Anal. Calcd for $C_{11}H_{11}N$: C, 84.03; H, 7.05; N, 8.91. Found: C, 83.90; H, 7.15; N, 8.84.

Attempted Preparation of 1-Phenyl-3H-pyrrolizine (XIII).—To a suspension of 0.46 g of sodium hydride (0.0199 mole, 0.89 g of a 52.6% dispersion in mineral oil) in 250 ml of anhydrous ether was added 3.6 g of 2-benzoylpyrrole (prepared by the method of Oddo[12]). The mixture was stirred for several hours to ensure complete conversion to the salt. To the suspended salt was added 7.2 g (0.0199 mole) of the vinyl salt II while the mixture was cooled in an ice bath. The slurry was stirred with continued cooling for 4 hr. The salts were removed by filtration and the ether was distilled. The pot residue consisted of a brown tar, which was found to contain triphenylphosphine oxide by thin layer chromatography. No crystalline material could be obtained from the mass by sublimation or recrystallization from a wide range of solvents. Column chromatography on silica gel with benzene eluent gave only a dark oil which could not be characterized. The nmr spectra of the oil did not agree with compound XIII.

Acknowledgment.—This investigation was supported in part by a Public Health Service Grant GM 12692-01 and a Public Health Service Predoctoral Fellowship (to K. K. L.) for which we are most grateful.

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Trialkyl Phosphates. I. Halogenation of Trialkyl Phosphites in the Presence of Alcohols

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Trialkyl phosphates can be prepared in high yield and purity by the halogenation of trialkyl phosphites in the presence of the corresponding alcohols. The principal side reactions, which can all be suppressed, are isomerization of the phosphite and cleavage of the phosphite and phosphate by hydrogen halide. Competition of the alcohol for the halogen was observed in only one case. A mechanism involving the direct alcoholysis of a quasi-phosphonium intermediate, $(RO)_3PX_2$, is proposed. Phosphonous esters, phosphinous esters, and tertiary phosphines can also be oxidized in this manner.

The oxidation of trialkyl phosphites to trialkyl phosphates can be accomplished with a variety of oxidizing agents, both organic and inorganic.[2] Direct oxidation with air or oxygen is possible in some cases, but the lower trialkyl phosphites, such as triethyl phosphite, are not appreciably attacked unless a catalyst is employed.[3] An interesting development in recent years has been the emergence of indirect methods of oxidation employing an organic halide in combination with an alcohol. The organic halides which have been employed for this purpose are carbon tetrachloride,[4,5] bromotrichloromethane,[4] carbon tetrabromide,[6] chloroform,[7] monobromocyanoacetamide,[8] and hexachlorocyclopentadiene.[9] In the absence of the alcohols these reactions all follow entirely different paths.

We have investigated the use of the halogens themselves for this purpose and have found the halogenation of a trialkyl phosphite in the presence of the corresponding alcohol to be a useful method for preparing trialkyl phosphates in high yield and purity. In most cases, competition of the alcohol for the halogen is not observed. The stoichiometry of the reaction is given in eq 1.

$$(RO)_3P + X_2 + ROH \longrightarrow (RO)_3PO + RX + HX \qquad (1)$$

In the absence of the alcohol, the product of the reaction of a trialkyl phosphite with a halogen is a dialkyl phosphorohalidate.[10,11]

When gaseous chlorine was passed into a dilute solution of trimethyl phosphite in methanol, a product which appeared to be trimethyl phosphate was obtained in 56.5% yield.[12] A gas chromatographic analysis, however, showed that it consisted of trimethyl phosphate (82%), dimethyl methylphosphonate (11%), and other minor impurities (7%). Dimethyl methylphosphonate is the product of self-isomerization of the trimethyl phosphite, catalyzed perhaps by the methyl chloride which is evolved as a by-product (eq 1, $R = CH_3$; $X = Cl$). The extent of self-isomerization was reflected also in the chlorine consumption, which was 12% less than the theoretical for this reaction.

The need for the excess of methanol is demonstrated in Table I, which shows the effect of reducing the molar

TABLE I

EXTENT OF DEALKYLATION AS A FUNCTION OF THE ALCOHOL TO PHOSPHITE RATIO

Moles of CH_3OH/ mole of $(CH_3O)_3P$	$(CH_3O)_2PHO$, %
30	0.2
15	0.3
5	7.3
1	19.3

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[8] T. Mukaiyama, C. Mitsunobu, and T. Obata, *J. Org. Chem.*, **30**, 101 (1965).

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[11] A notable exception is tris(2,2,2-trichloroethyl) phosphite, which forms a stable adduct with chlorine: H. N. Rydon and B. L. Tonge, *ibid.*, 4682 (1957); see also W. Gerrard, W. J. Green, and R. J. Phillips, *ibid.*, 1148 (1954); W. Gerrard and B. H. Howe, *ibid.*, 505 (1955).

[12] Trimethyl phosphate is extraordinarily sensitive to acid degradation. We discovered later that the yields in many of our earlier experiments could have been improved simply by stripping the acidic methanol solutions at the lowest possible temperature.

ratio of methanol to trimethyl phosphite in the chlorination of trimethyl phosphite at 25–30°.

The amount of dimethyl phosphite formed as a by-product increased substantially as the methanol to trimethyl phosphite ratio approached the stoichiometric 1:1. Dimethyl phosphite is formed by a side reaction between the trimethyl phosphite and the by-product hydrogen chloride.[13] The function of the excess alcohol is to complex the hydrogen chloride as the oxonium salt.[14] A 5- to 15-fold excess of alcohol was desirable in this case, but might not be so critical with alcohols less sensitive than methanol.

The effect of substituting other halogens for the chlorine is demonstrated in Table II, which shows the extent of dimethyl phosphite formation as a function of the halogen.

Table II

Extent of Dealkylation as a Function of the Halogen

Halogen	$(CH_3O)_2PHO$, %
Cl_2	0
Br_2	4.0
I_2	35.9

In the iodine experiment, the consumption of iodine abruptly ceased when less than half of the calculated amount had been added. The distilled product was a mixture of almost equal parts of dimethyl phosphite and trimethyl phosphate. The use of a base, triethylamine, to neutralize the hydrogen iodide (eq 1, R = CH_3; X = I) resulted in a viscous, nitrogen-containing product. Reversing the order of addition, however, so that the trimethyl phosphite was never present in excess, effectively suppressed the dealkylation of the phosphite. The consumption of iodine was close to the theoretical, and the amount of dimethyl phosphite formed was reduced to 1.5%.

In the chlorination experiments, reversing the order of addition served to suppress the self-isomerization of the phosphite. This was accomplished experimentally by passing the chlorine into the methanol at a steady rate at 0–10° and adding the trimethyl phosphite simultaneously but separately at a rate just sufficient to maintain a faint tinge of color (procedure B). The trimethyl phosphate prepared by this method did not contain any dimethyl methylphosphonate.

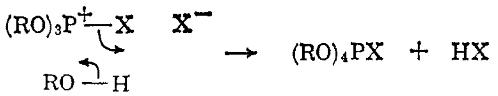
Using this technique, the synthesis was extended to other trialkyl phosphates, $(RO)_3PO$, where R = ethyl, *n*-propyl, *n*-butyl, isobutyl, 2-chloroethyl, 2-phenethyl, 2-ethylhexyl, and stearyl, and to their higher organophosphorus counterparts, diethyl phenylphosphonate, ethyl diphenylphosphinate, and triphenylphosphine oxide.[15] Yields were in the 90–100% range and product purity was often over 98%.

The only reaction in which the alcohol appeared to compete with the phosphite for the chlorine was the one involving a secondary alcohol, isopropyl alcohol. The chlorination of triisopropyl phosphite in isopropyl alcohol gave products containing substantial amounts of chlorine. In one experiment a product of the chlorination of isopropyl alcohol, *sym*-dichloroacetone, was actually isolated. These experiments suggest that some alcohols may be too sensitive to halogens to be of use in the present synthesis, but difficulties from this source were not nearly as severe as originally expected. The literature on this subject is surprisingly sparse.[16]

The initial step in this reaction must be an attack by the halogen on either the phosphite or the alcohol. A reaction with the alcohol would generate an alkyl hypohalite. Trialkyl phosphites are known to react with alkyl hypochlorites under conditions equivalent to those of the present synthesis[17] (eq 2).

$$(RO)_3P + ROX \longrightarrow (RO)_4PX \qquad (2)$$

We consider it more likely, however, that the halogen reacts with the phosphite, generating a quasiphosphonium intermediate, $(RO)_3PX_2$ or $(RO)_3\overset{+}{P}X\ X^-$, which in the presence of the excess alcohol undergoes an alcoholysis to a new quasiphosphonium compound (eq 3).



$$\begin{matrix}(RO)_3\overset{+}{P}-X & X^- \\ RO-H & \end{matrix} \longrightarrow (RO)_4PX + HX \qquad (3)$$

The final step in both mechanisms is the Arbuzov breakdown of the quasiphosphonium compound to the trialkyl phosphate by attack of X^- on one of the ester groups (eq 4).

$$(RO)_4PX \longrightarrow (RO)_3PO + RX \qquad (4)$$

Similar mechanisms have been suggested for the reactions of trialkyl phosphites with organic halides and alcohols,[4-6] and also for the reaction of triphenylphosphine with carbon tetrachloride[4] or halogens[15,18] in the presence of alcohols.

As a further extension of this work, we investigated the use of other chlorinating agents for the chlorination of trialkyl phosphites in alcohols, including thionyl chloride, sulfuryl chloride, cupric chloride, and hexachloroethane, but the results were not so satisfactory.

We also investigated briefly the behavior of a dialkyl phosphite in this reaction. The chlorination of dibutyl phosphite in butanol required a higher temperature (25–30°), but nevertheless gave tributyl phosphate in 76% yield. The stoichiometry was probably the following (eq 5).

$$(RO)_2PHO + X_2 + ROH \longrightarrow (RO)_3PO + 2\,HX \qquad (5)$$

Finally, we found that the halogenation–alcoholysis reaction could be carried out in stepwise fashion with almost the same results. The reaction of trimethyl phosphite with chlorine at 0–10° in the absence of a solvent gave an 86% yield of dimethyl phosphorochloridate, which, added dropwise to methanol at 0–10° and worked up in the usual manner, gave trimethyl phosphate in 87% yield. Similar results were obtained with dimethyl phosphoroiodidate.

The chlorination of other phosphorus-containing compounds in the presence of alcohols, including

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[13] W. Gerrard and E. G. G. Whitbread, *J. Chem. Soc.*, 914 (1952).

[14] H. D. Orloff, C. J. Worrel, and F. X. Markley, *J. Am. Chem. Soc.*, **80**, 734 (1958).

[15] The halogenation of triphenylphosphine in alcohols was described recently by G. A. Wiley, R. L. Hershkowitz, B. M. Rein, and B. C. Chung, *ibid.*, **86**, 964 (1964).

[16] R. Stroh, "Methoden der Organischen Chemie (Houben-Weyl)," Vol. V, Part 3, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, 1962, p 599.

[17] (a) K. A. Petrov and G. A. Sokol'skii, *Zh. Obshch. Khim.*, **26**, 3377 (1956); (b) D. B. Denney and R. R. DiLeone, *J. Am. Chem. Soc.*, **84**, 4737 (1962).

[18] G. A. Wiley, B. M. Rein, and R. L. Hershkowitz, *Tetrahedron Letters*, 2509 (1964).

elemental phosphorus itself, will be described in part II of this series.

Experimental Section[19]

Reagents.—Five of the trialkyl phosphites were prepared by transesterification reactions:[20] trimethyl phosphite and triisobutyl phosphite from triphenyl phosphite; and tri-*n*-propyl phosphite, tris(2-ethylhexyl) phosphite, and tristearyl phosphite from the trimethyl phosphite. Tris(2-phenethyl) phosphite was prepared by the reaction of 2-phenylethanol with phosphorus trichloride in the presence of triethylamine.[21] Dibutyl phosphite was prepared from tributyl phosphite by treatment with anhydrous hydrogen chloride.[20] Diethyl phenylphosphonite[22] and ethyl diphenylphosphinite[23] were prepared from the corresponding chlorides by reaction with ethanol in the presence of dimethylaniline. The remainder of the reagents were obtained from commercial sources and used without further purification.

Methods of Analysis.—Trialkyl phosphite and dialkyl phosphite content were measured by iodine titration.[24] Gas chromatographic analyses were run on a Burrell K-2 instrument, using the 20% SE-30 on Chromosorb W column described for trimethyl phosphite.[25] Infrared spectra were taken on a Beckman IR-4 spectrophotometer, liquids neat and solids in Nujol.

Chlorination of Trialkyl Phosphites in Alcohols.—The preparation of trimethyl phosphate from trimethyl phosphite is typical of each procedure. The same 30:1 molar ratio of alcohol to phosphite, reaction temperature, etc., was used for all of the phosphate esters.

A. Direct Addition.—Chlorine was passed into a solution of trimethyl phosphite (24.8 g, 0.2 mole) in methanol (250 ml) at 0–10° until the chlorine color was no longer discharged. The solution was allowed to warm to room temperature and then stripped on a steam bath under water-pump vacuum. The residue (25.6 g, n^{23}_{D} 1.4043) contained no dimethyl phosphite or trimethyl phosphite (Table II). Distillation gave 14.6 g (52%) of trimethyl phosphate in four fractions boiling over the range 76–88° (10 mm), but with fairly constant refractive index (n^{23}_{D} 1.3962–1.3972). The undistilled residue (7.5 g, n^{23}_{D} 1.4333) was large. The infrared spectrum of the distillate showed that it was mostly trimethyl phosphate, but the presence of small, but sharp bands at 7.6 (P-CH$_3$) and 8.0 μ (P=O)[26] indicated that some dimethyl methylphosphonate was present.

A large-scale run made under identical conditions gave the same results. A 22-l. flask was charged with 1935 g (15.5 moles) of trimethyl phosphite and 16 l. (400 moles) of methanol, cooled to 0–10° by means of a Dry Ice–acetone bath, and chlorinated at a rapid rate until the color was no longer discharged. This required 966 g (13.6 moles) of chlorine (88% of theory). The addition was completed in 1.5 hr. Work-up of the product gave 1233 g (56.5%) of trimethyl phosphate, bp 64–100° (0.2 mm), n^{20}_{D} 1.3970, acidity 8.2 mg of KOH/g.

Anal. Calcd for $C_3H_9O_4P$: P, 22.1. Found: P, 22.0.

A gas chromatographic analysis of this product showed that it contained 82% of trimethyl phosphate, 11% of dimethyl methylphosphonate, and other minor impurities.

Tri-*n*-propyl phosphate was similarly prepared from tri-*n*-propyl phosphite (3.2 moles), chlorine, and *n*-propyl alcohol. The product, bp 74–87° (1.25–0.1 mm), n^{20}_{D} 1.4179, was obtained in 96.5% yield: acidity, 0.33 mg of KOH/g; purity by gas chromatography, 84%.

Anal. Calcd for $C_9H_{21}O_4P$: P, 13.8. Found: P, 13.4.

The presence of di-*n*-propyl *n*-propylphosphonate in the product was not verified, but it was probably the major impurity. The high yield of product in this run reflects the difference in sensitivity between the methyl and *n*-propyl esters to acid degradation during stripping.

B. Simultaneous Addition.—A 1-l., four-neck flask equipped with dropping funnel, reflux condenser, thermometer, and inlet tube extending to the bottom of the flask was charged with 480 g (15 moles) of methanol and cooled to 0–10° in a Dry Ice–acetone bath. Chlorine was passed in under the surface at a steady rate and, when the solution was yellow, trimethyl phosphite (62.0 g, 0.5 mole) was run in from the dropping funnel at a rate just sufficient to maintain a yellow tinge. At the end of the addition, which took 20 min, the solution, permanently colored by the excess chlorine, was allowed to warm to room temperature. The solvent was then stripped off on a steam bath under water pump vacuum, leaving a colorless residue (62.7 g, n^{21}_{D} 1.4058) which gave on distillation 36.1 g (52%) of trimethyl phosphate, bp 70–74° (10 mm), n^{25}_{D} 1.3940, the remainder (22.1 g) being a viscous, brown, undistillable oil. The characteristic absorption bands of dimethyl methylphosphonate were absent in the infrared spectrum of this product.

It was suspected that the low yield of trimethyl phosphate in this experiment might be due to acid degradation during work-up. A reaction run under identical conditions but modified only in the stripping procedure, the flask being kept at as near room temperature as possible during the stripping of the solvent, gave 61.6 g (88%) of **trimethyl phosphate**, bp 75–80° (10 mm), n^{20}_{D} 1.3963, d^{20}_{4} 1.2127, and left only 4.6 g of undistilled residue [lit.[27,28] bp 62° (5 mm); n^{20}_{D} 1.39630, 1.3967; d^{20}_{4} 1.2144]. The purity of the product was exceptionally good: acidity, 0.3 mg of KOH/g; hydrolyzable chlorine, 0.01%; dialkyl phosphite, nil; major component by gas chromatography, 100 mole %.

Anal. Calcd for $C_3H_9O_4P$: P, 22.1. Found: P, 22.5.

A similar reaction between triethyl phosphite, chlorine, and ethanol gave a 91% yield of **triethyl phosphate**, bp 86–88 (8 mm), n^{20}_{D} 1.4052, d^{20}_{4} 1.0703 [lit.[27] bp 75.5° (5 mm), n^{20}_{D} 1.40533, d^{20}_{4} 1.0695]. Purity, in the order given above, was 1.1, <0.02, nil, and 99.8.

Tri-*n*-propyl phosphate, bp 86–88° (1.25 mm), n^{20}_{D} 1.4173, d^{20}_{4} 1.0115 [lit.[27] bp 107.5° (5 mm), n^{20}_{D} 1.41646, d^{20}_{4} 1.0121], was obtained in 100% yield. Purity was (as above) 1.9, 0.8 (total Cl), . . ., and 98.8.

Tri-*n*-butyl phosphate, bp 148–150° (9 mm), n^{20}_{D} 1.4246, d^{20}_{4} 0.9771 [lit.[27,29] bp 138.5° (6 mm), 148.5° (8 mm); n^{20}_{D} 1.42496, 1.4247; d^{20}_{4} 0.9766], was obtained in only 50% yield owing to an inadvertent loss in work-up. Purity, given as above, was 0.5, nil, 0.1, and 98.9.

Triisobutyl phosphate, bp 90–92° (0.75 mm), n^{20}_{D} 1.4192, d^{20}_{4} 0.9661 [lit.[27] bp 117° (5.5 mm), n^{20}_{D} 1.41931, d^{20}_{4} 0.9681], was obtained in 99% yield from triisobutyl phosphite, chlorine, and isobutyl alcohol. Purity, given as above, was . . ., 0.2 (total Cl), . . ., and 100. The acidity could not be determined because the compound hydrolyzed when titrated with base.

Tris(2-chloroethyl) phosphate, bp 146° (1 mm), n^{20}_{D} 1.4734, d^{20}_{4} 1.420 [lit.[30] bp 180° (5 mm), n^{20}_{D} 1.4731, d^{20}_{4} 1.4256], was prepared in 96% yield. Purity, given as above, 2.3, . . ., nil, 94.0.

Anal. Calcd for $C_6H_{12}Cl_3O_4P$: Cl, 37.3; P, 10.9. Found: Cl, 36.7; P, 10.8.

Also prepared as undistilled liquids were **tris(2-phenethyl) phosphate**, n^{20}_{D} 1.5513, d^{20}_{4} 1.1401 (lit.[21] n^{24}_{D} 1.5498, d^{20}_{4} 1.148), in 100% yield and **tris(2-ethylhexyl)phosphate**, n^{20}_{D} 1.4452, d^{20}_{4} 0.9913 (lit.[31] n^{20}_{D} 1.4434, d^{20}_{20} 0.9260), in 93% yield.

Tristearyl Phosphate.—This preparation required some modification, as the phosphite and the alcohol are both solids. A slurry of tristearyl phosphite (25.1 g, 0.03 mole) and stearyl alcohol (40.5 g, 0.15 mole) in 250 ml of benzene was chlorinated at 25–30° until the chlorine consumption ceased, was filtered, and was stripped of volatiles under vacuum. The residue was triturated in a mortar under acetone, filtered, washed with acetone, and dried, giving 32.9 g (98%) of tristearyl phosphate as a white, waxy solid, mp 55.5–57.5° (lit.[32] mp 72°) after one recrystallization from either acetone or ethanol. The product was

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[19] Melting points were determined using a Fisher-Johns apparatus and are corrected.

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[24] Technical Data Sheet No. 819A, "Analytical Methods for Tridecyl Phosphite," Hooker Chemical Corp., Niagara Falls, N. Y., 1959.

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[29] B. A. Arbuzov and V. S. Vinogradova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 459 (1947).

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shown by infrared analysis and by gas chromatography to be a 1:1 adduct of tristearyl phosphate and stearyl alcohol.

Anal. Calcd for $C_{72}H_{149}O_5P$: C, 76.80; H, 13.34; P, 2.75. Found: C, 76.15; H, 13.15; P, 2.22.

The stearyl alcohol could be removed by vacuum stripping to 200° (0.05 mm), but not without considerable degradation of the phosphate.

Diethyl Phenylphosphonate.—The reaction of diethyl phenylphosphonite (19.8 g, 0.1 mole), chlorine, and 138 g (3.0 moles) of anhydrous ethanol, following procedure B, gave 13.0 g (61%) of diethyl phenylphosphonate: bp 118–121° (1.4 mm); $n^{20}{}_{D}$ 1.4973; $d^{20}{}_{4}$ 1.1611; acidity, 3.8 mg of KOH/g.

Anal. Calcd for $C_{10}H_{15}O_3P$: P, 14.5; Cl, nil. Found: P, 13.8; Cl, 1.3 (total), 0.08 (hydrolyzable).

The literature gives bp 117–118° (1.5 mm), $n^{20}{}_{D}$ 1.4970, d^{25} 1.1152, for this compound.[33]

Ethyl Diphenylphosphinate.—Ethyl diphenylphosphinite (6.6 g, 0.029 mole) was chlorinated in 39.6 g (0.86 mole) of anhydrous ethanol according to procedure A, giving 6.1 g (87%) of ethyl diphenylphosphinate: bp 160° (0.4 mm); mp 39–41°; acidity, 7.1 mg of KOH/g.

Anal. Calcd for $C_{14}H_{15}O_2P$: P, 12.6; Cl, nil. Found: P, 12.6; Cl, 0.4 (total), 0.08 (hydrolyzable).

The literature gives bp 173–175° (1.5 mm),[33a] mp 165°.[34] The high melting point reported by Michaelis has been questioned,[35] but no alternative value has hitherto been given.

Triphenylphosphine Oxide.—Chlorine was passed into a slurry of 26.2 g (0.1 mole) of triphenylphosphine in 200 ml of anhydrous ethanol at 25–35° until the color became permanent. The solution was then stripped under reduced pressure, leaving a white solid. This was washed with 1:1 hexane–benzene and dried, giving 28.3 g (100%) of triphenylphosphine oxide, mp 155.5–157°, identified by its infrared spectrum.

Chlorination of Triisopropyl Phosphite in Isopropyl Alcohol.—This was one of the few reactions in which competition of the alcohol for the chlorine was a significant factor. The procedure followed was procedure B, triisopropyl phosphite (41.6 g, 0.2 mole) and chlorine being added simultaneously to 360 g (6.0 moles) of isopropyl alcohol at 0–10°. Distillation of the product gave the following fractions: (a) 8.7 g, bp 60–88° (10 mm), $n^{23}{}_{D}$ 1.4386 (*Anal.* Found: Cl, 28.5; P, 7.1.); (b) 21.9 g, bp 94–98° (10 mm), $n^{23}{}_{D}$ 1.4204 (*Anal.* Found: Cl, 13.8; P, 10.6.); (c) 7.8 g, bp 98–103° (10 mm), $n^{23}{}_{D}$ 1.4149 [*Anal.* Found: Cl, 7.6 (total), 0.32 (hydrolyzable); P, 11.6.]; and (d) a residue, 7.8 g. Fraction a contained a strong carbonyl band in the infrared spectrum at 5.73 μ.

In another experiment, the first distillate fraction partly crystallized in the receiver. The crystals, washed with hexane and dried, melted at 41–42° and were strongly lachrymatory. This product was identified by its infrared spectrum as *sym*-dichloroacetone.

Anal. Calcd for $C_3H_4Cl_2O$: Cl, 55.9. Found: Cl, 55.8.

Use of Other Halogens. a. Bromine.—Bromine was added dropwise to a solution of trimethyl phosphite (24.8 g, 0.2 mole) in methanol (250 ml) at 0–10° until the bromine color was no longer discharged. The solution was allowed to warm to room temperature and then stripped on a steam bath under water-pump vacuum. The residue (27.0 g, $n^{23}{}_{D}$ 1.4009) contained no trimethyl phosphite but 4.0% of dimethyl phosphite (Table II). Distillation of this product gave 15.3 g (55%) of trimethyl phosphate, bp 73–78° (10 mm), $n^{23}{}_{D}$ 1.3939.

Anal. Calcd for $C_3H_9O_4P$: P, 22.1. Found: P, 21.9.

b. Iodine.—A 0.25 *M* solution of iodine in methanol was added dropwise to a solution of trimethyl phosphite (24.8 g, 0.2 mole) in methanol (100 ml) at 0–10° until the iodine color was no longer discharged. This point was unexpectedly reached before half of the calculated amount of iodine had been added. The solution was stripped on a steam bath under water-pump vacuum, giving 25.1 g of crude residue which contained 1.1% of trimethyl phosphite and 35.9% of dimethyl phosphite (Table II). The product was distilled, giving 19.5 g of distillate, bp 44–50° (1 mm), $n^{23}{}_{D}$ 1.3987, whose infrared spectrum showed it to be a mixture of dimethyl phosphite and trimethyl phosphate, with bands at 4.1 (P–H) and 7.8–7.9 μ (P=O). The P–CH$_3$ band at 7.6 μ was absent.

When the order of addition was reversed, the crude stripped product was found to contain no trimethyl phosphite and only 1.5% of dimethyl phosphite. On distillation, it afforded 8.4 g (60%) of trimethyl phosphate, bp 80–87° (10 mm), $n^{22}{}_{D}$ 1.3950–1.3956, in three fractions.

Anal. Calcd for $C_3H_9O_4P$: P, 22.1. Found: P, 23.0.

The first experiment was then repeated with 20.2 g (0.2 mole) of triethylamine present in the trimethyl phosphite solution. The iodine end point was reached at 85% of the calculated value, but no amine salt separated. The solvent was stripped off as before, leaving a syrupy residue which partly crystallized when rubbed with ether. The mixture was filtered and the crystals were washed with ether and dried: 12.9 g (28% as triethylamine hydriodide). The filtrate separated into two layers, the lower layer being a viscous, yellow, undistillable liquid, 27.3 g, $n^{22}{}_{D}$ 1.4538 [*Anal.* Found: N, 4.6, P, 27.9 (P:N ratio 3:1).]. The identity of this substance was not established.

Chlorination of Dibutyl Phosphite in Butanol.—Dibutyl phosphite (38.8 g, 0.2 mole) and chlorine were added simultaneously to 444 g (6.0 moles) of butanol at 0–10°, following procedure B. When the addition was complete, the solution was allowed to warm to room temperature. A test for dibutyl phosphite was positive.[36] The chlorination was resumed and chlorine was passed in at 25–30° until the test was negative. The solution was then stripped under water-pump vacuum and distilled, giving 25.7 g (76%) of tributyl phosphate, bp 95–98° (0.3 mm), $n^{25}{}_{D}$ 1.4232.

Anal. Calcd for $C_{12}H_{27}O_4P$: P, 11.7. Found: P, 10.7.

A low-boiling fraction, bp 60–65° (0.6 mm), $n^{25}{}_{D}$ 1.4145, was also obtained in substantial amount (27.7 g). It contained no phosphorus, and its infrared spectrum showed no hydroxyl or carbonyl absorption. Its identity was not established.

Two-Step Reactions. a. Dimethyl Phosphorochloridate.—Dimethyl phosphorochloridate, bp 59–60° (4 mm), $n^{22}{}_{D}$ 1.4100, was prepared in 86% yield by the chlorination of trimethyl phosphite in the absence of a solvent.[10,37] The chloridate (21.7 g, 0.15 mole) was added dropwise to 144 g (4.5 moles) of methanol at 0–10° over a 10-min period. The solution was allowed to warm to room temperature, stripped carefully to avoid degradation, and distilled, giving 18.2 g (87%) of trimethyl phosphate, bp 74–78° (10 mm), $n^{23}{}_{D}$ 1.3941.

Anal. Calcd for $C_3H_9O_4P$: P, 22.1. Found: P, 21.7.

A similar experiment in which the reaction mixture was stripped on a steam bath gave a 65% yield of trimethyl phosphate and left a substantial undistilled residue.

b. Dimethyl Phosphoroiodidate.—A 0.1 *M* solution of dimethyl phosphoroiodidate in ether was prepared by the iodination of trimethyl phosphite in ether as described by McCombie, *et al.*[38] The solution was transferred to a dropping funnel and added dropwise to 250 ml of methanol over a 30-min period at 0–10°. During the addition the solution turned an orange-red color, but the color lightened to a pale yellow when the reaction mixture was stripped.[39] The residue (13.7 g) was distilled, giving 7.8 g (56%) of trimethyl phosphate, bp 84–86° (10 mm), $n^{23}{}_{D}$ 1.3945.

Anal. Calcd for $C_3H_9O_4P$: P, 22.1. Found: P, 21.5.

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[36] A simple qualitative test for dialkyl phosphites can be performed as follows. To a few drops of the solution to be tested add 1 ml of benzene and 0.5 ml of triethylamine. Shake until homogeneous and then add 1 drop of 0.1 *N* iodine in benzene. The color will be discharged in about 5 sec if a dialkyl phosphite is present. Alcohols and trialkyl phosphites interfere.

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[39] Dialkyl phosphoroiodidates decompose easily to phosphorus iodides, which are red (PI_3) or orange (P_2I_4). These may have been formed during the addition and destroyed during the stripping by the warm acidic methanol.