Polymerization of II *with styrene.* A solution of II (0.05 g.), styrene (0.5 ml.), and α,α'-azodiisobutyronitrile (0.01 g.) in 2 ml. of benzene under nitrogen set to a gel on heating overnight at 60°. After filtration and washing with benzene, 0.30 g. of golden-brown polymer was obtained. It was swollen by boiling carbon tetrachloride, and by toluene and butyl acetate at 100°, but did not dissolve.

cis-2,4,6-Tris(2-chloroethyl)-s-trithiane (XI). Hydrogen sulfide was passed into a solution of 33.6 g. (0.60 mole) of acrolein in 200 ml. of ether, previously saturated with hydrogen chloride, for 20 hr. at −20 to −10°. After warming to room temperature overnight, the mixture was treated with benzene and water, the benzene layer was separated, dried over magnesium sulfate, and freed of solvent by distillation. The residue was crystallized from ethyl acetate, then from ethyl acetate—*n*-hexane to give 5.08 g. of XI (8%), m.p. 115.0–116.0°. Further recrystallization from ethyl acetate raised the melting point to 130.0–131.5°.

Anal. Calcd. for $C_9H_{15}Cl_3S_3$: C, 33.18; H, 4.64; S, 29.52. Found: C, 33.94; H, 5.14; S, 30.20.

The rather unsatisfactory analysis probably resulted from loss of chloride during recrystallization. However, both its proton magnetic resonance spectrum and formation of the phenylthio derivative (XII) served to confirm the assigned structure.

cis-2,4,6-Tris(2-phenylthioethyl)-s-trithiane (XII). A sample (0.20 g., 0.62 mmole) of XI was treated with sodium thiophenoxide as described above for I. Since the product did not crystallize from the filtered reaction mixture, the solvent was removed by distillation and the residue was crystallized from ether to give 0.20 g. (59%) of XII, m.p. 70.0–74.0°. Further crystallization from *n*-hexane gave colorless needles, m.p. 82.5–83.0°.

Anal. Calcd. for $C_{27}H_{30}S_6$: C, 59.30; H, 5.53; S, 35.17. Found: C, 59.39; H, 5.95; S, 35.48.

2,4,6-Triethylidene-s-trithiane (XIII). To a solution of 0.18 g. (0.0046 g.-atom) of potassium in 10 ml. of *t*-butyl alcohol was added 0.50 g. (1.5 mmoles) of XI and 0.01 g. of 2,6-di-*t*-butyl-4-methylphenol. The solution was refluxed for 1 hr. The next day the solvent was removed *in vacuo* at 25°, and the residue was distilled to give 0.25 g. (76%) of an orange liquid, b.p. 109° at 0.15 mm.

Anal. Calcd. for $C_9H_{12}S_3$: C, 49.96; H, 5.59. Found: C, 49.56; H, 5.95.

The infrared spectrum (taken on an Infracord) had a band at 7.28 μ assignable to a methyl group.

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[CONTRIBUTION NO. 632 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., INC.]

Reaction of Thiocyanates with Trialkyl Phosphites

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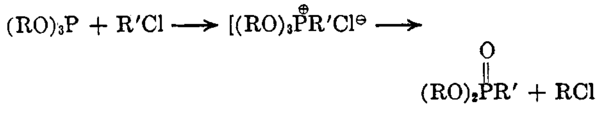
Trialkyl phosphites, $(RO)_3P$, react with alkyl and aryl thiocyanates, R'SCN, to give the alkylnitrile, RCN, and the corresponding thiophosphate, $(RO)_2\overset{O}{\overset{\|}{P}}SR'$. The reaction is believed to occur by an ionic mechanism involving displacement of the cyanide ion by nucleophilic attack of the phosphorus on sulfur.

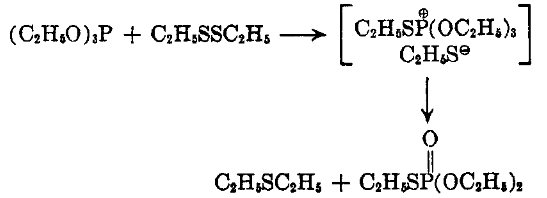
Trivalent phosphorus compounds, such as the trialkyl phosphites, are strong nucleophiles and will readily displace halide from an alkyl halide. The intermediate quasiphosphonium salt subsequently eliminates alkyl halide with simultaneous formation of the corresponding dialkyl alkylphosphonate. This reaction, first observed by Arbuzov,



$$(RO)_3P + R'Cl \longrightarrow [(RO)_3\overset{\oplus}{P}R'Cl^{\ominus}] \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}R' + RCl$$

has received the attention of numerous experimenters[1] and has been extended to the displacement of groups other than halides.

Recently, nucleophilic attack of trialkyl phosphites on alkyl disulfides and sulfenyl chlorides has been reported[2] and discussed in a review.[3] In the case of ethyl disulfide, the reaction is a typical displacement of ethyl mercaptide ion from the sulfur of the disulfide followed by deethylation of the quasiphosphonium salt by ethyl mercaptide



$$(C_2H_5O)_3P + C_2H_5SSC_2H_5 \longrightarrow \begin{bmatrix} C_2H_5S\overset{\oplus}{P}(OC_2H_5)_3 \\ C_2H_5S^{\ominus} \end{bmatrix} \downarrow C_2H_5SC_2H_5 + C_2H_5S\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$$

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[1] (a) G. M. Kosolapoff, *Organophosphorus Compounds*, John Wiley and Sons, Inc., New York, 1950, Chap. 7. (b) For a recent review of the mechanism of this reaction, see A. Y. Garner, E. C. Chapin, and P. M. Scanlon, *J. Org. Chem.*, **24**, 532 (1959).

[2] (a) H. I. Jacobson, R. G. Harvey, and E. V. Jensen, *J. Am. Chem. Soc.*, **77**, 6064 (1955). (b) D. C. Morrison, *J. Am. Chem. Soc.*, **77**, 181 (1955). (c) D. C. Morrison, Abstracts of American Chemical Society Meeting held in Chicago, September 1958, page 87P. (d) K. A. Petrov, G. A. Sokolsky, and B. M. Polees, *J. Gen. Chem. U.S.S.R.* (English transl.), **26**, 3765 (1956). (e) The reactions of various types of organic phosphinyl disulfides and diselenides with trialkyl phosphites and sodium dialkyl phosphites are described by J. Michalski and J. Wieczorkowski, *J. Chem. Soc.*, 885 (1960); J. Michalski, J. Wieczorkowski, J. Wasiak, and B. Pliszka, *Roczniki Chem.*, **33**, 247 (1959); J. Michalski and J. Wieczorkowski, *Bull. Acad. polon. Sci., Classe III*, **5**, 917 (1957).

[3] A. J. Parker and N. Kharasch, *Chem. Revs.*, **59**, 621 (1959).

ion. A similar mechanism is proposed for the sulfenyl halide reaction in which an alkyl halide and a trialkyl thiophosphate are formed.

Trialkyl- and triarylphosphines have also been shown to react with disulfides[3,4] and sulfenyl halides,[2c] but, as expected, are much weaker nucleophiles than phosphites. In the case of disulfides, the final step of the reaction involves dealkylation of the intermediate salt by the mercaptide ion so that the over-all reaction appears to be a simple desulfurization.

$$R_3P + R'SSR' \longrightarrow [R_3\overset{\oplus}{P}SR'\overset{\ominus}{S}R'] \longrightarrow R_3PS + R'SR'$$

All of the above reactions are thought to proceed by an ionic mechanism (although a radical mechanism has been suggested for the reaction of phosphines with disulfides). Free radical-induced reactions of trialkyl phosphites and phosphines with mercaptans, disulfides, and sulfenyl halides have also been reported.[5] It has been proposed that the radical $RS\cdot$ attacks the phosphorus and that the thionophosphate, $SP(OR)_3$, is subsequently formed by loss of $R\cdot$. The alkyl radical can propagate the chain and as a result is converted to RH, RSR, or RCl, corresponding to the starting material.

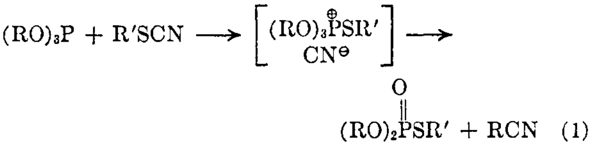
The reactions of trialkylphosphines with alkyl thiocyanates[6] and isothiocyanates[7] were reported in the early literature. The following equations indicate the proposed reaction course, but insufficient experimental data were given to allow proper

$$C_2H_5SCN + 2(C_2H_5)_3P \longrightarrow (C_2H_5)_3PS + (C_2H_5)_4\overset{\oplus}{P}CN^{\ominus}$$

$$RNCS + R_3P \longrightarrow R_3PS + RNC$$

evaluation of this work. Nucleophilic displacement of cyanide ion from thiocyanates by the anion of dialkyl phosphites[2e,8] and by mercaptide ion as well as other reagents[9a] has been reported.

Accordingly, it would be expected that trialkyl phosphites would react with thiocyanates to displace cyanide ion and this has now been found to occur.[9b] Thus, when a trialkyl phosphite is heated with an alkyl or aryl thiocyanate, an exothermic reaction occurs and the nitrile and thiophosphate (See equation 1) are formed in yields of 40–80% (see Table I). By analogy to the nucleophilic

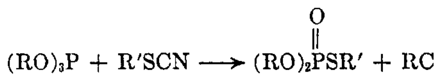


$$(RO)_3P + R'SCN \longrightarrow \left[\begin{matrix}(RO)_3\overset{\oplus}{P}SR' \\ CN^{\ominus}\end{matrix}\right] \longrightarrow (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}SR' + RCN \quad (1)$$

reactions of trialkyl phosphites described above, it is suggested that the mechanism is the same as that proposed for the Arbuzov-type reactions of trialkyl phosphites with disulfides and sulfenyl halides.

A free-radical mechanism is considered unlikely since the reaction could not be induced by ultraviolet irradiation at room temperature and was not inhibited by diphenylamine. A thionophosphate, $(RO)_3P{=}S$, would be the expected product if the reaction follows a radical course. The thiophosphates were identified by correspondence of their physical properties with those reported in the literature, and, in one case, by comparison with

TABLE I



$$(RO)_3P + R'SCN \longrightarrow (RO)_2\overset{\overset{\displaystyle O}{\|}}{P}SR' + RCN$$

Reactants		% Yield of RCN	% Yield of Thiophosphate
CH_3 12.4 g.[a]	$C_6H_5CH_2$ 14.9 g.[a]	68[b]	—[c]
CH_3[d] 12.4 g.	$C_6H_5CH_2$ 14.9 g.	56[b]	—
C_2H_5 16.6 g.	CH_3 7.3 g.	76[e]	81[f]
C_2H_5 16.6 g.	C_2H_5 8.7 g.	76[e]	90[g]
C_2H_5 16.6 g.	$C_6H_5CH_2$ 14.9 g.	59[e]	80[h]
C_2H_5 16.6 g.	C_6H_5 13.5 g.	36[e]	69[i]
C_2H_5 16.6 g.	p-$(CH_3)_2NC_6H_4$ 17.8 g.	37[e]	—
C_6H_5 30.4 g.	$C_6H_5CH_2$ 14.9 g.	0	0

[a] In every experiment, 0.10 mole of phosphite ester and thiocyanate were employed. [b] B.p. 80–81°, n_D^{25} 1.3427. [c] Decomposed during distillation. [d] Diphenylamine (1.0 g.) added as free-radical inhibitor. Reaction course appeared unchanged. [e] B.p. 95°, or 53° (105 mm.), n_D^{25} 1.3630. [f] B.p. 122° (18 mm.), n_D^{25} 1.4559; lit.,[2a] b.p. 145–150° (50 mm.). [g] B.p. 132° (22 mm.), n_D^{25} 1.4545; lit.[2a], b.p. 110° (11 mm.), n_D^{25} 1.4552. [h] B.p. 130° (0.6 mm.), n_D^{25} 1.5245. [i] B.p. 120° (0.75 mm.), n_D^{25} 1.5227. *Anal.* Calcd. for $C_{10}H_{15}O_3PS$: C, 48.8; H, 6.14; P, 12.6; S, 13.0. Found: C, 48.8; H, 5.93; P, 12.8; S, 12.7; lit.,[2b] b.p. 182–186° (30 mm.).

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[4] (a) A. Schonberg and M. Z. Barakat, *J. Chem. Soc.*, 892 (1949). (b) F. Challenger and D. Greenwood, *J. Chem. Soc.*, 26 (1950).

[5] (a) F. W. Hoffmann, R. J. Ess, T. C. Simmons, and R. S. Hanzel, *J. Am. Chem. Soc.*, **78**, 6414 (1956). (b) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **79**, 5326 (1957). (c) C. Walling, Abstracts of Organic Chemistry Symposium held at Seattle, Wash., June 1959, page 88.

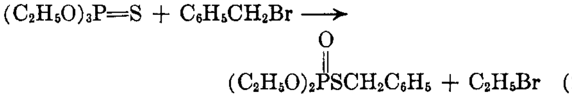
[6] A. W. Hofmann, *Ann.*, Supp. **1**, 53 (1861).

[7] A. W. Hofmann, *Ber.*, **3**, 766 (1870).

[8] G. Schrader, U. S. Patent **2,640,847** (June 1953); *Chem. Abstr.*, **48**, 5206 (1954).

[9] (a) E. Müller, *Methoden der Organisches Chemie* (Houben-Weyl), Vol. **9**, Sulfur, Selenium and Tellerium Compounds, Georg Thieme Verlag, Stuttgart, 1955, pp. 69 and 866. (b) Since submittal of this paper, it was brought to our attention that a similar result was reported recently in a communication by J. Michalski and J. Wieczorkowski, *Bull. Acad. polon. Sci.*, *Classe III*, **4**, 4279 (1956). Several examples using triethyl and tributyl phosphites and diethyl ethyl phosphonate with ethyl and benzyl thiocyanate were given. A mechanistic scheme similar to that proposed below was suggested but no experimental evidence was provided.

an authentic sample of *O,O*-diethyl-*S*-benzyl thiophosphate prepared by the known reaction[10]



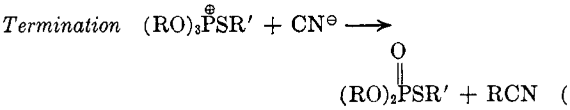
$$(C_2H_5O)_3P{=}S + C_6H_5CH_2Br \longrightarrow (C_2H_5O)_2\overset{\overset{O}{\|}}{P}SCH_2C_6H_5 + C_2H_5Br \qquad (2)$$

As expected in this type of reaction, triaryl phosphites do not react. Since aryl as well as alkyl thiocyanates may be used, an alternative ion chain mechanism outlined below seems improbable. The propagation step (Equation 4)

$$\textit{Initiation} \qquad (RO)_3P \xrightarrow{[S]} (RO)_3P{=}S \qquad (3)$$

$$\textit{Propagation} \quad (RO)_3P{=}S + R'SCN \longrightarrow (RO)_3\overset{\oplus}{P}SR'\ SCN^{\ominus} \qquad (4)$$

$$(RO)_3P + SCN^{\ominus} \longrightarrow (RO)_3P{=}S + CN^{\ominus} \qquad (5)$$



$$\textit{Termination} \quad (RO)_3\overset{\oplus}{P}SR' + CN^{\ominus} \longrightarrow (RO)_2\overset{\overset{O}{\|}}{P}SR' + RCN \qquad (6)$$

involves a known displacement-type reaction (Equation 2), but an aryl thiocyanate would not undergo such a nucleophilic displacement readily. An attempt to react $(EtO)_3P{=}S$ with ϕCH_2SCN by heating to 180° gave chiefly recovered starting material. Bartlett and Davis[11] have reported that triphenylphosphine will not react with thiocyanate ion.

A possible alternative course for the reaction is displacement of thiocyanate instead of cyanide ion. No indication of this nucleophilic displacement on carbon instead of sulfur was observed.

EXPERIMENTAL

Materials. Trimethyl, triethyl, and triphenyl phosphites and *O,O,O*-triethyl thionophosphate were obtained from Virginia-Carolina Chemical Corp. and were freshly distilled before use. Methyl, ethyl, and benzyl thiocyanates were obtained from Eastman Chemical Products, Inc., and were also distilled. Phenyl thiocyanate and dimethylaminophenyl thiocyanate were prepared by literature procedures.[12,13]

Reaction of phosphite esters with thiocyanates. The results from the reactions of the phosphite esters and thiocyanates are summarized in Table I. The general procedure is illustrated by the reaction of triethyl phosphite with benzyl thiocyanate.

A solution of 14.9 g. (0.10 mole) of benzyl thiocyanate in 16.6 g. (0.10 mole) of triethyl phosphite in a 50-ml. flask fitted with a thermometer, magnetic stirrer, and reflux condenser was gradually heated under a nitrogen atmosphere in an oil bath. When the reaction temperature reached approximately 80°, an exothermic reaction occurred and the internal temperature rose rapidly to approximately 120°. The oil bath temperature was then gradually increased to 140–150° during 1 hr. The product was distilled through a 12-in. spinning-band distillation column to give 3.22 g. of propionitrile, b.p. 95°, n_D^{25} 1.3629, and 20.9 g. of *O,O*-diethyl-*S*-benzyl thiophosphate, b.p. 128–130° (0.6 mm.), n_D^{25} 1.521 to 1.526. An intermediate fraction of 3.6 g., b.p. 67° (130 mm.) to 128° (0.6 mm.), was not characterized but would appear from examination of the infrared spectrum to contain diethyl ethylphosphonate, usually formed as a by-product in reactions of triethyl phosphite.

The nitrile fractions were characterized by comparison of their infrared spectra with those of authentic samples. The diethylbenzyl thiophosphate isolated from the above reaction was characterized by comparison of its infrared spectrum with that of an authentic sample prepared as described below. The other thiophosphate esters isolated were characterized by spectra and comparison to physical constants in the literature, and, in certain cases, by analysis. It was observed that heating of the thiophosphate esters for prolonged periods or at high temperatures during distillation resulted in decomposition to intractable tars.

O,O-Diethyl-S-benzyl thiophosphate. The general procedure[10] for reaction of the thionophosphates with an alkyl halide was modified because of the nature of the reactants. *O,O,O*-Triethyl thionophosphate (9.1 g., 0.045 mole) was placed in a flask fitted with an addition funnel and a distillation head with a receiver cooled in an ice bath. Benzyl bromide (7.5 g., 0.044 mole) was added gradually from the addition funnel as the reaction temperature was increased from 150° to 190° by use of an oil bath. After 30 min. heating at 190°, a total of 3.0 g. (61%) of ethyl bromide collected in the receiver. The reaction mixture was fractionally distilled at reduced pressure. A forerun of approximately 5 g. containing recovered starting material was discarded and the product, *O,O*-diethyl-*S*-benzyl thiophosphate, b.p. 137–138° (0.9 mm.), n_D^{25} 1.5241, was collected; 7.3 g. (64%).

Anal. Calcd. for $C_{11}H_{17}O_3PS$: C, 50.8; H, 6.59; P, 11.9; S, 12.3. Found: C, 51.2; H, 6.44; P, 12.0; S, 12.1.

In the infrared spectrum, absorptions characteristic of ethyl and benzyl groups were noted as well as strong absorption at 7.9 μ assigned to P=O stretching vibrations.

Attempted radical-induced reaction of trimethyl phosphite with benzyl thiocyanate. A solution of 14.9 g. (0.10 mole) of benzyl thiocyanate and 12.4 g. (0.10 mole) of trimethyl phosphite was irradiated overnight in a quartz tube under a nitrogen atmosphere using a low-pressure mercury resonance lamp.

The infrared spectrum of the resulting reaction mixture was identical with that of the starting solution in the 4–5 μ region. The main change in the spectrum was the appearance of a strong absorption at 7.9 μ, characteristic of P=O stretching vibration. Apparently, only the known rearrangement of trimethyl phosphite to dimethyl methylphosphonate had occurred in part. As a control experiment, the crude reaction product obtained by heating trimethyl phosphite with benzyl thiocyanate was found to have an infrared spectrum grossly different from that of the starting solution. In particular, the SCN absorption at 4.6 μ had diminished to almost zero and the CN absorption at 4.4 μ had appeared.

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(10) P. S. Pishchimuka, *J. Russ. Phys. Chem. Soc.*, **44**, 1406 (1912); see Reference 1a, p. 234.

(11) P. D. Bartlett and R. E. Davis, *J. Am. Chem. Soc.*, **80**, 2513 (1958).

(12) L. Gatterman and W. Haussknecht, *Ber.*, **23**, 738 (1890); A. Hantzsch and B. Hirsch, *Ber.*, **29**, 947 (1896).

(13) *Org. Syntheses*, **Coll. Vol. II**, 574 (1943).