176. *Organophosphorus Compounds of Sulphur and Selenium. Part XIII.* Action of Hydrogen Sulphide on Dialkyl and Diaryl Phosphorochloridites. New Synthesis of Dialkyl and Diaryl Thiophosphites and Tetra-alkyl Thiopyrophosphites.*†

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Reaction of hydrogen sulphide with dialkyl and diaryl phosphorochloridites in the presence of tertiary amines leads to the corresponding thiophosphites. In suitable conditions, tetra-alkyl thiopyrophosphites can be isolated as intermediates.

One of the most important groups of esters containing phosphorus are dialkyl phosphites $(RO)_2P{\cdot}OH$. Although they are usually referred to as phosphites, a tautomeric equilibrium is said to exist between the ter- and the quinque-valent forms, with a considerable predominance of the latter.

Kabachnik and Mastryukova recently obtained dialkyl thiophosphites by action of phosphorus sulphides on alcohols. They showed that dialkyl thiophosphites have properties similar to those of dialkyl phosphites, and suggested a tautomeric equilibrium: $(RO)_2P{\cdot}SH \rightleftharpoons (RO)_2PH{:}S$. Like the analogous oxygen compounds, dialkyl thiophosphites have only weak nucleophilic activity, though the sodium or potassium salts are strongly nucleophilic and exhibit the unsaturated character of tervalent phosphorus compounds.[1] They readily add sulphur and selenium,[2] and can be alkylated [3] or added to activated double bonds.[4] Useful as they are in synthesis of organophosphorus compounds, availability of dialkyl thiophosphites has been limited up till now, since Kabachnik and Mastryukova's procedure can be applied only to simple aliphatic alcohols, and the thiophosphites formed are isolated in rather small yields from complex mixtures of sulphur-containing products.

We showed earlier that reaction of dialkyl phosphorochloridates react with hydrogen sulphide in the presence of tertiary bases affords a convenient preparation of tetra-alkyl thiopyrophosphates [5,6] and similar anhydrides,[7] apparently by way of a salt of a phosphorus thioacid. We have now shown that when hydrogen sulphide is allowed to react with dialkyl phosphorochloridites at room temperature in the presence of tertiary amines, (equation *a*), dialkyl thiophosphites are formed in good yield and, under specific conditions, tetra-alkyl thiopyrophosphites can be isolated as intermediate products. The use of pure starting esters was not always necessary: in certain cases, the reaction with hydrogen sulphide occurs with the crude phosphorochloridite obtained by reaction of the alcohol and phosphorus trichloride in the presence of a tertiary amine. For instance, di-4-nitrobenzyl thiophosphite was obtained in good yield by saturating with hydrogen sulphide a mixture prepared by adding a solution of 2 mols. of 4-nitrobenzyl alcohol in 3 mols. of *NN*-diethylaniline to a benzene solution of 1 mol. of phosphorus trichloride. Anhydrous conditions are necessary for good yields of pure thiophosphites. Water reacts with dialkyl phosphorochloridites even in absence of tertiary amines, yielding dialkyl phosphites: removal of the latter is rather difficult owing to proximity of the boiling points of phosphites and thiophosphites; on the other hand, purification of the solid thiophosphites by crystallization presented no difficulties.

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* Part XII, *Roczniki Chem.*, in the press.

† Preliminary communication, *Roczniki Chem.*, 1955, **25**, 960.

[1] Kabachnik and Mastryukova, *Izvest. Akad. Nauk S.S.S.R. Otdel. khim. Nauk*, 1952, 727.

[2] *Idem, ibid.*, 1953, 163.

[3] *Idem, ibid.*, 1956, 193.

[4] Pudovik and Kovyrzina, *Zhur. obshchei Khim.*, 1954, **24**, 307.

[5] Fiszer and Michalski, *Roczniki Chem.*, 1951, **25**, 514.

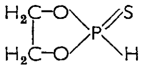
[6] Fiszer, Michalski, and Wieczorkowski, *ibid.*, 1953, **27**, 482.

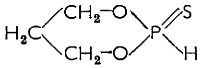
[7] Michalski and Skowronska, *ibid.*, 1956, **30**, 799.

The method described below afforded simple dialkyl thiophosphites in yields of 70—90%. Physical constants of the compounds were in general agreement with those given by Kabachnik and Mastryukova.[1] Their structure was confirmed by transforming them into dialkyl phosphorochloridothionates by sulphuryl chloride. We explored our method with special reference to preparation of thiophosphites, which were difficult or impossible to obtain by the previous method.

We obtained in good yield cyclic thiophosphites (I) and (II); these compounds are less stable than simple thiophosphites. Compound (I) decomposes violently even at 100°, and

(I)





(II)

impure preparations do so at still lower temperatures, but they can be purified by evaporative distillation at about 50°/10^{-1} mm. The six-membered ring analogue (II) is slightly more stable, and can be distilled under reduced pressure. When pure it is crystalline (m. p. 34°). Diphenyl thiophosphite was obtained as a high-boiling oil which was purified by evaporative distillation; its structure was confirmed by conversion into diphenyl phosphorochloridothionate. Di-4-bromobenzyl and di-4-nitrobenzyl thiophosphites were obtained crystalline. All these thiophosphites were neutral in aqueous solutions.

As mentioned above, dialkyl phosphorochloridates with hydrogen sulphide in the presence of tertiary amines yield tetra-alkyl thiopyrophosphates as the main products.[5] The evidence below suggests that reaction of dialkyl phosphorochloridites with hydrogen sulphide may involve four steps:

$$(RO)_2PCl + H_2S + R'_3N \longrightarrow (RO)_2PHS + R'_3N,HCl \quad \dots\dots\dots \quad (a)$$

$$(RO)_2PHS + R'_3N \rightleftharpoons (RO)_2P{\cdot}S^- \; R'_3NH^+ \;\; \text{(III)} \quad \dots\dots\dots \quad (b)$$

$$(RO)_2P{\cdot}S^- \; R'_3NH^+ + (RO)_2PCl \longrightarrow (RO)_2P{\cdot}S{\cdot}P(OR)_2 \;\; \text{(IV)} + R'_3N,HCl \quad \dots\dots \quad (c)$$

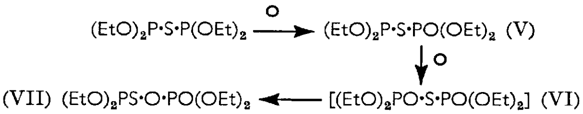
$$(RO)_2P{\cdot}S{\cdot}P(OR)_2 + H_2S(+ R'_3N) \longrightarrow 2(RO)_2PHS \quad \dots\dots\dots\dots\dots \quad (d)$$

The course of the reaction depends on the type of tertiary amine used. In the presence of a weak base of the pyridine type reactions (*b*) and (*c*) do not occur, formation of dialkyl thiophosphites being adequately represented by (*a*). Pyridine and dialkylanilines are presumably too weak bases to provide a concentration of the salt (III) adequate for condensation (*c*). When a stronger base is used, *e.g.*, triethylamine, the reaction involves all four steps, at least to some extent. The evidence is as follows: No tetraethyl thiopyrophosphite (IV; R = Et) was isolated when diethyl phosphorochloridite reacted with 0·5 mol. of hydrogen sulphide in the presence of pyridine. Attempts to condense diethyl phosphorochloridite with diethyl thiophosphite in the presence of pyridine or diethylaniline also failed; after 24 hours, only a slight amount of amine hydrochloride was precipitated from the ethereal or benzene solution, and phosphorochloridite could be recovered. With triethylamine or a similar tertiary amine and less than 1 mol. of hydrogen sulphide some tetra-alkyl thiopyrophosphite was isolated in addition to diethyl thiophosphite. Condensation of diethyl thiophosphite with diethyl phosphorochloridite in the presence of triethylamine leads to the tetra-alkyl thiopyrophosphite in good yield. The latter reacts with hydrogen sulphide in the presence of a catalytic amount of triethylamine, diethyl thiophosphite being formed. No tetraethyl thiopyrophosphite was isolated when diethyl phosphorochloridite was allowed to react with hydrogen sulphide in considerable excess in the presence of triethylamine.

The reaction of hydrogen sulphide with dialkyl phosphorochloridites in the presence of triethylamine or a similar tertiary amine is unsuitable for synthesis of tetra-alkyl thiopyrophosphites. The latter compounds, however, are conveniently prepared by condensation of dialkyl phosphorochloridites with dialkyl thiophosphites, as represented by (*b*) and (*c*). Tetraethyl thiopyrophosphite is a viscous and colourless oil. Its reactivity is shown by reaction (*d*) in the presence of a tertiary base in catalytic amounts, and in the vigorous reaction with water to yield an equimolar mixture of dialkyl phosphite and dialkyl thiophosphite.

The reactions referred to illustrate the known tendency of organophosphorus compounds to pass from the tervalent to the quinquevalent state, and resemble the corresponding reactions of tetraethyl pyrophosphite.

Tetra-alkyl thiopyrophosphites react also with carboxylic acids, producing mixed anhydrides. This will be the subject of a separate communication.



$$\begin{tikzcd} & \mathrm{(EtO)_2P{\cdot}S{\cdot}P(OEt)_2} \arrow[r, "\mathrm{O}"] & \mathrm{(EtO)_2P{\cdot}S{\cdot}PO(OEt)_2}\ \mathrm{(V)} \arrow[d, "\mathrm{O}"] \\ \mathrm{(VII)}\ \mathrm{(EtO)_2PS{\cdot}O{\cdot}PO(OEt)_2} & & \mathrm{[(EtO)_2PO{\cdot}S{\cdot}PO(OEt)_2]}\ \mathrm{(VI)} \arrow[ll] \end{tikzcd}$$

Tetraethyl thiopyrophosphite is readily oxidised in air (to tetraethyl thiopyrophosphate) and requires to be handled in nitrogen or carbon dioxide.

The infrared spectrum of the oxidation product indicates thiono-structure (VII): bands at 809 and 952 cm.$^{-1}$ correspond to the P=S and P–O–P group respectively; in physical properties the ester resembles the tetraethyl thiopyrophosphate prepared by other methods.[6,8]

All attempts to synthesize compounds containing the system $>$P(O)–S–P(O)$<$ have invariably given isomeric compounds $>$P(S)–O–P(O)$<$.[8] Evidently, even when the starting compound almost certainly contains the system P–S–P, addition of oxygen leads to combinations with thionic sulphur. It seems likely that the transient symmetrical compound (VI) rearranges; however, since oxidation of tetra-alkyl thiopyrophosphites is undoubtedly a two-stage process, rearrangement may occur already with the first oxidation product, the mixed anhydride (V). We failed to isolate pure mixed anhydrides of this type, but the behaviour of the mixture after incomplete oxidation suggests their formation.

EXPERIMENTAL

Extracts were dried over $MgSO_4$. Hydrogen sulphide was dried over P_2O_5.

Dialkyl Hydrogen Thiophosphites.—Dialkyl phosphorochloridite[9] (0·1 mole) and pyridine (0·1 mole) or other tertiary amine (triethylamine, *NN*-diethylaniline) in benzene (75 ml.) was stirred and hydrogen sulphide was passed in slowly for 3 hr. Reaction was exothermic, but the temperature was kept at +5°. The precipitated amine hydrochloride was filtered off. The filtrate was washed with ice-cold water (2 × 25 ml.), dried, and evaporated *in vacuo*, and the dialkyl hydrogen thiophosphite distilled as colourless liquid. Thus were obtained: diethyl (12·8 g., 83%), b. p. 75—76°/14 mm., n_D^{20} 1·4608 (Found: P, 20·0. Calc. for $C_4H_{11}O_2PS$: P, 20·1%) (Kabachnik and Mastryukova,[1] b. p. 67·5—68·5°/12 mm., n_D^{20} 1·4597), di-n-propyl (12·5 g., 67%), b. p. 100°/13 mm., n_D^{20} 1·4620 (Found: P, 16·7. Calc. for $C_6H_{15}O_2PS$: P, 16·8%) (*idem*, b. p. 62—63°/3 mm., n_D^{20} 1·4581), and di-n-butyl hydrogen thiophosphite (16·0 g., 76%), b. p. 81—83°/3 mm., n_D^{20} 1·4608 (Found: P, 14·5. Calc. for $C_8H_{19}O_2PS$: P, 14·7%) (*idem*, b. p. 89—90°/4 mm., n_D^{20} 1·4583).

Di-n-propyl Phosphorochloridothionate.—Sulphuryl chloride (4·5 g.) in benzene (10 ml.) was added dropwise with stirring to di-n-propyl hydrogen thiophosphite (6·0 g.) in benzene (30 ml.) at 5° and the whole stirred for 1 hr. Benzene was removed *in vacuo* and di-n-propyl phosphorochloridothionate (5·0 g.) distilled; it had b. p. 113—114°/14 mm., n_D^{20} 1·4684 (Found: P, 14·5. Calc. for $C_6H_{14}O_2PSCl$: P, 14·3%); Fletcher *et al.*[10] reported b. p. 70—75°/1 mm., n_D^{25} 1·4672.

Diphenyl Hydrogen Thiophosphite.—Diphenyl phosphorochloridite[11] (16·1 g.) and pyridine

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[8] McIvor, Grant, and Hubley, *Canad. J Chem.*, 1956 **34**, 1611; cf. Jones, Katritzky, and Michalski, *Proc. Chem. Soc.*, 1959, 321.

[9] Cook, Ilet, Saunders Stacey, Watson, Wilding, and Woodcock, *J.*, 1949, 2921.

[10] Fletcher, Hamilton, Hechenbleikner, Hoegberg, Beatrice, Sertl, and Cassaday, *J Amer. Chem. Soc.*, 1950, **72**, 2461.

[11] Forsman and Lipkin *ibid.*, 1953, **75**, 3145.

(5·6 g.) in benzene (50 ml.) were stirred and hydrogen sulphide was passed in slowly for 2·5 hr. at 5°. Pyridine hydrochloride was filtered off and the filtrate was washed with ice-cold water (2 × 25 ml.) and dried. Evaporation *in vacuo* yielded *diphenyl hydrogen thiophosphite* (11·5 g., 70%) as undistillable oil, n_D^{20} 1·5855. It was purified by evaporative distillation at 70°/0·001—0·005 mm., then having n_D^{20} 1·5878, d_4^{20} 1·2191 (Found: P, 12·1. $C_{12}H_{11}O_2PS$ requires P, 12·3%).

Diphenyl Phosphorochloridothionate.—Crude thiophosphite (13·5 g.) obtained in the previous experiment in benzene (50 ml.) was stirred, and sulphuryl chloride (8·2 g.) in benzene (10 ml.) was added dropwise at 0°. After the whole had been stirred for 1 hr. benzene and gaseous products were removed *in vacuo*; crystallisation of the residue from hot ethanol gave diphenyl phosphorochloridothionate (6·1 g.), m. p. 67°. The product showed no m. p. depression when mixed with the product prepared by Ephraim's method.[12]

Ethylene Hydrogen Thiophosphite (I).—Ethylene phosphorochloridite [13] (20·1 g.) and pyridine (12·5 g.) in benzene (120 ml.) were stirred and hydrogen sulphide was passed in slowly for 2·5 hr. at 5°. Pyridine hydrochloride was filtered off. The filtrate was washed with ice-cold water (2 × 25 ml.) and dried. After removal of solvent *in vacuo* crude *ethylene hydrogen thiophosphite* (12·0 g., 60%), n_D^{20} 1·5438, was obtained. Evaporation at 55—65°/0·7 mm. gave a product having n_D^{20} 1·5401, d_4^{20} 1·4063 (Found: P, 25·1. $C_2H_5O_2PS$ requires P, 25·0%).

Trimethylene Hydrogen Thiophosphite (II).—As in the previous experiment, hydrogen sulphide was passed into trimethylene phosphorochloridite [13] (12·5 g.) and pyridine (10·0 g.) in benzene (60 ml.). The *thiophosphite* (8·5 g., 69%) distilled and had b. p. 60°/0·02 mm., m. p. 34° (Found: P, 22·0. $C_3H_7O_2PS$ requires P, 22·4%).

Di-4-bromobenzyl Hydrogen Thiophosphite.—A solution of 4-bromobenzyl alcohol (15·0 g.) and *NN*-diethylaniline (17·9 g.) in benzene (75 ml.) was added with stirring to phosphorus trichloride (5·5 g.) in benzene (25 ml.) at 5°. After being stirred for 15 min. the mixture was saturated with hydrogen sulphide for 5 hr. at 5°. The precipitated diethylaniline hydrochloride was filtered off and the filtrate was concentrated *in vacuo* to 50 ml., and aniline hydrochloride was filtered off again. The filtrate was treated with light petroleum (150 ml.), and the layers were separated. The petroleum layer was removed and the oily layer was extracted with hot benzene (2 × 25 ml.). The combined extracts were evaporated under reduced pressure to dryness. Crystallisation of the residue from light petroleum–benzene gave *di-4-bromobenzyl hydrogen thiophosphite* (9·0 g., 51%), as colourless plates, m. p. 84° (Found: S, 7·4. $C_{14}H_{13}O_2PSBr_2$ requires S, 7·4%).

Di-4-nitrobenzyl Hydrogen Thiophosphite.—A solution of 4-nitrobenzyl alcohol (10·0 g.) and diethylaniline (15·0 g.) in benzene (80 ml.) and ether (20 ml.) was added dropwise with stirring to phosphorus trichloride (4·5 g.) in ether (20 ml.) at 5°.[14] After being stirred for 1 hr. the mixture was saturated with hydrogen sulphide for 3·5 hr. at 5°. The precipitated diethylaniline hydrochloride was filtered off. The solvent was evaporated *in vacuo*. Crystallisation of the residue gave *di-4-nitrobenzyl hydrogen thiophosphite* (7·3 g., 60%) as yellowish needles, m. p. 135° (from benzene) (Found: P, 8·5. $C_{14}H_{13}O_6N_2PS$ requires P, 8·4%).

Tetraethyl Thiopyrophosphite.—(*a*) Diethyl phosphorochloridite [9] (31·2 g.) and triethylamine (20·2 g.) in benzene (80 ml.) were stirred and hydrogen sulphide (*ca.* 2500 ml.) was passed in during 1·5 hr. at 5°. The precipitated triethylamine hydrochloride was filtered off under nitrogen. From the filtrate after removal of benzene *in vacuo* were obtained diethyl hydrogen thiophosphite (10·5 g.), b. p. 68—69°/10 mm., n_D^{20} 1·4606, and tetraethyl thiopyrophosphite (7·5 g.), b. p. 64—65°/0·05 mm.

(*b*) Diethyl phosphorochloridite (16·2 g.) in benzene (20 ml.) was added dropwise with stirring to the solution of diethyl hydrogen thiophosphite (16·0 g.) and triethylamine (11·0 g.) in benzene (80 ml.) at 20° and the whole was stirred for 45 min. Triethylamine hydrochloride was filtered off and washed with benzene (2 × 25 ml.) under nitrogen or carbon dioxide which had been deoxygenated and dried. From the combined filtrates benzene was removed *in vacuo*. Distillation of the residue gave *tetraethyl thiopyrophosphite* (19·5 g., 71%), b. p. 66—68°/0·05 mm. (Found: P, 22·1. $C_8H_{20}O_4P_2S$ requires P, 22·7%).

Action of Hydrogen Sulphide on Tetraethyl Thiopyrophosphite.—The compound (10·0 g.)

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[12] Ephraim *Ber.*, 1911, **44**, 631.

[13] Arbuzov, Zoroastrova, and Rizpolozhenskii, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1948, 208.

[14] Fölsch, *Acta Chem. Scand.*, 1956, **4**, 686.

obtained in the previous experiment in benzene (40 ml. + 2 drops of triethylamine) was cooled and hydrogen sulphide was passed into the solution with stirring for 1 hr. at 10°. The solvent was removed *in vacuo*. Distillation of the residue gave diethyl hydrogen thiophosphite (8·0 g., 71%), b. p. 75—76°/14 mm., n_D^{20} 1·4602 (Found: P, 20·1. Calc. for $C_4H_{11}O_2PS$: P, 20·1%).

Action of Water on Tetraethyl Thiopyrophosphite.—Water (0·8 g.) in ether (100 ml.) was added to tetraethyl thiopyrophosphite (13·4 g.) and the whole was stirred for 15 min. Ether was removed *in vacuo*. Distillation of the residue gave a mixture (9·0 g.), b. p. 80—82°/20 mm., n_D^{20} 1·4356, of diethyl hydrogen phosphite and thiophosphite. The refractive index calculated for an equimolar mixture is n_D^{20} 1·4360.

Action of Oxygen on Tetraethyl Thiopyrophosphite.—Tetraethyl thiopyrophosphite (13·5 g.) in benzene (15 ml.) was stirred and dry oxygen was passed in slowly for 2·5 hr. at 70—80°. The solvent was removed under reduced pressure. Fractional distillation of the residue gave tetraethyl thiopyrophosphate (4·5 g.), b. p. 86—88°/0·1 mm., n_D^{25} 1·4495 (Found: P, 20·1. Calc. for $C_8H_{20}O_6P_2S$: P, 20·2%). Fiszer *et al.*[6] reported b. p. 82—83°/0·05 mm., n_D^{25} 1·4495.

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