458. *The Organic Chemistry of Phosphorus. Part I. Some New Methods for the Preparation of Alkyl Halides.**

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Triphenyl phosphite methiodide has been shown to react with alcohols, thus :

$$(PhO)_3PMeI + ROH \longrightarrow RI + PhOH + Me{\cdot}PO(OPh)_2$$

The reaction gives good yields of alkyl iodides from a wide variety of alcohols; alkyl chlorides can be prepared similarly from triphenyl phosphite benzylochloride, $(PhO)_3P(CH_2Ph)Cl$. Alkyl halides can also be prepared conveniently and in good yield according to the general equation :

$$(PhO)_3P + ROH + XHal \longrightarrow RHal + X{\cdot}PO(OPh)_2 + PhOH$$

where X = alkyl or hydrogen; poor yields are obtained where X = NH_4,Na, or Li. These reactions are of value as new methods for the preparation of alkyl halides; their mechanisms are briefly discussed.

The work described in this paper had its origin in a general investigation of the influence of structure on the Arbusov reaction (Arbusov, *J. Russ. Phys. Chem. Soc.*, 1906, **38**, 687; cf. Michaelis and Kähne, *Ber.*, 1898, **31**, 1048) in which an alkyl halide reacts with a trialkyl phosphite, thus :

$$(RO)_3P + R'Hal \longrightarrow R'{\cdot}PO(OR)_2 + RHal$$

(for a comprehensive review of this reaction see G. M. Kosolapoff, " Organophosphorus Compounds," John Wiley & Sons, New York, 1950, p. 121). If R = R′ the reaction becomes formally catalytic, a small amount of an alkyl halide, RHal, serving to convert a large amount of a trialkyl phosphite, $(RO)_3P$, into the isomeric dialkyl alkylphosphonate, $R{\cdot}PO(OR)_2$. This was realised by the earlier workers (Arbusov, *loc. cit.*; Arbusov and Razumov, *Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1945, 167) but direct experimental evidence is scanty and we record experiments which show that as little as 0·01 mol. of methyl iodide will bring about the isomerisation of trimethyl phosphite; methyl sulphate is as effective for this purpose as methyl iodide.

The intervention of the " quasi-phosphonium " compound, $(RO)_3PR'Hal$, in the reaction was postulated by Arbusov (*loc. cit.*) and this view has been generally accepted; it is supported by Kosolapoff's finding (*J. Amer. Chem. Soc.*, 1944, **66**, 109) that the curve

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* The work described in this paper has been the subject of a preliminary communication (*Chem. and Ind.*, 1951, 313), and of two patent applications (B.P. Appln. 20,639/1950 and 2889/51).

relating the production of RHal to the reaction time is sigmoid and by the not entirely satisfactory kinetic work of Zawidski and Staronka (*Bull. int. Acad. Sci. Cracovie, A*, 1915, 319). In the complete reaction scheme

$$(RO)_3P + R'Hal \longrightarrow (RO)_3PR'Hal \quad . . . . \quad (i)$$

$$(RO)_3PR'Hal \longrightarrow R'{\cdot}PO(OR)_2 + RHal \quad . . . . \quad (ii)$$

all the evidence points to the second stage being normally the rate-determining one; thus the action of methyl iodide on triethyl phosphite produces almost exclusively diethyl methylphosphonate, presumably because stage (i) has gone to completion before any appreciable amount of ethyl iodide has been liberated in stage (ii), and it is only when RHal is much more reactive than R'Hal that any competition between the two halides for the available phosphite is observed (*e.g.*, in the reaction between triethyl phosphite and ethylene dibromide; Ford-Moore and Williams, *J.*, 1947, 1465).

In the case of triaryl phosphites both stages of the reaction are slow and it is easy to isolate the intermediate quasi-phosphonium compound (Michaelis and Kähne, *loc. cit.*, Broeker, *J. prakt. Chem.*, 1928, **118**, 287). It seemed important to study the chemistry of these compounds and we accordingly prepared triphenyl phosphite methiodide,* $(PhO)_3PMeI$; by rapid working with exclusion of moisture, we obtained this compound as needles, m. p. 146° (Michaelis and Kähne, *loc. cit.*, give m. p. 70—75°). In an attempt to determine the nature of the phosphorus–iodine bond in this compound, we treated it with alcoholic silver nitrate; precipitation of silver iodide was slow, and not instantaneous as with methyltriphenylphosphonium iodide. In order to exclude the possibility that the time-dependent production of silver iodide was due to reaction of the silver nitrate with methyl iodide formed by dissociation, the compound was treated with cold ethanol and methyl iodide was sought in the product; surprisingly, ethyl iodide was formed, together with phenol and diphenyl methylphosphonate.

This promised a method for the preparation of alkyl iodides and therafter we concerned ourselves mainly with the preparative aspect of the reaction. Triphenyl phosphite methiodide was found to react with a wide variety of alcohols according to the equation:

$$(PhO)_3PMeI + ROH \longrightarrow RI + PhOH + Me{\cdot}PO(OPh)_2$$

This appears to be quite general.

The preparative procedure is very simple; the alcohol and the methiodide, which need not be purified, are merely mixed in equivalent proportions; cooling may be necessary with the more reactive, and gentle warming with the less reactive, alcohols; the product is worked up either by direct distillation or by washing out the phenol with alkali, followed by distillation or crystallisation. Working on the 0·05—0·1-molar scale the yields of iodide obtained from thirteen alcohols varied from 60 to 95%; no attempt was made to establish optimal conditions and it seems likely that 90% yields will generally be attainable. The method is satisfactory with primary, secondary, and tertiary alcohols, unsaturated alcohols, glycols, and ethyl lactate; conversion of the last-named into ethyl α-iodopropionate in excellent yield makes this useful reagent much more accessible than it has been by the older and less direct methods (Bodroux and Taboury, *Bull. Soc. chim.*, 1907, **1**, 910; Kenyon, Phillips, and Turley, *J.*, 1925, **127**, 414). The direct production, albeit in poor yield, of cholesteryl iodide from cholesterol is of interest since this iodide has previously only been obtained indirectly (Beynon, Heilbron, and Spring, *J.*, 1936, 907; Helferich and Günther, *Ber.*, 1939, **72**, 338; Shoppee and Summers, *J.*, 1952, 1786).

Michaelis and Kähne (*loc. cit.*) also prepared triphenyl phosphite benzylochloride, $(PhO)_3P(CH_2Ph)Cl$, as an uncrystallisable oil, and we have used this substance to prepare *n*-hexyl chloride and 2-chloro-octane in excellent yield from the corresponding alcohols; there is not doubt that this method, too, is general.

Attempts to prepare tribenzyl phosphite methiodide failed owing to its immediate decomposition into benzyl iodide and dibenzyl methylphosphonate.

It is not necessary to isolate the quasi-phosphonium compound and alkyl chlorides,

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* We prefer this non-committal name to the systematic alternatives, methyltriphenoxyphosphonium iodide for the electrovalent and triphenyl methylphosphoranoiodidotrioate for the covalent structure.

bromides, and iodides can be readily prepared by merely refluxing together equimolecular quantities of triphenyl phosphite, an alcohol, and an alkyl halide, thus :

$$(PhO)_3P + ROH + R'Hal \longrightarrow RHal + R'\cdot PO(OPh)_2 + PhOH \quad . \quad . \quad . \quad . \quad (iii)$$

It is necessary, in order to avoid competition between R'Hal and RHal for unchanged phosphite, for R'Hal to be more reactive than RHal, unless the latter is removed as fast as it is formed (an example of this procedure is given on p. 2231) ; the most convenient halides for preparative use are benzyl chloride, benzyl bromide, and methyl iodide, although others can be used (examples will be found in the Experimental section). The reactants are best heated together by use of an electric mantle since the temperature can this conveniently be slowly raised as the usually more volatile R'Hal is used up; if the temperature is not raised during the reaction the yield may be much reduced or the necessary reaction time unduly prolonged; the progress of the reaction can be followed conveniently by observing the internal temperature of the gently refluxing reaction mixture. A wide variety of alkyl halides has been prepared in this way in yields varying from 60 to 99%; yields of 90% should be attainable in most cases. In general this method is more convenient than that employing the preformed quasi-phosphonium compound, although the latter may be preferable when the alcohol or iodide is heat-sensitive (*e.g.*, in the preparation of *cyclo*hexyl and *tert.*-butyl iodides). The new method gives excellent results with sterically hindered alcohols which are difficult to convert into halides by conventional methods; thus *neo*pentyl iodide was obtained from the alcohol in 74% yield, a great improvement over earlier methods (Whitmore, Whittle, and Harriman, *J. Amer. Chem. Soc.*, 1939, **61**, 1585), and 1 : 3-di-iodo-2 : 2-dimethylpropane in 85% yield from the corresponding glycol (conventional methods fail for this preparation; the dibromide was obtained in 35% yield by Whitmore, Popkin, Bernstein, and Wilkins, *J. Amer. Chem. Soc.*, 1941, **63**, 124). Other phosphites may replace triphenyl phosphite; thus *n*-butyl iodide was obtained in 40% yield from triethyl phosphite, butanol, and methyl iodide, but was accompanied by much ethyl iodide produced by the direct Arbusov reaction between triethyl phosphite and methyl iodide.

Equation (iii) can be generalised, thus :

$$(PhO)_3P + ROH + XHal \longrightarrow RHal + X\cdot PO(OPh)_2 + PhOH \quad . \quad . \quad . \quad . \quad (iv)$$

and we report here our results for the cases where X = H, NH_4, Li, and Na; work is in progress on the case where X = Halogen (cf. B.P. Appln. 20,205/1951) and our results will be reported later. A number of alkyl chlorides, including unsaturated alkyl chlorides, have been prepared in moderate to good yield (45—100%) by passing dry hydrogen chloride into a mixture of an alcohol and triphenyl phosphite. *n*-Butyl halides have also been prepared by heating *n*-butyl alcohol and triphenyl phosphite with ammonium chloride, sodium chloride, lithium bromide, and sodium iodide; the yields were poor except with ammonium chloride, which gave a 63% yield.

Several plausible mechanisms for the reaction between triphenyl phosphite methiodide and an alcohol can be envisaged, but the evidence available is hardly sufficient to enable a definite conclusion to be reached. Mechanisms which would lead to the intermediate formation of hydrogen iodide seem to be excluded by our finding that dimethylaniline ethiodide, rather than the hydriodide, is produced when triphenyl phosphite methiodide reacts with ethanol in the presence of dimethylaniline. An acceptable mechanism must also accommodate our observation that configurational inversion accompanies the formation of 2-iodo-octane from octan-2-ol; the very considerable racemisation which accompanies inversion is doubtless due to the prolonged contact of the alkyl iodide with iodide ions (cf. Hughes, Juliusberger, Masterman, Topley, and Weiss, *J.*, 1935, 1527). The mechanism which we adopt as a working hypothesis is the following, in which ester interchange is followed by the second stage of the normal Arbusov reaction :

$$(PhO)_3PMeI + ROH \longrightarrow (PhO)_2(RO)PMeI + PhOH$$
$$(PhO)_2(RO)PMeI \longrightarrow Me\cdot PO(OPh)_2 + RI$$

The great strength of the phosphorus–carbon bond would seem to rule out the possibility that the first stage is composite, involving initial dissociation of the methiodide into its components.

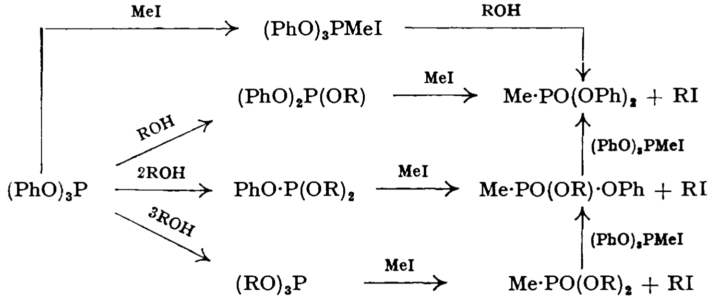
The three-component reaction (equations iii and iv) is demonstrably more complex, ester-interchange playing an important part. Ester-interchange between triphenyl phosphite and many alcohols occurs very readily; thus, the odour of trimethyl phosphite becomes apparent within a few minutes of mixing triphenyl phosphite and methanol at room temperature. Ester-interchange between equimolecular proportions of triphenyl phosphite and *n*-butyl alcohol yields one molecular proportion of phenol together with all the possible phosphites, *viz.*, tri-*n*-butyl phosphite, di-*n*-butyl phenyl phosphite, *n*-butyl diphenyl phosphite, and triphenyl phosphite. The action of methyl iodide on the resulting mixture of phosphites occurs in two stages, the first of which undoubtedly proceeds by the normal Arbusov mechanism but is incapable of giving rise to the high observed yields of alkyl halide. This is followed by a slower liberation of more *n*-butyl iodide which can only be accounted for by reaction between triphenyl phosphite methiodide and butyl methylphosphonates produced in the first stage; the occurrence of such a reaction has been independently established in the case of dimethyl methylphosphonate which reacts readily with triphenyl phosphite methiodide, thus :

$$Me{\cdot}PO(OMe)_2 + 2(PhO)_3PMeI \longrightarrow 2MeI + 3Me{\cdot}PO(OPh)_2$$

Alkyl iodides are also formed by the action of triphenyl phosphite methiodide on trialkyl phosphites, *e.g.* :

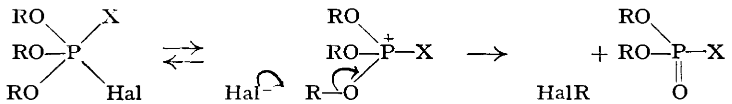
$$(BuO)_3P + (PhO)_3PMeI \longrightarrow BuI + Me{\cdot}PO(OBu)_2 + (PhO)_3P$$

but this reaction is unlikely to be of any importance in the three-component reaction since the Arbusov reaction with alkyl phosphites is much faster than the formation of triphenyl phosphite methiodide. The three-component reaction between triphenyl phosphite, an alcohol and methyl iodide probably involves all the reactions summarised in the following scheme :



the extent to which each participates depending on the reactivity of ROH.

All the reactions involve a stage identical with the second stage of the normal Arbusov reaction. The absence of rearrangement in the formation of the *neo*pentyl halides and the configurational inversion which accompanies the formation of the 2-halogeno-octanes suggest that the process is of this *S*2 type :



The absence of configurational inversion in the formation of the cholesteryl halides is paralleled by the similar anomaly observed with other reagents and is no doubt to be explained in the same way (cf. Shoppee, *J.*, 1946, 1147). The formation of unrearranged *neo*pentyl halides from *neo*pentyl alcohol is of interest in view of the widely held opinion that reactions involving *neo*pentyl–oxygen bond fission are invariably accompanied by rearrangement (cf. Whitmore, *J. Amer. Chem. Soc.*, 1932, **54**, 3274); since our experiments were completed, Sommer, Blankman, and Miller (*J. Amer. Chem. Soc.*, 1951, **73**, 3542) have observed similar absence of rearrangement in *S*2 conversions of *neo*pentyl alcohol into *neo*pentyl halides.

An *S*2 mechanism for the second stage of the Arbusov reaction is further supported by experiments with mixed trialkyl phosphites which react with methyl iodide with the liberation, as alkyl iodide, of the least electron-releasing alkyl group (methyl in preference to ethyl, and ethyl in preference to *iso*propyl); similar observations were also made in the reactions of the same mixed phosphites with water.

EXPERIMENTAL

For all values of α, $l = 1$.

Isomerisation of Trimethyl Phosphite.—(*a*) Trimethyl phosphite (McCombie, Saunders, and Stacey, *J.*, 1945, 380) (0·1 mol.) was refluxed with methyl iodide at 100° for 30 min. After a brief induction period, a vigorous reaction set in and was complete within 5 min. Distillation gave methyl iodide, collected in a trap at −80°, and dimethyl methylphosphonate, b. p. 63°/10 mm. (Found : C, 28·9; H, 7·3. Calc. for $C_3H_9O_3P$: C, 29·1 ; H, 7·3%). The yields were as follows :

Molar ratio, phosphite : iodide	Methyl iodide formed (%)	Phosphonate formed (%)
1 : 1	92	90
2 : 1	79	88
10 : 1	77	93
100 : 1	—	80

(*b*) Trimethyl phosphite (6·2 g., 0·05 mol.) and methyl sulphate (0·06 g., 0·0005 mol.) were heated under reflux at 100° for 15 min. Visible reaction commenced after 2 min. and was complete after 5 min. Distillation gave trimethyl phosphite (0·5 g., 8% ; recovered from trap at −80°) and dimethyl methylphosphonate, b. p. 66°/12 mm. (5·0 g., 81%).

Triphenyl Phosphite Methiodide.—Triphenyl phosphite (31 g.) and methyl iodide (21 g.) were heated (electric mantle) under reflux, with the exclusion of moisture, for 36 hr.; the temperature of the refluxing mixture rose from 70° to 115° during the reaction. Treatment of the product with anhydrous ether gave small yellowish-brown needles of the methiodide which were repeatedly washed with anhydrous ether and finally dried and weighed *in vacuo* (42 g., 94%). Large colourless crystals can be obtained by seeding the mixture after 3 hr. The pure compound is obtained as follows : The crude material is warmed gently with " AnalaR " acetone, and the saturated solution obtained by decantation is rapidly treated with an equal volume of dry ether; the methiodide separates in beautiful flat needles which are collected by centrifugation, washed several times with anhydrous ether, and dried in a vacuum-desiccator (P_2O_5). Two such crystallisations gave pure *triphenyl phosphite methiodide*, m. p. 146° (Found : C, 50·5; H, 4·2; I, 27·2. $C_{19}H_{18}O_3PI$ requires C, 50·45; H, 4·0; I, 28·1%). In the recrystallisation it is essential to minimise the time of contact with acetone and to work rapidly and with rigorous exclusion of moisture. The crude material was used for all the experiments described below; it was stored under ether, and dried and weighed *in vacuo* immediately before use.

Reaction of Triphenyl Phosphite Methiodide with Ethanolic Silver Nitrate.—A solution of the methiodide (7·95 g.) in absolute ethanol (30 ml.) was treated with saturated ethanolic silver nitrate (150 ml.). The precipitated silver iodide was filtered off after 3 min., washed with alcohol and ether, dried, and weighed; further crops were recovered from the filtrate at various times. The total yields of silver iodide were :

Time, mins.	3	6	10	20	80	150	1440
AgI, %	67	73	76	79	86	92	100

In a control experiment, triphenylphosphine methiodide (204·5 mg.) gave 118·3 mg. (99·6%) of silver iodide after 3 min.; no further precipitate was obtained from the filtrate.

Reaction of Triphenyl Phosphite Methiodide with Ethanol.—The methiodide (21 g.) was dissolved in absolute ethanol (35 ml.) by shaking for a few min.; distillation gave fractions (i) b. p. 65—79°/760 mm., (ii) b. p. 45—60°/0·04 mm., and (iii) b. p. 138—140°/0·04 mm. Fraction (i) was diluted with water (3 vols.), and the heavy oil which separated was dried ($CaCl_2$) and distilled; it had b. p. 72° and was identified as ethyl iodide (4·5 g., 62%) by conversion into ethyldimethylphenylammonium iodide, m. p. 136—137°. Fraction (ii) solidified and was completely soluble in sodium hydroxide solution; it was identified as phenol by conversion into 2 : 4 : 6-tribromophenol, m. p. 95—96°. Fraction (iii) was washed twice with 2N-sodium hydroxide and with water; on cooling in ice, diphenyl methylphosphonate (10·5 g., 91%) crystallised (m. p. 35—36°).

In a second experiment, volatile material was distilled off at 0·5 mm. and collected in a trap at −80°. The condensate was refluxed with dimethylaniline (6 g.) and gave ethyldimethylphenylammonium iodide (8·5 g., 66%), m. p. 132—133°. The residue was repeatedly washed with 2N-sodium hydroxide and water; the insoluble diphenyl methylphosphonate (9·9 g., 86%) solidified on cooling (m. p. 35°); acidification of the alkaline washings gave phenol (4 g., 96%), m. p. 39—40°, characterised as 2 : 4 : 6-tribromophenol, m. p. 93—94°.

Preparation of Alkyl Iodides from Triphenyl Phosphite Methiodide.—The alcohol was cautiously added to the calculated amount of crude triphenyl phosphite methiodide; cooling was necessary with the more reactive, and gentle warming with the less reactive, alcohols. After completion of the reaction, the alkyl iodide was isolated by one of the following procedures :

(A) The iodide was distilled directly from the reaction mixture under reduced pressure and collected in a trap at −80°. The condensate was repeatedly washed with water, dried (minimum quantity of Na_2SO_4 or K_2CO_3), and redistilled. This is the most convenient procedure for iodides with b. p.s substantially below that of phenol.

(B) The iodide and phenol were distilled directly, under reduced pressure, from the reaction mixture. The distillate, alone or admixed with ether, was repeatedly washed with ice-cold dilute sodium hydroxide solution and water, dried, and distilled.

(C) The reaction mixture was taken up in ether, and the phenol removed by repeated washing with dilute sodium hydroxide solution and water; drying and distillation then gave the iodide and diphenyl methylphosphonate.

The results of some experiments, on the 0·05—0·1-molar scale, are summarised in the Table.

Iodide	Conditions	Isolation	Yield (%)	B. p.*	Characterisation
*iso*Propyl	Room temp.	A	75	86—87°	*iso*Propylpyridinium iodide, m. p. 112—113° (decomp.)
n-Butyl	Room temp., 30 min.	A	72	130	n_D^{19} 1·4980; *n*-butylquinolinium iodide, m. p. 174°
sec.-Butyl	Room temp., 2 hr.	A	60	115—120	n_D^{18} 1·4980
tert.-Butyl	50—60°; 1 hr.	A	76 †	(i) 85—95 (ii)95—100	(i) n_D^{21} 1·4703 (ii) n_D^{21} 1·4885
1-Methylheptyl	Steam-bath 20 hr. Ether (450 ml./mol.) added	A	80	45—50 (0·8)	(Found: I, 52·8. Calc. for $C_8H_{17}I$: I, 52·9%); $\alpha_D^{20·4}$ + 0·1° [from (−)-octan-2-ol, $\alpha_D^{20·4}$ − 7·83°]
,,	80—100°, 1 hr.	A	65	99—100 (8)	$\alpha_D^{22·1}$ − 0·4° [from (+)-octan-2-ol, $\alpha_D^{21·4}$ + 7·72°]
*cyclo*Hexyl	Room temp.; 18 hr.	A	75	67 (8)	$n_D^{23·5}$ 1·5465
Allyl	0°; 30 min.	A	84	102—103	Allyldimethylphenylammonium iodide, m. p. 85°
Crotyl	0°; 30 min.	A	83	55—56 (40—45)	Crotyldimethylphenylammonium iodide, m. p. 113—114°
Benzyl	Room temp., 1 hr.	B	95	M. p. 23°	Benzyldimethylphenylammonium iodide, m. p. 165·5°
1-Phenylethyl	Room temp., 1 hr.	C	74	7—80 (2)	—
2-Phenylethyl	Room temp., 1 hr.	B	70 †	(i) 105—107 (11) (ii) 107—111 (11) (iii) 111—115 (11)	(i) n_D^{18} 1·5830 (ii) n_D^{18} 1·5910 (iii) n_D^{18} 1·6010
1 : 3-Di-iodopropane	Room temp., 2 hr.	B	95	50—51° (0·5)	n_D^{21} 1·6420
Ethyl α-iodopropionate	Room temp., 12 hr.	A	92	65—66 (8)	(Found : I, 56·0. Calc. for $C_5H_9O_2I$: I, 55·7%) $n_D^{20·5}$ 1·5000

* Pressure (mm.) in parentheses, if not 1 atm.

† In these cases, the iodide was contaminated with alcohol and the yield has been calculated from the refractive indices of the various fractions.

Cholesteryl Iodide.—Cholesterol (9·5 g.) was intimately mixed with triphenyl phosphite methiodide (12 g.); methyl iodide (10 ml.) was added and the mixture warmed to 50—60°, under reflux, for 1 hr. Next morning, the product was extracted with light petroleum (b. p. 40—60°; 100 ml.). The extract was evaporated and the residual syrup stirred with water (100 ml.); the water-insoluble fraction was washed with a little acetone and then dissolved in hot acetone (200 ml.). An oil which separated on cooling was removed and the solution kept at 2° for 2 days, whereupon it deposited cholesteryl iodide in needles, m. p. 99—100°; further crops were obtained by partial evaporation and cooling, the total yield being 3·6 g. (30%). Recrystallisation from ethyl acetate gave the pure iodide, m. p. 105°, $[\alpha]_D^{21·2}$ −12·7° (*c* 3·86 in $CHCl_3$) (Found : C, 65·3; H, 9·1; I, 25·5. Calc. for $C_{27}H_{45}I$: C, 65·3; H, 9·1; I, 25·6%).

Preparation of Alkyl Chlorides from Triphenyl Phosphite Benzylochloride.—*Triphenyl phosphite benzylochloride* (cf. Michaelis and Kähne, *Ber.*, 1898, **31**, 1050). This was prepared by heating triphenyl phosphite (34 g.) and benzyl chloride (13 g.) at 170—175° for 60 hr. The syrupy product was washed twice with light petroleum (b. p. 40—60°), then dried and weighed *in vacuo* (yield, 25 g.).

n-*Hexyl chloride.* *n*-Hexyl alcohol (5·5 g.) was mixed with the benzylochloride (25 g.); the exothermic reaction was moderated by cooling in ice. The mixture was then distilled under reduced pressure into a trap at −80°. The condensate (9 g.) was washed with N-sodium hydroxide and water, dried, and distilled, giving *n*-hexyl chloride (6 g., 95%), b. p. 132—136°, $n_D^{21\cdot5}$ 1·4230, characterised as *S*-*n*-hexyl*iso*thiuronium picrate, m. p. 155—156°.

2-*Chloro-octane.* Triphenyl phosphite benzylochloride (10 g.), mixed with (+)-octan-2-ol (2 g.; $\alpha_D^{21\cdot4}$ +7·72°), was kept at room temperature overnight. Distillation gave impure 2-chloro-octane which was washed with 2N-sodium hydroxide and water, dried, and distilled, yielding (−)-2-chloro-octane (1·8 g., 79%), b. p. 60°/13 mm., n_D^{20} 1·4275, $\alpha_D^{22\cdot4}$ −24·72°.

Tribenzyl Phosphite.—Phosphorus trichloride (23 g.) was added during 20 min. to a well-stirred, water-cooled mixture of benzyl alcohol (54 g.), dimethylaniline (61 g.), and anhydrous ether (100 ml.). The precipitated dimethylaniline hydrochloride was filtered off and washed thoroughly with anhydrous ether. Two fractional distillations of the filtrate and washings gave (i) dibenzyl hydrogen phosphite (8 g.), b. p. 145—160°/0·05 mm. (Found: C, 64·0; H, 5·75. Calc. for $C_{14}H_{15}O_3P$: C, 64·1; H, 5·75%), (ii) a mixture (10 g.), b. p. 160—180°/0·05 mm. (Found: C, 66·5; H, 5·9%), and (iii) *tribenzyl phosphite* (18 g., 31%), b. p. 180—195°/0·05 mm. (Found: C, 70·9; H, 6·1. $C_{21}H_{21}O_3P$ requires C, 71·6; H, 6·0%), which solidified and crystallised from light petroleum in long needles, m. p. 52° (Found: C, 71·2; H, 6·3%). No addition compound was found when tribenzyl phosphite was heated with methyl iodide at 100° for 30 hr.; the same reactants gave benzyl iodide when heated at 150° for 3 hr.

Preparation of Alkyl Halides from Triphenyl Phosphite, an Alkyl Halide, and an Alcohol.—A mixture of these reactants was refluxed, preferably by use of an electric heating-mantle, for the appropriate time. The product was worked up by one of three general methods outlined on p. 2229.

Some preparative experiments, on the 0·05—0·1-molar scale, are summarised in the annexed Tables.

Preparation of alkyl iodides.

Iodide	Iodide used (molar ratio, phosphite : iodide : alcohol), reaction conditions	Isolation	Yield (%)	B. p.*	Characterisation
Ethyl	MeI (1 : 2 : 1), steam-bath, 60 hr.	A	80	65—72°	Ethyldimethylphenylammonium iodide, m. p. 131°
n-Butyl	MeI (1·1 : 1·7 : 1), mantle, 60 hr.	A	90	129—130	n_D^{19} 1·5000
sec.-Butyl	MeI (1·1 : 1·5 : 1), mantle, 39 hr.	A	66	117—120	$n_D^{19\cdot5}$ 1·4985
1-Methylheptyl	(*a*) MeI (1 : 2·2 : 1), mantle, 24 hr.	B	76	40 (0·5)	$\alpha_D^{23\cdot6}$ − 0·1° [from (+)-octan-2-ol, $\alpha_D^{21\cdot4}$ + 7·72°]
,,	(*b*) MeI (1 : 6 : 1), mantle, 24 hr.	B	—	43—49 (0·7)	$\alpha_D^{15\cdot5}$ + 23·5° [from (−)-octan-2-ol, $\alpha_D^{20\cdot4}$ − 7·83°]
Allyl	MeI (1 : 1·5 : 1), mantle, 40 hr.	A	70	101—103	n_D^{21} 1·5540 (yield corr. for contamination with MeI); allylquinolinium iodide, m. p. 175°
2-Phenylethyl	MeI (1·1 : 1·5 : 1), mantle, 48 hr.	C	99	94—95 (1·5)	$n_D^{22\cdot5}$ 1·5990
*cyclo*Hexyl	MeI (1·1 : 1·5 : 1), mantle, 48 hr., 75—110°	B	42	63—65 (6)	n_D^{17} 1·5490
1 : 3-Di-iodo-propane	MeI (2·2 : 3 : 1), steam-bath, 30 hr.	B	80	65 (0·8)	n_D^{23} 1·6370 (redistillation gave a 46% yield of material with n_D^{20} 1·6430)
1:3-Di-iodo-2:2-dimethyl-propane	MeI (2·2 : 3 : 1), mantle, 39 hr., 75—130°	C	85	70—75 (0·9)	n_D^{17} 1·5935; I, 76·8% †
*neo*Pentyl	MeI (1 : 1·4 : 1), mantle, 24 hr., 75—130°	B	74	61—62 (50)	n_D^{23} 1·4888; ββ-dimethylbutyranilide, m. p. 129—130°
Ethyl α-iodo-propionate	MeI (1·1 : 1·5 : 1), mantle, 48 hr.	B	77	64—65 (8)	n_D^{20} 1·5000

* Pressure (mm.) in parentheses, if not 1 atm.

† Redistillation gave pure 1 : 1-*di-iodo*-2 : 2-*dimethylpropane*, b. p. 70°/1 mm., n_D^{17} 1·5950 (Found: I, 77·9. $C_5H_{10}I_2$ requires I, 78·4%).

Preparation of alkyl bromides.

Bromide	Bromide used (molar ratio, phosphite : bromide : alcohol), reaction conditions	Isolation	Yield (%)	B. p.	Characterisation
n-Butyl	CH_2PhBr (1·1 : 1·1 : 1), mantle, 46 hr., 140°	A	95	101°	n_D^{20} 1·4400
Allyl	CH_2PhBr (1·1 : 1·1 : 1), mantle, 48 hr., 140—130°	A	66	70—71	n_D^{21} 1·4670
1 : 3-Di-iodopropane	CH_2PhBr (2·2 : 2·2 : 1), mantle, 48 hr., 140°	B	85	70—75°/20 mm.	n_D^{27} 1·5220 *
Ethyl α-iodopropionate	CH_2PhBr (1·1 : 1·1 : 1), mantle, 62 hr., 160°	B	80	158—159	n_D^{18} 1·4445 (Found : Br, 44·2. Calc. for $C_5H_9O_2Br$: Br, 44·2%)
n-Butyl	$CH_2Br{\cdot}CO_2Et$ (1 : 1 : 1), mantle, 64 hr., 140—150°	A	58	100—102	n_D^{23} 1·4330
n-Butyl	$CH_2Br{\cdot}CH_2Br$ (1·05 : 1 : 1·05), sand-bath, 60 hr., 150°	B	40	100—122	Product contaminated with ethylene dibromide; yield calc. from n_D of the various fractions

* Redistillation gave a product, b. p. 164—165°, n_D^{18} 1·5235 (Found : Br, 79·4. Calc. for $C_3H_6Br_2$: Br, 79·25%).

Preparation of alkyl chlorides.

Chloride	Chloride used (molar ratio, phosphite : chloride : alcohol), reaction conditions	Isolation	Yield (%)	B. p.	Characterisation
n-Butyl	CH_2PhCl (1 : 1 : 1), mantle, 64 hr., 140—150°	A	65	78—79°	n_D^{25} 1·4010
Allyl	CH_2PhCl (1·1 : 1·1 : 1), mantle, 48 hr., 140—125°	A	59	44—45	n_D^{20} 1·4150
1 : 3-Di-iodopropane	CH_2PhCl (2·2 : 2·2 : 1), mantle, 48 hr., 170—180°	B	79	119—121	n_D^{20} 1·4470 *
Ethyl α-iodopropionate	CH_2PhCl (1·1 : 1·05 : 1), mantle, 60 hr., 175—180°	B	77	50—52°/8 mm.; 140—143	n_D^{20} 1·4220
n-Hexyl	CCl_4 (1 : 1 : 1), sand-bath, 60 hr., 150°	A	31	80—130	Contaminated with CCl_4; yield calc. from n_D of the various fractions

* Found : Cl, 63·7. Calc. for $C_3H_6Cl_2$: Cl, 62·8%. Distillation of the high-boiling residue gave diphenyl benzylphosphonate (77%), b. p. 210°/1 mm., needles, m. p. 61—62° (from light petroleum) (Found : C, 70·0; H, 5·4. Calc. for $C_{19}H_{17}O_3P$: C, 70·4; H, 5·3%)

Methyl iodide from triphenyl phosphite, n-*butyl iodide, and methanol.* Triphenyl phosphite (68 g., 0·22 mole), *n*-butyl iodide (40 g., 0·22 mole), and anhydrous methanol (6·4 g., 0·20 mole) were heated with an electric heating-mantle, the methyl iodide produced being continuously removed through a 3-ft. column packed with Fenske helices; the temperature of the mixture rose from 165° to 185° during the experiment (24 hr.), but the distillation temperature never exceeded 41°. The distillate (20 g.; n_D^{21} 1·5195) was washed twice with water, dried, and distilled, yielding methyl iodide (16 g., 56%), b. p. 42—43°, n_D^{20} 1·5290, characterised as trimethylphenylammonium iodide, sublimes at 215—220°.

n-*Butyl bromide from triphenyl phosphite, methyl bromide, and* n-*butyl alcohol.* Methyl bromide was passed slowly through a sintered-glass plate, into a mixture of triphenyl phosphite

(50 g., 0·16 mole) and *n*-butyl alcohol (11 g., 0·15 mole) heated under reflux with an electric heating-mantle; the temperature of the refluxing mixture fell from 155° to 135° during the experiment (12 hr.). Distillation into a trap cooled to −80°, followed by washing and redistillation through a 3-in. Fenske column, gave *n*-butyl bromide (13 g., 63%), b. p. 101·5°, n_D^{20} 1·4400.

n-*Butyl iodide from triethyl phosphite, methyl iodide, and* n-*butyl alcohol.* Triethyl phosphite (16·6 g., 0·1 mole), methyl iodide (14·2 g., 0·1 mole), and *n*-butyl alcohol (22·2 g., 0·1 mole) were heated under reflux on the steam-bath for 1 hr. Distillation gave 10 g. (64%) of somewhat impure ethyl iodide, b. p. 55—75°, n_D^{20} 1·5080, and 8·3 g. (45%) of crude *n*-butyl iodide; the latter, on redistillation gave 6·7 g. (36%) of the substantially pure iodide, b. p. 110—130°, n_D^{20} 1·4935.

Preparation of Alkyl Chlorides from Triphenyl Phosphite, Hydrogen Chloride, and an Alcohol.— A stream of dry hydrogen chloride was passed into an equimolecular mixture of triphenyl phosphite and an alcohol, usually without cooling, until there appeared to be no further reaction. The reaction product was then worked up by one of the standard procedures (p. 2229).

Some preparative experiments on the 0·1-molar scale are summarised in the following Table.

Chloride	Reaction conditions	Isolation	Yield (%)	B. p.	Characterisation
n-Butyl	No cooling, 1·5 hr.	A	76	77—79°	n_D^{17} 1·4025
Allyl	No cooling, 1·5 hr.	A	46	45—46	n_D^{20} 1·4160
Crotyl	No cooling, 1·5 hr.	A	72	80—85	$n_D^{21\cdot5}$ 1·4325 (mainly crotyl chloride, but contained some 1-methylallyl chloride)
1-Methylheptyl	Phosphite–alcohol mixture kept overnight before passage of HCl for 1 hr.	B	44	53—56°/8—10 mm.	$\alpha_D^{22\cdot2}$ + 18·8° [from (−)-octan-2-ol, $\alpha_D^{20\cdot4}$ − 7·83°]
2-Phenylethyl	No cooling, 2 hr.	C	76	82—84°/10—12 mm.	—

Cholesteryl chloride. Dry hydrogen chloride was passed for 30 min. through a mixture of triphenyl phosphite (5 g.) and cholesterol (2 g.), stirred at 60—70°; a clear yellow solution was obtained after a few min. The product was treated with acetone (20 ml.), and the cholesteryl chloride (1 g.) which separated filtered off and washed with acetone; dilution of this filtrate with water gave a further 1·2 g. of chloride. Recrystallisation from ethyl acetate gave pure cholesteryl chloride in needles, m. p. 95°, $[\alpha]_D^{20}$ −33·3° (*c* 3·188 in $CHCl_3$) (Found: C, 79·95; H, 11·1; Cl, 8·65. Calc. for $C_{27}H_{45}Cl$: C, 79·95; H, 11·1; Cl, 8·75%); there was no depression of m. p. on admixture with authentic (chromatographically purified) cholesteryl chloride having m. p. 94° and $[\alpha]_D^{20}$ −32·6° (*c* 3·224 in $CHCl_3$).

Preparation of Alkyl Halides from Triphenyl Phosphite, an Alcohol, and Inorganic Halides.— n-*Butyl chloride from ammonium chloride.* Triphenyl phosphite (34 g.), *n*-butyl alcohol (7·4 g.), and ammonium chloride (6 g.) were heated under reflux at 140° for 84 hr.; ammonia was evolved during the reaction. The filtered product was distilled, giving 5·8 g. (63%) of *n*-butyl chloride, b. p. 77—78°, n_D^{23} 1·4015.

n-*Butyl chloride from sodium chloride.* Triphenyl phosphite (34 g.), *n*-butyl alcohol (7·4 g.), and sodium chloride (6 g.) were heated at 170—180° for 120 hr. Distillation gave 1·5 g. (16%) of *n*-butyl chloride, b. p. 78°, n_D^{23} 1·4015.

n-*Butyl bromide from lithium bromide.* Triphenyl phosphite (34 g.), *n*-butyl alcohol (7·4 g.), and lithium bromide (9·6 g.) were heated at 140° for 64 hr. Distillation gave 5·5 g. (40%) of *n*-butyl bromide, b. p. 101—102°, n_D^{24} 1·4395.

n-*Butyl iodide from sodium iodide.* Triphenyl phosphite (34 g.), *n*-butyl alcohol (7·4 g.), and sodium iodide (16·5 g.) were heated at 160—170° for 64 hr. Distillation yielded 3·4 g. (18·5%) of *n*-butyl iodide, b. p. 130—132°, n_D^{25} 1·4980.

Reaction between Triphenyl Phosphite Methiodide and Ethanol in the Presence of Dimethylaniline.—A mixture of triphenyl phosphite methiodide (7·0 g.), absolute ethanol (1·5 g.), and dimethylaniline (3 g.) was warmed on the steam-bath for 15 min. Dilution with ether yielded ethyldimethylphenylammonium iodide (3·8 g., 88%), m. p. 115—117°, raised to 131° (not depressed on admixture with an authentic specimen) on recrystallisation from ethanol.

Ester Interchange between Triphenyl Phosphite and n-*Butyl Alcohol.*—(*a*) Triphenyl phosphite (68 g., 0·22 mole) and *n*-butyl alcohol (14·8 g., 0·20 mole) were heated at 100° for 16 hr. Fractionation gave (i) 18·5 g., b. p. 60—80°/10 mm., mainly phenol (0·20 mole), (ii) 7·5 g., b. p. 80—120°/10 mm., n_D^{25} 1·4580, mainly tri-*n*-butyl phosphite (0·03 mole) (Found: C, 57·2; H, 9·4. Calc. for $C_{12}H_{27}O_3P$: C, 57·6; H, 10·1%), (iii) 7·8 g., b. p. 120—140°/10 mm., n_D^{25} 1·4840, a mixture of tri-*n*-butyl and di-*n*-butyl phenyl phosphites (Found : C, 59·8; H, 8·4. Calc. for $C_{14}H_{23}O_3P$: C, 62·2; H, 8·6%), (iv) 9·0 g., b. p. 140—170°/10 mm., n_D^{25} 1·5302, mainly *n*-butyl diphenyl phosphite (0·03 mole) (Found : C, 64·8; H, 6·9. Calc. for $C_{16}H_{19}O_3P$: C, 66·2; H, 6·6%), (v) 4·1 g., b. p. 170—180°/10 mm., n_D^{25} 1·5819, a mixture of *n*-butyl diphenyl and triphenyl phosphites, and (vi) 28 g., residue, n_D^{25} 1·5815, similar to (v) (authentic triphenyl phosphite had n_D^{25} 1·5975).

(*b*) Triphenyl phosphite (68 g., 0·22 mole) was mixed with *n*-butyl alcohol (14·8 g., 0·20 mole) and the mixture kept at room temp. for 30 min. Distillation gave 18 g. (96%) of phenol, b. p. 60—110°/10 mm., and a mixture of phosphites which was heated under reflux for 3 hr. with methyl iodide (13 g.); distillation into a trap cooled at −80° gave *n*-butyl iodide (13 g., 35%), n_D^{23} 1·4990. The residue was heated with more methyl iodide (28 g.) for 24 hr. Distillation then gave a further 15·1 g. (41%) of *n*-butyl iodide, b. p. 125—131°, n_D^{23} 1·4980.

Reaction between Triphenyl Phosphite Methiodide and Dimethyl Methylphosphonate.—A mixture of triphenyl phosphite methiodide (23 g.) and dimethyl methylphosphonate (3 g.) was heated under reflux for 1 hr., the internal temperature falling from 120° to 100°. Distillation gave 5 g. of rather impure methyl iodide, b. p. 42—44°, n_D^{20} 1·5055, characterised as trimethylphenylammonium iodide, platelets (from alcohol), subliming at 220°.

*Reaction between Triphenyl Phosphite Methiodide and Tri-*n*-butyl Phosphite.*—Tri-*n*-butyl phosphite (2·5 g.) was added to triphenyl phosphite methiodide (5 g.); the methiodide dissolved readily on shaking, with some evolution of heat. Distillation gave *n*-butyl iodide (1·8 g., 88%), b. p. 125—132°, n_D^{23} 1·4970.

Preparation and Reactions of Some Mixed Trialkyl Phosphites.—*Ethyl dimethyl phosphite.* A mixture of ethyl phosphorodichloridite (147 g.; b. p. 117—118°) (Razumov, *J. Gen. Chem., U.S.S.R.*, 1944, **14**, 464) and anhydrous ether (500 ml.) was cooled in a freezing-mixture and treated portionwise, under a condenser, with a suspension of sodium methoxide (from powdered sodium, 46 g., and anhydrous methanol, 64 g.) in anhydrous ether (500 ml.). After the addition was complete, the mixture was kept at room temperature, with occasional shaking, for 1 hr.; sodium chloride was then filtered off rapidly and washed with anhydrous ether. Distillation of the filtrate and washings yielded the crude ester (107 g., 77%), b. p. 60—70°/10 mm., which, on refractionation through a 3-ft., vacuum-jacketed, Fenske column, gave pure *ethyl dimethyl phosphite* (56 g., 40·5%), b. p. 124—127° (Found : C, 34·7; H, 8·1%; equiv., 138·0. $C_4H_{11}O_3P$ requires C, 34·7; H, 8·0%; equiv., 138·0). [This equivalent, like the others quoted below, was determined as follows :—The ester (*ca.* 150 mg.) was heated at 100° under reflux with 70% alcoholic N-sodium hydroxide (5 ml.) for 1 hr.; the excess of alkali was back-titrated, after dilution, with 0·1N-hydrochloric acid (bromophenol-blue); with this indicator only one acidic group of phosphorous acid is titrated. In our experience equivalents are better criteria of purity of alkyl phosphites than elementary analyses, which often give unsatisfactory and non-concordant results.]

Ethyl dimethyl phosphite (27·6 g.) was heated under reflux for 1 hr. with methyl iodide (28·4 g.). Fractional distillation gave methyl iodide (27·5 g., 97%), b. p. 42·5—43°, characterised as trimethylphenylammonium iodide, m. p. 218—220°, and methylpyridinium iodide, m. p. 116—117°, and *ethyl methyl methylphosphonate* (27·0 g., 98%), b. p. 74—75°/15 mm. (Found : C, 34·3; H, 8·0%; equiv., 137·8. $C_4H_{11}O_3P$ requires C, 34·7; H, 8·0%; equiv., 138·0).

Ethyl dimethyl phosphite (13·8 g.) was stirred with water (2·0 g.) in acetone (10 ml.) for 30 min.; hydrolysis was accompanied by the evolution of heat. After 1 hr., distillation gave three phosphorus-containing fractions : (i) b. p. 65—73°/15—17 mm., 1·3 g. (Found : equiv., 123·5), (ii) b. p. 73—75°/15—17 mm., 9·0 g. (Found : C, 28·9; H, 7·0%; equiv., 124·0), and (iii) b. p. 75—77°/15—17 mm., 1·3 g. (Found : equiv., 126·4). Fraction (ii) was clearly *ethyl methyl hydrogen phosphite* ($C_3H_9O_3P$ requires C, 29·05; H, 7·25%; equiv., 124·0), and fractions (i) and (iii) were less pure samples of it; the total yield was 93·5%.

Diethyl methyl phosphite. The preparation of this mixed ester from diethyl phosphorochloridite and sodium methoxide or from ethyl phosphorodichloridite or phosphorodibromidite and sodium ethoxide was unsatisfactory. The following was the procedure finally adopted :

A mixture of anhydrous methanol (32 g.) and dimethylaniline (121 g.) was added, with ice-cooling, during 1 hr., to a well-stirred mixture of phosphorus trichloride (137 g.) and anhydrous ether (1 l.). Next, a mixture of anhydrous ethanol (92 g.) and dimethylaniline (242 g.) was added similarly during 2 hr. More ether (500 ml.) was then added and the dimethylaniline hydrochloride filtered off and washed twice with anhydrous ether. The filtrate and washings were distilled and the fraction of b. p. 50—90°/10—15 mm. was twice refractionated through a

3-ft. Fenske column, yielding *diethyl methyl phosphite* (35 g., 23%), b. p. 136—139° (Found : C, 38·6; H, 8·5%; equiv., 152·6. $C_5H_{13}O_3P$ requires C, 39·5; H, 8·55%; equiv., 152·0).

Diethyl methyl phosphite (10 g.) and methyl iodide (8·5 g.) were refluxed on the steam-bath for 30 min. Distillation gave methyl iodide (6·8 g., 79%), b. p. 41—50°, characterised as trimethylphenylammonium iodide, m. p. 215°, and methylpyridinium iodide, m. p. 116°, and diethyl methylphosphonate (6 g., 60%), b. p. 190—192°, n_D^{23} 1·4110 (Found : C, 38·1; H, 8·6%; equiv., 152·0. Calc. for $C_5H_{13}O_3P$: C, 39·5; H, 8·55%; equiv., 152·0).

Diethyl methyl phosphite (10 g.) was heated on the steam-bath for 30 min. with water (1·5 g.) in acetone (10 ml.). Distillation gave 5·3 g. (58%) of diethyl hydrogen phosphite, b. p. 65—66°/8 mm., n_D^{21} 1·4070 (Found : C, 33·2; H, 7·7%; equiv., 137·2. Calc. for $C_4H_{11}O_3P$: C, 34·75; H, 8·0%; equiv., 138·0).

*Ethyl di*iso*propyl phosphite.* A mixture of *iso*propyl alcohol (120 g.) and dimethylaniline (242 g.) was added during 80 min. to a well-stirred, ice-cooled mixture of ethyl phosphorodichloridite (130 g.) and anhydrous ether (500 ml.). After the mixture had been stirred at room temperature for a further 30 min., the dimethylaniline hydrochloride was filtered off and washed with ether. Removal of the ether and fractionation of the residue through a 3-ft. Fenske column gave *ethyl di*iso*propyl phosphite* (97 g., 50%), b. p. 69—71°/10 mm. (Found : C, 49·7; H, 10·05%; equiv., 192·1. $C_8H_{19}O_3P$ requires C, 49·5; H, 9·9%; equiv., 194·0).

This ester (19·5 g.) was refluxed at 100° for 30 min. with methyl iodide (14·2 g.); the reaction was very vigorous. Distillation gave ethyl iodide (12 g., 77%), b. p. 71—73°, n_D^{20} 1·5125, and di*iso*propyl methylphosphonate (17 g., 94%), b. p. 75—76°/5 mm., n_D^{20} 1·4158 (Found : C, 46·8; H, 9·35. Calc. for $C_7H_{17}O_3P$: C, 46·7; H, 9·5%).

Ethyl di*iso*propyl phosphite (19·5 g.) and water (2 g.) in acetone (10 ml.) were refluxed on the steam-bath for 14 hr. Distillation gave di*iso*propyl hydrogen phosphite (12·5 g., 75%), b. p. 89—90°/10 mm. (Found : C, 42·9; H, 9·3%; equiv., 159·3. Calc. for $C_6H_{15}O_3P$: C, 43·4; H, 9·1%; equiv., 166·0).

The majority of the microanalyses were carried out under the direction of Mr. F. H. Oliver in the microanalytical laboratory of the Organic Chemistry Department, Imperial College.

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