The Reaction of Elemental Phosphorus with Alkanethiolates in the Presence of Tetrachloromethane

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White phosphorus in a finely divided form reacts with sodium alkanethiolates in the presence of the corresponding thiol and an excess of tetrachloromethane to give high yields of the trithioite, $(RS)_3P$, and trichloromethane. When a stoicheiometric quantity of sodium ethanethiolate was used, triethyl phosphorotrithioite together with diethyl phosphorochloridodithioite and diethyl trichloromethylphosphonodithioite were isolated as major products. A minor side reaction between thiolate ions and tetrachloromethane leads to the formation of dialkyl disulphide and trialkyl trithio-orthoformate. A reaction scheme for the formation of these products is suggested.

THE reactions of elemental phosphorus have been widely studied over a long period of time in attempts to develop satisfactory syntheses of organophosphorus compounds. Most reactions lead to mixtures of products owing to the large number of possible intermediates formed in the breakdown of the tetrahedral structure of white phosphorus.[1]

The revival of interest in the subject in recent years, particularly by Grayson [2] and by Rauhut,[3] was stimulated mainly by the growing importance of trialkylphosphines in organic synthesis. It has become apparent that P_4 is an extremely weak nucleophile, but an active electrophile. Nucleophilic attack on phosphorus, however, leads to the formation of a highly reactive phosphide ion which captures protons and most Lewis acids to give a variety of intermediates which decompose in a complex manner.

Thus Grignard reagents [4] and other organometallics [5] produce mixtures of phosphines usually in low yield, together with diphosphines and polyphosphines as significant side-products. Similarly hydroxide [6] and alkoxide [7] ions lead to products derived mainly from phosphorus and hypophosphorous acids together with phosphine and diphosphine.

More satisfactory syntheses have been developed by trapping the intermediate phosphide ions with appropriate electrophiles, e.g. alkyl halides,[4,5] activated olefins,[8] and aldehydes.[9] Thus Rauhut [8] obtained high yields of tris-(2-cyanoethyl)phosphine oxide by the action of hydroxide ions on phosphorus in the presence of acrylonitrile in ethanol, and the reaction with acryl-

$$P_4 + 2\ KOH + 4\ H_2O + 9\ CH_2{=}CHCN \longrightarrow$$
$$3\ (CNCH_2CH_2)_3PO + K_2HPO_3 \quad (1)$$
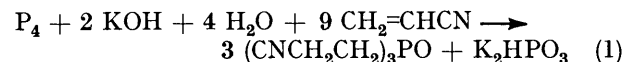
amide gave high yields of the corresponding phosphine oxide.

The related reaction with paraformaldehyde [9] in aqueous ethanol gives almost equimolar mixtures of hydroxymethyl-, bishydroxymethyl-, and hydroxymethyl(methyl)-phosphonic acids. According to Maier [9] the first step involves the attack by a hydroxide ion on P_4, followed by addition of the phosphine formed to formaldehyde.

In a consideration [10] of other electrophiles which may suitably trap the intermediate phosphide ion, we turned our attention to halogen compounds, in particular,

tetrachloromethane. This reacts rapidly with phosphines, aminophosphines, and similar phosphorus nucleophiles, and hence it is likely that it can compete effectively with the proton of a hydroxylic component of the
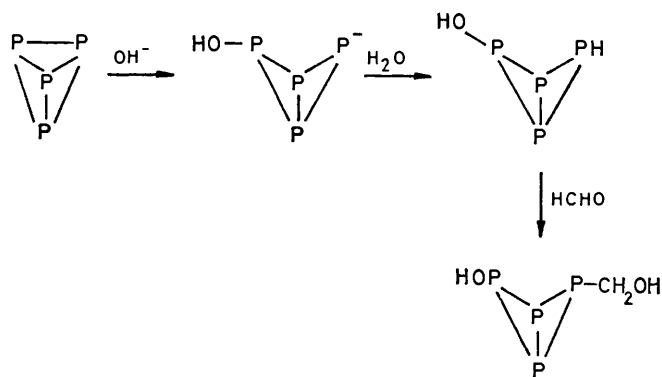
reaction mixture. The chlorophosphine thus produced reacts rapidly with the nucleophile, and hence, by a series of processes of this kind, a high degree of nucleophilic substitution on phosphorus may be achieved.

In this way, high yields of trialkylphosphite are obtained by the reaction of alkoxide ions with white phosphorus in the presence of tetrachloromethane.[10] This reaction is probably initiated in the following way.
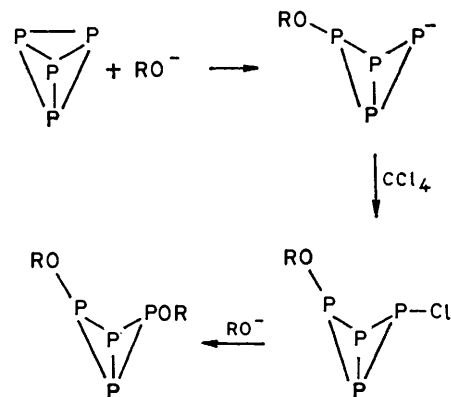

The trialkylphosphite so formed reacts more slowly with tetrachloromethane to give trialkyl phosphate,[11] and hence the yield of phosphite decreased on prolonged treatment.

We have extended these investigations to the reaction

of alkanethiolates in the presence of thiol and tetra-chloromethane, under similar conditions. High yields of trialkyl phosphorotrithioites are obtained, and although side products are formed in the accompanying, slower reaction between thiolate ions and tetrachloro-methane,[12] the trithioite does not oxidise further.
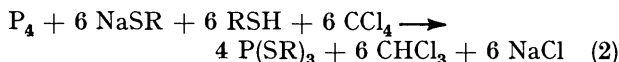
Trialkyl phosphorotrithioites can be prepared directly from white phosphorus and dialkyl disulphides [13] at elevated temperatures, probably by a homolytic process. In the presence of a catalytic quantity of hydroxide however, a rapid reaction leads to the trithioite in high yield, presumably by a mechanism similar to that described above.
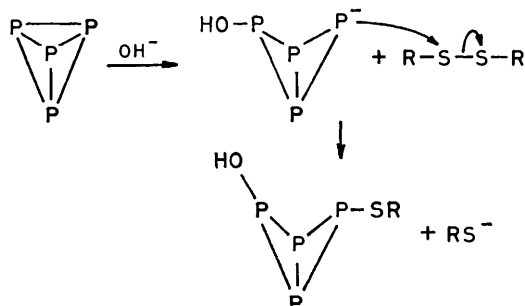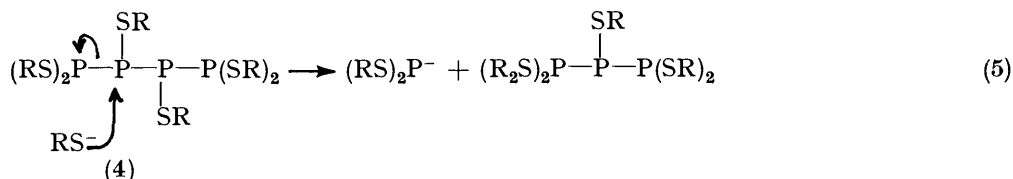

It appears, therefore, that the combination of a base with an appropriate electrophile can lead to a highly specific reaction with elemental phosphorus, with minimal formation of side-products.

RESULTS AND DISCUSSION

Elemental phosphorus, in the form of fine sand, was allowed to react with sodium alkanethiolate in carbon tetrachloride under two sets of conditions. In the first (Method 1), an equivalent quantity of sodium alkane-thiolate was used, according to equation (2).
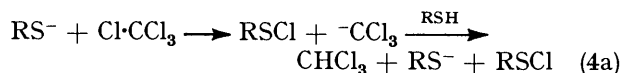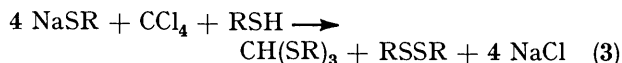
$$P_4 + 6\ NaSR + 6\ RSH + 6\ CCl_4 \longrightarrow$$
$$4\ P(SR)_3 + 6\ CHCl_3 + 6\ NaCl \quad (2)$$

The reaction, as monitored by the formation of tri-chloromethane and by g.l.c. analysis, was slow, and in the case of sodium ethoxide, a maximum yield of 37% of triethyl phosphorotrithioite (1, R = Et) was obtained

fractional distillation. The contribution of the side-reactions decreases as the concentration of the alkane-thiolate increases. The dialkyl disulphide (2) and trialkyl trithio-orthoformates (3) are derived from the direct reaction between the alkanethiolate and tetra-chloromethane [12] involving the attack of thiolate ions on the chlorine atom as in equations (4a) and (4b). The

$$4\ NaSR + CCl_4 + RSH \longrightarrow$$
$$CH(SR)_3 + RSSR + 4\ NaCl \quad (3)$$

$$RS^- + Cl \cdot CCl_3 \longrightarrow RSCl + {}^-CCl_3 \xrightarrow{RSH}$$
$$CHCl_3 + RS^- + RSCl \quad (4a)$$

$$RS^- + RSCl \longrightarrow RSSR + Cl^- \quad (4b)$$

trithio-orthoformate (3) is presumably formed by the reaction between trichloromethane and alkanethiolate ions, either by direct substitution or more likely by the formation of an intermediate carbene which is then trapped by alkanethiolate ions.

Control experiments show that these reactions proceed at room temperature at a rate commensurate with their formation as minor products in the reaction in the presence of elemental phosphorus. By increasing the alkanethiolate concentration, the reaction with phos-phorus is accelerated and proceeds to completion.
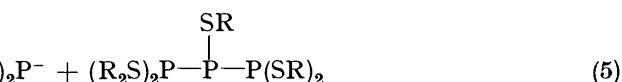
The diethyl phosphorochloridodithioite (Table 1)

TABLE 1

[31]P N.m.r. data of products formed by the reaction of sodium ethoxide (Method 1)

Product	δ_P [a]	$^3J_{PH}$/Hz	Multiplicity	Relative intensity [b]
(EtS)$_2$PCl [c]	184.5	11	Quintet	1
(EtS)$_2$PCCl$_3$	121.6	11	Quintet	1
(EtS)$_3$P [d]	113.9	9	Septet	2

[a] In p.p.m.; low-field shifts with respect to H_3PO_4 are designated as positive. [b] Measured from the noise-decoupled spectrum; approximate values. [c] Lit.,[14] δ_P 186.2; $^3J_{PH}$ ca. 11 Hz. [d] Lit.,[15] δ_P (neat) 115.6; $^3J_{PH}$ 9.1 Hz.

formed using method 1 is probably formed by the reaction of alkanethiolate ions with an intermediate (4) produced by the breakdown of the P_4 structure (see the Scheme) to give a phosphide ion which reacts rapidly

$$(RS)_2P\text{—}P\text{—}P\text{—}P(SR)_2 \longrightarrow (RS)_2P^- + (R_2S)_2P\text{—}P\text{—}P(SR)_2 \quad (5)$$

after prolonged treatment (4 d). In addition, side-products probably derived from the reaction between tetrachloromethane and the alkanethiolate [12] were observed.

In the second method (Method 2), when two equi-valents of the alkanethiolate were used, high yields of trialkyl phosphorotrithioite were obtained (97% from ethanethiolate and 82% from n-butanethiolate). These triesters were separated from the reaction mixture by

with tetrachloromethane as in equations (5) and (6). The exclusive production of triethyl phosphorotrithioite (1; R = Et) under optimum conditions (Method 2)

$$(RS)_2P^- + Cl\text{—}CCl_3 \longrightarrow (RS)_2PCl + {}^-CCl_3 \quad (6)$$
$$(5)$$
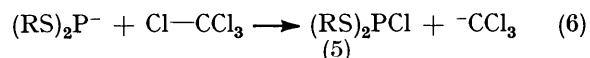
indicates that chloride ion is displaced rapidly by ethanethiolate ion from intermediates containing a P–Cl bond. With 1 equiv. of ethanethiolate ion, part
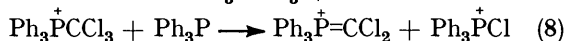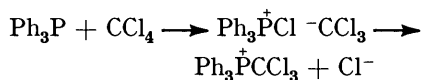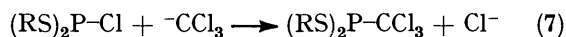
of this is used in the reaction with tetrachloromethane, and since ethanethiol reacts very slowly with diethyl phosphorochloridodithioite at room temperature, a low yield of the triester is produced.

Evidence for the participation of the trichloromethyl anion is provided by the detection of diethyl trichloromethylphosphonodithioite (6). This is produced by the attack of the $^-CCl_3$ ion on electrophilic phosphorus, probably in the form of the chloro-compound (5) formed in reaction (6).

A similar reaction occurs between triphenylphosphine and tetrachloromethane,[16] and between diphenylphosphinous amides and bromotrichloromethane.[17]

In the presence of an excess of sodium alkanethiolate,

the reaction shown in equation (7) does not occur, and it is unlikely that earlier intermediates containing P–Cl bonds react in this way, since products containing both

$$(RS)_2P\text{–}Cl + {}^-CCl_3 \longrightarrow (RS)_2P\text{–}CCl_3 + Cl^- \quad (7)$$

$$Ph_3P + CCl_4 \longrightarrow Ph_3\overset{+}{P}Cl\ {}^-CCl_3 \longrightarrow$$
$$Ph_3\overset{+}{P}CCl_3 + Cl^-$$

$$Ph_3\overset{+}{P}CCl_3 + Ph_3P \longrightarrow Ph_3\overset{+}{P}{=}CCl_2 + Ph_3\overset{+}{P}Cl \quad (8)$$

a chlorine atom and a trichloromethyl group directly bonded to phosphorus are not formed. In the early stages, therefore, displacement of chloride ion by ethanethiolate anion and capture of the $^-CCl_3$ ion by the
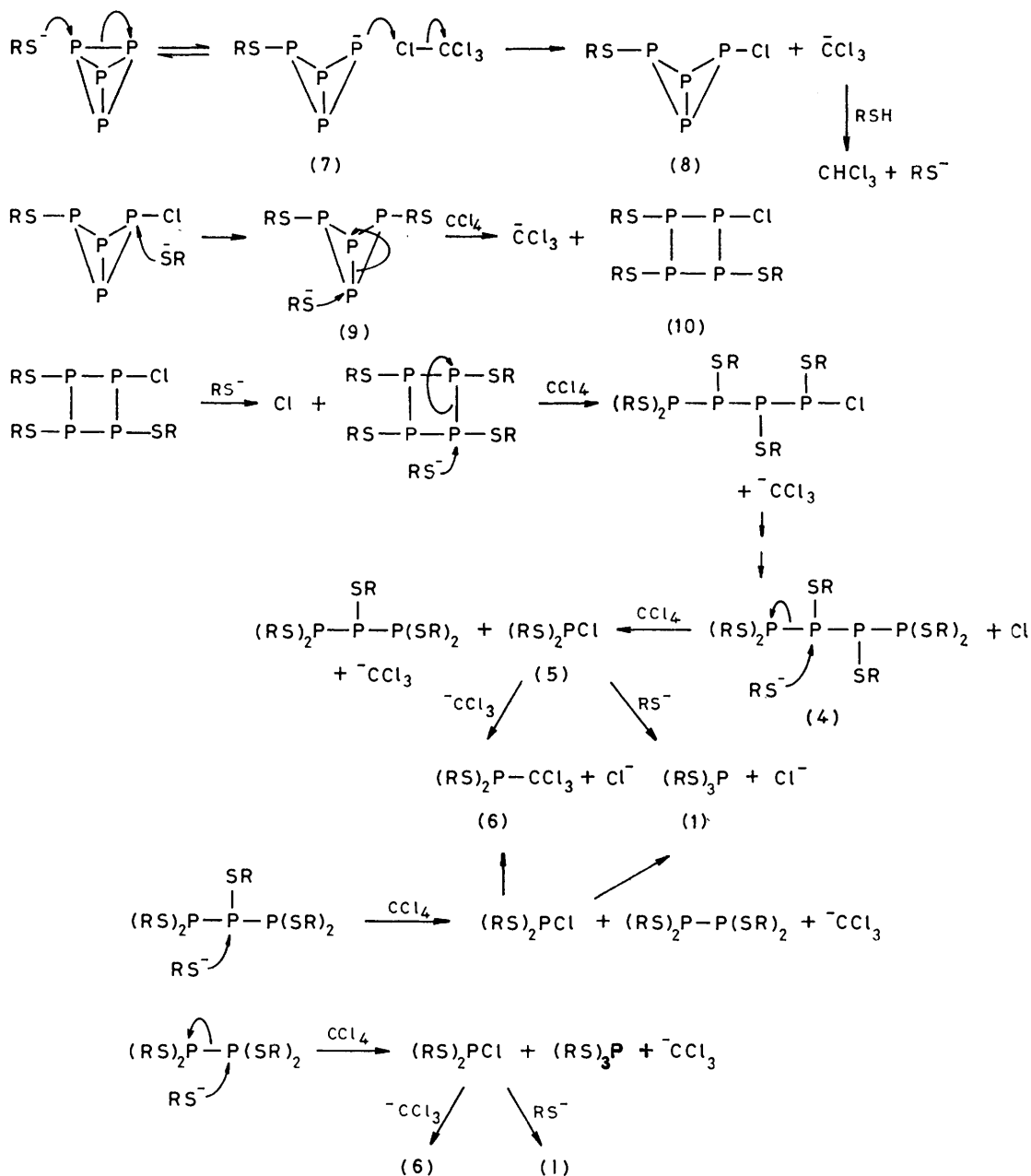
thiol occur exclusively. In the later stages, when the concentration of alkanethiolate is very low, displacement of chloride ion by the trichloromethyl carbanion competes more effectively.

The absence of intermediates in the analogous reaction with alkoxides [10] is explained by the reactions of chloro-intermediates with alcohol which proceed rapidly at room temperature. This generates acid which leads to the decomposition of trialkyl phosphite and the formation of dialkyl phosphite.

On the basis of these observations, a scheme for the overall reaction of elemental phosphorus with thiolate ions is proposed.

Chloride ion is rapidly displaced from (8) to give (9) which decomposes by attack on either a substituted or unsubstituted phosphorus atom. The former process would give rise to an intermediate which retains a strained three-membered ring, while the latter process would result in release of this ring strain. For this reason, we suggest that the alkanethiolate anion reacts at an unsubstituted phosphorus atom to give a four-membered ring in the anionic form, which eventually produces (10).

Although compounds of this type have not been reported in the literature to date, the closely related tetra-alkylcyclotetraphosphines are well known,[18] and have been postulated as intermediates in reactions of elemental phosphorus with nucleophiles; [1-3] and tetra-butylcyclotetraphosphine is the major product of the reaction of n-butylmagnesium bromide with phosphorus in the presence of n-butyl bromide.[5]

Attack by an alkanethiolate ion on (10) produces (4), which may react either at the mono- or the di-substituted phosphorus atom. Reaction at the terminal disubstituted atom would, by the appropriate series of processes, ultimately lead to a mixture of trialkyl phosphorotrithioite and dialkyl phosphorochloridodithioite in the ratio 3 : 1. Since the latter reacts further, a higher ratio would be expected. Thus the ratio of 2 : 1 observed using method 1 (Table 1), indicates that nucleophilic attack occurs at the phosphorus atom substituted by one alkanethiolate group, which is reasonable on steric grounds. The final step in the reaction scheme has already been discussed [equations (5)—(7)] and the route followed clearly depends on the reaction conditions.

Aromatic thiolates do not react with elemental phosphorus. This lack of reactivity can be explained by internal displacement of thiolate, which is a good leaving group, by phosphide ion in the initial intermediate (8; R = Ph). The competing reaction with tetrachloromethane is thereby essentially eliminated.

EXPERIMENTAL

Melting points were recorded on a hot-stage apparatus. N.m.r. spectra were recorded using a JEOL PS-100 spectrometer operating in the continuous-wave mode for ^{1}H spectra at 100 MHz and in the Fourier-transform mode for ^{31}P spectra at 40 MHz and ^{13}C spectra at 25 MHz. Internal

SiMe$_4$ was used as reference for the ^{1}H and ^{13}C spectra, and external 85% H$_3$PO$_4$ for the ^{31}P spectra. All shifts to high frequency of the standards were designated positive.

Product Analysis by G.L.C.—The reactions were carried out as described below and after a given period, usually 1 h, n-dodecane (3.25 g) was added as an internal standard for the g.l.c. analyses, which were performed at regular intervals. A Pye 104 chromatograph fitted with a flame-ionisation detector was used, with 1.5-m columns of internal diameter 4 mm. The following packings were used: SE 30 (3% silicone SE 30 on Chromosorb W AW-DMES, 60—80 mesh); QF 1 (10% QF 1 fluorosilicone oil on Chromosorb W, AW-DMCS, 60—80 mesh); and PESA [5% polyethylene glycol adipate (+2% phosphoric acid) on Chromosorb W AW-DMCS, 80—100 mesh]. Before use, each column was conditioned for 48 h at 5 °C below the maximum operating temperature. The composition of the reaction mixture at any given time was obtained from a calibration graph of the molar ratio of compound to standard against the ratio of the appropriate peak areas obtained by weighing the cut out peaks. The temperature and carrier-gas flow rate were varied so that analyses could be made under various experimental conditions. The compound of shortest retention time was measured first, and immediately after the peak had been recorded, the conditions appropriate for the next compound were set.

Each measurement was made three times and the mean value taken. The accuracy of the analyses depended on the response ratio of the particular product and the internal standard. For the phosphorus compounds, disulphides, and trithio-orthoformates, this varied between 1 : 1 and 1 : 2. For these compounds the errors, expressed as a percentage of the maximum yield, were *ca.* 1—5%. The response ratio for chloroform was low (*ca.* 1 : 20 for dibutyl ether and *ca.* 1 : 4 for n-dodecane) resulting in less accurate measurements.

Reaction of Phosphorus with Sodium Ethanethiolate and Carbon Tetrachloride in the Presence of Ethanethiol (Method 1).—(a) *Reaction products by ^{31}P n.m.r. spectroscopy.* Sodium ethanethiolate (2.52 g, 0.030 mol) was added slowly under nitrogen to a stirred solution of white phosphorus (0.62 g, 0.005 mol) prepared in the form of a fine sand, in carbon tetrachloride (300 ml) containing ethanethiol (3 ml, 0.041 mol), during 10 min at room temperature. The apparatus was sealed under nitrogen and the mixture stirred for 48 h. At this point a sample of the reaction mixture was analysed by g.l.c. [SE 30, 150 °C]. The major product was shown to be triethyl phosphorotrithioite, by comparison of its retention time with that of an authentic sample prepared by the method of Lippert and Reid,[19] and another product was shown to be diethyl phosphorochlorido-dithioite, also prepared by an independent method.[20]

A noise-decoupled spectrum of a sample of the filtered reaction mixture showed three lines, assigned to the following products: triethyl phosphorotrithioite, δ_P(CDCl$_3$) 114.1 [lit.,[15] δ_P(neat) 115.6]; diethyl phosphorochlorido-dithioite, δ_P(CDCl$_3$) 184.5 (lit.,[14] δ_P 186.2); and diethyl trichloromethylphosphonodithioite, δ_P(CDCl$_3$) 121.6.

The reaction mixture was filtered through Kieselguhr and the residue, after removal of solvent, was treated with hydrogen peroxide (3%) and acetic acid. The mixture was neutralised with ammonia, and the ethereal extract dried (MgSO$_4$). The ^{31}P n.m.r. spectrum showed two signals, a quintet due to diethyl trichloromethylphosphono-dithioate, δ_P 69.9 ($^3J_{PH}$ 13.2 Hz), and a septet due to triethyl

phosphorotrithioate, δ_P 63.9 ($^3J_{PH}$ 15.4 Hz) [lit.,[15] δ_P(neat) 61.3, $^3J_{PH}$ 15.3 Hz].

(b) *Reaction products by g.l.c. analysis.* The reaction was repeated under the same conditions using white phosphorus (0.83 g, 0.007 mol), and sodium ethanethiolate (3.37 g, 0.040 mol). After 1 h, n-dodecane (0.50 g) was added as an internal standard and the formation of products followed quantitatively by g.l.c. After 3 h, trichloromethane (0.01 mol) and triethyl phosphorotrithioite (0.001 mol) (1) were detected. After 24 h, trichloromethane (0.2 mol), (1) (0.008 mol), disulphide (0.004 mol), and tri-thioorthoformate (0.004 mol) were found. These yields did not change significantly on prolonged treatment. The theoretical yield of (1) is 5.73 g (0.027 mol), from which a maximum product yield of 37% was calculated.

Reaction of Phosphorus with Sodium Ethanethiolate and Carbon Tetrachloride in the Presence of Ethanethiol (Method 2).—A solution of white phosphorus (1.27 g, 0.010 mol) in carbon tetrachloride (400 ml) containing an excess of ethanethiol (15 ml, 0.203 mol) was allowed to react with sodium ethanethiolate (10.32 g, 0.123 mol) at room temperature. After 18 h, a sample of the reaction mixture was analysed by g.l.c. Chloroform [SE 30 (35 °C)], PEGA (50 °C)], diethyl disulphide [SE 30 (50 °C) and QF 1 (50 °C)], triethyl trithio-orthoformate [SE 30 (110 °C) and QF 1 (159 °C)], and triethyl phosphorotrithioite [SE 30 (150 °C), and QF 1 (159 °C)] were identified as products by comparison of their retention times on the first column with those of the authentic materials, and were confirmed as products by the same procedure on the second column. No diethyl phosphorochloridodithioite was detected, and a noise-decoupled [31]P n.m.r. spectrum of a filtered sample of the reaction mixture showed only one resonance, with δ_P 113.7, due to triethyl phosphorotrithioite [lit.,[15] δ_P(neat) 115.6].

Diethyl disulphide was isolated from the reaction mixture by preparative g.l.c., m/e 122 (M^+); triethyl trithio-orthoformate was isolated in the same way, m/e 196 (M^+); δ(CDCl$_3$) 1.28 (9 H, t, $^3J_{HH}$ 7.5 Hz, Me), 2.73 (6 H, q, CH$_2$), and 4.86 (1 H, s, CH). The separation was effected using a 1.6-m preparative column (15% QF 1 fluorosilicone oil on Chromosorb W AW-DMCS). A sample size of 30 μl was employed, the oven temperature was set at 110 °C, and was increased to 130 °C after the elution of diethyl disulphide. Samples of both compounds isolated for spectroscopic analysis were re-analysed by g.l.c., to confirm their purity. Authentic diethyl disulphide was obtained commercially, while authentic triethyl trithio-orthoformate was prepared from the condensation of ethanethiol with ethyl formate (72% yield), by the method of Holmberg. The product was a colourless oil, b.p. 78—80 °C at 0.4 mmHg (lit.,[21] 133 °C at 21 mmHg, 119 °C at 12 mmHg) (Found: C, 42.8; H, 8.3%. Calc. for C$_7$H$_{16}$S$_3$: C, 42.9; H, 8.2%); m/e 196 (M^+);

The reaction was repeated with white phosphorus (1.31 g, 0.011 mol), sodium ethanethiolate (10.64 g, 0.127 mol), ethanethiol (15 ml, 0.203 mol), and carbon tetrachloride (400 ml). After 18 h, the crude reaction mixture was filtered through Kieselguhr under nitrogen and the residue from rotary evaporation of the filtrate was divided into two equal portions. Reduced-pressure distillation of the first portion gave triethyl phosphorotrithioite (3.06 g, 68%), b.p. 84—86 °C at 0.4 mmHg (lit.,[19,22] b.p. 140—143 °C at 18 mmHg, 85 °C at 0.6 mmHg); m/e 214 (M^+); a noise-decoupled [31]P n.m.r. spectrum showed one resonance, δ_P(CDCl$_3$) 114.1 [lit.,[15] δ_P(neat) 115.6]; g.l.c. showed

slight contamination of the product by triethyl trithio-orthoformate. The second portion of crude material was treated with hydrogen peroxide (3%) and acetic acid, by the method of Lippert and Reid,[19] in order to oxidise the triethyl phosphorotrithioite to triethyl phosphorotrithioate. The mixture was neutralised with ammonia, the ether extracts were dried (MgSO$_4$), and the concentrated residue was distilled under reduced pressure to give triethyl phosphorotrithioate (6.59 g, 68%), b.p. 104—106 °C at 0.3 mmHg (lit.,[19] b.p. 165—168 °C at 15 mmHg). Authentic triethyl phosphorotrithioate for comparison was prepared by the oxidation of authentic triethyl phosphorotrithioite using the method of Lippert and Reid;[19] m/e 230 (M^+).

Control Experiment to Investigate the Effect of Sodium Ethanethiolate on Carbon Tetrachloride in the Absence of Phosphorus.—Sodium ethanethiolate (8.04 g, 0.096 mol) and ethanethiol (10 ml, 0.135 mol) were added to carbon tetrachloride (300 ml), and the mixture was stirred under nitrogen at room temperature. After 48 h, n-dodecane (3.21 g) was added as an internal standard and a sample of the reaction mixture was analysed by g.l.c. Chloroform [SE 30 (350 °C) and PEGA (50 °C)], diethyl disulphide [SE 30 (50 °C), QF 1 (69 °C)], and triethyl trithio-orthoformate [SE 30 (150 °C), QF 1 (159 °C)] were identified as products, by comparison of their retention times on the first column with those of the authentic materials and were confirmed as products by the same procedure, on the second column. The quantitative results are presented in Table 2.

TABLE 2

Reaction of sodium ethanethiolate with carbon tetrachloride and the corresponding thiol (RSH) at room temperature.

Thiol	Reaction time/d	Products *		
		CHCl$_3$	EtSSEt	CH(SEt)$_3$
EtSH	2	0.03	0.024	0.005
Bu^{n}SH	4	0.05	0.044	0.007

* Yields given in mol.

Reaction of Phosphorus with Sodium n-Butanethiolate and Carbon Tetrachloride in the Presence of n-Butanethiol (Method 2).—(a) *Identification of products.* Sodium n-butanethiolate (16.80 g, 0.150 mol) was added during 5 min under nitrogen to a stirred solution of white phosphorus (1.55 g, 0.013 mol) in carbon tetrachloride (400 ml) containing an excess of n-butanethiol (27 ml, 0.251 mol), at room temperature. After 15 min the apparatus was sealed under nitrogen and the mixture was stirred at room temperature for 48 h. At this point, a sample of the reaction mixture was analysed by g.l.c. Chloroform [SE 30 (35 °C) and PEGA (50 °C)], di-n-butyl disulphide [SE 30 (100 °C) and QF 1 (125 °C)], tri-n-butyl trithio-orthoformate [SE 30 (200 °C) and QF 1 (200 °C)], and tri-n-butyl phosphorotrithioite [SE 30 (200 °C) and QF 1 (200 °C)] were identified as products, by comparison of their retention times on the first column with those of the authentic materials and were confirmed as products, by the same procedure, on the second column. A noise-decoupled [31]P n.m.r. spectrum of a filtered sample of the reaction mixture showed one resonance, δ_P 116.3, due to tri-n-butyl phosphorotrithioite (lit.,[14] δ_P 116.1).

Authentic di-n-butyl disulphide was prepared for comparison (yield 69%), b.p. 106—107 °C at 14 mmHg (lit.,[23] b.p. 84 °C at 3 mmHg). Tri-n-butyl trithio-orthoformate

was prepared by the condensation of n-butanethiol with n-butyl formate, using the procedure of Holmberg (yield 56%); [21] b.p. 133—134 °C at 0.4 mmHg (lit.,[24] b.p. 147—148 °C at 1.0 mmHg). Tri-n-butyl phosphorotrithioite was prepared by the method of Lippert and Reid (yield 51%); [19] b.p. 134—136 °C at 0.4 mmHg (lit.,[19,25] b.p. 174—180 °C at 15 mmHg; 144 °C at 0.3 mmHg) (Found: C, 48.1; H, 9.2%. Calc. for $C_{12}H_{27}PS_3$: C, 48.3; H, 9.1%); m/e 298 (M^+).

(b) *Isolation of tri-n-butyl phosphorotrithioite.* The above reaction was repeated with white phosphorus (1.28 g, 0.010 mol), sodium n-butanethiolate (13.89 g, 0.124 mol), n-buthanethiol (25 ml, 0.232 mol), and carbon tetrachloride (400 ml). After 48 h, the crude reaction mixture was filtered through Kieselguhr under nitrogen and the concentrated residue distilled, after filtration under reduced pressure, to give tri-n-butyl phosphorotrithioite (8.68 g, 71%), b.p. 125—127 °C at 0.5 mmHg (lit.,[19] b.p. 174—180 °C at 15 mmHg); m/e 298 (M^+); a noise-decoupled ^{31}P n.m.r. spectrum showed one resonance, $\delta_P(CDCl_3)$ 116.7 (lit.,[14] δ_P 116.1); g.l.c. showed slight contamination of the product by tri-n-butyl trithio-orthoformate. A portion of the product (8.5 g, 0.029 mol) was then treated with hydrogen peroxide (3%) and acetic acid, by the method of Lippert and Reid,[19] to give tri-n-butyl phosphorotrithioate (5.21 g, 58%), b.p. 162—164 °C at 1.0 mmHg (lit.,[26] 166.5 °C at 1.0 1.0 mmHg) (Found: C, 45.7; H, 8.7%. Calc. for $C_{12}H_{27}$-OPS_3: C, 45.8; H, 8.7%); m/e 314 (M^+); a noise-decoupled ^{31}P n.m.r. spectrum showed one resonance, $\delta_P(CDCl_3)$ 63.8 (lit.,[26] δ_P +62.7); $\delta(CCl_4)$ 2.98 (6 H, dt, $^3J_{PH}$ 15.4, $^3J_{HH}$ 6.9 Hz, SCH$_2$) [lit.,[15] $\delta(CCl_4)$ 2.94 ($^3J_{PH}$ 15.2, $^3J_{HH}$ 7.0 Hz)]. Authentic tri-n-butyl phosphoro-trithiolate was prepared, for comparison from authentic tri-n-butyl phosphorotrithioite by the method of Lippert and Reid (yield 62%); [19] b.p. 143—144 °C at 0.4 mmHg (lit.,[27] b.p. 166.5 °C at 1.0 mmHg) (Found: C, 45.9; H, 8.9%. Calc. for $C_{12}H_{27}OPS_3$: C, 45.8; H, 8.7%); m/e 314 (M^+).

Control Experiment to Investigate the Combined Effect of Sodium n-Butanethiolate and n-Butanethiol on Carbon Tetrachloride, in the Absence of Phosphorus.—Sodium n-butanethiolate (11.49 g, 0.103 mol) and n-butanethiol (10 ml, 0.093 mol) were added to carbon tetrachloride (300 ml), and the mixture was stirred under nitrogen at room temperature. After 4 d, n-dodecane (3.21 g) was added as an internal standard and a sample of the reaction mixture was analysed by g.l.c. Chloroform [SE 30 (35 °C), PEGA (50 °C)], di-n-butyl disulphide [SE 30 (100 °C), QF 1 (125 °C)], and tri-n-butyl trithio-orthoformate [SE 30 (200 °C), QF 1 (200 °C)] were identified as products, by comparison of their retention times on the first column with those of the authentic materials and were confirmed as products, by the same procedure, on the second column. The quantitative results are presented in Table 2.

Analysis of Residues.—The solids which were deposited from the reactions of elemental phosphorus with sodium alkanethiolates were collected on sintered-glass crucibles, washed with carbon tetrachloride, and dried to constant weight by vacuum desiccation (0.1 mmHg) at room temperature. The residues were found to be involatile, water-soluble solids, with a sodium chloride content of >85% in each case. The residue from the reaction of elemental phosphorus with sodium n-butanethiolate contained 10% of the original phosphorus. An undecoupled ^{31}P n.m.r. spectrum of a sample of the same residue, in D_2O, showed a 1 : 1 doublet due to phosphite anion, δ_P 4.7 ($^1J_{PH}$ 662 Hz) and a singlet due to phosphate anion, δ_P 0.1, the former signal being by far the more intense.

Treatment of Phosphorus with Sodium Benzenethiolate and Carbon Tetrachloride, in the Presence of Benzenethiol (Method 2). Sodium benzenethiolate (16.23 g, 0.123 mol) was added during 5 min under nitrogen at room temperature) to a stirred solution of white phosphorus (1.27 g, 0.010 mol) in an excess of carbon tetrachloride (300 ml) containing benzenethiol (6.76 g, 0.061 mol). Samples of the mixture were analysed by g.l.c. [SE 30 (35 °C), QF 1 (220 °C)] after 2, 3, 5, and 24 h, and after 1 week, but no chloroform, triphenyl phosphorotrithioite, or other product was detected. Samples of authentic triphenyl phosphorotrithioite, in carbon tetrachloride, were passed through the QF 1 column at 220 °C to give the authentic retention time and to prove the stability of the compound on the column at that temperature. The authentic material was prepared from phosphorus trichloride and benzenethiol by the method of Michaelis and Linke (yield 56%); [28] m.p. 71—73 °C (from ethanol) (lit.,[28] m.p. 76—77 °C) (Found: C, 60.5; H, 4.3%. Calc. for $C_{16}H_{15}PS_3$: C, 60.3; H, 4.2%); m/e 358 (M^+); a noise-decoupled ^{31}P n.m.r. spectrum showed one resonance, $\delta_P(CDCl_3)$ +132.0 (lit.,[26,29] δ_P 130.0, 133.3).

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