

was stirred and refluxed for 39 hr. and hydrolyzed with 500 ml. of 1:1 hydrochloric acid. The ether was removed by distillation and the residue was heated on a steam bath for 1 hr., with occasional shaking. The aqueous phase was separated and extracted with three 100-ml. portions of ether. The extracts and organic phase were combined, dried over anhydrous magnesium sulfate, and concentrated. The residue was distilled to give 3.8 g. (2.4%) of *t*-butyl pentyl ketone, b.p. 45–55° (1 mm.), n_D^{25} 1.4190–1.4240; semicarbazone, m.p. 139–140° (lit.⁶ m.p. 140–140.5°); 2,4-dinitrophenylhydrazone, m.p. 76–77° (lit.⁶ m.p. 99–100°); and 46 g. of an intractable tar.

Anal. Calcd. for $C_{16}H_{24}O_4N_4$: C, 57.13; H, 7.19; N, 16.66. Found: C, 57.09; H, 7.14; N, 16.18.

(6) F. C. Whitmore, C. I. Noll, and V. C. Meunier, *J. Am. Chem. Soc.*, **61**, 683 (1939).

Preparation of *t*-Alkylphosphonic Dichlorides¹

T. H. SIDDALL, III, AND C. A. PROHASKA

Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, South Carolina

Received May 3, 1963

The aluminum chloride-catalyzed reaction of alkyl halides with phosphorus trichloride^{2a,b} has broad utility for the synthesis of *sec*-alkylphosphonic dichlorides. However, the usefulness of this reaction for the straightforward synthesis of *t*-alkylphosphonic dichlorides appeared to be limited to the preparation of *t*-butylphosphonic dichloride. Kosolapoff and Crofts³ found that

are still only 40–50%. In all cases the foreshots obtained in distillation under high vacuum were small, and as much as half of the high-boiling material remained as a heel even when bath temperatures were raised to over 100° at about 0.2-mm. pressure. We have not studied any range of experimental conditions in an attempt to improve yields, since our object was to obtain about 50 g. of pure product without regard to optimizing conditions for yield.

Experimental

One mole of alkyl bromide was added slowly to 1 mole of phosphorus trichloride plus 1 mole of anhydrous aluminum chloride in 400 ml. of methylene chloride at about 0°. After the reaction mixture had been stirred overnight at room temperature, the mixture was poured slowly, with good manual agitation, over a mixture of ice and solid carbon dioxide. The mixture with ice was allowed to warm up slowly to between –20 and –10°, and the phases were separated in a separatory funnel. After the mixture was dried with anhydrous calcium chloride, the methylene chloride was pumped off from the organic phase and distillation carried out at about 0.2 mm.

The three *t*-alkylphosphonic dichlorides that were prepared in this manner are listed in Table I. All three compounds are clear, colorless liquids at room temperature. Proton magnetic resonance spectrograms for these compounds and for *t*-butylphosphonic dichloride (all 10% by volume in carbon tetrachloride) were obtained with the Varian Associates Model 4300 B spectrometer at 40 Mc. The doublet for the β -methyl protons occupies the same position for all three of the higher *t*-alkylphosphonic dichlorides (41.1 and 67.4 c.p.s. downfield from tetramethylsilane as an internal standard) but is displaced to 44.3 and 69.1 c.p.s. for the *t*-butylphosphonic dichloride. From the spectrograms it is estimated that the three higher phosphonic dichlorides

TABLE I
t-ALKYLPHOSPHONIC DICHLORIDES

Compound	C, %		H, %		P, %		Cl, %		Yield of high boilers, %	Yield of product, %	Approximate ^a b.p. at 0.2–0.3 mm., °C.
	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.			
2-Methylbutyl-2-phosphonic dichloride	31.6	31.7	5.9	5.9	16.0	16.4	36.3	37.5	50	32	55
3-Methylamyl-3-phosphonic dichloride	34.6	35.5	6.7	6.5	14.5	15.3	34.3	34.9	50	40	70
3-Methylheptyl-3-phosphonic dichloride	40.8	41.6	7.3	7.4	12.9	13.4	29.9	30.7	40	22	90

^a Crude measurements made during purification of compounds.

starting with *t*-amyl chloride, a mixture of *t*-butyl- and amylphosphonic dichlorides was obtained and the separation of these two products by fractional distillation was difficult. Experiments in this laboratory confirmed these results; we were never able to prepare *t*-amylphosphonic dichloride that, by proton magnetic resonance spectrograms, was free of *t*-butylphosphonic dichloride. However, the finding of Kinnear and Perren^{2b} that isobutyl chloride gave *t*-butylphosphonic dichloride suggested that 1-halo-2-alkylalkanes could be used to prepare *t*-alkylphosphonic dichlorides.

Our investigations show that the use of 1-halo-2-alkylalkanes apparently provides a general preparation of *t*-alkylphosphonic dichlorides by the reaction of Kinnear and Perren. The yields of pure products are only 20–40%, while the yields of gross high-boiling material

contain not more than a few per cent of the *t*-butyl compound. Even the small peaks to the lowfield side of the main doublet for these compounds may not be due to the *t*-butyl doublet, but may be due to other protons in these molecules.

The Photoinitiated Oxidation of Tertiary Phosphites

J. B. PLUMB AND C. E. GRIFFIN

Department of Chemistry, University of Pittsburgh, Pittsburgh 13, Pennsylvania

Received April 25, 1963

During a study of the photochemical phenylation of tri-*n*-butyl phosphite with iodobenzene,¹ we observed the formation of a significant amount of a third ma-

(1) The information contained in this article was developed during the course of work under contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

(2) (a) J. P. Clay, *J. Org. Chem.*, **16**, 892 (1951); (b) A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

(3) P. C. Crofts and G. M. Kosolapoff, *J. Am. Chem. Soc.*, **73**, 3379 (1953).

(1) For a preliminary report of this study, see J. B. Plumb and C. E. Griffin, *J. Org. Chem.*, **27**, 4711 (1962).

terial in addition to the expected products, di-*n*-butyl phenylphosphonate and di-*n*-butyl *n*-butylphosphonate. A mass balance on the identified products accounted quantitatively for the iodine and phenyl groups of iodobenzene; thus, among the known starting materials, tri-*n*-butyl phosphite could be the only source of the third product. Further experiments indicated that formation of the product was suppressed by rigorous exclusion of oxygen from the reaction vessel, suggesting that, in the presence of air, oxidation of the phosphite to phosphate had occurred. Vapor phase chromatography (v.p.c.) and infrared spectroscopy confirmed the identity of the third product as tri-*n*-butyl phosphate.

We have now investigated the photoinitiated air oxidation of several lower trialkyl phosphites and triphenyl phosphite and have found that quantitative uptake of oxygen occurs readily, forming the corresponding tertiary phosphates with little contamination from side products.

The only photoinitiated air oxidation of a trivalent organophosphorus compound studied previously was that of triphenylphosphine to the corresponding oxide² which was described as involving a "long-lived but reactive intermediate (possibly a peroxide)." It has also been shown that γ -radiation readily catalyzes the air oxidation of triisopropyl phosphite to the phosphate.³ Other reagents which have recently found use for the oxidation of tertiary phosphites include dinitrogen tetroxide,⁴ ozone,⁵ alkoxy radicals,⁶ peroxides and air,⁶ azobisisobutyronitrile and air,⁷ and nitric oxide,⁸ the last four by radical mechanisms.

The air oxidation of triethyl phosphite is reported to be unsuccessful,⁴ although that of tris(β -cyanoethyl) phosphite⁹ apparently proceeds readily at 78°. We found that the conversion of tri-*n*-butyl phosphite (I) to phosphate in the absence of solvent occurred to the extent of 45% during twenty hours oxidation by dry air in the dark at 50–55°, while in the presence of ultraviolet light, but under otherwise identical conditions, tri-*n*-butyl phosphate (II) was formed quantitatively in five hours. In a comparable two-hour irradiative oxidation, II was obtained in 63% yield; the addition of 2 mole % of hydroquinone to I decreased the yield of II to 1.7% under otherwise identical reaction conditions (two-hour reaction time).

When I was irradiated in the presence of oxygen instead of air, the resulting exothermic reaction caused the temperature of the reaction mixture to rise above 100°; no comparable exothermicity was observed for the air oxidations. Quantitative v.p.c. analysis of aliquots from the reaction mixture indicated an almost linear increase in the concentration of II with time from 0–100% reaction; a quantitative yield of II was obtained in seventy minutes under these conditions.

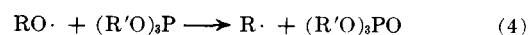
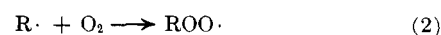
The photoinitiated air oxidation of a series of lower trialkyl phosphites, (RO)₃P (R = methyl, ethyl, isopropyl), closely followed the behavior of I; all were

oxidized quantitatively to the corresponding phosphates in twenty hours at 50–60°. The oxidation of triphenyl phosphite was markedly slower, although a satisfactory yield (79%) of triphenyl phosphate was obtained in 168 hours.

In all cases where oxidations were allowed to run to completion the only impurities observed in the product were traces of the alcohol and the corresponding dialkyl phosphite, (RO)₂P(O)H. These materials were probably formed by inadvertent hydrolysis of the trialkyl phosphite during handling or by the action of incompletely dried air. Their concentrations were usually less than 2% (determined by total peak area in vapor phase chromatograms). The only impurity observed in the photoinitiated oxidation of I with oxygen was 2–3% of di-*n*-butyl phosphate (III); the presence of III was detected by v.p.c., and its identity was confirmed by paper chromatography. This material could arise either by hydrolysis of the product II by traces of moisture under the conditions employed or by oxidation of di-*n*-butyl phosphite (formed either by hydrolysis of the reactant I, or present as an impurity in I). In order to determine the possibility of the formation of III by the second route, the photoinitiated oxidation of di-*n*-butyl phosphite (IV) with oxygen was attempted. Under conditions which lead to the rapid and complete oxidation of I, IV remained unchanged. No di-*n*-butyl phosphate was produced, but a small amount (ca. 4%) of tri-*n*-butyl phosphate (II) was detected. This finding suggests that a small amount of di-*n*-butyl phosphite may have undergone oxidation to the phosphate III; subsequent esterification of III by traces of 1-butanol known to be present in the di-*n*-butyl phosphite would lead to the formation of II. Thus no choice as to the mode of formation of III in the oxidation of I can be made; however, this study does indicate that a secondary phosphite appears to be quite resistant to oxidation under conditions favorable for the rapid photoinitiated oxidation of trialkyl phosphites.

The experimental simplicity of the method and the high yields and purity of products obtained in these oxidations indicate the synthetic utility of this procedure. The character of this oxidation differs from the peroxide⁶ and azobisisobutyronitrile⁷ initiated oxidations only in the manner of initiation; some synthetic advantages may be realized since the products are free of initiator or oxidant fragments.

The marked catalytic effect of ultraviolet irradiation and the inhibition of oxidation effected by traces of hydroquinone clearly indicate that the reaction proceeds by a free radical mechanism, in all probability a chain propagated process. The formation of any long-lived reactive intermediate such as those formed in the photoinitiated oxidation of triphenylphosphine² and the ozone oxidation of trialkyl phosphites⁵ appears unlikely because of the linear dependence of phosphate concentration on time. A similar linear dependence has been observed by Coe³ in γ -initiated oxidations. In order to account for the features observed, we suggest the following mechanism.



(2) P. D. Bartlett, E. F. Cox, and R. E. Davis, *J. Am. Chem. Soc.*, **83**, 103 (1961).

(3) D. G. Coe, *Nature*, **181**, 1519 (1958).

(4) J. R. Cox and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 5441 (1958).

(5) Q. E. Thompson, *ibid.*, **83**, 845 (1961).

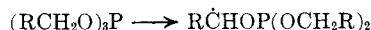
(6) C. Walling and R. Rabinowitz, *ibid.*, **81**, 1243 (1959).

(7) M. B. Floyd and C. E. Boozer, *ibid.*, **85**, 984 (1963).

(8) L. P. Kuhn, J. O. Doali, and C. Wellman, *ibid.*, **82**, 4792 (1960).

(9) E. V. Kuznetsov and R. K. Valetdinov, *Tr. Kazansk. Khim.-Tekhnol. Inst.*, No. **21**, 167 (1956); *Chem. Abstr.*, **51**, 11985 (1957).

A similar radical chain mechanism has been postulated for the autoxidation of trialkylphosphines,^{7,10} triphenylphosphine,⁷ and tributyl phosphite.⁷ The attack of alkoxy radicals on phosphites to yield phosphates and alkyl radicals has been demonstrated clearly.^{6,11} The propagating radicals, R·, formed in step 1 and necessary for initiation of the chain process may arise from a number of sources. Radicals of the type RCHOH could arise from traces of the corresponding alcohol present in the trialkyl phosphite; the presence of such radicals is well established in photolytic reactions involving primary or secondary alcohols.¹² Minute traces of alcohol could usually be detected by v.p.c. even after the most careful distillation of the starting trialkyl phosphites over sodium in a stream of dry nitrogen. Alternatively, the initiating and propagating radical may be produced by removal of an α -hydrogen from the trialkyl phosphite itself (see following).



A similar attack in the autoxidation of carboxylic esters has been postulated.^{13a} Analogous initiation steps for the oxidation of triphenyl phosphite would be expected to be highly inefficient^{13b}; the combination of initiation inefficiency and the absorption of energy by the aryl phosphite would account for the lower reactivity of triphenyl phosphite.

Experimental¹⁴

Materials and Procedures.—The tertiary phosphites were obtained from commercial sources and were distilled from sodium in an atmosphere of dry nitrogen prior to use. Authentic samples of trialkyl phosphates and other reaction products were obtained from commercial sources and distilled before use. The purity of all materials was confirmed by v.p.c. and infrared analysis.

V.p.c. analyses were carried out with a 0.25-in. o.d. 6-ft. stainless steel column packed with either 20% Carbowax 20M (for analysis of trimethyl, isopropyl, and *n*-butyl phosphite reactions) or 20% silicone rubber S.E. 30 (for triethyl and phenyl phosphite reactions) on 60–80-mesh Chromosorb P. Column temperatures from 175° (for trimethyl phosphite oxidations) to 250° (for triphenyl phosphite) were employed; the carrier gas was helium. Quantitative analyses were based on integrated peak areas using standard mixtures of authentic materials for calibration. In all cases, clean separations of all the components of the reaction mixtures were obtained and the phosphites and phosphates gave symmetrical peaks with no evidence of tailing.

Photoinitiated Air Oxidation of Tri-*n*-butyl Phosphite (I).—Tri-*n*-butyl phosphite (7.1 g., 28.4 mmoles) was placed in a 125-ml. two-necked Vycor flask equipped with an air inlet tube which

dipped into the liquid, a magnetic stirrer, a reflux condenser, and a thermometer which dipped into the liquid. Air was passed successively through concentrated potassium hydroxide solution and concentrated sulfuric acid and dried over phosphorus pentoxide before passing into the reaction vessel. With a continuous stream of dry air at a flow rate of 20 ml./min., the phosphite was stirred and irradiated for 20 hr. with an unfiltered 100-w. mercury resonance lamp (Hanovia 8A-1 quartz lamp). The lamp was placed 5 cm. from the reaction vessel; a reaction temperature of 50–60° was maintained during the course of the reaction. The infrared spectrum of the product was identical to that of an authentic sample of tri-*n*-butyl phosphate (II). V.p.c. analysis indicated that no traces of I remained, and the major peak in the chromatogram was identified as II. Three minor peaks, two of which were identified as 1-butanol and di-*n*-butyl phosphite, accounted for less than 4% of the total peak area on the chromatogram; the third peak was not identified. The weight of product was 7.3 g., 97% (based on $\text{I} + 0.5 \text{O}_2 \rightarrow \text{II}$).

Under conditions otherwise identical to this experiment, reduction in reaction time to 10 and 5 hr. gave the same results. In each case the yield of II was 99.5%. Further reduction in reaction time to 2 hr. led to the formation of the phosphate in 63.1% yield. Other than a total of 2% of the impurities noted above, the remainder of the material was unchanged I.

In the dark, a 20-hr. oxidation of I at 50–55° under the standard conditions gave a 45.4% conversion to phosphate. Unchanged I and traces of 1-butanol and di-*n*-butyl phosphite were the only other components observed.

Inhibition of Oxidation of I.—The oxidation of 7.1 g. (28.4 mmoles) of I was carried out under the conditions described in the preceding section in the presence of 0.0625 g. of hydroquinone (2 mole %); reaction time was 2 hr. Quantitative v.p.c. analysis of the reaction mixture indicated a yield of 1.69% of phosphate. Unchanged I was the major component of the reaction mixture, and the usual trace impurities were observed.

Photoinitiated Oxidation of I with Oxygen.—Tri-*n*-butyl phosphite (12.5 g., 50 mmoles) was oxidized by the general procedure as described using a stream of dry oxygen (20 ml./min.) instead of air. The reaction was exothermic; the temperature of the reaction mixture rose steadily, reaching a maximum of 103° after 50 min., then gradually falling to 50°. Samples (0.1 ml.) were taken periodically from the reaction mixture through a rubber septum and analyzed quantitatively by v.p.c. The analyses indicated that the concentration of phosphate in the mixture increased almost linearly with time and that oxidation was complete after 60 min. Samples taken after this period of irradiation contained no unchanged I and gave a single major peak identified as the phosphate. One minor impurity was detected by v.p.c. and identified as di-*n*-butyl phosphate (2–3%) by paper chromatography. Paper chromatography was carried out on Whatman no. 1 paper employing a one-dimensional ascending technique; the mobile phase consisted of 60 ml. of acetone, 35 ml. of water, and 5 ml. of concentrated ammonium hydroxide. Di-*n*-butyl phosphate had an R_f value of 0.82, and identity and quantitative estimation was obtained by comparison with known solutions of di-*n*-butyl phosphate in tri-*n*-butyl phosphite.

Photoinitiated Air Oxidation of Other Tertiary Phosphites.—The air oxidation of four other tertiary phosphites was carried out under the conditions initially described for the oxidation of I. Trimethyl, triethyl, and triisopropyl phosphites were oxidized (20 hr.) to give the corresponding phosphates in 94–99% yield. The maximum amount of impurity detected in any run was 2%.

Triphenyl phosphite was oxidized for 88 hr.; analysis showed the reactant, triphenyl phosphite, and a trace of phenol to be the only materials present in the reaction mixture. Quantitative v.p.c. analysis showed 25.7% of the phosphate in the mixture; analysis of the mixture for triphenyl phosphite by the method of Thompson⁵ gave a value of 21.0%. In a similar oxidation carried out for 168 hr., triphenyl phosphate was obtained in 79.2% yield.

Acknowledgment.—This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under grant no. AF-AFOSR-62-48. We are indebted to Drs. A. D. F. Toy and D. Bernhart for providing paper chromatographic data.

(10) S. A. Buckler, *J. Am. Chem. Soc.*, **84**, 3093 (1962).

(11) Walling and Rabinowitz⁶ reported that the autoxidation of triethyl phosphite could be initiated by peroxides and proposed a mechanism identical to that cited in equations 1–4.

(12) W. H. Urry, F. W. Stacey, E. S. Huyser, and O. O. Juveland, *ibid.*, **76**, 450 (1954); H. L. J. Backstrom and A. Steneryr, *Acta Chem. Scand.*, **13**, 8 (1958); J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patterson, G. Rechtenwald, and R. B. Martin, *J. Am. Chem. Soc.*, **81**, 1068 (1959); V. Franzen, *Ann.*, **633**, 1 (1960).

(13)(a) E. G. E. Hawkins, "Organic Peroxides," D. Van Nostrand Company, Inc., Princeton, N. J., 1961, pp. 386, 390–391; (b) pp. 397–401.

(14) Determinations of infrared spectra were carried out with Perkin-Elmer Model 21 and Beckman IR-8 spectrophotometers. V.p.c. analyses were performed on an F and M Model 500 chromatograph. We are indebted to the Victor Chemical Works, Monsanto Chemical Company, and Hooker Chemical Corporation for samples of phosphites and phosphates.