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.), $n^{25}D$ 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.

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

Preparation of *t*-Alkylphosphonic Dichlorides[1]

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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 Crofts[3] found that 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 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 reremained 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 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.

TABLE I

t-ALKYLPHOSPHONIC DICHLORIDES

	C, %		H, %		P, %		Cl, %		Yield of high boilers,	Yield of product,	Approxi-. mate[a] b.p at 0.2–0.3
Compound	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	%	%	mm., °C.
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.

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[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).

The Photoinitiated Oxidation of Tertiary Phosphites

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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-

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