Organophosphorus Compounds. Part CXXXVI.[1] Thiopyrophosphate Synthesis by Condensation of Oxophosphoranesulphenyl Chlorides with Trialkyl Phosphites and their Structural Analogues

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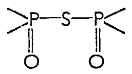
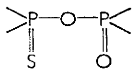
Oxophosphoranesulphenyl chlorides react readily with esters of tercovalent phosphorus acids giving, in addition to thiopyrophosphate systems $>P(O){-}S{-}P(O)<$, acid chlorides and *O*-esters $>P(S)OR$. The symmetrical thiopyrophosphates are converted into their unsymmetrical isomers, $>P(O){-}O{-}P(S)<$, during the isolation procedure. The reaction is seen to involve nucleophilic attack by the phosphorus atom on the sulphur atom of the oxophosphoranesulphenyl chloride, and formation of a quasiphosphonium complex which decomposes by two parallel paths.

All the methods so far reported for the synthesis of tetra-alkyl monothiopyrophosphates lead to the thermodynamically stable unsymmetrical thioxo-isomers (B).[2-9]



(A)



(B)

The structure (B) was confirmed by spectroscopic means,[10-12] particularly n.m.r.,[13] and behaviour towards nucleophilic reagents.[2-8] Since a preliminary report of the present results,[14,15] both isomers (A) and (B) of the fully esterified thiopyrophosphates derived from neopentyl glycol have been synthesised. The isomer (A) with the symmetrical dioxo-structure is stable at room temperature.[14] Indeed our most recent studies have revealed that even open-chain symmetrical tetra-alkyl monothiopyrophosphates can be isolated from the reaction of piperidinesulphenyl chloride with dialkyl phosphites at a sufficiently low temperature.[16]

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Studies of dialkoxyoxophosphoranesulphenyl chlorides $(RO)_2P(O)SCl$ (I) suggested a new synthetic route to thiopyrophosphates based on the reaction of (I) with trialkyl phosphites $(RO)_3P$ (II). If nucleophilic attack by the phosphorus atom takes place at the sulphur atom of the sulphenyl chloride (I), the symmetrical thiopyrophosphate isomer (A) would be formed. Such a synthesis would be analogous to that of *OOS*-trialkyl thiophosphates, which may be represented by an Arbusov reaction scheme:[17]

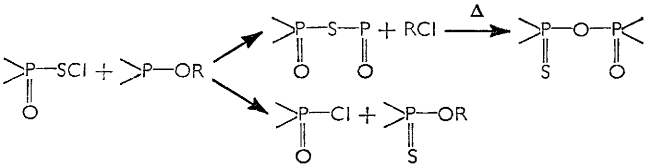
$$R'SCl + P(OR)_3 \longrightarrow [R'SP(OR)_3]^+Cl^- \longrightarrow R'SP(O)(OR)_2 + RCl$$

Procedure and Results.—Oxophosphoranesulphenyl chlorides (I) react as readily with trialkyl phosphites (II) as with the structural analogues containing a C–P bond. Such reactions are carried out in inert solvents, for example light petroleum or benzene, and are noticeably exothermic. In all reactions described here, the temperature was maintained between 0 and 5°.

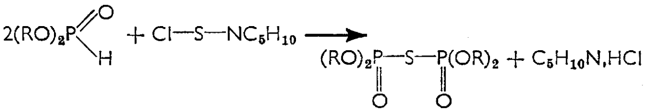
Starting material		Products	Yield (%)	B.p. (m.).	n_D
$(EtO)_2P(O)SCl$	$(EtO)_3P$	$(EtO)_2P(S)\cdot O\cdot P(O)(OEt)_2$	15	83—84°/0·05 mm.	1·4480 [a]
		$(EtO)_2P(O)Cl$ identified as $(EtO)_2P(O)NHPh$	40	M.p. 92—92·5°	
		$(EtO)_3PS$	70	94·5/12 mm.	1·4480 [b]
$(EtO)_2P(O)SCl$	$(PhO)_3P$	$(EtO)_2P(O)Cl$	72	84/12 mm.	1·4200 [a]
		$(PhO)_3PS$	74	135—140/0·05 mm. M.p. 92—93°	
$(EtO)_2P(O)SCl$	$EtP(OEt)_2$	$(EtO)_2P(S)\cdot O\cdot P(O)(OEt)Et$	71	85/0·04 mm.	1·4560 [a]
		$(EtO)_2P(O)Cl$ identified as $(EtO)_2P(O)NHPh$	17·5	M.p. 92—92·5	
		$EtP(S)(OEt)_2$	20	86/13 mm.	1·4558 [b]
$(EtO)_2P(O)SCl$	$PhP(OEt)_2$	$(EtO)_2P(S)\cdot O\cdot P(O)(OEt)Ph$	70	120—122/0·05 mm.	1·5044 [a]
		$(EtO)_2P(O)Cl$	10	86—87/14 mm.	1·4200 [b]
		$PhP(S)(OEt)_2$	20	72—73/0·02 mm.	1·5220 [a]
$Et(EtO)P(O)SCl$	$(EtO)_3P$	$Et(EtO)P(O)\cdot O\cdot P(S)(OEt)_2$	7	85—87/0·05 mm.	1·4580 [b]
		$Et(EtO)P(O)Cl$ identified as $Et(EtO)P(S)\cdot O\cdot P(O)(OEt)Et$	45	110—112/0·5 mm.	1·4660 [a]
		$(EtO)_3PS$	51	87—89/12 mm.	1·4500 [b]
$MeC(O)SCl$	$(EtO)_3P$	$MeCOCl$	50	50—53 mm.	
		$(EtO)_3PS$	70	99—101/17 mm.	1·4480 [b]
$(PrO)_2P(O)SCl$	$(PrO)_3P$	$(PrO)_2P(S)\cdot O\cdot P(O)(OPr)_2$	16	87—88/0·01 mm.	1·4370 [a]
		$(PrO)_2P(O)Cl$ identified as $(PrO)_2P(O)NH\cdot Ph$	41	M.p. 96°	
		$(PrO)_3PS$	72	125/11 mm.	1·4505

[a] At 25°. [b] At 20°

The action of (II) and structural analogues on (I) is complex and does not always yield a thiopyrophosphate-type compound as the main product. Two pairs of products have been observed, and their formation may be represented as follows:



The products were separated by distillation and identified either by their physical properties and i.r. spectra or, if necessary, by transformation into characteristic derivatives. A typical procedure involved the preliminary separation of thiopyrophosphates of type (B) from acid chlorides and *O*-esters by distillation. The latter two products proved difficult to separate by distillation, so the chloride was converted either into the corresponding amide or, by the action of hydrogen sulphide in the presence of tertiary amine, into the corresponding thiopyrophosphate of type (B).[18] Symmetrical monothiopyrophosphates (A) are unstable to heat, and distillation always led to full isomerisation into systems (B). However the intermediate formation of type (A) isomers was fully confirmed by t.l.c. Suitable model compounds were prepared independently by reaction of dialkyl phosphites with piperidinesulphenyl chloride:[16]



$$2(RO)_2P(O)H + Cl{-}S{-}NC_5H_{10} \longrightarrow (RO)_2P(O){-}S{-}P(O)(OR)_2 + C_5H_{10}N,HCl$$

The Table summarises the results of the reactions of diethoxyoxophosphoranesulphenyl chloride with triethyl and triphenyl phosphites and with diethyl ethyl- and phenylphosphonites. The results of the reactions of *P*-ethoxy-*P*-ethyloxophosphoranesulphenyl chloride and of 1-oxoethanesulphenyl chloride, MeCOSCl, with triethyl phosphite are also shown. Because of the nature of the isolation procedure, the yields are approximate.

Discussion.—In accord with observed facts, an ionic mechanism may be proposed involving nucleophilic displacement by phosphite at the sulphur atom of the oxophosphoranesulphenyl chloride:

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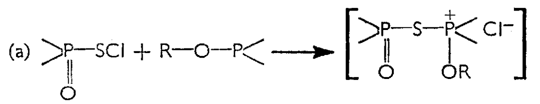
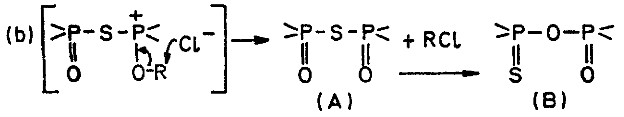
[17] D. C. Morrison, *J. Amer. Chem. Soc.*, 1955, **77**, 181.

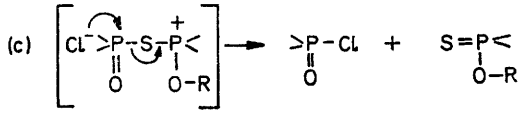
[18] J. Michalski and A. Skowrońska, *Roczniki Chem.*, 1956, **30**, 799.



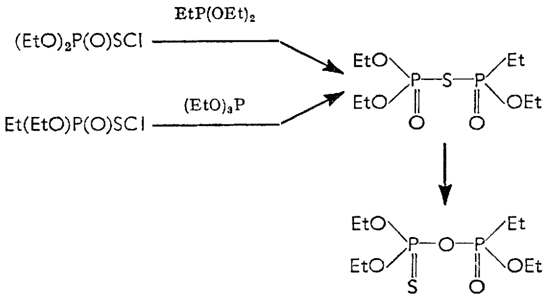
(III)

The intermediate quasiphosphonium complex (III) may break down in two ways, as represented by (b) and (c). According to pathway (b) chloride ion removes an alkyl group adjacent to the phosphonium phosphorus atom, forming the symmetrical thiopyrophosphate of type (A). A second site for nucleophilic attack by chloride ion is the phosphinyl group; this reaction (c) would lead to an acid chloride and an *O*-ester. The proposed scheme for decomposition of the quasiphosphonium complex (III) is analogous to that for breakdown of the complex formed by reaction of acyl disulphides with esters of tervalent phosphorus acids.[19] The mode of breakdown of (III) depends on the nature of the substituents. The reaction between triethyl phosphite and diethoxyoxophosphoranesulphenyl chloride gave tetraethyl thiopyrophosphate in only 15% yield, the main products being diethyl phosphorochloridate and triethyl phosphorothionate. Thus the complex breaks down predominantly according to path (c). The same oxophosphoranesulphenyl chloride reacts with diethyl ethylphosphinite affording 70% of the thioxo-anhydride and the products corresponding to decomposition (c) in 20% yield. When *P*-ethyl-*P*-ethoxyoxophosphoranesulphenyl chloride was used as starting material, however, reaction with triethyl phosphite proceeded mainly by path (c). A rational explanation of the difference may be found in the enhanced electron deficiency at the phosphorus atom caused by replacement of an alkoxy- by an alkyl group.



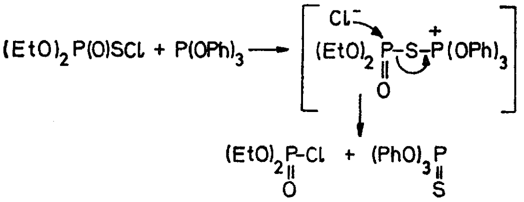


It is interesting that the last two reactions described led to the same thio-anhydride as the main product. Its structure was confirmed by hydrolysis and chromatography of the reaction mixture.

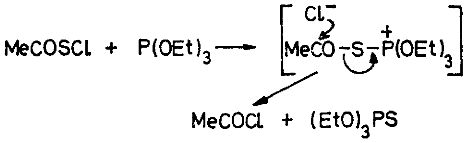


The mechanism of isomerisation of symmetrical thiopyrophosphate systems is beyond the scope of this paper and will be discussed separately.

As expected, the reaction between triphenyl phosphite and diethoxyoxophosphoranesulphenyl chloride follows path (c) alone. The bond between an oxygen atom and a phenyl group is strong, and nucleophilic attack by chloride anion on the phenyl group does not take place.

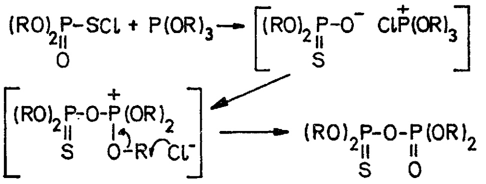


The reaction between 1-oxoethanesulphenyl chloride and triethyl phosphite was studied for comparative purposes. Attack by chloride anion is directed entirely on the acetyl group in the quasiphosphonium complex.



Removal of the acetyl group from a complex of the type (III) apparently occurs more readily than that of a phosphoryl group.

An alternative ionic mechanism for the reactions under discussion involves nucleophilic attack of the phosphorus atom on positive chlorine.[20] This scheme does not explain the formation of symmetrical thiopyrophosphate (A) and other products. However in the reaction of diethoxythioxophosphoranesulphenyl chloride with triethyl phosphite[21] the mechanism involving positive halogen attack seems to be partially operative. A mechanism based on homolytic fission is unlikely because of the absence of appropriate side products. In any case such a process would lead to the same quasiphosphonium complex as just described.



$$(RO)_2P(O)SCl \longrightarrow (RO)_2P(O)S\cdot + Cl\cdot$$

$$(RO)_2P(O)S\cdot \xrightarrow{(RO)_3P} (RO)_2P(O)\cdot S\cdot P(OR)_3 \xrightarrow{(RO)_2P(O)SCl}$$

$$(RO)_2P(O)\cdot S\cdot \overset{+}{P}(OR)_3Cl^- + (RO)_2P(O)S\cdot$$

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[20] B. Miller, 'Topics in Phosphorus Chemistry,' vol. II, Interscience, New York, London, and Sydney, 1965, p. 155.

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EXPERIMENTAL

Benzene was dried over sodium hydride and distilled. I.r. spectra were recorded with a U.R. model 10 (Zeiss) spectrophotometer for liquid films.

Diethoxyoxophosphoranesulphenyl chloride,[22] *P*-ethoxy-*P*-ethyloxophosphoranesulphenyl chloride,[23] 1-oxoethanesulphenyl chloride,[24] triethyl phosphite,[25] triphenyl phosphite,[26] diethyl ethylphosphonite,[27] and diethyl phenylphosphonite [28] were prepared by literature methods.

Reactions of Diethoxyoxophosphoranesulphenyl Chloride (I) *with Trialkyl Phosphite and its Analogues.—General procedure.* Diethoxyoxophosphoranesulphenyl chloride (0·15 mole) in benzene (30 ml.) was added dropwise to a solution of an appropriate phosphorus ester (0·15 mole) in benzene (100 ml.) with vigorous stirring. The temperature of the exothermic reaction was kept at 0—5° (ice–salt bath). The solvent and gaseous products were evaporated off *in vacuo*. The mixtures were separated by distillation.

(a) *Reaction with triethyl phosphite.* T.l.c. of the mixture [Kieselgel G (Merck); benzene–acetone–chloroform (4 : 3 : 1); spots developed 5% with aqueous silver nitrate and 2% ethanolic Bromothymol Blue sprays followed by u.v. illumination] gave three spots: (i) orange, *sym*-tetraethyl thiopyrophosphate, R_F 0·49; (ii) dark grey, diethyl phosphorochloridate, R_F 0·72; and (iii) yellow, triethyl phosphorothionate, R_F 0·88. [Authentic samples of *sym*-tetraethyl thiopyrophosphate (prepared by reaction of diethyl phosphite with piperidinesulphenyl chloride), diethyl phosphorochloridate, and triethyl phosphorothionate have R_F values 0·50, 0·72, and 0·88, respectively.]

The reaction mixture was distilled to afford two fractions: (*a*) b.p. 92—98°/18 mm. (41 g.), and (*b*) b.p. 85—90°/0·05 mm. (7·5 g.). To fraction (*a*) in benzene (30 ml.) aniline (0·25 mole) was added at 0°. After a few hours the precipitate was filtered off and washed with benzene. The benzene solution was evaporated and the residue was distilled to yield triethyl phosphorothionate (20·8 g., 70%), b.p. 50—51°/0·9 mm., n_D^{20} 1·4480 (lit.,[29] b.p. 94·5°/12 mm., n_D^{20} 1·4480) (Found: P, 15·7. Calc. for $C_6H_{15}O_3PS$: P, 15·65%). The precipitate was extracted with boiling benzene. Evaporation of the extract gave diethyl phenylphosphoramidate (13·7 g., 40%), m.p. and mixed m.p. 92—93° (from water). The residue was identified as aniline hydrochloride.

Redistillation of the fraction (*b*) afforded tetraethyl thiopyrophosphate (6·9 g., 15%), b.p. 83—84°/0·05 mm., n_D^{25} 1·4480 (lit.,[30] b.p. 82—84°/0·04 mm., n_D^{25} 1·4495), $\nu_{max.}$ 1290 (P=O), 946 (P–O–P), and 615 (P=S) cm.$^{-1}$ (Found: P, 19·9. Calc. for $C_8H_{20}O_6P_2S$: P, 20·2%).

(b) *Reaction with diethyl ethylphosphonite.* Products were separated as in (a) to give diethyl ethylphosphonothionate (7·7 g., 28%), b.p. 86°/13 mm., n_D^{25} 1·4520 (lit.,[28] b.p. 81°/10 mm., n_D^{20} 1·4558) (Found: P, 17·25. Calc. for $C_6H_{15}O_2PS$: P, 17·05%); diethyl phenylphosphoramidate (6·0 g., 71%), m.p. 92°; triethyl ethylthiopyrophosphonate (30·8 g., 71%), b.p. 85°/0·04 mm., n_D^{25} 1·4560, $\nu_{max.}$ 1268 (P=O), 946 (P–O–P), and 600 (P=S) cm.$^{-1}$ (Found: P, 21·1. Calc. for $C_8H_{20}O_5PS$: P, 21·4%).

Hydrolysis of triethyl ethylthiopyrophosphonate. Triethyl ethylthiopyrophosphonate (8·7 g., 0·03 mole) in benzene (50 ml.) was refluxed for 10 hr. with water (1 g., 0·06 mole). The solvent was evaporated off *in vacuo* and the residue was distilled to yield a mixture of ethyl hydrogen ethylphosphonate and diethyl hydrogen phosphorothionate. The acids were identified by ascending paper chromatography [Whatman no. 1 paper; propanol–aqueous ammonia–water (6 : 3 : 1); developed by spraying with Hanes and Isherwood's reagent [31]]. Two spots were obtained: R_F 0·80 and 0·89. Authentic samples of ethyl hydrogen ethylphosphonate and diethyl hydrogen phosphorothionate have R_F values 0·80 and 0·89, respectively.

(c) *Reaction with diethyl phenylphosphonite.* Distillation of the reaction mixture gave diethyl phosphorochloridate (2·6 g., 10%), b.p. 86—87°/14 mm., n_D^{20} 1·4200 (lit.,[32] b.p. 86°/12 mm., n_D^{25} 1·4162) (Found: P, 17·85. Calc. for $C_4H_{10}ClO_3P$: P, 18·0%); diethyl phenylphosphonothionate (7·0 g., 20%), b.p. 72—73°/0·02 mm., n_D^{25} 1·5220 (Found: P, 13·35. Calc. for $C_{10}H_{15}O_2PS$: P, 13·5%); and triethyl phenylthiopyrophosphonate (35·3 g., 70%), b.p. 120—122°/0·05 mm., n_D^{25} 1·5044, $\nu_{max.}$ 1275 (P=O), 945 (P–O–P), and 600 (P=S) cm.$^{-1}$ (Found: P, 18·3. Calc. for $C_{12}H_{20}O_5P_2S$: P, 18·4%).

(d) *Reaction with triphenyl phosphite.* Fractionation of the reaction mixture gave diethyl phosphorochloridate (18·6 g., 72%), b.p. 84°/12 mm., n_D^{25} 1·4200; triphenyl phosphorothionate (38 g., 74%), b.p. 134—140°/0·05 mm., m.p. 47·5—48° (lit.,[33] b.p. 241°/11 mm., m.p. 48°) (Found: P, 9·2. Calc. for $C_{18}H_{15}O_3PS$: P, 9·0%).

Reaction of Dipropoxyoxophosphoranesulphenyl Chloride with Tripropyl Phosphite.—Dipropoxyoxophosphoranesulphenyl chloride (29·15 g., 0·1 mole) in benzene (30 ml.) was added dropwise to a solution of tripropyl phosphite (20 g., 0·1 mole) in benzene (100 ml.). The temperature was kept at *ca.* 0°. The solvent and propyl chloride were removed *in vacuo*. T.l.c. of the mixture [benzene–acetone–chloroform (4 : 3 : 1), developed with 5% aqueous silver nitrate and 2% ethanolic Bromothymol Blue followed by u.v. illumination] showed the presence of *sym*-tetrapropyl thiopyrophosphate, R_F 0·57, dipropyl phosphorochloridate, R_F 0·75, and tripropyl phosphorothionate R_F 0·90. The products were separated as described for the reaction of diethoxyoxophosphoranesulphenyl chloride with triethyl phosphite, to give tripropyl phosphorothionate (17·25 g., 72%), b.p. 125°/11 mm., n_D^{25} 1·4505 (lit.,[29] b.p. 123·5—124·5°/10 mm., n_D^{25} 1·4502) (Found: P, 12·7. Calc. for $C_9H_{21}OPS$: P, 12·9%); dipropyl phenylphosphoramidate (10·5 g., 41%), m.p. 96°; and tetrapropyl thiopyrophosphate (5·8 g., 16%), b.p. 87—88°/0·01 mm., n_D^{25} 1·4370 (lit.,[34] b.p. 94—95°/0·01 mm., n_D^{25} 1·4363),

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[33] H. B. Gottlieb, *J. Amer. Chem. Soc.*, 1932, **54**, 748.

[34] B. Fiszer, J. Michalski, and J. Wieczorkowski, *Roczniki Chem.*, 1953, **27**, 482.

$\nu_{max.}$ 1295 (P=O), 950 (P–O–P), and 618 (P=S) cm.$^{-1}$ (Found: P, 16·95. Calc. for $C_{12}H_{28}O_6PS$: P, 17·1%).

Reaction of P-*Ethoxy*-P-*ethyloxophosphoranesulphenyl Chloride with Triethyl Phosphite*.—A solution of *P*-ethoxy-*P*-ethyloxophosphoranesulphenyl chloride (33·9 g., 0·18 mole) in benzene (50 ml.) was added dropwise to triethyl phosphite (29·9 g., 0·18 mole) in benzene (50 ml.) with vigorous stirring. The temperature was kept at 0—5°. The mixture was stirred at room temperature for 1 hr.; the solvent and ethyl chloride were then removed *in vacuo*. Distillation of the residue gave two fractions: (i) b.p. 70—90°/13 mm. (41·5 g.); and (ii) b.p. 85—90°/0·3 mm. (8·0 g.). To fraction (i) in benzene (100 ml.), pyridine (7·1 g., 0·09 mole) was added and dry hydrogen sulphide was passed through for 2 hr. at 8—10°. The precipitate was filtered off and washed with benzene. The benzene solution was washed with water, dilute hydrochloric acid, and water again, and then dried ($MgSO_4$). The solvent was evaporated off and the residue was fractionated to give triethyl phosphorothionate (19 g., 51%), b.p. 87—89°/12 mm., n_D^{20} 1·4500) (Found: P, 15·95. Calc. for $C_6H_{15}O_3PS$: P, 15·65%); diethyl ethylthiopyrophosphonate (11 g., 45%), b.p. 110—112°/0·5 mm., n_D^{25} 1·4660) (lit.,[35] b.p. 119—120°/0·8 mm., n_D^{25} 1·4652), $\nu_{max.}$ 1968 (P=O), 945 (P–O–P), and 600 (P=S) cm.$^{-1}$ (Found: P, 22·3. Calc. for $C_8H_{20}O_4P_2S$: P, 22·6%). Redistillation of fraction (ii) gave triethyl ethylthiopyrophosphonate (4 g., 7%), b.p. 85—87°/0·05 mm., n_D^{20} 1·4580 (Found: P, 21·2. Calc. for $C_8H_{20}O_5P_2S$: P, 21·4%).

Reaction of Oxoethanesulphenyl Chloride with Triethyl Phosphite.—Oxoethanesulphenyl chloride (22·0 g., 0·2 mole) in benzene (50 ml.) was added dropwise to triethyl phosphite (33·2 g., 0·2 mole) at −5 to 0°. Fractional distillation of the mixture through a short Fenske column yielded acetyl chloride, b.p. 50—53° (7 g., 50%; identified as acetanilide, m.p. 113—114°), and triethyl phosphorothionate, b.p. 99—101°/17 mm., n_D^{20} 1·4480 (lit.,[29] b.p. 94·5°, n_D^{20} 1·4480).

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[35] J. Michalski and A. Skowrońska, *Roczniki Chem.*, 1956, **30**, 799.