821. *Organophosphorus Compounds of Sulphur and Selenium. Part X.* Action of Sulphuryl Chloride on Alkyl Hydrogen Alkylphosphonothioates and Dialkylphosphinothioic Acids. Synthesis of* P-*Alkoxy*-P-*alkyloxophosphoranesulphenyl Chlorides.*

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Reaction of sulphuryl chloride with alkyl hydrogen alkylphosphonothioates leads to *P*-alkoxy-*P*-alkyloxophosphoranesulphenyl chlorides or bis(alkoxyalkylphosphinyl) disulphides, depending on the amount of reagent used. The products are thermally unstable and yield on decomposition alkyl alkylphosphonochloridates or thionoanhydrides.

Dialkylphosphinothioic acids with sulphuryl chloride give dialkylphosphinyl chlorides or the thionoanhydrides.

Earlier reports[1] from this laboratory described a new type of organophosphorus compounds, namely, dialkoxyoxophosphoranesulphenyl chlorides, $(RO)_2PO{\cdot}SCl$.† Some *P*-alkoxy-*P*-alkyl- (II) and dialkyl-oxophosphoranesulphenyl chlorides $R_2PO{\cdot}SCl$ have now been investigated. Although only the compounds (II) have been isolated, the remaining results appear worth reporting.

The method used previously for preparing dialkoxyoxophosphoranesulphenyl chlorides involved treatment of dialkylphosphorothioates $(RO)_2PS{\cdot}OH$ or bis(dialkoxyphosphinyl) disulphides $[(RO)_2PO{\cdot}S]_2$ with chlorine or, more conveniently, sulphuryl chloride.[1] When sulphuryl chloride and *O*-alkyl hydrogen alkylphosphonothioates (I) (prepared from alkyl hydrogen alkylphosphonites [2]) were used in equimolar proportions, the sulphenyl chlorides (II) were formed. When the amount of chlorinating agent used was halved, bis(alkoxyalkylphosphinyl) disulphides (III) were produced; these were readily converted

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

† This and similar nomenclature is based on the hypothetical parent compound, phosphorane PH_5 (*J.*, 1952, 5122), and the radical phosphenyl $PH_2(O)$–.

[1] Lenard and Michalski, *Roczniki Chem.*, 1956, **30**, 655; Lenard-Borecka and Michalski, *ibid.*, 1957, **31**, 1269; Michalski, Lenard-Borecka, Musierowicz, and Skowronska, XVIth Internat. Congr. Pure Appl. Chem., Paris, 1957, Handbook Vol. II, p. 108.

[2] Michalski and Skowronska, *Roczniki Chem.*, 1956, **30**, 799.

into the chlorides (II) by sulphuryl chloride. The disulphides (III) were also obtained by condensation of the acids (I) with the chlorides (II) (reaction *b*).

$$\underset{\text{(I)}}{\mathrm{R(RO)PS{\cdot}OH}} + \mathrm{SO_2Cl_2} \longrightarrow \underset{\text{(II)}}{\mathrm{RPO(OR){\cdot}SCl}} + \mathrm{HCl} + \mathrm{SO_2} \quad \ldots\ldots \quad (a)$$

$$\mathrm{RPO(OR){\cdot}SCl} + \mathrm{HOSP(OR)R} \longrightarrow \underset{\text{(III)}}{\mathrm{[RPO(OR){\cdot}S{\cdot}]_2}} + \mathrm{HCl} \quad \ldots\ldots \quad (b)$$

$$\mathrm{[RPO(OR){\cdot}S{\cdot}]_2} + \mathrm{SO_2Cl_2} \longrightarrow \mathrm{2RPO(OR){\cdot}SCl} + \mathrm{SO_2}$$

The yields of chloride (II), isolated by distillation, were lower than expected (30—70%), owing to thermal decomposition which was very fast at 80° but required a few days at room temperature:

$$\mathrm{RPO(OR){\cdot}SCl} \longrightarrow \mathrm{S} + \mathrm{RPO(OR)Cl}\ \text{(IV)}$$

The alkyl alkylphosphonochloridates (IV) formed agreed in properties with those obtained from alkyl hydrogen alkylphosphonites.[2] The disulphides (III) were also unstable, decomposing rapidly at 100° and within several days at room temperature, to yield sulphur and the alkoxyalkylphosphinyl alkoxyalkylphosphinothioyl anhydrides (V):

$$\mathrm{[RPO(OR){\cdot}S{\cdot}]_2} \longrightarrow \mathrm{S} + \mathrm{RPS(OR){\cdot}O{\cdot}PRO(OR)}\ \text{(V)}$$

The structure of these products (V) was confirmed by comparing their properties with those of compounds obtained by action of hydrogen sulphide on alkyl alkylphosphonochloridates (IV) in the presence of tertiary bases.[3] The infrared spectra of compounds (V) prepared by the latter route indicate the thiono-structure shown.[4]

The action of sulphuryl chloride on dialkylphosphinothioic acids $R_2PS{\cdot}OH$ failed, however to yield dialkyloxophosphoranesulphenyl chlorides $R_2PO{\cdot}SCl$. For reasons given below it is probable that these chlorides were in fact formed but were too unstable to be isolated.

Our investigations were concerned with diethylphosphinothioic acid $Et_2PS{\cdot}OH$ [obtained by alkaline hydrolysis of diethylphosphinothioyl chloride $Et_2P(S)Cl$] and with dibenzylphosphinothioic acid [prepared by adding sulphur to dibenzylphosphine oxide $(Ph{\cdot}CH_2)_2PHO$]. Chlorination of acids $R_2PS{\cdot}OH$ was carried out under conditions analogous to those used for acids (I).

Sulphuryl chloride and diethylphosphinothioic acid in equimolar proportions afford diethylphosphinyl chloride (VI) in good yield:

$$\mathrm{Et_2PS{\cdot}OH} + \mathrm{SO_2Cl_2} \longrightarrow \mathrm{S} + \mathrm{HCl} + \mathrm{SO_2} + \mathrm{Et_2P(O){\cdot}Cl}\ \text{(VI)}$$

Reaction of diphenylphosphinothioic acid[5] is similar. Reaction with 0·5 mol. of sulphuryl chloride yields the anhydride (VII):

$$\mathrm{2Et_2PS{\cdot}OH} + \mathrm{SO_2Cl_2} \longrightarrow \mathrm{S} + \mathrm{2HCl} + \mathrm{SO_2} + \mathrm{Et_2P(S){\cdot}O{\cdot}P(O)Et_2}\ \text{(VII)}$$

In both these cases elemental sulphur is formed. Liberation of sulphur is evident even at 0° and is very rapid at room temperature.

These facts, analogy with the chlorination of thioacids of phosphorus investigated earlier, and additional observations reported below make it legitimate to propose the annexed scheme. According to this the thioanhydride (VII) may be produced either by decomposition of the disulphide or by condensation of diethylphosphinyl chloride with diethylphosphinothioic acid, this chloride being produced by decomposition of the unstable sulphenyl chloride, and the disulphide by condensation of the sulphenyl chloride with diethylphosphinothioic acid. In the final stage of the reaction, the thioanhydride decomposes to sulphur and diethylphosphinyl chloride. The last reaction also appears

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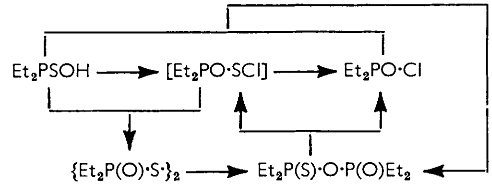
[3] Michalski, *ibid.*, 1955, **29**, 960.

[4] Coe, Perry, and Brown, *J.*, 1957, 3604.

[5] Craig, U.S.P. 2,724,726.

to proceed in two stages. In the first, one molecule each of diethylphosphinyl chloride and the sulphenyl chloride are produced; in the second the latter chloride decomposes to



diethylphosphinyl chloride and sulphur. In conformity with the proposed scheme diethylphosphinothioic acid was found to condense with diethylphosphinyl chloride:

$$Et_2PO{\cdot}Cl + HO{\cdot}PSEt_2 \longrightarrow Et_2P(S){\cdot}O{\cdot}P(O)Et_2 + HCl$$

and the thioanhydride with sulphuryl chloride gave diethylphosphinyl chloride:

$$Et_2P(S){\cdot}O{\cdot}P(O)Et_2 + SO_2Cl_2 \longrightarrow 2Et_2PO{\cdot}Cl + SO_2 + S$$

Both reactions have general implications in respect of the system $>P(S){\cdot}OP(O)<$ and will be investigated further.

The thioanhydride (VII) obtained in the reactions referred to above proved identical with that systhesized earlier [2] by treating diethylphosphinyl chloride with hydrogen sulphide in the presence of tertiary amines. We ascribe to it a structure with thionic sulphur linkage, in analogy with the compounds (V) and the thiopyrophosphates.

Sulphuryl chloride and dibenzylphosphinothioic acid afford dibenzylphosphinyl chloride and sulphur:

$$(Ph{\cdot}CH_2)_2PS{\cdot}OH + SO_2Cl_2 \longrightarrow (Ph{\cdot}CH_2)_2PO{\cdot}Cl + S + SO_2 + HCl$$

When 0·5 mol. of sulphuryl chloride was used, no secondary reactions were noted and unchanged dibenzylphosphinothioic acid was present. Observation of the reactions presents some difficulties owing to the susceptibility of dibenzylphosphinyl chloride to hydrolysis. These experiments do not warrant any conclusions as to the course of secondary processes resembling those noted for the diethyl analogue. They confirm, however, the instability of group $>PO{\cdot}SCl$ combined with two radicals by direct phosphorus–carbon links. The stability of the system decreases as alkoxy-groups are replaced by alkyl.

EXPERIMENTAL

Extracts were dried over $MgSO_4$. Carbon was determined by McCready and Hassid's procedure.[6]

P-*Ethoxy*-P-*ethyloxophosphoranesulphenyl Chloride*.—Sulphuryl chloride (27 g.) in benzene (30 ml.) was added dropwise to a solution of ethyl ethylphosphonothioic acid [2] (30·8 g.) in benzene (100 ml.). Reaction was exothermic but the temperature was kept at −5° to 0°. The solvent and gaseous products were removed under reduced pressure. The *sulphenyl chloride* was distilled *in vacuo* as a yellow liquid (26 g., 70%), b. p. 33—34°/0·5 mm., n_D^{20} 1·4800, d_4^{20} 1·2312 (Found: P, 15·9; Cl, 18·7. $C_4H_{10}O_2ClSP$ requires P, 16·4; Cl, 18·8%).

n-*Butyl Hydrogen Ethylphosphonothioate*.[7, 2]—*n*-Butyl hydrogen ethylphosphonite [2] (74·3 g.) was added to a solution from sodium (11 g.) in anhydrous *n*-butyl alcohol (150 ml.). Sulphur (15 g.) was added slowly with cooling. Unchanged sulphur was then filtered off, the filtrate evaporated *in vacuo* to dryness, and the crude sodium salt dissolved in water (50 ml.) and acidified with 20% hydrochloric acid (90 ml.). The free acid was extracted with benzene (3 × 70 ml.). The extracts were evaporated *in vacuo* and distillation of the residue gave n-*butyl hydrogen ethylphosphonothioate* (51·5 g., 56%), b. p. 76°/0·06 mm., n_D^{25} 1·4821, d_4^{25} 1·0683 (Found: P, 16·9. $C_6H_{15}O_2SP$ requires P, 17·0%).

P-n-*Butoxy*-P-*ethyloxophosphoranesulphenyl Chloride*.—Sulphuryl chloride (13·5 g.) in

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[6] McCready and Hassid, *Ind. Eng. Chem. Anal.*, 1942, **14**, 526.

[7] Foss, *Acta Chem. Scand.*, 1947, **1**, 8; Kabachnik, Kurochkin, Mastryukova, Joffe, Popov, and Rodionova, *Doklady Akad. Nauk S.S.S.R.*, 1955, **104**, 861.

benzene (40 ml.) was added dropwise to *n*-butyl hydrogen ethylphosphonothioate (18 g.) diluted with benzene (60 ml.). The temperature of the exothermic reaction was kept at −10° to −5°. The solvent was evaporated and the *sulphenyl chloride* distilled *in vacuo* as a yellow liquid (11·8 g., 55%), b. p. 74°/0·4 mm., n_D^{25} 1·4528 (Found: P, 14·7. $C_6H_{14}O_2ClSP$ requires P, 14·3%).

Thermal Decomposition of P-*Ethoxy*-P-*ethyloxophosphoranesulphenyl Chloride*.—*Ethyl ethylphosphonochloridate*. The chloride (26·4 g.) was heated in a vacuum-still at 60—70°/*ca*. 1 mm. Precipitation of sulphur and distillation were observed. The ethyl ethylphosphonochloridate formed (15·5 g., 71%) was distilled *in vacuo*, having b. p. 35—36°/0·2 mm., n_D^{20} 1·4402 (Found: P, 19·6; Cl, 22·5. Calc. for $C_4H_{10}O_2ClP$: P, 19·7; Cl, 22·6%). Michalski and Skowronska [2] give b. p. 53—54°/1 mm., n_D^{25} 1·4378.

Bis-(P-*ethoxy*-P-*ethylphosphinyl*) *Disulphide*.—(i) Sulphuryl chloride (5·15 g.) in benzene (20 ml.) was added dropwise to ethyl hydrogen ethylphosphonothioate (11·75 g.) in benzene (60 ml.) at 0°. The solvent and gaseous products were removed *in vacuo* and the residue gave the *disulphide* as a pale yellow oil (11·7 g., 98%), n_D^{25} 1·5061 (Found: P, 20·7. $C_8H_{20}O_4S_2P_2$ requires P, 20·2%).

(ii) Ethoxyethyloxophosphoranesulphenyl chloride (9·47 g.) in benzene (100 ml.) was added dropwise to ethyl hydrogen ethylphosphonothioate (7·79 g.) in benzene (70 ml.) at −5° to 0°. The solvent and gaseous products were removed *in vacuo* and the residue gave the disulphide (15·2 g., 98%), n_D^{20} 1·5051 (Found: P, 20·2%).

Thermal Decomposition of Bis(*ethoxyethylphosphinyl*) *Disulphide*.—The disulphide (15·2 g.) was heated at 120°/*ca*. 0·05 mm. The crude anhydride (VII) which collected distilled as a pale yellow oil (10·2 g., 75%), b. p. 74—75°/0·05 mm., n_D^{25} 1·4744 (Found: P, 22·3. Calc. for $C_8H_{20}O_4SP_2$: P, 22·6%). Michalski and Skowronska [2] give b. p. 119—120°/0·8 mm., n_D^{25} 1·4652.

Diethylphosphinothioyl Chloride.—Sulphur (16·2 g.) was added portionwise to diethylchlorophosphine [9] (63·5 g.) in benzene (250 ml.) at 18—24°. The solvent was evaporated and the crude *diethylphosphinothioyl chloride* distilled as a colourless liquid (70·8 g., 89%), b. p. 94—95°/9 mm., n_D^{25} 1·5292 (Found: P, 19·8; Cl, 22·1. $C_4H_{10}ClSP$ requires P, 19·8; Cl, 22·6%).

Diethylphosphinothioic Acid.—An aqueous solution of sodium hydroxide (25 g. in 50 ml.) was added dropwise to diethylphosphinothioyl chloride (45 g.) at 30—40°. The resulting aqueous solution of sodium diethylphosphinothioate was acidified with 20% hydrochloric acid. *Diethylphosphinothioic acid* which separated was added to a benzene extract of the aqueous layer (3 × 50 ml.). The solvent was evaporated and the crude acid distilled as a colourless liquid (31 g., 78%), b. p. 67—68°/0·12 mm., n_D^{25} 1·5257 (Found: P, 22·3. $C_4H_{11}OSP$ requires P, 22·4%). The cyclo*hexylamine salt*, prepared in usual way, formed needles (from benzene), m. p. 145—147° (Found: P, 13·1; N, 5·9. $C_{10}H_{24}ONPS$ requires P, 13·1; N, 5·9%). The compound with m. p. 76° claimed by Strecker and Grosmann [10] as diethylphosphinothioic acid probably has a different structure.[11]

Action of Sulphuryl Chloride on Diethylphosphinothioic Acid.—(i) Sulphuryl chloride (14·6 g., 1 mol.) in benzene (50 ml.) was added dropwise to diethylphosphinothioic acid (15 g., 1 mol.) in benzene (50 ml.), the temperature being kept at −6° to −2°. Sulphur was precipitated. The solvent was evaporated and the diethylphosphinyl chloride was distilled as a colourless liquid (10·2 g., 61%), b. p. 96—98°/10 mm., n_D^{20} 1·4682 (Found: P, 21·8; Cl, 25·1. Calc. for $C_4H_{10}OPCl$: P, 22·3; Cl, 25·2%). Razumov, Mukhacheva, and Zaikonnikova [12] give b. p. 108—109·5°/16 mm., n_D^{20} 1·4647.

(ii) Sulphuryl chloride (6·5 g., 0·5 mol.) in benzene (20 ml.) was added dropwise to diethylphosphinothioic acid (13·4 g., 1 mol.) in benzene (30 ml.) at 0°. The mixture was then left for 1 hr. at room temperature. The precipitated sulphur was filtered off, and the thioanhydride distilled as a pale yellow oil (6·9 g., 59%), b. p. 94—95°/0·07 mm., n_D^{20} 1·5030 (Found: P, 25·6. Calc. for $C_8H_{20}O_2SP_2$: P, 25·6%). Michalski [3] gives b. p. 140°/0·5 mm., n_D^{25} 1·5056.

Condensation of Diethylphosphinyl Chloride with Diethylphosphinothioic Acid.—The acid (8 g.) in benzene (8 ml.) was added dropwise to the chloride (8·1 g.) in benzene (7 ml.) at 15—20°. Hydrogen chloride and solvent were removed under reduced pressure. Diethylphosphinic diethylphosphinothionic anhydride distilled as a pale yellow oil (12·4 g., 96%), b. p. 93—94°/0·05 mm., n_D^{20} 1·5037 (Found: P, 25·4. Calc. for $C_8H_{20}O_2SP_2$: P, 25·6%).

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[9] Beeby and Mann, *J.*, 1951, 413.

[10] Strecker and Grosmann, *Ber.*, 1916, **49**, 63.

[11] Kabachnik and Shepeleva, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1949, 56.

[12] Razumov, Mukhacheva, and Zaikonnikova, *Zhur. obshchei Khim.*, 1957, **27**, 754.

Action of Sulphuryl Chloride on the Preceding Anhydride.—Sulphuryl chloride (2·1 g.) in benzene (10 ml.) was added dropwise to the anhydride (3·7 g.) in benzene (10 ml.) at −2° to 0°. Precipitated sulphur was filtered off, and solvent evaporated. Diethylphosphinic chloride distilled as a colourless liquid (2·1 g., 48%), b. p. 104°/13 mm., n_D^{25} 1·4668 (Found: P, 22·3. Calc. for $C_4H_{10}OClP$: P, 22·3%).

Dibenzylphosphinothioic Acid.—To an alcoholic solution of sodium ethoxide (obtained from 3·35 g. of sodium in 100 ml. of ethanol) dibenzylphosphine oxide[13] (33 g.) in ethanol (200 ml.) was added. The mixture was stirred while sulphur (5·2 g.) was added portionwise at 30—35°. Stirring was continued for a further 2 hr. Excess of sulphur was filtered off, and the solvent evaporated at reduced pressure. *Sodium dibenzylphosphinothioate* crystallized from ethanol as needles, m. p. 232—236° (Found: P, 10·5. $C_{14}H_{14}OSPNa$ requires P, 10·9%). This salt (31 g.) was dissolved in water (200 ml.) and decomposed by excess of hydrochloric acid at 0°. The *dibenzylphosphinothioic acid* which separated crystallized from ethanol–benzene (1 : 10) as colourless plates, m. p. 190—191°, slightly soluble in benzene and carbon tetrachloride (Found: C, 64·3; S, 11·9. $C_{14}H_{15}OSP$ requires C, 64·1; S, 12·2%). The compound with m. p. 171° claimed by Strecker and Grosmann[10] as dibenzylphosphinothioic acid has probably a different structure.[11]

Action of Sulphuryl Chloride on Dibenzylphosphinothioic Acid.—Sulphuryl chloride (2·7 g., 1 mol.) dissolved in benzene (30 ml.) was added dropwise to a suspension of dibenzylphosphinothioic acid (5·24 g., 1 mol.) in carbon tetrachloride (120 ml.) −25° to −20°. The solid disappeared. When the solvent was evaporated under reduced pressure at 0°, sulphur was precipitated. This was filtered off. The dibenzylphosphinyl chloride present in the filtrate was difficult to purify owing to pronounced instability and was hydrolysed by a few drops of water to the dibenzylphosphinic acid. The product crystallized from benzene as plates, m. p. 191—193° (Found: C, 68·4. Calc. for $C_{14}H_{15}O_2P$: C, 68·3%). The acid showed no m. p. depression when mixed with a sample of acid prepared by Miller, Bradley, and Hamilton's method.[13]

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[13] Miller, Bradley, and Hamilton, *J. Amer. Chem. Soc.*, 1956, **78**, 5299.