0.1 mole) was heated with the phosphite (31.0 g., 0.1 mole) at 180° for 3 hr. Distillation gave unchanged substances.

Reaction of Phenyl Benzenethiosulphonate with Triethyl Phosphite.—(a) Triethyl phosphite (83 g., 0.5 mole) was added to a solution of phenyl benzenethiosulphonate (125 g., 0.5 mole) in benzene (100 ml.) at 20–25°. The solvent was removed under reduced pressure and on distillation *in vacuo* five fractions were obtained. Fraction (i) was pure triethyl phosphate (29.6 g.), b. p. 101°/15 mm., n_D^{25} 1.4068 (lit.,²² b. p. 90°/10 mm., n_D^{25} 1.4039) (Found: C, 39.7; H, 8.3; P, 16.6. Calc. for $C_6H_{15}O_4P$: C, 39.6; H, 8.3; P, 17.0%). Fraction (ii) (32.3 g.; b. p. 122–128°/25 mm.; n_D^{25} 1.4170) was composed of 91% of triethyl phosphate and 9% of ethyl benzenesulphonate (Found: C, 42.0; H, 8.5; P, 16.0. Calc. for mixture: C, 41.1; H, 8.1; P, 16.0%). Fraction (iii) (14.8 g., b. p. 96–106°/0.5 mm., n_D^{25} 1.5243) was composed of 90.5% of *OO*-diethyl *S*-phenyl phosphorothiolate and 9.5% of diphenyl disulphide (Found: C, 51.5; H, 5.8; P, 10.5. Calc. for mixture: C, 50.7; H, 5.9; P, 11.4%). The highest-boiling products were recognized as diphenyl disulphide (50.6 g.), m. p. and mixed m. p. 59°, and an excess of phenyl benzenethiosulphonate (41 g., 33%), m. p. and mixed m. p. 39°. With allowances for the composition of two mixtures, yields of triethyl phosphate, ethyl benzenesulphonate, *OO*-diethyl *S*-phenyl phosphorothiolate, and diphenyl disulphide were 65%, 3.4%, 11%, and 48%, respectively. The structure of the ethyl benzenesulphonate was confirmed by alkaline hydrolysis; the resulting sodium benzenesulphonate was converted into 2,4-dinitrodiphenyl sulphone, m. p. and mixed m. p. 156°. That of *OO*-diethyl *S*-phenyl phosphorothiolate was confirmed as follows: the mixture was dissolved in chloroform (50 ml.), and a solution of chlorine (7.2 g.) in chloroform (90 ml.) was added with stirring at –12°,¹¹ to give diethyl phosphorochloridate and benzenesulphenyl chloride. Ethylene was then passed through till the mixture was decolorized and the crude diethyl phosphorochloridate (2 g., b. p. 90–100°/18 mm.) was then distilled off and converted into the corresponding anilide, m. p. and mixed m. p. 94°.

(b) Triethyl phosphite (33.2 g., 0.2 mole) was added to a solution of phenyl benzenethiosulphonate (25.0 g., 0.1 mole) in benzene (30 ml.) at 25°. The solvent was removed under reduced pressure and on distillation *in vacuo* the product yielded: (i) triethyl phosphate (16.8 g.), b. p. 101°/13 mm., n_D^{25} 1.4133 (Found: C, 40.4; H, 8.3; P, 16.4. Calc. for $C_6H_{15}O_4P$: C, 39.6; H, 8.3; P, 17.0%); (ii) ethyl benzenesulphonate (5.0 g.), b. p. 58°/0.05 mm., n_D^{20} 1.5308 (Found: C, 56.1; H, 6.1. Calc. for $C_8H_{10}O_2S$: C, 56.4; H, 5.9%); (iii) *OO*-diethyl *S*-phenyl phosphorothiolate (17.5 g.), b. p. 87–88°/0.04 mm., n_D^{25} 1.5259 (Found: C, 49.3; H, 6.0; P, 12.0. Calc. for $C_{10}H_{15}O_3PS$: C, 48.8; H, 6.1; P, 12.6%); and (iv) diphenyl disulphide (2 g.), m. p. and mixed m. p. 59°.

Reaction of Ethyl n-Butanethiosulphonate with Sodium Diethyl Phosphite.—Sodium (3.4 g., 0.15 mole) was dissolved in a solution of diethyl phosphite (20.7 g., 0.15 mole) in benzene (150 ml.), and the solution treated with ethyl butanethiosulphonate (27.3 g., 0.15 mole) at 25–30° with cooling and stirring. The colourless suspension was extracted with water (3 × 50 ml.), the combined water extracts were washed with benzene (3 × 20 ml.), and the benzene extracts were combined with a benzene solution of the reaction mixture. The product was dried (Na_2SO_4), the solvent removed under reduced pressure, and the residue distilled *in vacuo* giving *OOS*-triethyl phosphorothiolate (24.5 g., 83%), b. p. 121–122°/15 mm., n_D^{20} 1.4570 (Found: C, 36.6; H, 7.6; P, 15.6. Calc. for $C_6H_{15}O_3SP$: C, 36.4; H, 7.6; P, 15.6%). The aqueous layer was evaporated to dryness under reduced pressure and the crude sodium

²¹ Beilstein's "Handbuch, etc.," 1928, Vol. 11, 34; Landau, *J. Amer. Chem. Soc.*, 1947, **69**, 1219.

²² Evans, Davies, and Jones, *J.*, 1930, 1310.

n-butanethiolate (11.6 g., 54%) was suspended in ethanol (100 ml.) and refluxed with 1-chloro-2,4-dinitrobenzene (16 g.), giving n-butyl 2,4-dinitrophenyl sulphone, m. p. and mixed m. p. 89°.

Reaction of Ethyl n-Butanethiosulphonate with Sodium Di-n-butyl Phosphite.—The thiosulphonate (27.3 g., 0.15 mole) was added to a benzene solution of the phosphite (0.15 mole), and the reaction carried out as in the preceding experiment, yielding *OO*-di-n-butyl *S*-ethyl phosphorothiolate (30.5 g., 80%), b. p. 162—164°/18 mm., n_D^{20} 1.4568, and sodium n-butanethiosulphonate (18.8 g., 86%). The phosphorothiolate was treated with chlorine in aqueous medium, affording ethanesulphonyl chloride, b. p. 66°/16 mm., n_D^{20} 1.4527, which was converted into the *p*-toluidide, m. p. and mixed m. p. 79°. The sodium butanethiosulphonate was condensed with 1-chloro-2,4-dinitrobenzene, giving the corresponding sulphone, m. p. and mixed m. p. 88°.

Reaction of Ethyl Benzenethiosulphonate with Sodium Diethyl Phosphite.—The phosphite (0.1 mole) in benzene was treated with the thiosulphonate (20.3 g., 0.1 mole) by the same procedure as before. The reaction yielded *OOS*-triethyl phosphorothiolate (14.0 g., 71%), b. p. 114°/12 mm., n_D^{20} 1.4566 (Found: P, 15.7. Calc. for $C_6H_{15}O_3SP$: P, 15.6%); and sodium benzenethiosulphonate (14.0 g., 85%), which was converted into 2,4-dinitrodiphenyl sulphone, m. p. and mixed m. p. 157°.

Reaction of Phenyl Benzenethiosulphonate with Sodium Diethyl Phosphite.—The phosphite (0.1 mole) in benzene was treated with phenyl benzenethiosulphonate (25.0 g., 0.1 mole), and the reaction carried out as previously described, giving *OO*-diethyl *S*-phenyl phosphorothiolate (17.0 g., 69%), b. p. 91°/0.05 mm., n_D^{20} 1.5238 (lit.,²³ b. p. 108°/0.2 mm., n_D^{16} 1.5240), and sodium benzenethiosulphonate (15.1 g., 92%) which was converted into 2,4-dinitrodiphenyl sulphone, m. p. and mixed m. p. 159°. The ester was treated with chlorine in aqueous medium, giving benzenesulphonyl chloride, b. p. 128—130°/20 mm., n_D^{20} 1.5458, and thence the *p*-toluidide, m. p. and mixed m. p. 110°.

Non-reaction of S-Ethyl Sodium Thiosulphate with Triethyl Phosphite.—(a) Triethyl phosphite (16.6 g., 0.1 mole) was refluxed under stirring with a suspension of *S*-ethyl sodium thiosulphate (16.4 g., 0.1 mole) in benzene (70 ml.) for 2 hr. The resulting mixture was cooled, the precipitate was filtered off, and washed with benzene, and the filtrate evaporated under reduced pressure. Distillation of the residue gave unchanged triethyl phosphite (11.7 g., 70%).

(b) A suspension of *S*-ethyl sodium thiosulphate (16.4 g., 0.1 mole) in triethyl phosphite (16.6 g., 0.1 mole) was heated at 110—120° till slight decomposition was observed (2 hr.). The resulting mixture was cooled and filtered, and the filtrate distilled *in vacuo*, giving unchanged phosphite (5.0 g., 30%), and a pitch-like, undistillable residue. No trace of *OOS*-triethyl phosphorothiolate was detected.

Reaction of S-Ethyl Sodium Thiosulphate with Sodium Diethyl Phosphite.—A solution of the phosphite (0.15 mole) in ethanol (100 ml.) was added with stirring to a suspension of the thiosulphate (24.6 g., 0.15 mole) in ethanol (100 ml.) at 20°. The temperature rose by about 10°. Ethanol was removed under reduced pressure, benzene (200 ml.) added, the suspension washed several times with water, and the benzene solution dried (Na_2SO_4). The solvent was removed under reduced pressure, and the product gave on distillation *OOS*-triethyl phosphorothiolate (3.2 g., 11%), b. p. 59—60°/0.4 mm., n_D^{20} 1.4570 (Found: P, 16.0. Calc. for $C_6H_{15}O_3SP$: P, 15.6%).

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²³ Lecoq and Todd, *J.*, 1954, 2383.