**1104.** *The Reactivity of Organophosphorus Compounds. Part XVII.*[1] *A Novel Oxidation of Some Tervalent Compounds: Reduction of Carbon Tetrachloride to Chloroform by Trialkyl Phosphites.*
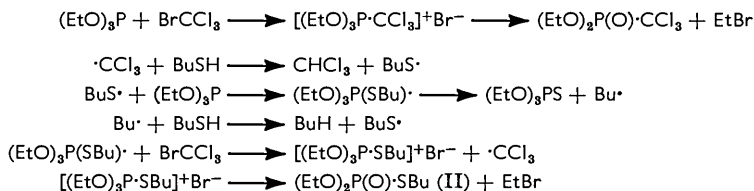
By A. J. Burn and J. I. G. Cadogan.

Trialkyl phosphites, $(RO)_3P$, react with alcohols, $R'OH$, in the presence of carbon tetrachloride or bromotrichloromethane to give the corresponding trialkyl phosphate, chloroform, and an alkyl halide (when $R = R'$). Small quantities of the dialkyl trichloromethylphosphonate are also formed under some conditions. Variation of the phosphite and alcohol ($R \neq R'$) leads to mixtures of phosphates, but when $R' = Bu^t$, oxidation to the phosphate $(RO)_3PO$ occurs. The results are discussed in terms of solvolysis of intermediate quasiphosphonium ions of the type $[(RO)_3P\cdot CCl_3]^+$. Similar reactions involving triphenylphosphine and triphenyl phosphite with ethanol and polyhalogenomethanes have been investigated.
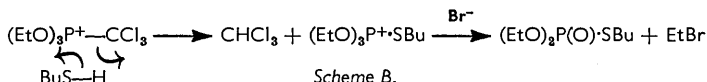
REACTIONS between trialkyl phosphites and polyhalogenomethanes were first reported by Kamai and his co-workers,[2] *e.g.*,

$$(EtO)_3P + BrCCl_3 \longrightarrow (EtO)_2P(O)\cdot CCl_3 \text{ (I)} + EtBr$$
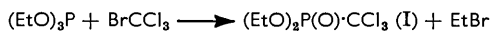
and it is now generally accepted that radical-chain processes are involved in this type of reaction.[3,4] If the above reaction is carried out in the presence of butane-1-thiol, high yields of *S*-butyl diethyl phosphorothiolate (II) and chloroform, with small amounts of the trichloromethylphosphonate (I) and triethyl phosphorothionate are obtained, by way of competing radical-chain processes (Scheme A) rather than by a solvolytic mechanism (Scheme B).[3,5]

$$(EtO)_3P + BrCCl_3 \longrightarrow [(EtO)_3P\cdot CCl_3]^+Br^- \longrightarrow (EtO)_2P(O)\cdot CCl_3 + EtBr$$

$$\cdot CCl_3 + BuSH \longrightarrow CHCl_3 + BuS\cdot$$

$$BuS\cdot + (EtO)_3P \longrightarrow (EtO)_3P(SBu)\cdot \longrightarrow (EtO)_3PS + Bu\cdot$$

$$Bu\cdot + BuSH \longrightarrow BuH + BuS\cdot$$

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

$$[(EtO)_3P\cdot SBu]^+Br^- \longrightarrow (EtO)_2P(O)\cdot SBu \text{ (II)} + EtBr$$

Scheme A.

$$(EtO)_3P^+\!\!-\!CCl_3 \longrightarrow CHCl_3 + (EtO)_3P^+\cdot SBu \xrightarrow{\ Br^-\ } (EtO)_2P(O)\cdot SBu + EtBr$$
$$\overset{\curvearrowleft\ \curvearrowright}{BuS\!-\!H} \qquad\qquad \textit{Scheme B.}$$

The results of corresponding reactions of trialkyl phosphites and related compounds with carbon tetrachloride or bromotrichloromethane in the presence of alcohols are now described. In this case also, in theory, alternative reaction paths corresponding to Schemes A and B can be followed. Thus a radical-chain process (Scheme C) is possible, whereby trichloromethyl radicals can react with the trialkyl phosphite to give a quasiphosphonium intermediate (III) which decomposes by nucleophilic dealkylation to the dialkyl trichloromethylphosphonate, *e.g.*, (I) (Scheme C). Also, trichloromethyl radicals can react with the alcohol by abstraction of an α-hydrogen atom to give chloroform and an α-hydroxyalkyl radical. Reaction of this radical with the phosphite would then be expected to give an α-hydroxyalkylphosphonate. That abstraction from the alcohol would occur at an
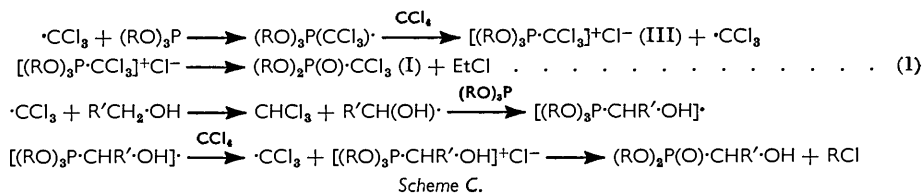
[1] Part XVI, Cadogan, Cameron-Wood, and Foster, *J.*, 1963. 2549.
[2] Kamai and Egorova, *J. Gen. Chem. (U.S.S.R.)*, 1946, **16**, 1521; Kamai, *Doklady-Akad. Nauk. S.S.S.R.*, 1951, **79**, 795.
[3] Bunyan and Cadogan, *J.*, 1962, 2953.
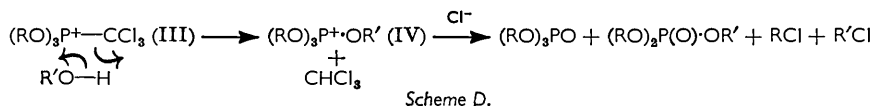[4] Cadogan, *Quart. Rev.*, 1962, **16**, 208.
[5] Cadogan and Foster, *J.*, 1961, 3071.

$$\cdot CCl_3 + (RO)_3P \longrightarrow (RO)_3P(CCl_3)\cdot \xrightarrow{\ CCl_4\ } [(RO)_3P\cdot CCl_3]^+Cl^- \text{ (III)} + \cdot CCl_3$$

$$[(RO)_3P\cdot CCl_3]^+Cl^- \longrightarrow (RO)_2P(O)\cdot CCl_3 \text{ (I)} + EtCl \quad \ldots \ldots \ldots \ldots \quad (1)$$

$$\cdot CCl_3 + R'CH_2\cdot OH \longrightarrow CHCl_3 + R'CH(OH)\cdot \xrightarrow{\ (RO)_3P\ } [(RO)_3P\cdot CHR'\cdot OH]\cdot$$

$$[(RO)_3P\cdot CHR'\cdot OH]\cdot \xrightarrow{\ CCl_4\ } \cdot CCl_3 + [(RO)_3P\cdot CHR'\cdot OH]^+Cl^- \longrightarrow (RO)_2P(O)\cdot CHR'\cdot OH + RCl$$

Scheme C.

α-hydrogen atom rather than at the hydroxylic hydrogen atom (cf. the corresponding reaction with alkanethiols) follows from the work of Urry and his co-workers,[6] who showed that radical induced addition of alcohols to olefins proceeded as follows:

$$RCH_2\cdot OH \longrightarrow RCH(OH)\cdot \xrightarrow{\ R'CH:CH_2\ } R'CH\cdot CH_2\cdot CHR\cdot OH \xrightarrow{\ RCH_2\cdot OH\ } R'CH_2\cdot CH_2\cdot CHR\cdot OH$$

The alternative reaction scheme (D) requires the formation of the same quasiphosphonium salt (III), either by a radical-chain process or by heterolytic displacement, which can then decompose [reaction (1)], or undergo solvolysis to give chloroform and a new quasiphosphonium intermediate (IV) which in turn reacts by nucleophilic dealkylation to

$$(RO)_3P^+\!\!-\!\!CCl_3 \text{ (III)} \longrightarrow (RO)_3P^+\!\cdot OR' \text{ (IV)} \xrightarrow{\ Cl^-\ } (RO)_3PO + (RO)_2P(O)\cdot OR' + RCl + R'Cl$$
$$\underset{R'O-H}{\curvearrowright\curvearrowright} \qquad \underset{CHCl_3}{+}$$

Scheme D.

give the observed products. Thus, for reaction of triethyl phosphite with carbon tetrachloride and ethanol, both Schemes C and D predict the formation of diethyl trichloromethylphosphonate and chloroform, while Scheme C predicts the formation of diethyl 1-hydroxyethylphosphonate and Scheme D that of triethyl phosphate. Experiment has now shown that Scheme D is operative since, for example, reaction of an equimolar mixture of triethyl phosphite, ethanol, and carbon tetrachloride at the boiling point (3½ hr.) gave triethyl phosphate (89%), diethyl trichloromethylphosphonate (11%), and chloroform.

Reactions of trialkyl phosphites with polyhalogenomethanes in the presence of alcohols.

| Halide	R in (RO)₃P	R' in R'OH	(RO)₃PO	(RO)₂(R'O)PO	(R'O)₂(RO)PO	(R'O)₃PO	(RO)₂P(O)CCl₃
CCl₄ (1)	Et (1)	Et (1)	89	—	—	—	11
CCl₄ (3)	Et (1)	Et (3)	97·5	—	—	—	2·5
CCl₄ (2)	Et (1)	Et (4)	100	—	—	—	—
CCl₄ (2)	Et (1)	Me (4)	25	45	30	—	—
BrCCl₃ (2)	Et (1)	Me (4)	28	54	18	—	—
CCl₄ (2)	Et (1)	Allyl (4)	56	36	8	—	—
CCl₄ (1)	Et (1)	Allyl (1)	72	20	Trace	—	8
BrCCl₃ (2)	Et (1)	Allyl (4)	67	27	3	—	3
BrCCl₃ (2)	Et (1)	Bu (4)	14	45	33	8	Trace
CCl₄ (3)	Et (1)	Bu (3)	13	37	36	12	2
BrCCl₃ (2)	Et (1)	Buᵗ (4)	98	—	—	—	Trace
CCl₄ (1)	Allyl (1)	Et (1)	24	37	32	7	—
CCl₄ (2)	Allyl (1)	Et (4)	6	16	34	44	—
CCl₄ (2)	Allyl (1)	Bu (4)	4	10	32	54	—
CCl₄ (2)	Bu (1)	Et (4)	26	36	28	10	—
CCl₄ (2)	Bu (1)	Allyl (4)	65	27	5	3	—
CCl₄ (2)	Bu (1)	Buᵗ (4)	81	—	—	—	—
CCl₄ (2)	Et (1)	Buᵗ (4)	80	—	—	—	Trace
CCl₄ (2)	Allyl (1)	Allyl (4)	79	—	—	—	—
CCl₄ (2)	Bu (1)	Bu (4)	99	—	—	—	—
CCl₄ (2)	Et (1)	C₆H₁₁ (4)	20	80	—	—	—
CCl₄ (2)	Allyl (1)	Buᵗ (4)	62				
CCl₄ (2)	Me (1)	Me (4)	43				

* Molar proportions in parentheses.

⁶ Urry, Stacey, Huyser, and Juveland, *J. Amer. Chem. Soc.*, 1954, **76**, 450.

In further accord with Scheme D, an increase in the proportion of ethanol [$(EtO)_3P : EtOH : CCl_4 : : 1 : 4 : 2$] led to the suppression of the trichloromethylphosphonate and to an almost quantitative yield of triethyl phosphate. Under similar conditions triallyl, tributyl, and trimethyl phosphite were oxidised in high yield to the corresponding phosphates by carbon tetrachloride in allyl alcohol, butanol, and methanol, respectively. The reaction is therefore of value as a method of oxidation of phosphites to phosphates under neutral anhydrous conditions.

It is of interest that diethyl methylphosphonite can similarly be converted into diethyl methylphosphonate, thus indicating that solvolysis of the $P \cdot CCl_3$ group occurs but that of the PMe group does not. The latter conclusion is confirmed by the isolation of diethyl methylphosphonate from the Arbusov reaction, in ethanol, of triethyl phosphite and methyl iodide, which involves the same intermediate [$(EtO)_3PMe^+$].

According to Scheme D, reactions between a phosphite, carbon tetrachloride, and an alcohol containing different alkyl groups should lead to a mixture of products consequent upon selective dealkylation of the unsymmetrical quasiphosphonium ion (IV). Such selectivity would be expected to depend mainly on the relative electrophilicities of the α-carbon atoms of the groups involved, and also on a statistical factor. To test this, such reactions have been carried out and the composition of the mixture of products has been determined in each case by gas–liquid chromatography and in many cases confirmed by isolation. The results are summarised in the Table and are considered to be compatible with Scheme D. Thus, an equimolar mixture of carbon tetrachloride, triethyl phosphite, and allyl alcohol gives triethyl phosphate (72%), allyl diethyl phosphate (20%), and diethyl trichloromethylphosphonate (8%), together with allyl chloride and chloroform, indicating loss of the more electrophilic allyl group. The use of a greater proportion of allyl alcohol, which would be expected to suppress the formation of diethyl trichloromethylphosphonate, led, unexpectedly, to the formation of an additional product, diallyl ethyl phosphate. A similar effect was noted in the corresponding reaction of triallyl phosphite with ethanol in carbon tetrachloride, which gave a mixture of all four possible phosphates. Similar complications occurred in most of the reactions involving phosphites and alcohols containing different alkyl groups. Such results indicate that more extensive solvolysis of the quasiphosphonium intermediate is involved than was at first envisaged, leading in some cases to complete replacement of the alkoxy-groups in the phosphite by alkoxy-groups derived from the alcohol (Scheme E).
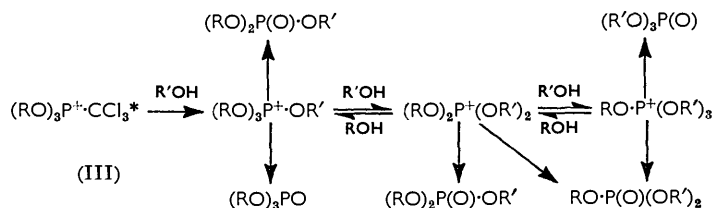

Scheme E.

* Intermediates such as [$(RO)_2P(CCl_3) \cdot OR'$]$^+$ are discounted because products such as $(RO)(R'O)P(O) \cdot CCl_3$ were not formed to a detectable extent.

In further accord with Scheme D, substitution of carbon tetrachloride by the more reactive bromotrichloromethane led only to an increase in the rate of the reaction and not to an appreciable change in the composition of the mixture of the products.

It could be argued, however, that the products of these reactions could arise by prior transesterification of the phosphite, followed by reaction of the unsymmetrical phosphite with carbon tetrachloride to give a quasiphosphonium salt which then reacts as in Scheme D, thus:
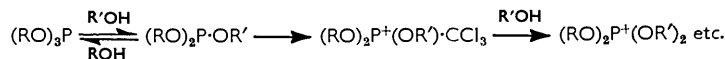
Control experiments have shown, however, that transesterification of phosphite does not occur under the mild conditions required for the reactions described above, as would be expected from the results of Hoffmann and his co-workers [7] who have studied the transesterification process in the absence of halogenomethanes. Similarly, it has been shown that transesterification of trialkyl phosphates does not occur under these conditions, in accord with the report [8] that triethyl phosphate and butanol do not react at 160°, except in the presence of butoxide ions. Further, diethyl trichloromethylphosphonate does not react with ethanol to give triethyl phosphates and chloroform.

In the reactions so far discussed, the alkyl groups in the key quasiphonium intermediates (e.g., IV) have either been identical, or of not widely differing reactivities in the dealkylation step. Hence it was only in the former case that oxidations of preparative value [(RO)$_3$P $\longrightarrow$ (RO)$_3$PO] were achieved. The use of t-butyl alcohol overcame this difficulty, however, because the quasiphosphonium ion in these cases preferentially decomposed with the loss of the highly electrophilic t-butyl group, probably in an S_N1 process. Thus triethyl, tributyl, and triallyl phosphite were readily oxidised in the presence of t-butyl alcohol and carbon tetrachloride or bromotrichloromethane to the corresponding phosphates in high yields, thus providing a second method of preparative value, the tetrahalide being reduced in each case to chloroform.

The reaction of triphenyl phosphite with ethanol in carbon tetrachloride or bromotrichloromethane gave chloroform, phenol, triethyl phosphate, and a mixture of phosphates believed to consist of the various ethyl phenyl phosphates and triphenyl phosphate. This suggests that here again repeated solvolysis of the intermediate trichloromethyltriphenoxyphosphonium salt occurred. In this case, however, it is possible that transesterification of the phosphite occurred before reaction with the polyhalogenomethane, since the former reaction is more rapid than the analogous reaction of trialkyl phosphites. In either event the greater tendency for replacement of a phenoxy-group is in accord with the higher stability of the corresponding anion in this case. Similar results were obtained when tri-(2-chloroethyl) phosphite was allowed to react with carbon tetrachloride and ethanol, when ethylene chlorhydrin and triethyl phosphate were obtained.

It is necessary to comment on the difference between the mechanisms which operate when trialkyl phosphites react with carbon tetrachloride in alcohols on the one hand, compared with alkanethiols on the other. In the latter case, reaction by way of a chain-transfer process is in accord with the very high reactivity of alkanethiols as chain-transfer reagents, whereas alcohols are among the least reactive.[9] It is noteworthy that in the reaction of triethyl phosphite with bromotrichloromethane carried out in the presence of *both* ethanol and butane-1-thiol,* i.e., under conditions where competition between Schemes A and D could occur, triethyl phosphate (14%) and S-butyl diethyl phosphorothiolate (II) (86%) were formed. This indicates that the thioloquasiphosphonium ion has a longer life in ethanol than the corresponding trichloromethyl intermediate, as expected [(EtO)$_3$P$^+$–SR $\longleftrightarrow$ (EtO)$_3$P=SR$^+$], so that dealkylation by chloride ion occurs before solvolysis by ethanol. Since similar thioloquasiphosphonium intermediates are involved in the Pishchimuka reaction of alkyl halides with phosphorothionates [10] the reaction of methyl iodide with ethyl NN'-dicyclohexylphosphorodiamidothionate (V) was carried out in ethanol. In agreement with the observations described above, solvolysis of the thiolophosphonium ion did not occur but dealkylation to give S-methyl NN'-dicyclohexylphosphorodiamidothioate (VI) took place. Our experiments do not allow us to decide, however, whether the quasiphosphonium intermediate (III) is formed by a heterolytic or homolytic route in the presence of alcohols.

* This experiment was kindly carried out by Dr. P. J. Bunyan.

[7] Hoffmann, Ess, and Usinger, *J. Amer. Chem. Soc.*, 1956, **78**, 5817.
[8] Rueggeberg and Chernack, *J. Amer. Chem. Soc.*, 1948, **70**, 1802.
[9] Walling, " Free Radicals in Solution," Wiley, New York, 1959.
[10] Burn and Cadogan, *J.*, 1961, 5532.

In addition to reactions of trialkyl and triphenyl phosphites with alcohols and poly-halogenomethanes, those of triphenylphosphine have been examined. Recently it has been shown that triphenylphosphine reacts with carbon tetrachloride,[11] bromoform,[12]

(V)   (VI)
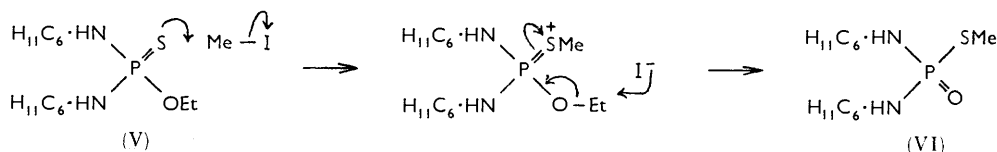
and carbon tetrabromide.[13] Rabinowitz and Marcus have shown [11] that dichloromethyl-enetriphenylphosphorane (VII) is an intermediate in the first reaction, which presumably proceeds by way of a phosphonium intermediate which decomposes as shown:
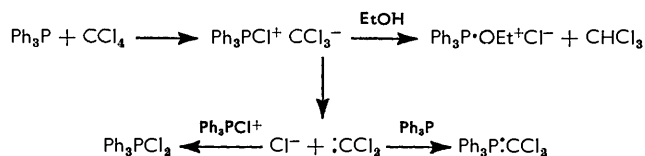

(VII)
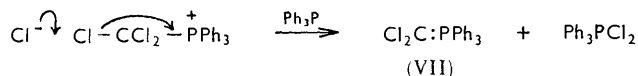
The corresponding reaction when carried out in ethanol would be expected under Scheme D to proceed by way of the same phosphonium intermediate, thus:

$$Ph_3P^+ \cdot CCl_3 \xrightarrow{ROH} CHCl_3 + Ph_3P^+ \cdot OR \text{ (VIII)} \xrightarrow{Cl^-} Ph_3PO + RCl$$
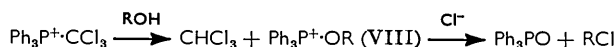
Subsequent decomposition of the quasiphosphonium salt (VIII) formed by solvolysis can then proceed only by dealkylation. This has been confirmed by experiment; tri-phenylphosphine reacts, for example, with carbon tetrachloride or bromotrichloromethane in ethanol to give high yields of triphenylphosphine oxide.

An alternative explanation of our reaction with triphenylphosphine and of that of Rabinowitz and Marcus involves nucleophilic attack on positive halogen to give a triphenylhalogenophosphonium cation and the trichloromethyl anion, subsequent solvolysis of the former by ethanol, and dealkylation in the usual way. Reaction of the anion with ethanol in our case then yields chloroform while decomposition could give dichlorocarbene and hence dichloromethylenetriphenylphosphorane.

$$Ph_3P + CCl_4 \longrightarrow Ph_3PCl^+ CCl_3^- \xrightarrow{EtOH} Ph_3P \cdot OEt^+Cl^- + CHCl_3$$

$$Ph_3PCl_3 \xleftarrow{Ph_3PCl^+} Cl^- + :CCl_2 \xrightarrow{Ph_3P} Ph_3P:CCl_3$$

The corresponding route involving triethyl phosphite is discounted because it is incompatible with the formation of diethyl trichloromethylphosphonate.

On the other hand, bromoform did not react under these conditions with triphenyl-phosphine in ethanol. Ramirez and McKelvie [12] had earlier noted that the reaction between the phosphine and bromoform was slow. They reported that reaction in boiling benzene occurred only in the presence of dibenzoyl peroxide, to give dibromomethyltriphenylphos-phonium bromide [(Ph₃P·CHBr₂)⁺Br⁻], and concluded that a free-radical reaction initiated by the peroxide had taken place. The phosphonium bromide was also formed in a reaction at the boiling point in the absence of benzene and peroxide. Since there is ample evidence [4] that triphenylphosphine and dibenzoyl peroxide react by heterolysis, the reaction between bromoform and triphenylphosphine has now been re-examined. In accord with expectation we were unable to initiate a reaction with dibenzoyl peroxide in benzene at 80°. Reaction occurred in the absence of benzene at the boiling point (150°), however, and a product

[11] Rabinowitz and Marcus, *J. Amer. Chem. Soc.*, 1962, **84**, 1312.
[12] Ramirez and McKelvie, *J. Amer. Chem. Soc.*, 1957, **79**, 5829.
[13] Ramirez, Desai, and McKelvie, *J. Amer. Chem. Soc.*, 1962, **84**, 1745.

having the same characteristics as those attributed by Ramirez and McKelvie to dibromo-methyltriphenylphosphonium bromide was obtained.

It is possible that Ramirez and McKelvie's reaction in benzene was initiated by peroxidic impurities other than dibenzoyl peroxide. In this connection it is noteworthy that Bartlett, Cox, and Davis have shown [14] that triphenylphosphine itself yields an unidentified, long-lived but reactive product with oxygen in certain circumstances.

EXPERIMENTAL

Gas–Liquid Chromatography.—Measurements were carried out with the following instruments: (a) a Pye " Argon " chromatograph, using argon as carrier gas and 4 ft. columns (APL, PEGA). The APL column was packed with Apiezon L on Celite 545, and the PEGA column with poly(ethylene glycol adipate) on Celite 545; (b) a Perkin-Elmer " Fraktometer " Model 116, using nitrogen or hydrogen as carrier gas, and a 2-metre column (" C ") consisting of silicone oil (DC 200) on Celite 545.

Reagents.—All phosphites and phosphates used were tested for purity by gas–liquid chromatography. The following trialkyl phosphites (Albright & Wilson Ltd.) were redistilled before use: triethyl phosphite, b. p. 55—56°/15 mm., n_D^{20} 1·4135 (lit.,[15] b. p. 52°/14 mm., $n_D^{17·5}$ 1·4140); tri-n-butyl phosphite, b. p. 118—122°/10 mm., n_D^{27} 1·4294 (lit.,[16] b. p. 122°/12 mm., n_D^{19} 1·4321); triallyl phosphite, b. p. 88—89°/10 mm., n_D^{25} 1·4570 (lit.,[17] b. p. 52—54°/0·25 mm., n_D^{25} 1·4556); tri-(2-chloroethyl) phosphite, b. p. 109—110°/0·1 mm., n_D^{25} 1·4845 (lit.,[18] b. p. 112—115°/2·5 mm., n_D^{20} 1·4818). Triethyl phosphate and tri-n-butyl phosphate (British Drug Houses), triallyl phosphate (Albright & Wilson Ltd.), and tri-(2-chloroethyl) phosphate (L. Light and Co. Ltd.) were used for identification of reaction products without further purification. The alcohols, carbon tetrachloride, chloroform, and bromotrichloromethane were also used without further purification unless otherwise stated.

Ethyl Dimethyl Phosphate.—Ethyl phosphorodichloridate (8·15 g.) in ether (Na dried, 50 ml.) was added dropwise to a magnetically-stirred solution of sodium methoxide in methanol, formed by dissolving sodium (2·3 g.) in methanol (20 ml.). The mixture was set aside for 24 hr., light petroleum (b. p. 40—60°; 300 ml.) was added, and the precipitate of sodium chloride was filtered off. Distillation of the filtrate gave ethyl dimethyl phosphate (5·23 g., 68%), b. p. 80—82°/10 mm., n_D^{22} 1·3996 (Found: C, 31·3; H, 7·2. Calc. for $C_4H_{11}O_4P$: C, 31·2; H, 7·2%).

Diallyl ethyl phosphate, b. p. 55—57°/0·1 mm., n_D^{25} 1·4335 (lit.,[19] b. p. 72°/1—2 mm., n_D^{25} 1·4350), and dibutyl ethyl phosphate, b. p. 70—75°/0·05 mm., n_D^{25} 1·4172 (lit.,[8] b. p. 95—96°/3—4 mm., n_D^{20} 1·4182), were similarly prepared from ethyl phosphorodichloridate.

Methyl phosphorodichloridate (47·2 g.), b. p. 67—68°/10 mm., n_D^{23} 1·4320, was prepared by the dropwise addition of methanol (22 g.) to phosphorus oxychloride (102 g.) in light petroleum (b. p. 40—60°; 100 ml.). After an initial vigorous evolution of hyrogen chloride the solution was boiled (2 hr.), allowed to cool, and degassed with nitrogen (4 hr.). Preparation of diethyl methyl phosphate, b. p. 90°/10 mm., n_D^{25} 1·3390, from methyl phosphorodichloridate, was similar to that of the dialkyl ethyl phosphates. The product was shown by gas–liquid chromatography to be contaminated with small quantities of triethyl phosphate and dimethyl ethyl phosphate which could not be removed by distillation.

Allyl Diethyl Phosphate.—Triethylamine (11·1 g.) was added dropwise to a magnetically-stirred mixture of diethyl phosphite (13·8 g.), allyl alcohol (6·1 g.), and carbon tetrachloride (30·3 g.). Within 5 min. a vigorous reaction occurred causing the reaction mixture to boil; a white precipitate also appeared during this time. After the vigorous reaction had subsided, light petroleum (b. p. 40—60°; 200 ml.) was added, followed by boiling under reflux for 3 hr. Filtration and distillation gave allyl diethyl phosphate (9·1 g., 47%), b. p. 70—72°/0·05 mm., n_D^{25} 1·4204. Toy and Cooper [20] reported b. p. 63°/0·05 mm., n_D^{25} 1·4216.

[14] Bartlett, Cox, and Davies, *J. Amer. Chem. Soc.*, 1961, **83**, 103.
[15] Ford-Moore and Williams, *J.*, 1947, 1465.
[16] Gerrard, *J.*, 1940, 1464.
[17] Young, Wood, Joyce, and Anderson, *J. Amer. Chem. Soc.*, 1956, **78**, 2126.
[18] Kabachnik and Rossiiskaya, *Izvest. Akad. Nauk. S.S.S.R. Otdel. khim. Nauk*, 1946, 295 (*Chem. Abs.*, 1948, **42**, 7241).
[19] Steinberg, *J. Org. Chem.*, 1950, **15**, 637.
[20] Toy and Cooper, *J. Amer. Chem. Soc.*, 1954, **76**, 2191.

Butyl diethyl phosphate, b. p. 68—78°/0·1 mm., n_D^{25} 1·4110 (lit.,[19] b. p. 100—101°/2—3 mm., n_D^{25} 1·4085), was prepared similarly but in low (15%) yield. A better preparation is as follows: triethyl phosphite (33·2 g.) and butanol (7·4 g.), after 7 hr. at 140—160°, gave butyl diethyl phosphite (58%), b. p. 80—82°/10 mm., n_D^{25} 1·4180. Hydrogen peroxide (100 vol.; 4 ml.) was added to a solution of the phosphite (1·94 g.) in methanol (15 ml.). After 10 min. at the boiling point, distillation gave butyl diethyl phosphate (87%), b. p. 70—72°/0·2 mm., n_D^{24} 1·4115.

S-methyl *NN'*-dicyclohexylphosphorodiamidothioate, m. p. 175°, was prepared from ethyl *NN'*-dicyclohexylphosphorodiamidothionate, m. p. 76°, by reaction with methyl iodide for 24 hr. at room temperature as described by Burn and Cadogan.[10] The same reactants, after reaction in ethanol for a similar period, gave the same product.

Reactions of Trialkyl Phosphites with Polyhalogenomethanes in the Presence of Alcohols.— Representative examples of these reactions are described. Details of related reactions in which the proportions and nature of the reactants were varied are given in the Table.

In addition to their isolation, the identities of the reaction products were confirmed by gas–liquid chromatography, the retention times being compared with those of authentic samples. In determination of the concentrations of the products, calibrations using weighed authentic mixtures were not carried out in all cases, for the following reasons: (*a*) Several of the phosphates could not be obtained in a sufficiently pure state and contained small amounts of unsymmetrical phosphates. (*b*) The low-boiling halide products were subject to loss by evaporation during reflux, and were mainly examined only to check the course of the reaction in a few cases. (*c*) Alcohols did not respond well on the gas–liquid chromatogram under conditions suitable for the analysis of halides. In view of these circumstances the concentrations of the phosphates were measured directly from the peak areas of the chromatograms, assuming the detector response to be in the same proportion to the concentration for each of a given group of chemically similar esters formed in a single reaction, and are given as the mole percentage of total phosphate formed. Similar assumptions were made in determining the halide concentrations, which are also given as the mole percentage of total halide present, and merely the presence of an alcohol was noted.

(i) Triethyl phosphite (3·32 g., 1 mol.), ethanol (0·92 g., 1 mol.), and carbon tetrachloride (3·1 g., 1 mol.) were boiled under reflux on a water-bath for 3½ hr. Gas–liquid chromatography (Perkin-Elmer) at 192°, using a 2 metre " C " column and nitrogen carrier gas flow 15 ml./min., indicated the formation of diethyl trichloromethylphosphonate (11%; relative retention time 2·23) and triethyl phosphate (89%; 1·0). Analysis of the low-boiling products using the same apparatus at 62°, with hydrogen carrier-gas (flow 50 ml./min.), indicated carbon tetrachloride (15%; 3·15), chloroform (85%; 2·18) and ethanol (1·0). An early peak (0·82) was attributed to ethyl chloride but was not confirmed.

(ii) Triethyl phosphite (3·32 g., 1 mol.), ethanol (3·68 g., 4 mol.), and carbon tetrachloride (6·16 g., 2 mol.) were boiled under reflux for 3½ hr. Analysis (Pye) at 150° (APL column, argon flow 30 ml./min.) indicated diethyl trichloromethylphosphonate ($\ll$1%; 3·77) and triethyl phosphate (100%; 1·0). Distillation gave triethyl phosphate (3·32 g., 92%), b. p. 92—96°/ 10 mm., n_D^{24} 1·4040 (correct infrared spectrum).

(iii) Triethyl phosphite (3·32 g., 1 mol.), allyl alcohol (1·16 g., 1 mol.), and carbon tetrachloride (3·1 g., 1 mol.) were boiled under reflux on a water-bath for 3½ hr. Analysis (Pye) at 150° (APL column, flow 40 ml./min.) indicated the presence of diethyl trichloromethylphosphonate (8%; 3·62), diallyl ethyl phosphate (trace; 2·16), allyl diethyl phosphate (20%; 1·45), and triethyl phosphate (72%; 1·0). Analysis of the low-boiling products (Perkin-Elmer) at 62° (" C " column, hydrogen carrier-gas, flow 50 ml./min.) indicated the presence of carbon tetrachloride (15%; 2·29), chloroform (53%; 1·7), allyl alcohol (1·48), allyl chloride (32%; 1·0), ethanol (trace). In a control reaction, triethyl phosphate (1·82 g., 1 mol.), allyl alcohol (2·32 g., 4 mol.), and carbon tetrachloride (3·1 g., 2 mol.) were boiled under reflux for 5 hr. Analysis under the above conditions showed that transesterification to give allyl phosphates did not occur.

(iv) Bromotrichloromethane (8·0 g., 2 mol.) was added to a mixture of triethyl phosphite (3·32 g., 1 mol.) and methanol (2·56 g., 4 mol.). A vigorous reaction occurred within 1 min. The results of the gas–liquid chromatographic analyses are given in the Table. Suitable control experiments established that triethyl phosphite and triethyl phosphate did not undergo transesterification with methanol under the above conditions.

(v) Triallyl phosphite (4·04 g., 1 mol.), allyl alcohol (4·64 g., 4 mol.), and carbon tetrachloride

(6·2 g., 2 mol.) were boiled under reflux for 10 hr. Distillation gave triallyl phosphate (3·44 g., 79%) b. p. 60—70°/0·1 mm., n_D^{25} 1·4480 (correct infrared spectrum).

(vi) Bromotrichloromethane (8·0 g., 2 mol.) was added to triethyl phosphite (3·32 g., 1 mol.) and t-butyl alcohol (5·9 g., 4 mol.). The mixture became only slightly warm within 15 min. and was boiled under reflux for a further 15 min. Analysis (Pye) at 150° (APL column, flow 40 ml./min.) indicated that the product was almost pure triethyl phosphate (1·0), with diethyl trichloromethylphosphonate (<1%; 3·65) and an unidentified peak (*ca.* 2%; 2·9). Distillation gave two fractions, (a) b. p. 35—65°/0·1 mm., n_D^{25} 1·4235 (2·05 g.), and (b) b. p. 76—80°/0·1 mm., n_D^{25} 1·4200 (0·75 g.), both of which had an infrared spectrum compatible with their consisting of triethyl phosphate with a little diethyl trichloromethylphosphonate. A residue of 0·7 g. was left. Similar results were obtained by the use of carbon tetrachloride as the polyhalogeno-methane.

(vii) Triallyl phosphite (2·02 g., 1 mol.), t-butyl alcohol (3·0 g., 4 mol.), and carbon tetra-chloride (3·1 g., 2 mol.) were boiled under reflux for 11½ hr. Analysis (Pye) at 175° (APL column flow 40 ml./min.) indicated the formation of triallyl phosphate and the disappearance of triallyl phosphite. Distillation gave triallyl phosphate (1·35 g., 62%), b. p. 120—122°/15 mm., n_D^{25} 1·4484 (correct infrared spectrum).

(viii) Tributyl phosphite (2·5 g., 1 mol.), t-butyl alcohol (2·96 g., 4 mol.), and carbon tetra-chloride (3·1 g., 2 mol.) similarly gave, after 11 hr. at the boiling point, tributyl phosphate (2·17 g., 82%), b. p. 92/0·1 mm., n_D^{25} 1·4290 (correct infrared spectrum and gas–liquid chromato-graphic retention time).

(ix) Diethyl methylphosphonite (6·8 g., 1 mol.) was added dropwise to a mixture of ethanol (9·2 g., 4 mol.) and carbon tetrachloride (15·4 g., 2 mol.) during 2 min. A vigorous reaction occurred after a further 2 min. After 2 hr. at the boiling point, distillation gave diethyl methyl-phosphonate (6·5 g., 86%), b. p. 68—71°/10 mm., n_D^{22} 1·4141 (correct infrared spectrum). An Arbusov reaction of triethyl phosphite, methyl iodide (2 mol.), and ethanol (4 mol.) gave the same product (99%).

(x) Trimethyl phosphite, carbon tetrachloride, and methanol similarly gave trimethyl phosphate (43%), b. p. 58—60°/10 mm., n_D^{25} 1·3960, after 3 hr. at the boiling point.

(xi) Tri-(2-chloroethyl) phosphite (2·69 g., 1 mol.), ethanol (1·84 g., 4 mol.), and carbon tetrachloride (3·08 g., 1 mol.) were boiled under reflux for 19 hr. Distillation gave ethylene chlorhydrin (1·08 g., 45%), b. p. 128—132°, and triethyl phosphate (1·18 g., 65%) (both with correct infrared spectrum). A third fraction (0·4 g.), b. p. 140—155°/0·1 mm., had an infrared spectrum identical with that of a mixture of triethyl phosphate and tri-(2-chloroethyl) phosphate.

(xii) Triphenyl phosphite (3·1 g., 1 mol.), ethanol (5 ml.), and bromotrichloromethane (4·0 g., 2 mol.) were boiled under reflux for 6 hr. Distillation gave a low-boiling fraction (<65°) which contained chloroform and ethyl bromide (g.l.c.) and a residue with a strong odour of phenol. This was dissolved in ether and extracted with 2N-sodium hydroxide to give phenol (2·0 g., 71%) (tribromo-derivative, m. p. 92°). Distillation of the neutral portion (1·4 g.) gave triethyl phosphate, b. p. 98—100°/10 mm., n_D^{23} 1·4070 (correct infrared spectrum), and a fraction, b. p. 140—175°/0·1 mm., which appeared to consist (infrared) of a mixture of the various ethyl phenyl phosphates with triphenyl phosphate.

(xiii) Triphenylphosphine (2·62 g., 1 mol.), ethanol (10 ml.), and carbon tetrachloride (3·1 g., 2 mol.) were boiled for 4 hr. Distillation gave a fraction (b. p. <78°) which was shown qualita-tively to contain ethanol, carbon tetrachloride, chloroform, and ethyl chloride. Recrystall-isation of the residue from benzene gave triphenylphosphine oxide (2·05 g., 74%), m. p. and mixed m. p. 158—159°, and a colourless unidentified powder (0·055 g.), m. p. 235—240° (cf. Rabinowitz and Marcus,[11] who isolated a trace of a compound, m. p. 239—241°, from the reaction of triphenylphosphine and carbon tetrachloride). Similar results were obtained from a reaction involving bromotrichloromethane instead of carbon tetrachloride. No reaction occurred when the polyhalogenomethane used was chloroform or bromoform under the above conditions.

Reactions of Triphenylphosphine with Bromoform.—Bromoform was freed from possible peroxide impurities by shaking with ferrous sulphate solution (3 × 100 ml.). It was then washed with water (3 × 100 ml.), dried (MgSO₄), passed through an alumina column, and distilled, the fraction of b. p. 50°/20 mm. being collected.

" AnalaR " benzene (Na dried) was boiled under reflux for several hours, and distilled under nitrogen, the fraction b. p. 79·5° being collected.

Triphenylphosphine (L. Light and Co. Ltd.) was recrystallised from ethanol–ether to constant m. p. 79—80°.

Triphenylphosphine (2·6 g., 1 mol.) was boiled under reflux for 30 min. in benzene (25 ml.) under nitrogen. To this boiling solution was then added bromoform (2·5 g., 1 mol.) and dibenzoyl peroxide (0·05 g., 0·02 mol.) in benzene (10 ml.). The reaction mixture was boiled under reflux for a further 30 min. and the benzene was then distilled off. Recrystallisation of the solid residue from ethanol–ether gave triphenylphosphine (2·0 g., 77% recovery), m. p. and mixed m. p. 78—79°.

In a similar experiment, using 0·1 mol. of peroxide per mol. of phosphine, the phosphine was recovered in 81% yield (2·1 g.), m. p. and mixed m. p. 78°.

Triphenylphosphine (4·62 g., 1 mol.), bromoform (4·45 g., 1 mol.), and dibenzoyl peroxide (0·11 g., 0·025 mol.) were boiled under reflux in benzene (10 ml.) in the dark under nitrogen for 30 min. Removal of the benzene and recrystallisation of the residue from ethanol gave triphenylphosphine (4·15 g., 90% recovery), m. p. and mixed m. p. 78—79°.

Triphenylphosphine (1·31 g., 1 mol.) and bromoform (4·25 g., 3 mol.) were heated to the boiling point, and after about 3 min. a sudden reaction occurred. The solution turned brown and began to boil, and white fumes were evolved. On cooling, a sticky residue was obtained and was put on to a silica chromatography column in chloroform solution (10 ml.). Elution with light petroleum (b. p. 40—60°; 200 ml.) gave bromoform (1·8 g.). Petroleum–benzene (400 ml.) and petroleum–chloroform (200 ml.) gave no product. Elution with pure chloroform (600 ml.) gave a solid (1·2 g.) which, recrystallised from chloroform–ethyl acetate, had m. p. 234—235° (1·1 g.); this compound had the same m. p. as that which Ramirez and McKelvie [12] formulated as $[Ph_3P \cdot CHBr_2]^+Br^-$.

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