573. *The Reactivity of Organophosphorus Compounds. Part XIII.*[1] *Radical-chain Transfer Reactions of Triethyl Phosphite: a New Phosphorothiolate Synthesis.*

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Re-investigation of the reaction between bromotrichloromethane and triethyl phosphite has revealed the formation of carbon tetrachloride as a main product; and reaction in the presence of butane-1-thiol has been shown to give *S*-butyl diethyl phosphorothioate in excellent yield. These and related reactions are discussed in terms of a radical-chain mechanism.

Radical-induced reduction of alkanethiols to alkanes by trialkyl phosphites was first reported by Hoffmann and his co-workers,[2] and the mechanism of the reaction was later investigated by Walling and Rabinowitz.[3] The latter workers established that the reduction proceeded by a chain mechanism in which thiyl radicals (RS·), formed by homolysis of the thiol, reacted with the phosphite to give an intermediate thiophosphoranyl radical (I) which then decomposed to give the corresponding trialkyl phosphorothionate and chain-carrying alkyl radical, thus:

$$\text{Scheme A:}\quad \begin{aligned} \text{RSH} &\longrightarrow \text{RS}\cdot \\ \text{RS}\cdot + (\text{EtO})_3\text{P} &\longrightarrow (\text{EtO})_3\text{P(SR)}\cdot\ \text{(I)} \\ (\text{EtO})_3\text{P(SR)}\cdot &\longrightarrow (\text{EtO})_3\text{PS} + \text{R}\cdot \qquad \text{(i} \\ \text{R}\cdot + \text{RSH} &\longrightarrow \text{RH} + \text{RS}\cdot \end{aligned}$$

It has also been shown that carbon tetrachloride reacts with trialkyl phosphite by a homolytic route,[4] although in this case the chain reaction is propagated in a different fashion (scheme B),[5] whereby the intermediate trichloromethylphosphoranyl radical (II) reacts by chain transference with carbon tetrachloride rather than by decomposition as in (i).

$$\text{Scheme B:}\quad \begin{aligned} \text{CCl}_4 &\xrightarrow{h\nu} \cdot\text{CCl}_3 + \text{Cl}\cdot \\ \cdot\text{CCl}_3 + (\text{EtO})_3\text{P} &\longrightarrow (\text{EtO}_3)\text{P(CCl}_3)\cdot\ \text{(II)} \\ (\text{EtO})_3\text{P(CCl}_3)\cdot + \text{CCl}_4 &\longrightarrow [(\text{EtO})_3\text{P}\cdot\text{CCl}_3]^+\text{Cl}^-\ \text{(III)} + \cdot\text{CCl}_3 \qquad \text{(ii} \\ [(\text{EtO})_3\text{P}\cdot\text{CCl}_3]^+\text{Cl}^- &\longrightarrow (\text{EtO})_2\text{P(O)}\cdot\text{CCl}_3\ \text{(IV)} + \text{EtCl} \end{aligned}$$

Cadogan and Foster [5] observed, however, that, when carbon tetrachloride and butane-1-thiol were allowed to compete in reaction with triethyl phosphite, *S*-butyl diethyl phosphorothioate (V; R = Bu) was isolated in addition to products corresponding to the simultaneous operation of schemes A and B, *i.e.*, triethyl phosphorothionate and diethyl trichloromethylphosphonate (IV). The presence of the phosphorothiolate (V) was rationalised as follows (scheme C):

$$\text{Scheme C:}\quad \begin{aligned} \text{RS}\cdot + (\text{EtO})_3\text{P} &\longrightarrow (\text{EtO})_3\text{P(SR)}\cdot\ \text{(I)} \\ (\text{EtO})_3\text{P(SR)}\cdot + \text{CCl}_4 &\longrightarrow [(\text{EtO})_3\text{P}\cdot\text{SR}]^+\text{Cl}^- + \cdot\text{CCl}_3 \qquad \text{(iii)} \\ [(\text{EtO})_3\text{P}\cdot\text{SR}]^+\text{Cl}^- &\longrightarrow (\text{EtO})_2\text{P(O)}\cdot\text{SR}\ \text{(V)} + \text{EtCl} \end{aligned}$$

i.e., the intermediate thiophosphoranyl radical (I), which in the absence of carbon tetrachloride decomposes to triethyl phosphorothionate [reaction (i)], is assumed to react by

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[1] Part XII, Bunyan and Cadogan, *J.*, 1962, 1304.

[2] Hoffmann, Ess, Simmons, and Hanzel, *J. Amer. Chem. Soc.*, 1956, **78**, 6414.

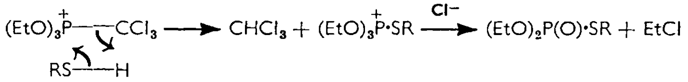
[3] Walling and Rabinowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 1243.

[4] (*a*) Kamai and Kharrasova, *Zhur. obschei Khim.*, 1957, **27**, 953; (*b*) Griffin, *Chem. and Ind.*, 1958, 415.

[5] Cadogan and Foster, *J.*, 1961, 3071.

abstraction [reaction (iii)] of chlorine, thus displacing a trichloromethyl radical in a chain-transfer step. An alternative explanation of these results involves thiol solvolysis of the intermediate trichloromethylphosphonium chloride (III), formed as in reaction (ii), thus:

Scheme D:



The experiments described in this paper were designed to distinguish between the possible paths C and D for the reaction of triethyl phosphite with a mixture of butane-1-thiol and polyhalogenomethanes. If the reaction proceeds by competition as in scheme C it follows that substitution of a more reactive chain transfer agent, *e.g.*, bromotrichloromethane,[6] for carbon tetrachloride should favour the displacement reaction (iii), with ultimate formation of phosphorothiolate (V), rather than the decomposition (i) to give thionate. On the other hand an increase in the chain-transfer constant of the polyhalogenomethane would also favour formation of diethyl trichloromethylphosphonate [reaction (ii)]. Under scheme C, however, it seemed probable that variation of the chain-transfer agent and also of the relative proportions of reactants might lead to the exclusive formation of one or other of the three possible products.

Competition reactions between triethyl phosphite (1 mol.*), butane-1-thiol, and polyhalogenomethanes.

	Reactants		Products (%) †				
Exp. no.	CXY_3 (mol.)	BuSH (mol.)	Total wt. (g.)	$(EtO)_3PS$	$(EtO)_2P(O)\cdot CCl_3$	$(EtO)_2P(O)\cdot SBu$	$(EtO)_3P$ accounted for (%)
1	$BrCCl_3$ 2	2	5·5	0	17	83	94
2	$BrCCl_3$ 3	2	5·8	1	31	68	99
3	$BrCCl_3$ 4	2	5·4	1	33	66	93
4	$BrCCl_3$ 2	4	5·4	0	7	93	95
5	$BrCCl_3$ 1·2	4	5·2	5	4	91	92
6	CCl_4 2	2	5·5	20	20	60	96
7	CCl_4 2	4	5·4	26	13	61	97
8	$CHCl_3$ 2	4	4·7	99·5	0·5 ‡	0	95

* 4·15 g. † Expressed as molar % of total weight. ‡ This fraction is unidentified because it had retention time equal to that of $(EtO)_2P(O)\cdot CHCl_2$.

The results, summarised in the Table, of the relevant experiments involving triethyl phosphite, butane-1-thiol, and polyhalogenomethanes, are considered to support the operation of scheme C. Thus, appreciable yields of triethyl phosphorothionate occur only with carbon tetrachloride and chloroform, which is in accord with their lower reactivity as chain-transfer agents, since it is only in these solvents that the intermediate thiophosphoranyl radical has a life sufficiently long to allow it to decompose to thionate. Further, this is the sole reaction which occurs with chloroform and butan-1-thiol, thus reflecting the considerably reduced reactivity of chloroform as a chain transfer agent [$k(CCl_4)/k(CHCl_3) = 180$ for styrene [7]]. In view of Griffin's report [8] that chloroform reacts homolytically with triethyl phosphite in the presence of dibenzoyl peroxide it is surprising that some participation of chloroform does not occur in the reaction carried out in the presence of butane-1-thiol. The nature of the reaction, if any, between chloroform and triethyl phosphite and that of the latter with dibenzoyl peroxide are therefore being re-investigated.

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[6] Walling, " Free Radicals in Solution," J. Wiley, N.Y., 1959.

[7] Gregg and Mayo, *J. Amer. Chem. Soc.*, 1948, **70**, 2373; 1953, **75**, 3530.

[8] Griffin, Amer. Chem. Soc. 135th Meeting, 1959, Abs., p. 69-O.

In further accord with scheme C the highest yields of phosphorothiolate (V) are obtained from experiments involving bromotrichloromethane. For a constant ratio of thiol to phosphite, an increase in concentration of bromotrichloromethane leads to an increase in diethyl trichloromethylphosphonate, *i.e.*, the possibility of the occurrence of reaction (ii) is increased. The use (experiments 4 and 5) of a low proportion of bromotrichloromethane with a high proportion of thiol favours the formation of high yields of phosphorothiolate and it is noteworthy that reduction of the proportion of bromotrichloromethane in the reaction mixture leads to the reappearance of triethyl phosphorothionate. In addition to the phosphorus esters formed in the above reactions, good yields of chloroform were also obtained. This is also in accord with scheme C which in consequence can be extended as follows:

$$(EtO)_3P(SR)\cdot + CCl_4 \longrightarrow [(EtO)_3P\cdot SR]^+Cl^- + \cdot CCl_3$$

$$\cdot CCl_3 + RSH \longrightarrow CHCl_3 + RS\cdot$$

$$RS\cdot + (EtO)_3P \longrightarrow (EtO)_3P(SR)\cdot\text{, etc.}$$

The alternative solvolytic mechanism (scheme D) does not account for these experimental observations since its operation should lead to the same ratio of thiolate to trichloromethylphosphonate, for a given concentration of reactants, for both carbon tetrachloride and bromotrichloromethane (compare experiments 1 and 4 with 6 and 7).

Similar experiments have been carried out with dibutyl disulphide in the place of butane-1-thiol. Disulphides are known to be chain-transfer agents but are less reactive than the corresponding thiols.[6] Jacobson, Harvey, and Jensen have shown[9] that disulphides react with trialkyl phosphites in what is generally believed to be a heterolytic

$$(RO)_3\overset{\curvearrowright}{P}\quad RS\overset{\curvearrowright}{\text{——}}SR \longrightarrow [RO)_3P\cdot SR]^+RS^- \longrightarrow (RO_2)P(O)\cdot SR + RSR \quad . \ . \ . \ . \ . \quad \text{(iv)}$$

process [reaction (iv)].[10] Walling and Rabinowitz[3] have shown, however, that the radical-induced reaction of disulphide with triethyl phosphite proceeds as follows:

$$RS\cdot SR \longrightarrow 2RS\cdot$$

$$(EtO)_3P + RS\cdot \longrightarrow (EtO)_3P(SR)\cdot \longrightarrow (EtO)_3PS + R\cdot$$

$$R\cdot + RS\cdot SR \longrightarrow RSR + RS\cdot$$

We have confirmed that this process occurs under the influence of ultraviolet radiation, whereas it does not proceed to a significant extent in the presence of dibenzoyl peroxide, and that the competition between dibutyl disulphide, triethyl phosphite, and bromotrichloromethane proceeds without participation of the disulphide, giving high-boiling products, one of which is formulated as tetraethyl dichloromethylenediphosphonate (VIII). This is anomalous in view of an earlier report[4b] that bromotrichloromethane and triethyl phosphite gave a good yield (88%) of diethyl trichloromethylphosphonate. A re-investigation of this reaction has now revealed the formation of carbon tetrachloride (>50%) and high-boiling products, again including one formulated as tetraethyl dichloromethylenediphosphonate (VIII), in addition to the previously reported ethyl bromide and diethyl trichloromethylphosphonate which was obtained in yields varying (35—55%) according to experimental conditions. The appearance of carbon tetrachloride is attributed to a hitherto undetected chain-transfer step in which a trichloromethyl radical is assumed to abstract a chlorine atom from the first-formed diethyl trichloromethylphosphonate to give a new radical (VI). This can now continue the chain in either or both of two ways, (*a*) by abstraction of a bromine atom from bromotrichloromethane [reaction (vi)] or (*b*) by

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[9] Jacobsen, Harvey, and Jensen, *J. Amer. Chem. Soc.*, 1955, **77**, 6064.

[10] For a review see Cadogan, *Quart. Rev.*, 1962, **16**, 208.

reaction with triethyl phosphite with subsequent reaction of the resulting phosphoranyl radical with bromotrichloromethane [reaction (vii)] in a variation of scheme B:

$$\cdot CCl_3 + (EtO)_3P \longrightarrow (EtO)_3P(\cdot CCl_3)\cdot \xrightarrow{BrCCl_3} [(EtO)_3P\cdot CCl_3]^+Br^- + \cdot CCl_3$$

$$[(EtO)_3P\cdot CCl_3]^+Br^- \longrightarrow (EtO)_2P(O)\cdot CCl_3 + EtBr$$

$$\cdot CCl_3 + (EtO)_2P(O)\cdot CCl_3 \longrightarrow (EtO)_2P(O)\cdot CCl_2\cdot \text{ (VI)} + CCl_4 \quad \text{. . . . . (v)}$$

$$(EtO)_2P(O)\cdot CCl_2\cdot + BrCCl_3 \longrightarrow (EtO)_2P(O)\cdot CCl_2Br \text{ (VII)} + \cdot CCl_3 \quad \text{. . . . . (vi)}$$

$$(EtO)_2P(O)\cdot CCl_2\cdot + (EtO)_3P \longrightarrow (EtO)_2P(O)\cdot CCl_2\cdot\dot{P}(OEt)_3$$

$$(EtO)_2P(O)\cdot CCl_2\cdot\dot{P}(OEt)_3 \xrightarrow[\text{(vii)}]{BrCCl_3} [(EtO)_2P(O)\cdot CCl_2\cdot P(OEt)_3]^+Br^- \longrightarrow (EtO)_2P(O)\cdot CCl_2\cdot P(O)(OEt)_2 \text{ (VIII)}$$

The possible products (VII) and (VIII) can similarly enter into subsequent reactions with trichloromethyl radicals and bromotrichloromethane, thus giving rise to complex products, as observed.

This rationalisation is supported by the observations that the reaction between bromotrichloromethane and triethyl phosphite is preceded by an induction period, whereas the addition of diethyl trichloromethylphosphonate to a mixture of these reactants causes an immediate and vigorous reaction with the formation of a much higher yield of carbon tetrachloride (0·71; cf. 0·48 mole/mole of phosphite).

EXPERIMENTAL

Gas–liquid chromatography was carried out with a Perkin–Elmer " Fraktometer," model 116, fitted with a high-sensitivity dual thermal-conductivity detector which normally gives a linear response. This was tested with mixtures of known composition wherever possible and found to be satisfactory. Analyses of the phosphorus ester reaction products were carried out with both a 1-m. column packed with " Apiezon L " on Celite (545) (1-m. Q. column) at 168°, and a 2-m. column packed with silicone oil on Celite (545) (2 m. C. column) at 191°. Nitrogen was the carrier gas. Lower-boiling materials were first removed from the reaction mixtures by distillation under reduced pressure, and then subjected to analysis with both a 2-m. column packed with " Apiezon L " on Celite (545) at 76°, and with a 2-m. column packed with didecyl phthalate on Celite 545 at 70°. Hydrogen was the carrier gas. All results are quoted as percentages by weight of the total product, unless otherwise stated.

Ultraviolet irradiations were performed under nitrogen, the reactants being contained in the annular space between a Pyrex tube (diameter 50 mm.) and a quartz tube (diameter 40 mm.). An " Hanovia " 755/63 low-pressure discharge tube (*ca.* 80% of radiation at 2537 Å) placed in the central tube acted as a low-intensity source. All irradiations were carried out at *ca.* 25°, with reactants previously degassed by passing nitrogen through them.

Triethyl phosphite fractionally distilled from sodium had b. p. 60°/15 mm., carbon tetrachloride had b. p. 76°, and bromotrichloromethane had b. p. 105°. Butane-1-thiol (Light and Co.) exhibited only one peak when subjected to gas–liquid chromatography and was used without further purification.

Di-n-butyl Disulphide.—Iodine (38 g.) in ethanol (200 ml.) was added slowly with stirring to a solution of butane-1-thiol (27 g.) in ethanol (300 ml.) and sodium (6·9 g.). After removal of the solvent by distillation, the residue was poured into water and extracted with ether, and the extract washed with 5% aqueous sodium hydroxide solution, dried ($CaSO_4$), and distilled, yielding di-n-butyl disulphide (21·6 g., 80%), b. p. 39—40°/0·07 mm.

Diethyl Dichloromethylphosphonate.—The dichloromethyl trichlorophosphonium chloroaluminate complex produced by the method of Kinnear and Perren[11] was subjected to ethanolysis in methylene chloride as described by Hoffmann, Simmons, and Glunz,[12] yielding *diethyl dichloromethylphosphonate* as a colourless liquid (23%), b. p. 82°/0·2 mm., n_D^{25} 1·4513 (Found: C, 27·4; H, 4·8. $C_5H_{11}Cl_2O_3P$ requires C, 27·2; H, 5·0%).

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[11] Kinnear and Perren, *J.*, 1952, 3437.

[12] Hoffmann, Simmons, and Glunz, *J. Amer. Chem. Soc.*, 1957, **79**, 3570.

Diethyl trichloromethylphosphonate[5] had b. p. 128°/14 mm., n_D^{20} 1·4620. Triethyl phosphorothionate[13] had b. p. 95°/12 mm., n_D^{20} 1·4480.

Reaction of Triethyl Phosphite with Bromotrichloromethane.—(i) Triethyl phosphite (4·15 g., 0·025 mol.) was added to bromotrichloromethane (9·9 g., 0·05 mol.), and after a short induction period (*ca.* 3—5 min.) a vigorous reaction occurred, which caused the mixture to boil and become red. When the reaction had subsided, the mixture was boiled under reflux for 1 hr., and after removal of the lower-boiling material [fraction (i); 4·45 g.], the residue (4·0 g.), which showed only one peak corresponding to diethyl trichloromethylphosphonate on gas–liquid chromatographic analysis (1-m. Q. column), was subjected to distillation to give the following fractions: (*a*) diethyl trichloromethylphosphonate (1·85 g.), b. p. 64°/0·03 mm., n_D^{25} 1·4545, identified by comparison of the infrared spectrum with that of an authentic specimen, (*b*) an oil (1·45 g.), b. p. 86—110°/0·04 mm., and (*c*) a residue (0·7 g.), which appeared to be partly a hygroscopic white solid, insoluble in organic solvents. Fraction (*b*) was further subjected to fractional micro-distillation and two main fractions were collected: (1) an oil, formulated as tetramethyl dichloromethylenediphosphonate, b. p. 88—92°/0·04 mm. (Found: C, 30·5; H, 6·4. Calc. for $C_9H_{20}Cl_2O_6P_2$: C, 30·3; H, 5·6%), and (2) an oil, b. p. 106—108°/0·04 mm. (Found: C, 31·8; H, 6·5%).

Analysis of the lower-boiling material [fraction (i)] showed it to consist of the following components, with quantities and relative retention times given in parentheses: ethyl bromide (0·0065 mol.; 1·00), chloroform (trace; 2·11), carbon tetrachloride (0·012 mol.; 2·74) and bromotrichloromethane (0·0095 mol.; 6·27). A considerable amount of ethyl bromide (b. p. 38°) was probably lost during the reaction and subsequent working-up.

(ii) By addition of triethyl phosphite (4·15 g.) dropwise during 20 min. to bromotrichloromethane (9·9 g.) boiling under reflux for 1 hr., and working-up as described above, there were obtained from the residue (4·4 g.): (*a*) diethyl trichloromethylphosphonate (2·9 g.), b. p. 68°/0·04 mm., n_D^{25} 1·4600, (*b*) an oil (0·9 g.), b. p. 80—110°/0·04 mm., and (*c*) a residue (0·6 g.). Analysis of the lower-boiling material [fraction (i)] showed ethyl bromide, carbon tetrachloride, and bromotrichloromethane in the molar ratio 0·16 : 0·43 : 0·41.

(iii) Triethyl phosphite (4·15 g., 0·025 mol.) was added to a mixture of bromotrichloromethane (10·9 g., 0·055 mol.) and diethyl trichloromethylphosphonate (6·4 g., 0·025 mol.); an immediate vigorous reaction ensued. When the reaction had subsided, the mixture was boiled under reflux for 1 hr., and after working-up as above there were obtained from the residue (9·7 g.): (*a*) diethyl trichloromethylphosphonate (7·0 g.), b. p. 64°/0·03 mm., n_D^{25} 1·4584, (*b*) an oil (1·7 g.), b. p. 70—110°/0·04 mm., and (*c*) a residue (1·0 g.). Fraction (*b*) was further subjected to fractional distillation and two main fractions were collected: (1) an oil, b. p. 88—92°/0·04 mm. (Found: C, 31·3; H, 6·3%), (2) an oil, b. p. 108—110°/0·04 mm. (Found: C, 28·4; H, 5·5%). Analysis of the lower-boiling material [fraction (i), 5·5 g.] showed the presence of ethyl bromide (0·0056 mol.), chloroform (trace), carbon tetrachloride (0·0176 mol.), and bromotrichloromethane (0·0113 mol.).

*Reaction of Triethyl Phosphite with Bromotrichloromethane and Butane-*1*-thiol.*—A series of reactions was carried out in which triethyl phosphite (4·15 g., 0·025 mol.) was added to various mixtures of bromotrichloromethane and butane-1-thiol shown in the Table. The mixtures were allowed to heat and cool spontaneously for 1 hr. and then were boiled under reflux for 1 hr. further. After removal of the lower-boiling products [fraction (i)] the residue were analysed by gas–liquid chromatography and found to contain triethyl phosphorothionate, diethyl trichloromethylphosphonate, and *S*-butyl diethyl phosphorothioate in the percentages shown in the Table.

The columns used and relevant relative retention times were as follows: phosphorothionate (1-m.Q. and 2-m.C., 1), trichloromethylphosphonate (1-m.Q., 2·9; 2-m.C., 1·75), *S*-butyl phosphorothioate (1-m.Q., 5·05; 2-m.C, 2·52). Distillation showed that in no case did more than 4% of the product have b. p. >75°/0·04 mm., whilst fractionation of the product of expt. 4 readily yielded pure *S*-butyl diethyl phosphorothioate (4·2 g., 75%), b. p. 74°/0·04 mm., n_D^{25} 1·4549 [Walling and Rabinowitz[3] report b. p. 102·5—103°/1·5 mm., n_D^{25} 1·4561]. Analysis of the lower-boiling products [fraction (i)] showed them to contain ethyl bromide, chloroform, butane-1-thiol, and bromotrichloromethane only. No carbon tetrachloride was detected. In expt. 5 the molar ratio of these components was 0·07 : 0·17 : 0·37 : 0·39, whilst that in

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[13] Cadogan and Moulden, *J.*, 1961, 5524.

expt. 3 was 0·02 : 0·12 : 0·80 : 0·06. In general, a crystal of dibenzoyl peroxide was added to assist initiation of the reaction but this was superfluous since the reactions readily proceeded without this.

In a control experiment bromotrichloromethane (9·9 g.), butane-1-thiol (18 g.) and diethyl trichloromethylphosphonate (12·8 g.) containing a trace of benzoyl peroxide were boiled under reflux for 2 hr. No detectable reaction occurred.

*Reaction of Triethyl Phosphite with Carbon Tetrachloride and Butane-*1-*thiol.*—The reaction was carried out as described above, with carbon tetrachloride in the place of bromotrichloromethane. The results are summarised in the Table.

*Reaction of Triethyl Phosphite with Chloroform and Butane-*1-*thiol.*—The addition of triethyl phosphite (4·15 g.) containing a trace of benzoyl peroxide to a mixture of chloroform (6·0 g., 0·05 mol.) and butane-1-thiol (9 g., 0·1 mol.) caused the temperature of the mixture to rise to *ca.* 60° during 30 min. The mixture was boiled under reflux for a further 90 min. and the solvent removed; the residue (4·7 g.) was shown to be triethyl phosphorothionate (95%), n_D^{25} 1·4412, by comparison of the infrared spectrum with that of an authentic specimen (n_D^{25} 1·4450). Gas–liquid chromatography revealed a trace (*ca.* 0·5%) of diethyl trichloromethylphosphonate or diethyl dichloromethylphosphonate, which could not themselves be separated.

Reaction of Triethyl Phosphite with Di-n-butyl Disulphide.—(i) *In the presence of benzoyl peroxide.* Benzoyl peroxide (0·24 g., 0·001 mol.) was added to a mixture of triethyl phosphite (4·15 g., 0·025 mol.) and di-n-butyl disulphide (4·46 g., 0·025 mol.) under nitrogen at 90°, and the temperature was maintained for 18 hr. Analysis of the product by gas–liquid chromatography indicated the presence of small amounts of triethyl phosphate, ethyl benzoate, triethyl phosphorothionate, and *S*-butyl phosphorothioate, in addition to large quantities of triethyl phosphite and di-n-butyl disulphide.

(ii) *In ultraviolet light* (cf. ref. 3). Triethyl phosphite (4·15 g.) and di-n-butyl disulphide (4·46 g.) were irradiated until samples withdrawn at regular intervals and subjected to analysis contained no triethyl phosphite (72 hr.). The main products were triethyl phosphorothionate and n-butyl sulphide. Some unchanged di-n-butyl disulphide remained, however, and a small quantity of *S*-butyl diethyl phosphorothioate was also detected.

(iii) *In the presence of bromotrichloromethane.* Triethyl phosphite (4·15 g.) was added to bromotrichloromethane (9·9 g., 0·05 mol.) and dibutyl disulphide (4·46 g.). After a short induction period (5—7 min.), a vigorous reaction occurred which caused the mixture to boil and become bright yellow. When the reaction had subsided, the mixture was boiled under reflux for 1 hr., and after the lower-boiling material [fraction (i)] had been removed by distillation, the residue (8·45 g.), which showed only one peak (di-n-butyl disulphide) on gas–liquid chromatography and contained no detectable amount of diethyl trichloromethylphosphonate, was distilled, and yielded the fractions: (*a*) impure di-n-butyl disulphide (4·4 g.), b. p. 42°/0·03 mm., identified by comparison of the infrared spectrum with that of an authentic specimen, (*b*) a yellow-red oil (3·00 g.), b. p. 64—120°/0·03 mm., and (*c*) a residue (1·00 g.). Fraction (*b*) which showed only a slight reaction for sulphur but a strong halogen reaction, was further subjected to fractional distillation and two major fractions of small boiling range were collected [the first was identified by infrared spectral correlations and elemental analysis], *viz.*: (*a*) tetraethyl dichloromethylenediphosphonate, b. p. 82—86°/0·03 mm. (Found: C, 30·3; H, 5·7. Calc. for $C_9H_{20}Cl_2O_6P_2$: C, 30·3; H, 5·6%); and (*b*) an oil, p. b 102—106°/0·03 mm. (Found: C, 34·15; H, 6·9%). In an earlier fraction, b. p. 65—75°/0·03 mm., a trace of *S*-butyl diethyl phosphorothioate was detected by gas–liquid chromatography. Analysis of the lower-boiling material [fraction (i)] showed it to consist of carbon tetrachloride and bromotrichloromethane in the molar ratio 0·35 : 0·65, together with traces of ethyl bromide and chloroform.

In a control experiment, bromotrichloromethane (9·9 g.) and di-n-butyl disulphide (4·46 g.) containing a trace of benzoyl peroxide were boiled under reflux for 1 hr. after being kept overnight at room temperature. No detectable reaction occurred.

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