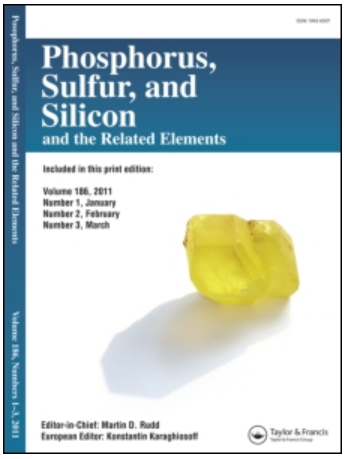

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THE PREPARATION OF TRIALKYL PHOSPHITES DIRECTLY FROM THE ELEMENT

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THE PREPARATION OF TRIALKYL PHOSPHITES DIRECTLY FROM THE ELEMENT

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The reaction between finely divided white phosphorus and several alkoxide ions in the presence of tetrachloromethane and excess of alcohol has been investigated under a variety of conditions. High yields of trialkylphosphite are obtained when two equivalents of alkoxide are used. With one equivalent of alkoxide, dialkylphosphonate is formed in comparable yield. Maximum yields of triester are obtained within 1–3 h at room temperature. Prolonged treatment results in the conversion of trialkylphosphite to phosphate by reaction with tetrachloromethane. Phenolate ions are unreactive under the same experimental conditions. The mechanism of the reaction is discussed.

INTRODUCTION

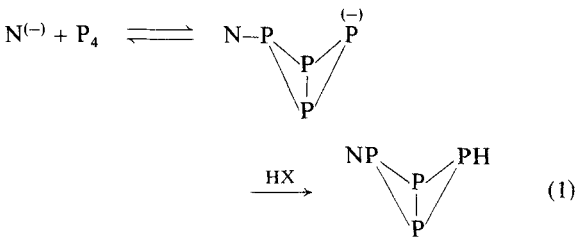
There has been much interest in the direct synthesis of organophosphorus compounds from elemental phosphorus for many years.[1] Early attempts were largely unsuccessful, as low yields of product were usually obtained and moreover complex mixtures presented difficulties of separation and purification.

Some progress has been made in recent years by using a combination of reagents, and we have recently developed a general approach to this problem.[2] In order to obtain high yields of particular product, various difficulties have to be overcome.

a) The insolubility of phosphorus in most organic solvents leads to heterogeneous reaction mixtures with the attendant problems of diffusion, local concentration, in particular of acid, and variable reaction times.

b) The molecule P_4 has a very low nucleophilic reactivity.[3]

c) The phosphorus molecule is highly electrophilic, but attack by a nucleophile produces a phosphide ion, itself highly nucleophilic. There are two major consequences of this. Either the phosphide ion displaces the nucleophile and no reaction occurs, or it is trapped by acid, (either Brönsted or Lewis) with the formation of two series of products, the one derived from phosphorus acid, the other derived from phosphine.



(1)

Thus, we find that phenoxide and thiophenoxide ions do not react with P_4 in the presence of tetrachloromethane, whereas alkoxide and thioalkoxide ions react almost quantitatively. This difference in behaviour can be attributed to the reversibility of the first stage of the reaction.

Hydroxide ions react slowly with P_4 to give a complex mixture of products[4] including phosphorous acid, phosphine and diphosphine as the intermediate phosphide ion is rapidly neutralized by water (Eq. 1). To counter this difficulty, most satisfactory syntheses employ an electrophilic reagent which can compete with the proton, if a protolytic solvent or reagent is used, to divert the reaction towards the required product, e.g. the reaction of organolithium compounds in the presence of alkyl halides,[5] and of

hydroxide ions in the presence of aldehydes,[6] acrylonitrile[7] or disulphides.[8]

We have developed a similar method[2] involving the reaction of nucleophiles, e.g. alkoxides, thioalkoxides and amines with white phosphorus in the presence of a positive halogen compound, in particular tetrachloromethane. In the following section the results of an experimental investigation of the reaction of several alkoxides are summarized.

RESULTS AND DISCUSSION

In view of the heterogeneous nature of the reaction, and complex mixture of reactants, the yields of the various organophosphorus compounds are highly dependent on the reaction conditions, and it is difficult to draw generalizations.

The reactions of methanol and *n*-butanol were carried out under a variety of conditions, and on analysis of the analytical data,[9] the following conclusions are drawn.

1) In most cases the maximum yield of trialkyl phosphite is observed within 1–2 h of mixing.

2) Low yields of trialkyl phosphite are usually obtained when one equivalent of sodium alkoxide is used. This is probably due to the generation of local acidity, as high yields of dialkyl phosphonate are produced, (Table I).

3) The yield of trialkyl phosphite decreases with time as the yield of trialkyl phosphate produced by further reaction of phosphite with tetrachloromethane increases (Table II).

The subsequent reaction to give phosphate is more marked in the case of the methyl and ethyl esters than in the case of *n*-butyl esters. Under optimum conditions 58% of tri-*n*-butylphosphite is formed in the absence of tri-*n*-butyl phosphate and di-*n*-butyl phosphonate (Table II).

In aqueous solution, very low yields (*ca.* 3%) of organophosphorus compounds are produced. A complex mixture of inorganic products including phosphoric, phosphorus and hypophosphorus acids is detected, and the organic component is a mixture of mono- and diesters of phosphorus and phosphonic acids with a trace of trialkyl phosphate (Table III).

A major difficulty was encountered in the separation of the trialkyl ester from the reaction mixtures. The lower esters formed constant boiling mixtures with the excess of alcohol and tetrachloromethane required for the preparation, and repeated distillations gave fractions which consisted of mixtures and decomposition products of the triesters.

TABLE I

Products of reaction of sodium *n*-butoxide (0.06 mol) with white phosphorus (0.009 mol) in *n*-butanol (50 ml) and tetrachloromethane (30 ml) at 25°.

Time (h)	Product (%)			Total
	$(BuO)_3P$	$(BuO)_3PO$	$(BuO)_2PHO$	
1	38	—	—	—
3	47	19	7	73
5	41	22	14	77
7	34	22	21	77
24	0	35	47	82

TABLE II

Products of reaction of sodium alkoxides (0.12 mol) and white phosphorus (0.009 mol) in alcohol (50 ml) and tetrachloromethane (30 ml) at 25°.

Time (h)	Product (%)					
	$(MeO)_3P$	$(MeO)_3PO$	$(EtO)_3P$	$(EtO)_3PO$	$(BuO)_3P$	$(BuO)_3PO$
1	82	—	76	7	—	—
3	74	7	68	6	58	0
6	75	7	63	12	55	0
24	39	36	39	—	—	—
144	—	—	7	85	41	18

TABLE III

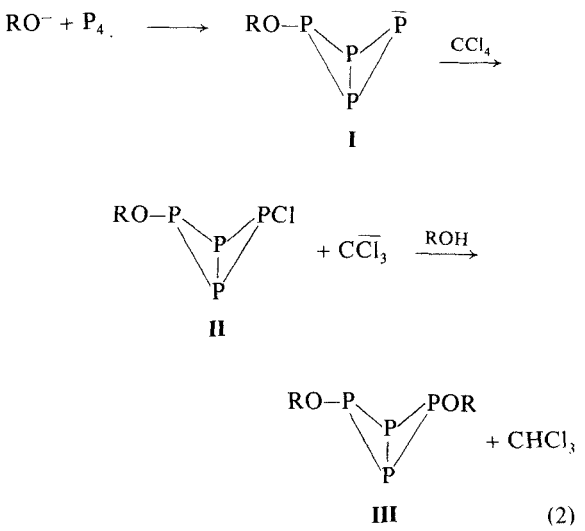
^{31}P Nmr data for the products of the reaction between sodium *n*-butoxide and elementary phosphorus in the presence of tetrachloromethane in aqueous solution

Assignment	δ_P	$^1J_{PH}$ (Hz)	$^3J_{HP}$ (Hz)	Multiplets	Line Intensities[a]
Organic Phase					
$(BuO)_2PHO$	7.7	700	8	dq	1.1
$BuO(HO)PHO$	5.1	673	8	dt	4.5
$(BuO)_3PO$	−0.6	—	—	m	1.0
$(BuO)_2(HO)PO$	−1.2	—	—	m (over-lapped)	2.3
$BuO(HO)_2PO$	−1.4	—	—	m (over-lapped)	3.7
Aqueous Phase					
H_3PO_4	0	—	—	s	1.0
H_3PO_3	3.2	640	—	d	10.4
H_3PO_2	8.6	530	—	t	5.4

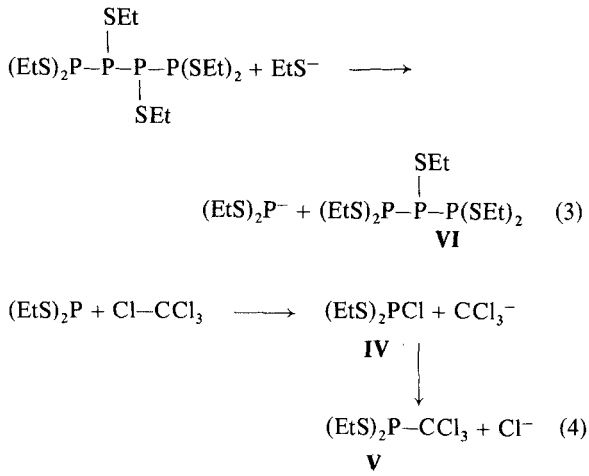
[a] Measured from the noise decoupled spectrum.

For this reason the triesters were reacted *in situ* with several reagents, in particular benzoyl chloride, dichloroacetaldehyde and phenacyl chloride and the resulting compounds isolated and analysed. (Experimental).

Although difficulty is experienced in isolating the triesters in high yield, it is clear thay they are formed in solution almost quantitatively under optimum conditions, and very little phosphorus is converted to inorganic phosphate. The reason for this high conversion lies in the high reactivity of the intermediate phosphide ion, **I**, towards tetrachloromethane resulting in the formation of a P–Cl compound, **II**, which in turn reacts rapidly with either alcohol or alkoxide ion to give the symmetrical diester, **III**.



(2)



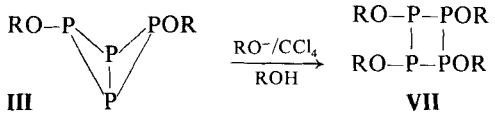
(3)

(4)

In the analogous reaction with thiolate ions in the presence of thiol,[10] intermediate phosphorus compounds, in particular diethyl phosphorochloridothiote, **IV**, and diethyl trichloromethylphosphonodithioite, **V**, are isolated. These are produced by the reaction of a disubstituted intermediate, e.g. **VI**, in the presence of a limited concentration of thiolate ions, and by further reaction of the chloridothioite with trichloromethyl anions formed *in situ*. The chlorodithioite, **IV**, is unreactive towards thiol, whereas the corresponding chloridite reacts rapidly with alcohol to give the ester (Eq. 2).

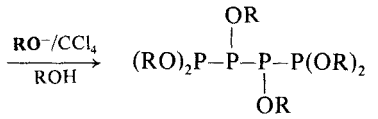
The initial product, **III**, reacts in a similar manner with alkoxide ions and tetrachloromethane. Of the two alternative sites, reaction at the unsubstituted phosphorus atom is preferred to reaction at the substituted phosphorus atom. The preferred reaction leads to a tetra-alkoxy cyclo tetraphosphine, **VII**, at

present unknown, related to tetra-alkyl cyclotetraphosphines which are in fact produced by the reaction of Grignard reagents with elemental phosphorus.[5,11]



III

VII



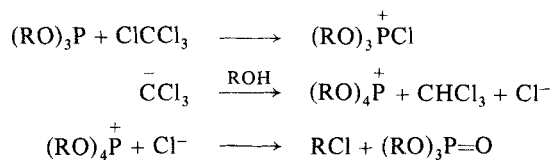
VIII

Further reaction gives the linear tetraphosphine, VIII, analogous to compound **VI** (Eq. 3).

By these series of processes the phosphorus tetrahedron is degraded to give trialkylphosphite as the major product.

Dialkyl phosphonate can be formed by protonation of the initial phosphide ion followed by successive reactions with alkoxide and tetrachloromethane. Alternatively, particularly in the later stages of the reaction, local acidity may develop and acid hydrolysis of trialkylphosphite may lead to dialkylphosphonate and alkyl halide in the well known Michaelis–Arbusov reaction.[12]

As the reaction proceeds the concentration of trialkylphosphite decreases as the yield of trialkylphosphate increases (Table II). This change is due to the reaction of phosphite with tetrachloromethane in the presence of alcohol.[13]



a reaction which has been widely studied mechanistically and synthetically.

EXPERIMENTAL

Reaction of finely divided phosphorus with sodium methoxide and tetrachloromethane in the presence of methanol

Method (*a*) Phosphorus sand (1.38 g, 0.011 mol) was prepared by melting a freshly cleaned piece of phosphorus under nitrogen in tetrachloromethane (30 ml) and cooling the rapidly stirred mixture in ice. A solution of sodium methoxide (3.61 g, 0.067 mol) in an excess of methanol (25 ml) was added dropwise under nitrogen with stirring and cooling to the phosphorus sand in tetrachloromethane. The reaction mixture became cloudy and after 30 min was milky in appearance. Then *n*-dodecane (0.39 g) was added as an internal standard and a sample of the reaction mixture was analysed by glc after various reaction times. Chloroform [SE 30 (35°), PEGA (80°)], methyl chloride [SE 30 (35°), QF 1 (50°)], dimethyl carbonate [QF 1 (50°), PEGA (80°)], trimethyl phosphite [SE 30 (35°), QF 1 (50°)], dimethyl phosphonate [SE 30 (50°), QF 1 (100°)], and trimethyl phosphate [SE 30 (50°), QF 1 (100°)] 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. After 48 h stirring at room temperature, unchanged phosphorus was still present in the reaction mixture.

Method (*b*) A solution of sodium methoxide (6.69 g, 0.124 mol) in an excess of methanol (50 ml) was added slowly at room temperature to phosphorus sand (1.28 g, 0.010 mol) in tetrachloromethane (30 ml), as in Method (a). In this case however the reaction appeared to proceed to completion with no phosphorus remaining unchanged. After 1 h, *n*-dodecane (0.39 g) was added as an internal standard and a sample of the reaction mixture was analysed by glc at various time intervals. Chloroform [SE 30 (35°), PEGA (80°)], trimethyl phosphite [SE 30 (35°), QF 1 (50°)], and trimethyl phosphate [SE 30 (50°), QF 1 (100°)] 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 trace of methyl chloride was detected and identified on the QF 1 column (50°) only. Nmr spectroscopy confirmed the presence of dimethyl phosphonate. A noise decoupled ^{31}P nmr spectrum of a filtered sample of the reaction mixture after completion, showed a line due to trimethyl phosphate, δ_P 1.6 [lit.[14,15] ($CDCl_3$) 2.4, (neat) 2.4] and one due to dimethyl phosphonate, δ_P 10.3 [lit.[16,17] (neat 11 ± 1)]. An undecoupled spectrum of the same sample showed the trimethyl phosphate signal as a ten-line multiplet, $^3J_{PH}$ 12 Hz (lit.[18,19] 12.2, 11.19 ± 0.2 Hz), and showed the dimethyl phosphonate signal as a doublet of septets, $^1J_{PH}$ 708, $^3J_{PH}$ 12 Hz (lit.[16,18] $^1J_{PH}$ 715, 696, $^3J_{PH}$ 12.2 Hz), with the upfield multiplet partially overlapping the trimethyl phosphate signal.

A control experiment to investigate the effect of methanolic sodium methoxide solution on tetrachloromethane, in the absence of phosphorus The procedure of method (b) was followed, but the reagents were mixed together in the absence of elemental phosphorus. Metallic sodium (2.76 g, 0.120 g atom), cleaned of its surface coating and weighed in dry diethyl ether, was allowed to react with an excess of methanol (50 ml), cooled by means of a cold-water bath. Tetrachloromethane (30 ml) was added and the mixture was stirred at room temperature. A white solid was gradually deposited and after 16 h, a sample of the reaction mixture was analysed by glc [SE 30 (35°)]. No chloroform was detected, but a trace of a compound was observed, which was shown to have the same retention time as authentic dimethyl carbonate, on two columns [QF 1 (50°), PEGA (80°)].

An attempted isolation of trimethyl phosphite, prepared from phosphorus White phosphorus (5.89 g, 0.048 mol) was allowed to react with sodium methoxide (30.77 g, 0.570 mol) in the presence of methanol (9.12 g, 0.285 mol) and an excess of tetrachloromethane (400 ml), as in method (b). Previous attempts to filter these reaction mixtures had proved difficult, so after the reaction mixture had been stirred for 3 h at room temperature under nitrogen, trimethyl phosphite and other volatile constituents were removed under vacuum (0.1 mmHg) and collected in a trap cooled by liquid nitrogen. At this stage, glc showed that no decomposition of the trimethyl phosphite produced had occurred. The vacuum-transferred material was then distilled at atmospheric pressure, using a 30 cm glass-filled fractionating column. A forerun was collected, then as the temperature rose to 74° the main fraction was collected. The temperature began to rise gradually and at 80° the final fraction was collected, the vapour temperature reaching a maximum of 95°. Samples of the main and final fractions were analysed by glc [QF 1 (50°)]. The main fraction consisted of tetrachloromethane contaminated with trimethyl phosphite. The final fraction consisted of trimethyl phosphite contaminated with tetrachloromethane.

A control experiment to investigate the possibility of separating a mixture of methanol, trimethyl phosphite and tetrachloromethane by fractional distillation Trimethyl phosphite (3.56 g, 0.029 mol) and methanol (1.38 g, 0.043 mol) were dissolved in tetrachloromethane (60 ml) and the solution was distilled at atmospheric pressure, using a 10 cm Vigreux fractionating-column. The first fraction was collected at 52° and as the vapour temperature began to rise, the main fraction was collected, during which the vapour temperature stabilised at 74°. An intermediate fraction was collected between 74° and 80°, then the final fraction was collected between 80° and 90°. Samples of the various fractions were analysed by glc [QF 1 (50°)]. The first fraction consisted only of methanol and tetrachloromethane. The main fraction, which contained no methanol, consisted of tetrachloromethane contaminated with trimethyl phosphite. The final fraction consisted of trimethyl phosphite contaminated with tetrachloromethane.

Reaction of trimethyl phosphite, prepared from phosphorus, *with benzoyl chloride* White phosphorus (5.94 g, 0.048 mol) was allowed to react with sodium methoxide (31.03 g, 0.575 mol) in the presence of methanol (9.20 g, 0.288 mol) and an excess of tetrachloromethane (400 ml). After the mixture had been stirred for 16 h at room temperature under nitrogen, trimethyl phosphite and other volatile constituents were removed under vacuum (0.1 mmHg) and collected in a trap cooled by liquid nitrogen. *n*-Decane (3.60 g) was added to the vacuum-transferred material (335 ml), as an internal standard and the amount of trimethyl phosphite present was estimated by glc (5.45 g, 23%). A portion of the vacuum-transferred material (155 ml, containing 0.020 mol trimethyl phosphite) was added dropwise under nitrogen with stirring and ice-cooling to benzoyl chloride (2.95 g, 0.021 mol). After the addition was complete, the mixture was stirred under nitrogen at room temperature for 30 min. The solvent was then removed by rotary evaporation and the residue was distilled under reduced pressure to give dimethyl benzoylphosphonate (4.28 g, 46%) as a pale green oil; bp 150–180° at 0.8 mmHg (lit.[20] 146° at 2.5 mmHg); $\delta(CCl_4)$ 4.05 (d, $^3J_{PH}$ 11 Hz, OCH_3) [lit.[20] (neat) 3.82 ($^3J_{PH}$ 11 Hz)]; $\nu_{max.}$ (film) 1655 (C=O), 1260 cm^{-1} (P=O) (lit.[20] 1650, 1258 cm^{-1}). A noise decoupled ^{31}P nmr spectrum of the product showed one line, δ_P ($CDCl_3$) 0.4 [lit.[21] ($CDCl_3$) 0.1]. The product was found to have the same retention time as authentic material[20] on two columns [SE 30 (75°), QF 1 (100°)].

Reaction of trimethyl phosphite, prepared from phosphorus, with dichloroacetaldehyde White phosphorus (5.12 g, 0.041 mol) was allowed to react with sodium methoxide (26.75 g, 0.495 mol) in the presence of methanol (8.00 g, 0.250 mol) and an excess of tetrachloromethane (347 ml), as in Method (b). After the reaction mixture had been stirred for 16 h at room temperature under nitrogen, *n*-decane (4.00 g) was added as an internal standard and the amount of trimethyl phosphite present was estimated by glc (9.73 g, 48%). At this point, the trimethyl phosphite and other volatile constituents were removed under vacuum (0.1 mmHg) and collected in a trap cooled by liquid nitrogen (vol. collected 250 ml). A portion of the vacuum-transferred material (64 ml, containing 0.020 mol trimethyl phosphite) was added rapidly to dichloroacetaldehyde polymer (2.26 g, 0.020 mol) to give a clear solution, after 16 h stirring at room temperature. Methyl chloride and the *E*- and *Z*-isomers of 2-chlorovinyl dimethyl phosphate were identified as products, by glc. Dimethyl phosphonate and trimethyl phosphate were also detected as impurities, all compounds being identified by comparison of their retention times on the QF 1 column (150°) with those of the authentic materials.† The residue from rotary evaporation of the reaction mixture was distilled under reduced pressure to give a mixture of the *E*- and *Z*-isomers of 2-chlorovinyl dimethyl phosphate (0.82 g, 22%); b.p. 120–140° at 22 mmHg (lit.[22] 60–61° at 0.08 mmHg); $\delta(CCl_4)$ 4.00, 4.03 (d $^3J_{PH}$ 12 Hz, OCH_3, *E*- and *Z*-isomers [lit.[22] (neat) 3.80 ($^3J_{PH}$ 11.5 Hz)], 6.05 (dd, $^3J_{HH}$ 4 Hz, OC=CH, *Z*-isomer‡) [lit.[24,25] (CCl_4) 5.605, 5.61 ($^3J_{HH}$ 4.3, 4.1 Hz)., 6.59 (dd, $^3J_{HH}$ 12 Hz OC=CH, *E*-isomer) [lit.[24,25] (CCl_4) 6.14, 6.16 ($^3J_{HH}$ 11.5, 11.15 Hz)], 7.23 (m, OCH=C, *E*- and *Z*-isomers) [lit.[22,24,25] (neat) 6.87, (CCl_4) 6.80, 6.78 (*E*-isomer); (neat) 6.96, (CCl_4) 6.84 (*Z*-isomer)]; ν_{max} (film) 1 640 (C=C), 1277 cm^{-1} (P=O) [lit.[26] (Calc.) 1286 cm^{-1}]. The *E*:*Z*-isomer ratio was shown to be 63 : 37, by integration of the 2-vinyl proton resonances.

The isolation of trimethyl phosphite, prepared from phosphorus as dimethyl 1-phenylvinyl phosphate by reaction with phenacyl chloride White phosphorus (5.64 g, 0.045 mol) was allowed to react with sodium methoxide (29.47 g, 0.546 mol) in the presence of methanol (8.73 g, 0.273 mol) and an excess of tetrachloromethane (382 ml), as in Method (b). After the reaction mixture had been stirred for 3 h at room temperature under nitrogen, *n*-decane (3.37 g) was added as an internal standard and the amount of trimethyl phosphite present was estimated by glc (11.99 g, 53%). At this point, the reaction mixture was filtered through Kieselguhr and the filtrate was added rapidly with stirring to an excess of phenacyl chloride (18.68 g, 0.121 mol). Slight effervescence occurred and an orange solution resulted, which faded to pale yellow after 5 min. The mixture was stirred for 16 h at room temperature, washed with water, and the organic phase dried ($MgSO_4$). The residue from rotary evaporation of the dried material, was distilled under reduced pressure to give, in addition to some unchanged phenacyl chloride, bp 126–132° at 16 mmHg (lit.[27] 133–134° at 20 mmHg), dimethyl 1-phenylvinyl phosphate (2.63 g, 12%), bp

† Pure samples of the individual *E*- and *Z*-isomers of 2-chlorovinyl dimethyl phosphate were kindly given to us by Dr. Grayson.

‡ Each of the 2-vinyl proton resonances was assigned to a particular isomer on the basis of the magnitude of $^3J_{HH}$.[23]

182–184° at 16 mmHg (lit.[28,29] 112–114° at 0.01 mmHg, 143° at 3.0 mmHg); a noise decoupled ^{31}P nmr spectrum of the product showed one line δ_P ($CDCl_3$) −4.3 (lit.[30] −4.22); δ(CCl_4) 7.52 (5H, m, C_6H_5), 5.27 (2H, m, $^4J_{PH}$ 2 Hz, C=CH_2), 3.74 (6H, d, $^3J_{PH}$ 11.5 Hz, OCH_3) [lit.[30] (CCl_4) 7.44 (C_6H_5), 5.21 ($^4J_{PH}$ ~ 2.3 Hz, C=CH_2), 3.75 ($^3J_{PH}$ 11.5 Hz, OCH_3)]; $\nu_{max.}$ (film) 1635 (C=C), 1280 cm^{-1} (P=O) [lit.[26] (calc.) 1286 cm^{-1}].

Reaction of finely divided phosphorus with sodium ethoxide and tetrachloromethane in the presence of ethanol—Method (b) This reaction was carried out in a similar way to the reaction with methanol, using (2.76 g, 0.120 g atom) with an excess of absolute ethanol (48 ml), phosphorus sand (1.03 g) in tetrachloromethane (30 ml).

A noise decoupled spectrum of the sample showed two lines, one due to triethylphosphite, δ_P 137.9 [lit,[17,31] (neat) 139 (±1), 136.9], and the other due to triethyl phosphate, δ_P −1.9 lit.[17,31] (neat) −1 ± 1, −0.9].

Reaction of triethyl phosphite, prepared from phosphorus, with α-chloroisobutyrophenone Absolute ethanol (20 ml) was added under nitrogen to a solution of white phosphorus (0.62 g, 0.005 mol) in an excess of tetrachloromethane (400 ml), cooled in ice. Sodium ethoxide (4.08 g, 0.060 mol) was added under nitrogen to the stirred mixture in one portion, and after 15 min the ice bath was removed and the apparatus was sealed under nitrogen. After 24 h, α-chloroisobutyrophenone (3.65 g, 0.020 mol) was added to the crude reaction mixture and the whole was heated under reflux on a water bath for 16 h. At this point, a sample of the cooled reaction mixture was analysed by glc. Diethyl phenyl-2,2-dimethylvinyl phosphate [SE 30 (150°), QF 1 (200°)] was identified as a product, by comparison of its retention time on the first column with that of the authentic material and this was confirmed by the same procedure on the second column. The yield was low however, and on distillation of the residue from rotary evaporation of the filtered reaction mixture, a material was isolated which was shown to be a mixture. A noise decoupled ^{31}P nmr spectrum of the isolated material showed a line due to diethyl phenyl-2,2-dimethylvinyl phosphate, δ_P ($CDCl_3$) −5.7, and a line due to triethyl phosphate, δ_P ($CDCl_3$) − 1.2 [lit.[17] (neat) −1 ± 1].

A sample of authentic diethyl phenyl-2,2-dimethylvinyl phosphate was prepared, for purposes of comparison, by the method of Borowitz and his co-workers,[32] bp 110–112° at 0.1 mmHg (lit.[32] 126–128° at 0.3 mmHg); a noise decoupled ^{31}P nmr spectrum of the authentic material showed one line, δ_P ($CDCl_3$) −5.8.

The isolation of triethyl phosphite, prepared from phosphorus, as diethyl 1-phenylvinyl phosphate by reaction with phenacyl chloride The reaction was carried out as in the preparation of dimethyl 1-phenylvinyl phosphate from white phosphorus (1.24 g), sodium ethoxide (8.16 g) in ethanol (40 ml), tetrachloromethane (400 ml) and phenacyl chloride (6.18 g). Diethyl 1-phenylvinyl phosphate (1.73 g, 17%) was isolated by fractional distillation, bp 108–110° at 4 nm (lit.[32,33] 110–118° at 0.15 nm; 112° at 0.01 nm).

A noise decoupled ^{31}P nmr spectrum of the product showed a major line, δ_P ($CDCl_3$) −6.6 [lit.[30] −10.00], and a minor line, δ_P 0.2; δ($CDCl_3$) 7.46 (m, C_6H_5), 5.24 (m, $^4J_{PH}$ 2.5 Hz, C=CH_2), 4.20 (dq, $^3J_{PH}$ 8.3 Hz, $^3J_{HH}$ 7.0 Hz, OCH_2), 1.34 (dt, $^3J_{HH}$ 7.0, $^4J_{PH}$ 1 Hz, CH_3) in close agreement with literature values.[30,34]

Reaction of phosphorus with sodium n-butoxide and tetrachloromethane in the presence of n-butanol—Method (a) A solution of sodium *n*-butoxide in *n*-butanol, prepared by the reaction of metallic sodium (1.38 g, 0.060 g atom) with an excess of *n*-butanol (50 ml) at room temperature, was added dropwise under nitrogen with stirring and cooling to phosphorus sand (1.15 g, 0.009 mol), in tetrachloromethane (30 ml). The mixture was stirred for 1 h at room temperature, *n*-dodecane (0.77 g) was added as an internal standard, and a sample of the reaction mixture was analysed by glc at various time intervals. Chloroform [SE 30 (35°), PEGA (50°)], *n*-butyl chloride [SE 30 (35°), QF 1 (50°)], di-*n*-butyl carbonate [SE 30 (100°), QF 1 (180°)], di-*n*-butyl phosphonate [SE 30 (125°), QF 1 (180°)], tri-*n*-butyl phosphite [SE 30 (125°), QF 1 (180°)], and tri-*n*-butyl phosphate [SE 30 (160°), QF 1 (180°)] 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.

Method (b) A solution of sodium *n*-butoxide in *n*-butanol, prepared by the reaction of metallic sodium (2.76 g, 0.120 g atom) with an excess of *n*-butanol (70 ml), was added to phosphorus sand (1.16 g, 0.009 mol), in a mixture of tetrachloromethane (12.97 g, 0.084 mol) and an an excess of di-*n*-butyl ether (25 ml), as in Method (a). On addition of the butoxide solution the reaction mixture became deep brown, in marked contrast to the reaction of elemental phosphorus with sodium methoxide in the presence of di-*n*-butyl ether and with sodium *n*-butoxide under various conditions. The colour faded gradually and after 3 days the reaction mixture was milky in appearance. After 3 h, *n*-dodecane (0.78 g) was added as an internal standard and samples of the reaction mixture was analysed by glc at various reaction times. Chloroform [SE 30 (35°), PEGA (50°)], tri-*n*-butyl phosphite [SE 30 (125°), QF 1 (180°)], and tri-*n*-butyl phosphate [SE 30 (160°), QF 1 (180°)] 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.

Preparation of tri-n-butyl phosphite from phosphorus—A solution of sodium *n*-butoxide in *n*-butanol was prepared by the reaction of metallic sodium (13.8 g, 0.600 g atom) with an excess of *n*-butanol (250 ml). A portion of this solution (215 ml) was added under nitrogen dropwise with stirring to phosphorus sand (4.02 g, 0.032 mol) in an excess of tetrachloromethane (150 ml), cooled by means of an ice-salt bath. After the addition was complete, the cooling bath was removed and the reaction mixture was stirred under nitrogen for 3 h. Chloroform and unchanged tetrachloromethane was removed under vacuum (0.1 mmHg) and collected in a trap cooled by liquid nitrogen. A sample of the vacuum transferred material was analysed by glc [SE 30 (160°)] and no tri-*n*-butyl phosphite was detected. The reaction mixture, after removal of the volatile components, was filtered through Kieselguhr under nitrogen and the reaction flask and residue was rinsed with a small quantity of dry diethyl ether. The ether washings were combined with the filtrate and the whole was dried ($MgSO_4$). Distillation of the residue from rotary evaporation of the dried material gave tri-*n*-butyl phosphite (4.48 g, 14%); bp 128–130° at 14 mmHg (lit.[35] 122° at 12 mmHg). (Found: C, 57.8; H, 11.1. Calc. for $C_{12}H_{27}O_3P$: C, 57.6; H, 10.9%); a noise decoupled ^{31}P nmr spectrum of the isolated tri-*n*-butyl phosphite showed one line, δ_P (C_6D_6) 138.2 [lit.[16,35] (neat) 139 (±1), 140 (±1)]; δ($CDCl_3$) 4.06 (6H, dt, $^3J_{PH}$ 8.23, $^3J_{HH}$ 6.86 Hz, OCH_2) (lit.[36] $^3J_{PH}$ 8.6 Hz).

Treatment of finely divided phosphorus with sodium phenoxide and tetrachloromethane in the presence of phenol Phosphorus sand in an excess of tetrachloromethane (140 ml) was prepared from a piece of white phosphorus (1.35 g, 0.011 mol) which had been cleaned, dried and weighed under nitrogen. Phenol (6.14 g, 0.065 mol) was added in one portion with stirring, and sodium phenoxide (7.58 g, 0.065 mol) was added over a period of about 5 min. At this point the apparatus was sealed under nitrogen and stirring was continued at room temperature. After 24 h, a sample was analysed by glc [SE 30 (35°, 245°)] but no chloroform, triphenyl phosphite, or other product was detected. The reaction mixture was then heated and stirred under reflux for a further 12 h. A sample of the cooled reaction mixture was analysed by glc [SE 30 (245°)] but again no products were detected.

Reaction of finely divided phosphorus with aqueous potassium hydroxide and tetrachloromethane, in the presence of n-Butanol (a) A solution of potassium hydroxide (12.74 g, 0.227 mol) in water (25 ml) was added dropwise with stirring to phosphorus sand (4.7 g, 0.038 mol) in a mixture of tetrachloromethane (35.02 g, 0.227 mol) and *n*-butanol (33.61 g, 0.455 mol), cooled by means of a cold-water bath. After 24 h at room temperature the reaction mixture, containing some unchanged phosphorus, was filtered through Kieselguhr and the two layers in the filtrate were separated. A sample of the organic phase was analysed by glc and two of the products were shown to be chloroform [SE 30 (35°), PEGA (50°)] and tri-*n*-butyl phosphate [SE 30 (160°), QF 1 (180°)]. No *n*-butyl chloride was detected by glc [SE 30 (35°)]. A noise decoupled ^{31}P nmr spectrum of a sample of the organic phase showed lines due to the mono- and di-*n*-butyl esters of phosphonic acid and to the mono-, di and tri-*n*-butyl esters of phosphoric acid, that due to *n*-butyl hydrogen phosphonate being the most intense in the spectrum. Assignments were made on the basis of the chemical shifts of the lines and of the multiplicity and coupling constants observed in an undecoupled spectrum of the same sample. These assignments and the data on which they are based are presented in Table 3. Qualitative analysis of the aqueous phase, which gave a pH 3 reaction to Universal Indicator paper, confirmed the presence of chloride as silver chloride and orthophosphate (as molydbate) anions. A noise decoupled ^{31}P nmr spectrum of a sample of the aqueous phase showed three lines, due to phosphoric acid, phosphorus acid, and hypophosphorus acid. Again assignments were based on the chemical shifts of the lines and on the multiplicity and coupling constants observed in an undecoupled spectrum of the same sample. The assignments and the data on which they are based are presented in Table 3. (b) A solution of potassium hydroxide (29.76 g, 0.531 mol) in water (100 ml) was added dropwise under nitrogen with stirring and ice-cooling to phosphorus sand (5.48 g, 0.044 mol), in a mixture of *n*-butanol (39.24 g, 0.530 mol) and an excess of tetrachloromethane (60 ml). After 24 h at room temperature, all of the phosphorus had been used up. The two phases were separated, the aqueous phase was extracted with 2 × 25 ml portions of tetrachloromethane, the extracts were combined with the organic phase, and the whole was dried ($MgSO_4$). A sample of the dried material was analysed by glc [SE 30 (35°), (160°)]. Chloroform, di-*n*-butyl carbonate and tri-*n*-butyl phosphate were detected as products, but *n*-butyl chloride and di-*n*-butyl phosphonate were not detected. The residue from rotary evaporation of the dry organic phase was distilled at atmospheric pressure. As in the previous experiment, once the unchanged *n*-butanol had been collected at 116–118° (lit.[37] 117.5°), the residue in the distilling flask was too low in volume to be distilled further. The residue (0.49 g) was shown by glc [SE 30 (160°)] to consist of tri-*n*-butyl phosphate contaminated with traces of other compounds, including di-*n*-butyl carbonate and di-*n*-butyl phosphonate. This represents less than 3% conversion into organophosphorus products. A noise decoupled ^{31}P nmr spectrum of the residue in tetrachloromethane, showed one major line and two minor ones. The major line was due to tri-*n*-butyl phosphate, δ_P 0.6 (lit.[38] 0.6), one of the minor lines was due to di-*n*-butyl phosphonate, δ_P −10.18 [lit.[39] (neat) −8 (±1), and the other was assigned to di-*n*-butyl phosphate δ_P 2.0 [lit.[40] (neat) 0 ± 0.5]. A noise decoupled ^{31}P nmr spectrum of a sample of the aqueous phase showed two lines. An undecoupled spectrum of the same sample showed a 1:1 doublet due to phosphite di-anion δ_P + 3.0, $^1J_{PH}$ 568 Hz, lit.[41] δ_P 3.3 $^1J_{PH}$ 567 Hz and a 1:2:1 triplet due to hypophosphite anion, δ_P −7.2 $^1J_{PH}$ 519 Hz, lit.[42] δ_P 7.3 $^1J_{PH}$ 518.

Reaction of finely divided phosphorus with aqueous potassium hydroxide and tetrachloromethane, in the presence of methanol A solution of potassium hydroxide (29.48 g, 0.525 mol) in water (100 ml) was added to phosphorus sand (5.45 g, 0.044 mol), in a mixture of methanol (16.82 g, 0.526 mol) and an excess of tetrachloromethane (60 ml), by the procedure used in section (b) of the previous experiment. After 24 h at room temperature, all of the phosphorus had been used up. The two phases were separated and the aqueous phase was extracted with 2× 25 ml portions of tetrachloromethane. During the extractions the separation into organic and aqueous phases was poor, therefore solid sodium chloride was added in order to break up the resulting emulsions. The extracts were combined with the organic phase and the whole was dried ($MgSO_4$). A sample of the dried material was analysed by glc [SE 30 (35°), PEGA (50°), QF 1 (100°)], and chloroform [SE 30 (35°), PEGA (50°)] was the only product to be detected. No dimethyl carbonate, dimethyl phosphonate or trimethyl phosphate was detected. An undecoupled ^{31}P nmr spectrum of a sample of the aqueous phase showed a 1:1 doublet due to the phosphite anion, δ_P −3.0 ($^1J_{PH}$ 568 Hz) and a 1:2:1 triplet due to the hypophosphite anion, δ_P −7.1 ($^1J_{PH}$ 519 Hz).

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REFERENCES

1. M. M. Rauhut, *Topics in Phosphorus Chemistry*, M. Grayson and E. J. Griffith, Interscience, New York 1964, Vol. 1, p. 1; L. Maier, *Fortsch. Chem. Forsch.* **19**, 1 (1971).
2. C. Brown, R. F. Hudson, G. Wartew and H. Coates, *J. Chem. Soc. Chem. Comm.* 7 (1978).
3. H. Boch, *Pure and Appl. Chem.* **44**, 343 (1975); G. Heckmann and E. Fluck, *Mol. Phys.* **23**, 175 (1972).
4. J. R. Van Wazer, *Phosphorus and Its Compounds*, Interscience, New York, 1958, Vol. I, p. 356.
5. M. M. Rauhut and A. M. Semsel, *J. Org. Chem.* **28**, 473 (1963).
6. L. Maier, *Z. Anorg. Chem.* **394**, 117 (1972); *Helv. Chim. Acta*, **50**, 1723 (1967); **52**, 827 (1969).
7. M. M. Rauhut, R. Bernheimer and A. M. Semsel, *J. Org. Chem.* **28**, 478 (1963).
8. Chisung Wu, *J. Am. Chem. Soc.* **87**, 2522 (1965).

9. For full details see G. A. Wartew, Ph.D Thesis, University of Kent, 1976.
10. C. Brown, R. F. Hudson and G. A. Wartew, *J. Chem. Soc. Perk.* **I** (1978).
11. A. H. Cowley and R. P. Pinnell, *Inorg. Chem.* **5**, 1463 (1966).
12. W. Gerrard and E. C. G. Whitbread, *J. Chem. Soc.* 914 (1952).
13. A. J. Burn and J. I. G. Cadogan, *J. Chem. Soc.* 5788 (1963).
14. F. Ramirez, O. P. Madan and C. P. Smith, *Tetrahedron*, **22**, 567 (1966).
15. R. A. Y. Jones and A. R. Katritzky, *Angew. Chem.* **74**, 60 (1962).
16. K. Moedritzer, *J. Inorg. Nuclear Chem.* **22**, 19 (1961).
17. J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, *J. Am. Chem. Soc.* **78**, 5715 (1956).
18. G. Mavel, *Compt. Rend.* **248**, 3699 (1959).
19. R. C. Axtmann, W. E. Shuler and J. H. Eberly, *J. Chem. Phys.* **31**, 850 (1959).
20. K. D. Berlin and H. A. Taylor, *J. Am. Chem. Soc.* **86**, 3862 (1964).
21. V. T. Rice, Ph.D. Thesis, University of Kent at Canterbury, 1973.
22. A. R. Stiles, C. A. Reilly, G. R. Pollard, C. H. Tieman, L. F. Ward, Jr., D. D. Phillips, S. B. Soloway and R. R. Whetstone, *J. Org. Chem.* **26**, 3960 (1961).
23. H. M. McConnell, C. A. Reilly and A. D. McLean, *J. Chem. Phys.* **24**, 479 (1956); S. Alexander, *J. Chem. Phys.* **28**, 358 (1958).
24. I. J. Borowitz, S. Firstenberg, E. W. R. Casper and R. K. Crouch, *J. Org. Chem.* **36**, 3282 (1971).
25. C. B. C. Boyce, S. B. Webb, L. Phillips and P. A. Worthington, *J. Chem. Soc. Perk.* **I**, 2881, 1973.
26. L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta* **20**, 247 (1964).
27. R. C. Weast, *Handbook of Chemistry and Physics* Chemical Rubber Co., Cleveland, Ohio, 47th edn., p. C-102.
28. P. A. Chopard, V. M. Clark, R. F. Hudson and A. J. Kirby, *Tetrahedron* **21**, 1961 (1965).
29. E. M. Gaydou, R. Freze and G. Buono, *Bull. Soc. Chim. France* 2279 (1973).
30. E. M. Gaydou, *Canad. J. Chem.* **51**, 3412 (1973).
31. N. Muller, P. C. Lauterbur and J. Goldenson, *J. Am. Chem. Soc.* **78**, 3557 (1956).
32. I. J. Borowitz, M. Anschel and S. Firstenberg, *J. Org. Chem.* **32**, 1723 (1967).
33. R. F. Hudson, P. A. Chopard and G. Salvadori, *Helv. Chim. Acta* **47**, 632 (1964).
34. R. D. Frampton, T. T. Tidwell and V. A. Young, *J. Am. Chem. Soc.* **94**, 1271 (1972).
35. L. F. Johnson and W. C. Jankowski, *Carbon-13 NMR Spectra. A Collection of Assigned, Coded and Indexed Spectra* (Wiley-Interscience, New York, 1972) spectrum no. 363.
36. A. R. Katritzky, J. M. Lagowski and J. A. T. Beard, *Spectrochim. Acta*, **16**, 964 (1960).
37. L. W. Daasch and D. C. Smith, *Analyt. Chem.* **23**, 853 (1951).
38. L. J. Bellamy and L. Beecher, *J. Chem. Soc.* 475, (1952).
39. L. L. Burger, *J. Phys. Chem.* **62**, 590 (1958).
40. R. C. Weast, *Handbook of Chemistry and Physics* (Chemical Rubber Co., Cleveland, Ohio) 47 th edn., p. C-474.
41. E. Fluck and H. Binder, *Z. Anorg. Chem.* **354**, 139 (1967).
42. R. A. Shaw and M. Woods, *Phosphorus* **1**, 191 (1971).