978. *Organophosphorus Compounds of Sulphur and Selenium. Part XXII.* Reactions of Organic Disulphides with Dialkyl Phosphites and Thiophosphites.*†

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Dialkyl phosphites and thiophosphites react only with acyl-type disulphides, but in the presence of amines, or as their sodium or potassium derivatives, and with alkyl disulphides, nucleophilic substitution at sulphur usually occurring. The phosphorothioic acid esters and mercaptides formed can interact, the latter acting as nucleophilic dealkylation agents. The low rate of dealkylation at room temperature, and the relatively high rate at 60—100°, enable neutral and acid esters to be prepared conveniently.

REACTIONS of trialkyl phosphites and their analogues with organic disulphides have been described [1,2] in terms of nucleophilic substitution at sulphur; they lead to compounds of the type $R_2PO{\cdot}SR'$, or, in certain cases, by secondary isomerisation also $R_2PS{\cdot}OR'$. Formation of an intermediate quasiphosphonium complex is assumed [1,2] and the complicated course of the reaction with acyl-type disulphides is explained by a dual possibility of stabilisation of the complex involved.[2]

Dialkyl phosphites and their sulphur derivatives also have nucleophilic character. Their structure is best expressed by assuming a tautometic equilibrium,[3] $(RO)_2PHO \rightleftharpoons (RO)_2P{\cdot}OH$, where the concentration of the active form with tervalent phosphorus is minute. A similar situation exists for dialkyl thiophosphites [4,5] and selenophosphites.[6] Free dialkyl phosphites exhibit nucleophilic activity only with regard to some reagents, such as halogens [7] and thiocyanogen.[8] Their alkali-metal derivatives, or the diesters in the presence of amines, show an activity comparable with that of triesters of tervalent phosphorus acids. The present paper concerns the reactions of dialkyl phosphites and thiophosphites with organic disulphides. Predictably, they react only with the acyl-type disulphides, which have an active S–S linkage; in the form of their alkali-metal derivatives or in the presence of organic bases they react readily with most types of organic disulphides.

Reactions of aliphatic and aromatic disulphides with sodium dialkyl phosphites and thiophosphites are exothermic and temperature and medium determine the final products.

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* Part XXI, *Roczniki Chem.*, 1962, **36**, 775. † Preliminary communication, *ibid.*, 1959, **33**, 247.

[1] Jacobson, Harvey, and Jensen, *J. Amer. Chem. Soc.*, 1955, **77**, 6064.
[2] Michalski and Wieczorkowski, *Bull. Acad. polon. Sci.*, Cl. III, 1957, **5**, 917.
[3] Milobendzki, *Ber.*, 1912, **45**, 292.
[4] Kabachnik and Mastryukova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1953, 163.
[5] Krawiecki and Michalski, *Roczniki Chem.*, 1957, **31**, 716.
[6] Krawiecki and Michalski, to be published.
[7] McCombie, Saunders, and Stacey, *J.*, 1945, 380; Atherton, Openshaw, and Todd, *J.*, 1945, 382.
[8] Michalski and Wieczorkowski, *Roczniki Chem.*, 1957, **31**, 585.

At low temperatures (0—40°) and in solvents such as benzene, the reaction can easily be stopped at the stage (a) or (b):

$$(RO)_2P{\cdot}ONa + R'S{\cdot}SR' \longrightarrow (RO)_2PO{\cdot}SR' + R'{\cdot}SNa \tag{a}$$

$$(RO)_2P{\cdot}SNa + R'S{\cdot}SR' \longrightarrow (RO)_2PS{\cdot}SR' + R'{\cdot}SNa \tag{b}$$

Reactions of sodium dialkyl phosphites and disulphides in boiling benzene led to sodium *OS*-dialkyl phosphorothioates and dialkyl sulphides, also in excellent yield:

$$(RO)_2P{\cdot}ONa + R'S{\cdot}SR' \longrightarrow (R'S)(RO)PO{\cdot}ONa + R'{\cdot}SR \tag{c}$$

Reactions of sodium dialkyl thiophosphites with disulphides are less affected by temperature and, even in boiling benzene, proceed essentially according to scheme (b). The process:

$$(RO)_2P{\cdot}SNa + R'S{\cdot}SR \longrightarrow (R'S)(RO)PS{\cdot}ONa + R'{\cdot}SR \tag{d}$$

requires a suitable polar solvent, *e.g.*, ethanol. Undoubtedly, equations (c) and (d) sum up two consecutive reactions, the first corresponding to (a) or (b), and the other being a special case of anionic dealkylation caused by the mercaptide anion formed:

$$(RO)_2PO{\cdot}SR' + R'SNa \longrightarrow (RO)(R'S)PO{\cdot}ONa + R'{\cdot}SR \tag{e}$$

This path was confirmed independently by allowing *S*-n-butyl *OO*-diethyl phosphorothiolate to react with sodium butyl sulphide in boiling benzene; the yield, however, was much lower. The inferior rate of dealkylation may be attributed to the low dispersion of the mercaptide in comparison with the colloidal suspension produced in reaction (a). Particular attention is due to a modification of the reaction, whereby dialkyl phosphites react with disulphides in the presence of amines. Secondary dealkylation is here generally avoided, and the yields are much the same as when sodium dialkyl phosphite is used.

As mentioned above, free dialkyl phosphites and thiophosphites react with disulphides which have particularly active S–S bond. One of the compounds in this class has earlier been reported by Michalski and Wieczorkowski, namely, thiocyanogen NC·S·S·CN:[8] it is a typical pseudohalogen and reacts with phosphites very much as the halogens do:

$$(RO)_2PHO + (SCN)_2 \longrightarrow (RO)_2PO{\cdot}NCS + HSCN$$

We find that bisdialkoxyphosphinyl disulphides (I), whose pseudohalogen character was noted by Foss,[9] react similarly with dialkyl phosphites, forming tetra-alkyl thiopyrophosphates and dialkyl hydrogen thiophosphoric acid:

$$(RO)_2PHO + (RO)_2PO{\cdot}S{\cdot}S{\cdot}PO(OR)_2\ (I) \longrightarrow (RO)_2PO{\cdot}O{\cdot}PS(OR)_2 + (RO)_2PO{\cdot}SH$$

Reaction between bisdialkoxyphosphinothioyl disulphides (II) and dialkyl phosphites takes a similar course:

$$(RO)_2PHO + (RO)_2PS{\cdot}S{\cdot}S{\cdot}PS(OR)_2\ (II) \longrightarrow (RO)_2PO{\cdot}S{\cdot}PS(OR)_2\ (III) + (RO)_2PS{\cdot}SH$$

The asymmetrical structure of the dithiopyrophosphate (III) obtained was confirmed by degradation with sodium alkoxides:

$$(RO)_2PO{\cdot}S{\cdot}PS(OR)_2 \xrightarrow{R'O^-} (RO)_2PO{\cdot}OR' + {}^-S{\cdot}PS(OR)_2$$

The dithiopyrophosphates (III) were identical with the products of condensation of dialkyl thiophosphites with dialkoxyoxophosphoranesulphenyl chlorides:[10]

$$(RO)_2PHS + ClS{\cdot}PO(OR)_2 \longrightarrow (RO)_2PO{\cdot}S{\cdot}PS(OR)_2 + HCl$$

Reaction of dialkyl phosphites or their sodium derivatives with the disulphides (I) or (II) in the presence of amines is more involved because of dealkylation. For example,

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[9] Foss, *Acta Chem. Scand.*, **1947**, **1**, 8.
[10] Michalski and Skowronska, to be published.

sodium dialkyl phosphites and the disulphide (II) at 5—15° yield tetra-alkyl dithiopyrophosphates and sodium *OO*-dialkyl phosphorodithioates:

$$\mathrm{(RO)_2P{\cdot}ONa + (RO)_2PS{\cdot}S{\cdot}S{\cdot}PS(OR)_2 \longrightarrow (RO)_2PO{\cdot}S{\cdot}PS(OR)_2 + (RO)_2PS{\cdot}SNa}$$

The result is similar to that with free phosphites. The secondary dealkylation is evident at as low a temperature as 30—40°, yielding the dithiopyrosulphate salt (IV) and the triester (V). The salt is soluble in water and can be converted into the acid, but attempts to isolate it in a pure state failed. Thermal decomposition led to formation of the ester (V) and a polymeric substance resembling metaphosphoric acid:

$$\begin{tikzcd}
\mathrm{(RO)_2PO{\cdot}S{\cdot}PS(OR)_2 + (RO)_2PS{\cdot}SNa} \arrow[r] & \mathrm{(RO)(NaO)PO{\cdot}S{\cdot}PS(OR)_2\ (IV) + (RO)_2PS{\cdot}SR\ (V)} \arrow[d] \\
 & \mathrm{(RO)_2PS{\cdot}SR + (NaPO_3)_n}
\end{tikzcd}$$

The above experiments explain the course of the phosphorodithioate synthesis recently described by Mel'nikov *et al.*,[11] in which bisdialkoxyphosphinothioyl disulphides in benzene are heated with dialkyl phosphites in the presence of triethylamine:

$$\mathrm{(RO)_2PHO + NEt_3 + (RO)_2PS{\cdot}S{\cdot}S{\cdot}PS(OR)_2 \longrightarrow 2(RO)_2PS{\cdot}SR + Et_3N,HPO_3}$$

The reaction of sodium dialkyl phosphite with bisdialkoxyphosphinyl disulphide is similar: first, a tetra-alkyl thiopyrophosphate and sodium *OO*-dialkyl phosphorothioate are formed; if the reaction is carried out in boiling toluene, secondary reaction, analogous to the dealkylation and pyrolysis above are observed. The final products are triethyl phosphorothiolate and a polymeric substance.

Tervalent phosphorus derivatives show marked affinity for sulphur owing both to the considerable polarizability of phosphorus and to use of 3*d* orbitals of sulphur. The reaction of dialkyl phosphites or their metallic derivatives with organic disulphides is a particular case of nucleophilic substitution at sulphur by a reagent having phosphorus as nucleophilic centre. The pronounced activity of acyl-type disulphides probably arises because the leaving group is a thermodynamically stable anion of a thioacid. The nucleophilic attack on S–S linkage in organic disulphides by sodium dialkyl phosphites has a counterpart in two other reactions. Foss[12] observed easy rupture of the linkage between sulphur atoms in the S_8 cyclic structure of elemental sulphur by sodium dialkyl phosphites. Similarly, fission of the S–S bond was involved in reactions of sodium dialkyl phosphites with esters of thiosulphonic acid and Bunte's salt studied in this Laboratory.[13]

EXPERIMENTAL

Extracts were dried over magnesium sulphate.

Reaction of Diphenyl Disulphide with Sodium Diethyl Phosphite.—Diphenyl disulphide (0·2 mole) in benzene (150 ml.) was added dropwise to a benzene solution of sodium diethyl phosphite (from 27·6 g. of diethyl phosphite and 4·6 g. of sodium) with stirring. Reaction was slightly exothermic and the temperature was kept at 15—20°. The suspension of sodium mercaptide was extracted with water (4 × 100 ml.). The solvent of the organic layer was removed and the residue distilled *in vacuo*, giving *OO*-diethyl *S*-phenyl phosphorothiolate (33 g., 67%), b. p. 115—116°/0·6 mm., n_D^{25} 1·5248 (lit.,[14] b. p. 108°/0·2 mm., n_D^{16} 1·5240) (Found: C, 48·5;

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[11] Mel'nikov, Shvetsova-Shilovskaya, and Kagan, *Zhur. obshchei Khim.*, 1960, **30**, 200.

[12] Foss, *Acta Chem. Scand.*, 1947, **1**, 12.

[13] Michalski, Modro, and Wieczorkowski, *J.*, 1960, 1665.

[14] Lecoq and Todd, *J.*, 1954, 2381.

H, 6·1; P, 12·6. Calc. for $C_{10}H_{15}O_3PS$: C, 48·8; H, 6·1; P, 12·6%). The aqueous layer was acidified with 20% hydrochloric acid (50 ml.) and extracted with ether (3 × 50 ml.). The solvent was removed and the residue distilled, giving thiophenol (14 g., 67%), b. p. 167—168°, n_D^{20} 1·5884.

Similarly were prepared: *OOS*-tri-n-butyl (83%), b. p. 167°/11 mm., n_D^{20} 1·4574 (lit.,[15] b. p. 168—172°/14 mm., n_D^{20} 1·4553) (Found: C, 50·7; H, 9·5; P, 10·9. Calc. for $C_{12}H_{27}O_3PS$: C, 50·7; H, 9·6; P, 11·0%), and *OO*-diethyl *S*-n-butyl phosphorothiolate (93%), b. p. 135—136°/13 mm., n_D^{19} 1·4578 (lit.,[16] b. p. 131—133°/11 mm., n_D^{20} 1·4580) (Found: P, 13·7. Calc. for $C_8H_{19}O_3PS$: P, 13·7%).

Reaction of Di-n-butyl Disulphide with Sodium Diethyl Thiophosphite.—Sodium diethyl thiophosphite was prepared from diethyl thiophosphite and sodium ethoxide in benzene. The alcohol was removed by partial evaporation. The reaction, carried out as previously described, yielded OO-*diethyl* S-*n-butyl phosphorodithioate* (33·5%), b. p. 145°/12 mm., n_D^{25} 1·4961 (Found: C, 39·5; H, 7·8; P, 12·4. $C_8H_{19}O_2PS_2$ requires C, 39·6; H, 7·9; P, 12·8%).

Similarly were prepared *OOS*-tri-n-butyl (84%), b. p. 146—148°/2·5 mm., n_D^{25} 1·4892 (lit.,[17] b. p. 148—149°/4 mm., n_D^{20} 1·4859) (Found: C, 48·1; H, 9·5; P, 10·3. Calc. for $C_{12}H_{27}O_2PS_2$: C, 48·6; H, 9·1; P, 10·4%), and OO-*di-n-propyl* S-*phenyl phosphorodithioate* (76%), b. p. 104—106°/0·005 mm., n_D^{20} 1·5486 (Found: C, 49·5; H, 6·5; P, 10·4. $C_{12}H_{19}O_2PS_2$ requires C, 49·6; H, 6·5; P, 10·7%.

Reaction of Diphenyl Disulphide with Sodium Diethyl Phosphite.—Diphenyl disulphide (0·2 mole) in benzene (150 ml.) was added dropwise with stirring to sodium diethyl phosphite (0·2 mole) in benzenene (150 ml.) at 80°. After 2 hr. the mixture was extracted with water (4 × 100 ml.). The solvent of the benzene layer was removed and the residue distilled, yielding ethyl phenyl sulphide (11 g., 87%), b. p. 201—203°, n_D^{20} 1·5647 (Found: C, 69·9; H, 7·2. Calc. for $C_8H_{10}S$: C, 69·5; H, 7·2%). The aqueous layer was acidified and extracted with benzene (3 × 70 ml.). The solvent was removed but the *O*-ethyl *S*-phenyl hydrogen phosphorothiolate (27 g., 82%) obtained was an undistillable oil; it was identified as cyclohexylamine salt, m. p. 130—131° (from benzene–light petroleum) (lit.,[14] m. p. 128—129°) (Found: C, 53·0; P, 9·6. Calc. for $C_{14}H_{24}NO_3PS$: C, 53·0; P, 9·8%).

Similarly were prepared *OS*-di-n-butyl (68%) [*cyclohexylamine salt*, m. p. 111—112° (Found: C, 52·0; H, 10·0; P, 9·6. $C_{14}H_{32}NO_3PS$ requires C, 51·7; H, 9·8; P, 9·5%)] and *O*-ethyl *S*-n-butyl hydrogen phosphorothiolate (66%) [*cyclohexylamine salt*, m. p. 125—126° (Found: O, 48·6; P, 10·3. $C_{12}H_{28}NO_3PS$ requires C, 48·5; P, 10·3%)].

Dealkylation of OO-*Diethyl* S-*n-Butyl Phosphorothiolate with Sodium n-Butyl Sulphide.*—Sodium butyl sulphide was suspended in a benzene solution of *OO*-diethyl *S*-n-butyl phosphorothiolate (0·2 mole) and the mixture was refluxed for 2 hr. The products were isolated as previously described. The experiment yielded butyl ethyl sulphide (38%), b. p. 141—142° (identified as sulphone, m. p. and mixed m. p. 49—50°), and *O*-ethyl *S*-n-butyl hydrogen phosphorothiolate (40%) (identified as cyclohexylamine salt, m. p. and mixed m. p. 125—126°).

Reaction of Di-n-butyl Disulphide with Sodium Di-n-butyl Thiophosphite.—Sodium dibutyl thiophosphite (0·05 mole) and dibutyl disulphide (8·9 g., 0·05 mole) in ethanol (80 ml.) were refluxed for 2 hr. The mixture was cooled and evaporated. The residue was dissolved in water (100 ml.) and extracted with benzene (3 × 25 ml.). The benzene of the extract was removed and the residue distilled, yielding di-n-butyl sulphide (3·5 g., 48%), b. p. 180—181°, n_D^{20} 1·4550. The aqueous layer was acidified. Extraction with benzene (3 × 20 ml.) afforded *OS*-di-n-butyl hydrogen phosphorodithioate (6 g., 50%) as an undistillable oil identified as *cyclohexylamine salt*, m. p. 174—175° (decomp.) (Found: C, 49·9; H, 9·9; P, 9·5. $C_{14}H_{32}NO_2PS_2$ requires C, 49·3; H, 9·4; P, 9·1%).

Reaction of Diphenyl Disulphide with Di-n-butyl Phosphite in Presence of Triethylamine.—Dibutyl phosphite (19·4 g., 0·1 mole) in benzene (100 ml.) was treated with triethylamine (10·1 g., 0·1 mole), and then with diphenyl disulphide (21·8 g., 0·1 mole) in benzene (100 ml.). The mixture was stirred for 2 hr. at 80°. The products were extracted with water (4 × 50 ml.). The solvent was removed from the benzene layer, and the residue distilled *in vacuo*, yielding OO-*di-n-butyl* S-*phenyl phosphorothiolate* (26 g., 86%), b. p. 118—119°/0·005 mm., n_D^{20} 1·5215 (Found: C, 55·6; H, 7·7; P, 10·2. $C_{14}H_{23}O_3PS$ requires C, 55·6; H, 7·6; P, 10·3%). The

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[15] Michalski and Wieczorkowski, to be published.
[16] Michalski and Wieczorkowski, *Roczniki Chem.*, 1959, **33**, 105.
[17] Kabachnik and Mastryukova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, **1952**, **727**.

aqueous layer was acidified and extracted with benzene (3 × 50 ml.). The benzene was removed and the residue distilled, giving thiophenol (6 g., 64%), b. p. 166—167°, n_D^{20} 1·5880.

Reaction of Bisdiethoxyphosphinyl Disulphide with Diethyl Phosphite.—Bisdiethoxyphosphinyl disulphide (67·6 g., 0·2 mole) in benzene (150 ml.) was treated with diethyl phosphite (27·6 g., 0·2 mole). Reaction was slightly exothermic and the temperature was kept at 20—25°. The mixture was washed with 5% aqueous sodium hydrogen carbonate and then with water. The benzene was removed and the residue distilled *in vacuo*, giving tetraethyl thiopyrophosphate (44 g., 72%), b. p. 78—80°/0·03 mm., n_D^{20} 1·4453 (Found: P, 20·3. Calc. for $C_8H_{20}O_6P_2S$: P, 20·3%). The aqueous solution, on acidification and extraction with benzene (3 × 70 ml.), yielded *OO*-diethyl hydrogen phosphorothioate (23 g., 68%), b. p. 62—63°/0·03 mm., n_D^{20} 1·4624 (lit.,[18] b. p. 106—107°/2·5 mm., n_D^{20} 1·4719) (Found: P, 18·2; Calc. for $C_4H_{11}O_3PS$: P, 18·2%).

Reactions of Bisdiethoxyphosphinothioyl Disulphide.—(*a*) *With di-n-butyl phosphite.* Bisdiethoxyphosphinothioyl disulphide (22·2 g., 0·066 mole) in benzene was treated with dibutyl phosphite (12·8, 0·006 mole) at 75—80°. After 2 hr. the mixture was cooled, the solvent was removed, and the residue distilled *in vacuo*, yielding *diethyl di-n-butyl dithiopyrophosphate* (19 g., 84%), b. p. 120—122°/0·01 mm., n_D^{20} 1·4920 (Found: C, 38·0; H, 7·3; P, 16·2. $C_{12}H_{28}O_5P_2S_2$ requires C, 38·1; H, 7·4; P, 16·4%), and *OO*-diethyl hydrogen phosphorodithioate (9 g., 81%), b. p. 99—101°/12 mm., n_D^{20} 1·5096 [*cyclohexylamine salt*, m. p. 94—95° (Found: C, 42·0; H, 8·4; P, 11·0. $C_{10}H_{24}NO_2PS_2$ requires C, 42·1; H, 8·4; P, 10·9%)].

(*b*) *With sodium diethyl phosphite.* The disulphide (37·0 g., 0·1 mole) was added dropwise to sodium diethyl phosphite (0·1 mole) in benzene (150 ml.). The mixture was stirred at 8—10° for 0·5 hr., then extracted with water (5 × 50 ml.). The solvent was removed from the organic layer and the residue distilled *in vacuo*, yielding tetraethyl dithiopyrophosphate (24·0 g., 75%), b. p. 103—105°/0·01 mm., n_D^{20} 1·4964 (lit.,[11] b. p. 114—115°/0·08 mm., n^{20} 1·4940) (Found: C, 29·8; H, 6·2; P, 19·4. Calc. for $C_8H_{20}O_5P_2S_2$: C, 29·8; H, 6·2; P, 19·2%). The aqueous layer, on acidification and extraction with benzene, yielded *OO*-diethyl hydrogen phosphorodithioate (14·0 g., 75%), b. p. 117—119°/19 mm., n_D^{20} 1·5074 (cyclohexylamine salt, m. p. and mixed m. p. 94—95°).

(*c*) *With sodium diethyl phosphite.* The disulphide (30·0 g., 0·08 mole) was added dropwise to sodium diethyl phosphite (0·08 mole) in benzene (150 ml.). The temperature of reaction was kept at 20—25° and the reaction carried out as described above, yielding *OOS*-triethyl phosphorodithioate (7·0 g., 41%), b. p. 127—129°/19 mm., n_D^{20} 1·4980 (lit.,[20] b. p. 74—77°/1 mm., n_D^{20} 1·5033) (Found: C, 33·7; H, 7·0; P, 14·4. Calc. for $C_6H_{15}O_2PS_2$: C, 33·6; H, 7·0; P, 14·5%), and tetraethyl dithiopyrophosphate [19] (12·0 g., 46%), b. p. 102—104°/0·02 mm., n_D^{20} 1·4925 (Found: C, 30·0; H, 6·7; P, 19·4. Calc. for $C_8H_{20}O_5P_2S_2$: C, 29·8; H, 6·2; P, 19·2%). The aqueous layer, on acidification and extraction with benzene, yielded an undistillable oil, recognized as a mixture of crystalline cyclohexylamine *OO*-diethyl phosphorodithioate (7·8 g., 35%), m. p. and mixed m. p. 94—95°, and an oil which in boiling benzene gave *OOS*-triethyl phosphorodithioate (4·6 g., 27%), b. p. 114—116°/11 mm., n_D^{20} 1·4986, and a polymeric substance containing phosphorus and resembling metaphosphoric acid.

Reaction of Diethyl Di-n-butyl Dithiopyrophosphate with Sodium n-Butoxide.—The ester (18·9 g., 0·05 mole) in benzene was treated with sodium butoxide (0·05 mole) in butanol (50 ml.), with stirring at 45—56°. After 1 hr. the solvent was removed. The residue was dissolved in benzene (100 ml.) and extracted with water (3 × 25 ml.), and the benzene was removed from the organic layer. The residue was distilled, giving tri-n-butyl phosphate (11·0 g., 83%), b. p. 165°/20 mm., n_D^{20} 1·4380 (lit.,[21] b. p. 138·5°/6 mm., n_D^{20} 1·4249) (Found: C, 53·7; H, 10·2; P, 11·8. Calc. for $C_{12}H_{27}O_4P$: C, 54·1; H, 10·1; P, 11·6%). The aqueous layer was acidified and extracted with benzene (3 × 20 ml.). The benzene was removed and the residue was distilled, yielding *OO*-diethylhydrogen phosphorodithioate (6·5 g., 73%), b. p. 101—102°/11 mm., n_D^{20} 1·5094 (cyclohexylamine salt, m. p. and mixed m. p. 94—95°).

Reaction of Bis(diethoxyphosphinyl) Disulphide with Sodium Diethyl Phosphite.—Sodium diethyl phosphite (0·05 mole) in toluene (100 ml.) was treated with the disulphide (16·9 g., 0·05 mole). The temperature was kept at 105—110°. After 2 hr. the mixture was cooled and

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[18] Kabachnik, Joffe, and Mastryukova, *Zhur. obshchei Khim.*, 1955, **25**, 684.

[19] Fiszer, Michalski, and Wieczorkowski, *Roczniki Chem.*, 1953, **27**, 482.

[20] Norman, LeSuer, and Mastin, *J. Amer. Chem. Soc.*, 1952, **74**, 161.

[21] Vogel and Cowan, *J.*, 1943, 16.

extracted with water (4 × 50 ml.). The toluene was removed, and the residue was distilled, giving *OOS*-triethyl phosphorothiolate (12 g., 63%), b. p. 117—119°/14 mm., n_D^{20} 1·4536 (lit.,[22] b. p. 122·5—123°/20 mm., n_D^{20} 1·4578) (Found: C, 36·6; H, 7·7. Calc. for $C_6H_{15}O_3PS$: C, 36·4; H, 7·6%). The aqueous extracts were combined and water was removed under reduced pressure. The residue was a polymeric substance containing phosphorus and resembling metaphosphoric acid.

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[22] Kabachnik and Mastryukova, *Zhur. obshchei Khim.*, 1955, **25**, 1924.