bicarbonate extract. The oil could not be recrystallized and did not form a solid 2,4-dinitrophenylhydrazone.

Registry No.—^{14}C-4-Bromophenyl N-phenylbenzimidate, 18746-06-0; ^{14}C-4-bromophenol, 18746-07-1; N-benzoyl-N-^{14}C-4-bromodiphenylamine, 18746-08-2; N-benzoyl-N-(4-bromophenyl)-4-aminobenzoic acid, 18753-77-0; α-^{3}H-allyl N-phenylbenzimidate, 18753-78-1; α-^{3}H-allyl alcohol, 18753-79-2; N-^{3}H-allyl-N-benzoylaniline, 18753-80-5.

Acknowledgment.—The Puerto Rico Nuclear Center is operated by the University of Puerto Rico for the U. S. Atomic Energy Commission.

Reactions of *t*-Butylperoxy Esters. VIII. The Preparation of Dialkyl *t*-Butylperoxy Phosphates[1]

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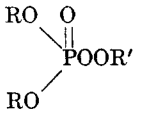
Analytically pure *t*-butylperoxy phosphates, $(RO)_2P(O)OOCMe_3$ (**1**, R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *n*-octyl, Ph, $PhCH_2$), are prepared by reaction of the corresponding dialkylchlorophosphates (**2**) with an aqueous potassium hydroxide solution of *t*-butyl hydroperoxide in the presence of petroleum ether (bp 20–40°). Only peroxy esters **1** (R = *n*-Pr, *i*-Pr) are distillable; other methods of purification are presented.

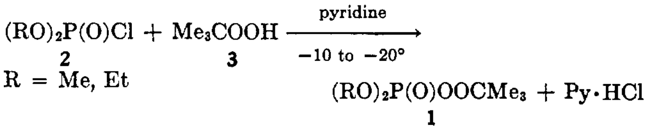
The chemistry of phosphoric acid peroxy esters of general structure **1** has to date received little attention.[2]



1

This scarcity of results is not surprising in view of the lack of suitable methods for preparation of these compounds and the difficulties encountered in their handling.

The first reported peroxy esters of phosphoric acid (**1**) were prepared by Rieche, Hilgetag, and Schramm.[3] Thus dimethyl or diethyl chlorophosphate (**2**, R = Me, Et) were allowed to react with *t*-butyl hydroperoxide (**3**) in the presence of excess anhydrous pyridine at −10 to −20° to produce dimethyl or diethyl *t*-butylperoxy phosphate (**1**, R = Me, Et).



$$\underset{\substack{\mathbf{2}\\ R\,=\,Me,\,Et}}{(RO)_2P(O)Cl} + \underset{\mathbf{3}}{Me_3COOH} \xrightarrow[-10\ \text{to}\ -20^\circ]{\text{pyridine}} \underset{\mathbf{1}}{(RO)_2P(O)OOCMe_3} + Py\cdot HCl$$

Harrison and Mageli[4] described a series of peroxy esters (**1**, R = Et, *n*-Bu, *n*-octyl, Ph; R′ = CMe_3, hexyl, cumyl, pinanyl) prepared by the reaction of **2** with hydroperoxides in the presence of aqueous solutions of alkali metal hydroxides. However, satisfactory analyses were obtained only for **1** (R = *n*-Bu, *n*-octyl; R′ = CMe_3).

As part of a general investigation of the chemical and biological properties of **1** it was necessary to develop methods for preparation of analytically pure peroxy ester in quantity.

Rieche and coworkers[3] successfully prepared **1** (R = Me, Et). Although we have been able to reproduce their work, this method is not generally applicable. Distillation of **1** is difficult. Only in the case of **1** (R = *i*-Pr) is it possible to distil 5 g or larger portions in good yield. Therefore, it is requisite that the crude peroxy ester be obtained in a form that is readily purified without distillation. Attempts to remove the excess pyridine by vacuum distillation, washing with water or sulfuric acid, and column chromatography were either unsuccessful or produced low yields of product. Several experiments in which a stoichiometric amount of 2,6-lutidine was substituted for the pyridine were tried. Since lutidine hydrochloride is less soluble than pyridine hydrochloride, removal of the organic base was not so difficult. However, yields of peroxy ester were low and an unidentified contaminant prevented purification.

The procedure of Harrison and Mageli[4] which eliminated the organic base seemed to be advantageous. However, in our hands the reported procedure has failed to yield products free of impurities.

We now report a generally applicable sequence that permits synthesis of **1** (R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *n*-octyl, Ph, $PhCH_2$) in yields varying from 30 to 80%. Reaction of chlorophosphate **2** with an aqueous potassium hydroxide solution of *t*-butyl hydroperoxide (**3**) in the presence of petroleum ether (bp 20–40°) produces the corresponding dialkyl *t*-butylperoxy

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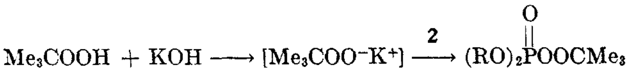
[1] (a) This investigation was supported by a grant from the Public Health Service, U. S. Department of Health, Education, and Welfare (GM 14932-01). (b) The results were presented in part in a talk at the International Symposium on the Chemistry of Organic Peroxides in Berlin, DDR, Sept 1967.

[2] G. Sosnovsky and J. H. Brown, *Chem. Rev.*, **66**, 529 (1966).

[3] (a) A. Rieche, G. Hilgetag, and G. Schramm, *Chem. Ber.*, **95**, 381 (1962); (b) *Angew. Chem.*, **71**, 285 (1959); (c) German Patent (East) 21,489 (1959); (d) German Patent 1,082,895 (1960).

[4] J. B. Harrison and O. L. Mageli, U. S. Patent 2,960,526 (1960).

phosphate (**1**). However, there is no general recipe for the preparation of these peroxy esters, and in each case the detailed procedure described in the Experimental Section must be followed. Salt **4** is prepared by pouring



$$\underset{\mathbf{3}}{Me_3COOH} + KOH \longrightarrow \underset{\mathbf{4}}{[Me_3COO^-K^+]} \xrightarrow{\mathbf{2}} \underset{\mathbf{1}}{(RO)_2\overset{O}{\overset{\|}{P}}OOCMe_3}$$

R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, *i*-Bu, *n*-octyl, Ph, $PhCH_2$

the appropriate amount of 100% **3** into a 20% (w/v) aqueous potassium hydroxide solution at 8–10°. This reaction is very exothermic and is moderated by the subsequent addition of the petroleum ether. It appears that the choice of solvent is critical to the succes of the method. Experiments in which pentane, ethyl ether, and benzene were substituted for petroleum ether yielded little or no reaction. The dialkyl chlorophosphate is added dropwise as rapidly as possible maintaining the reaction temperature between 8 and 12°. If the temperature is allowed to rise rapidly above 15°, or if the pH of the organic layer falls below pH 8, the corresponding dialkyl phosphate, $(RO)_2P(O)OH$ (**5**), is formed. Acid **5** should not be permitted to form since we have found[5] the decomposition of **1** to be catalyzed by **5**.

Contrary to a previous report[3a] we were unable to distil **1** (R = Me). It readily decomposes at room temperature and is most conveniently purified by crystallization from Skellysolve B at −70°. The white crystalline material obtained can be stored for a few days at 5° and several weeks at −20°.

Diethyl *t*-butylperoxy phosphate (**1**, R = Et) is distillable through a short-path distillation column in quantities of 5 g or less; however, it is more conveniently purified by removing the unreacted **3** at room temperature under high vacuum. This compound can be stored indefinitely at −20°.

Di-*n*-propyl *t*-butylperoxy phosphate (**1**, R = *n*-Pr) and diisopropyl *t*-butylperoxy phosphate (**1**, R = *i*-Pr) are readily distillable and are stable indefinitely at −20°.

Di-*n*-butyl *t*-butylperoxy phosphate (**1**, R = *n*-Bu) is undistillable and may be purified either by removing the volatile impurities under high vacuum at room temperature, or by chromatography on neutral alumina. Once pure, it is stable indefinately at −20°. Diisobutyl *t*-butylperoxy phosphate (**1**, R = *i*-Bu) and di-*n*-octyl *t*-butylperoxy phosphate (**1**, R = *n*-octyl) are readily purified by chromatography on neutral alumina using benzene–ethyl acetate (4:1, v/v) and benzene, respectively, as eluents.

Diphenyl *t*-butylperoxy phosphate (**1**, R = Ph) is too unstable to isolate. Although isolation of this material has been reported,[4] our experiments agree with those of Rieche and coworkers[3a] that this compound decomposes violently even at 0° under high vacuum. Dibenzyl *t*-butylperoxy phosphate (**1**, R = $PhCH_2$) also decomposes at room temperature. This product was identified by nmr and has not been isolated in pure form.

Experimental Section

t-Butyl hydroperoxide-90 (Lucidol Division, Wallace and Tiernan, Inc.) was concentrated by discarding the fraction up to bp 40° (40 mm). All other materials were best commercial grade used without further purification. The petroleum ether used had bp 20–40°.

Boiling points are uncorrected. Nmr spectra were obtained on a Varian A-60 or HA-100 spectrometer using an internal TMS standard; 60-MHz spectra were obtained on neat samples; 100-MHz spectra were obtained on 10% (v/v) samples in CCl_4. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill., and by Mr. W. Saschek.

We find the distillation of **1** (R = Me, Et, *n*-Pr) to be greatly facilitated by (a) washing the distillation vessel with 30% (w/v) aqueous NaOH, water, and then acetone before each distillation, and (b) washing the peroxy ester in petroleum ether with a cold 50% (v/v) aqueous ammonium hydroxide solution just prior to distillation.

Dialkyl Chlorophosphates 2. A General Procedure.[6]—To a solution of the alcohol (4.0 mol) in 350 ml of dry benzene was added dropwise at 8–10° a solution of 184 g (1.33 mol) of phosphorus trichloride in 350 ml of benzene. The mixture was stirred for 1 hr after the addition and then a solution of 180 g (1.33 mol) of sulfuryl chloride in 350 ml of benzene was added dropwise at 8–10°. The mixture was warmed to room temperature, concentrated, and distilled giving dialkyl chlorophosphate **2**, Table I.

TABLE I

DIALKYL CHLOROPHOSPHATES 2

R	Bp (mm), °C	$n^{25}D$	Yield, %	Lit.[a] $n^{25}D$
Me	80 (25)	1.4107	85	1.4107
Et	42 (0.2)	1.4146	66	1.4162
n-Pr	74 (0.3)	1.4236		1.4236
i-Pr	48 (1)	1.4146	78	1.4159
n-Bu	98 (0.26)	1.4281	92	1.4289
i-Bu	111 (12)	1.4262	60	1.4249

[a] See ref 6.

Dimethyl *t*-Butylperoxy Phosphate (1, R = Me).—To a solution of 7.16 g (0.11 mol) of potassium hydroxide in 29 ml of water at 10° was added in one portion 9.01 g (0.1 mol) of *t*-butyl hydroperoxide and then 60 ml of petroleum ether. The mixture was cooled to 13° and 12.9 g (0.09 mol) of **2** (R = Me) was added in one portion. The mixture was held at 20° for 10 min. The organic layer was washed with 50 ml of ice-cold 5% sodium chloride, and then with 50 ml of ice water, dried (Na_2SO_4), and concentrated at 10°. The oily residue was crystallized repeatedly from Skellysolve B giving 9.44 g (53%) of dimethyl *t*-butylperoxy phosphate (**1**, R = CH_3): mp 26°; $n^{25}D$ 1.4160; nmr δ 3.81 [d, 6, J = 18 Hz, $(CH_3O)_2P(O)$], 1.29 (s, 9, CH_3COO).

Anal. Calcd for $C_6H_{15}O_5P$: active oxygen, 8.13. Found: active oxygen, 8.3.

Diethyl *t*-Butylperoxy Phosphate (1, R = Et). A.—To a solution of 35 g (0.2 mol) of **2** (R = Et) in 100 ml of petroleum ether at −20° was added a solution of 34.0 g (0.22 mol) of *t*-butyl hydroperoxide in 24 g (0.3 mol) of anhydrous pyridine. The mixture was warmed to 25° and filtered. The filtrate was concentrated and the residual oil was dissolved in benzene. The benzene solution was washed with ice-cold water, concentrated, and distilled giving diethyl *t*-butylperoxy phosphate (**1**, R = Et): bp 66–67° (0.15 mm); $n^{25}D$ 1.4169 (lit.[3a] $n^{20}D$ 1.419–1.421).

Anal. Calcd for $C_8H_{19}O_5P$: C, 42.47; H, 8.47. Found: C, 42.19; H, 8.27.

B.—To a mixture of 14.32 g (0.22 mol) of potassium hydroxide, 58.08 g of water, 36.09 g (0.2 mol) of *t*-butyl hydroperoxide, and 120 ml of petroleum ether prepared as above was added at 9° 31.0 g (0.18 mol) of **2** (R = Et) over 5 min. The mixture was stirred at 9–15° for 30 min and the organic layer was washed with 100 ml of water, dried (Na_2SO_4), and concentrated. The residual oil was held at ambient temperature under vacuum until nmr and tlc showed no *t*-butyl hydroperoxide giving 21.06 g (53%) of diethyl *t*-butylperoxy phosphate (**1**, R = Et): $n^{25}D$ 1.4161; nmr

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[5] G. Sosnovsky and E. H. Zaret, unpublished result.

[6] B. Fiszer and J. Michalski, *Rocz. Chem.*, **26**, 688 (1952); R. A. McIvor, G. D. McCarthy, and G. A. Grant, *Can. J. Chem.*, **34**, 1819 (1956).

δ 1.32 (m, 6, $\mathbf{CH_3}CH_2O$), 4.16 (m, 4, $CH_3\mathbf{CH_2}O$), 1.28 [s, 9, $(CH_3)_3COO$].

Di-*n*-propyl *t*-Butylperoxy Phosphate (1, R = *n*-Pr).—To a mixture of 7.16 g (0.11 mol) of potassium hydroxide, 29 ml of water, 9.01 g (0.10 mol) of *t*-butyl hydroperoxide, and 100 ml of petroleum ether prepared as above was added 18.05 g (0.09 mol) of freshly distilled **2** (R = *n*-Pr) at 10°. The solution was stirred for 2.5 hr at ambient temperature. The organic layer was washed with 50 ml of cold water, dried (Na_2SO_4), concentrated, and distilled giving 16 g (70%) of di-*n*-propyl *t*-butylperoxy phosphate (**1**, R = *n*-Pr): bp 85–87° (0.3 mm); $n^{25}D$ 1.4219; nmr (CCl_4) δ 1.95 (t, 6, $\mathbf{CH_3}CH_2CH_2O$), 1.72 (m, 4, $CH_3\mathbf{CH_2}CH_2O$), 4.00 (m, 4, $CH_3CH_2\mathbf{CH_2}O$), 1.28 [s, 9, $(CH_3)_3COO$].

Anal. Calcd for $C_{10}H_{23}O_5P$: active oxygen, 6.3; mol wt, 254. Found: active oxygen, 6.1; mol wt, 250.

Diisopropyl *t*-Butylperoxy Phosphate (1, R = *i*-Pr). A.—To a solution of 40 g (0.2 mol) of **2** (R = *i*-Pr) in 100 ml of petroleum ether at −10 to −5° was added a solution of 20 g (0.22 mol) of *t*-butyl hydroperoxide in 20 g (0.25 mol) of anhydrous pyridine. The mixture was warmed to 25° and filtered. The filtrate was concentrated and the residual oil was dissolved in benzene. The benzene solution was washed with ice water, dried (Na_2SO_4), concentrated, and distilled giving 15 g (30%) of diisopropyl *t*-butylperoxy phosphate (**1**, R = *i*-Pr): bp 64–67° (0.1 mm); $n^{25}D$ 1.4148.

Anal. Calcd for $C_{10}H_{23}O_5P$: C, 47.24; H, 9.15; active oxygen, 6.3. Found: C, 47.13; H, 9.35; active oxygen, 6.2.

B.—To a mixture of 7.16 g (0.11 mol) of potassium hydroxide, 29 ml of water, 9.01 g (0.10 mol) of *t*-butyl hydroperoxide, and 50 ml of petroleum ether prepared as above was added at 8° 18.04 g (0.09 mol) of **2** (R = *i*-Pr) in one portion. The mixture was stirred at room temperature for 4 hr. The organic layer was washed with ice-cold water, dried (Na_2SO_4), concentrated, and distilled giving 11.8 g (51.5%) of diisopropyl *t*-butylperoxy phosphate (**1**, R = *i*-Pr): bp 76–78° (0.03 mm); $n^{25}D$ 1.4145; nmr δ 1.28 [d, 6, J = 6 Hz, $(\mathbf{CH_3})_2CHO$], 2.73 [m, 2, $(CH_3)_2\mathbf{CH}O$], 1.25 [s, 9, $(CH_3)_3COO$].

Di-*n*-butyl *t*-Butylperoxy Phosphate (1, R = *n*-Bu).—To a mixture of 7.16 g (0.11 mol) of potassium hydroxide, 29 ml of water, 9.01 g (0.10 mol) of *t*-butyl hydroperoxide, and 50 ml of petroleum ether prepared as above was added 15.44 g (0.07 mol) of **2** (R = *n*-Bu) at 8°. The temperature was raised to 26° over 2 hr. The organic layer was washed with ice-cold water, dried (Na_2SO_4), and concentrated. The residual oil was held at ambient temperature (0.1 mm) for 18 hr giving 14.56 g (77%) of di-*n*-butyl *t*-butylperoxy phosphate (**1**, R = *n*-Bu): $n^{25}D$ 1.4247 (lit.[4] $n^{25}D$ 1.4248); nmr δ 4.06 (m, 4, CH_2O), 1.28 [s, 9, $(CH_3)_3COO$].

Anal. Calcd for $C_{12}H_{27}O_5P$: C, 51.05; H, 9.64; active oxygen, 5.7. Found: C, 50.95; H, 9.52; active oxygen, 6.0.

Diisobutyl *t*-Butylperoxy Phosphate (1, R = *i*-Bu).—To a mixture of 7.16 g (0.11 mol) of potassium hydroxide, 29.04 g of water, 9.01 g (0.10 mol) of *t*-butyl hydroperoxide, and 50 ml of petroleum ether prepared as above was added at 8° 20.57 g (0.09 mol) of **2** (R = *i*-Bu). The mixture was stirred at room temperature for 7 hr. The organic layer was washed with cold water, dried (Na_2SO_4), concentrated, and chromatographed on neutral alumina using benzene–ethyl acetate (4:1 v/v) as eluent giving 12 g (47%) of diisobutyl *t*-butylperoxy phosphate (**1**, R = *i*-Bu): bp 99.5–100° (0.4 mm); $n^{25}D$ 1.4200; nmr (CCl_4) δ 0.95 [d, 12, J = 6 Hz, $(\mathbf{CH_3})_2CHCH_2O$], 1.94 [m, 2, $(CH_3)_2\mathbf{CH}CH_2O$], 3.76 [m, 4, $(CH_3)_2CH\mathbf{CH_2}O$], 1.28 [s, 9, $(CH_3)_3COO$].

Anal. Calcd for $C_{12}H_{27}O_5P$: C, 51.05; H, 9.64; active oxygen, 5.67. Found: C, 50.60; H, 9.26; active oxygen, 5.56.

Di-*n*-octyl *t*-Butylperoxy Phosphate (1, R = *n*-Octyl).—To a mixture of 7.16 g (0.11 mol) of potassium hydroxide, 29 ml of water, 9.01 g (0.10 mol) of *t*-butyl hydroperoxide, and 50 ml of petroleum ether prepared as above was added at 10° 20.48 g (0.09 mol) of **2** (R = *n*-octyl). The mixture was stirred at ambient temperature for 90 min. The organic layer was washed with cold water, dried (Na_2SO_4), concentrated, and chromatographed on neutral alumina using benzene as eluent giving 10.06 g (30%) of di-*n*-octyl *t*-butylperoxy phosphate (**1**, R = *n*-octyl): $n^{25}D$ 1.4389 (lit.[4] $n^{25}D$ 1.4380); nmr (CCl_4) δ 2.98 (m, 4, $-\mathbf{CH_2}O-$), 1.35 [s, 9, $(CH_3)_3COO$].

Anal. Calcd for $C_{20}H_{43}O_5P$: C, 60.88; H, 10.99. Found: C, 61.25; H, 10.85.

Diphenyl Chlorophosphate (2, R = Ph).—Compound **2** (R = Ph) was prepared by the method of Brigl and Müller.[7] Thus 18.8 g (0.2 mol) of phenol and 15.3 g (0.1 mol) of phosphorus oxychloride were heated to 230° over 5 hr. The brown oil obtained was distilled giving 11.0 g (41%) of diphenyl chlorophosphate (**2**, R = Ph): bp 102–105° (0.05 mm); $n^{25}D$ 1.5460 (lit.[8] $n^{25}D$ 1.5490).

Diphenyl *t*-Butylperoxy Phosphate (1, R = Ph).—To a mixture of 7.16 g (0.11 mol) of potassium hydroxide, 29 ml of water, 10.0 g (0.10 mol) of 90% *t*-butyl hydroperoxide, and 50 ml of petroleum ether prepared as above was added at 8° 24.17 g (0.09 mol) of **2** (R = Ph). The temperature was raised to 24° over 1.75 hr. The reaction mixture separated into three phases. The top two phases were separated, dissolved in anhydrous ether, washed with ice-cold water, dried (Na_2SO_4), and concentrated at 0° giving diphenyl *t*-butylperoxy phosphate (**1**, R = Ph): $n^{26}D$ 1.5133 (lit.[4] $n^{26}D$ 1.4996).

Anal. Calcd for $C_{16}H_{19}O_5P$: active oxygen, 5. Found: active oxygen, 5.2.

This material decomposes violently at 0° and should be handled with caution.

Dibenzyl chlorophosphate (2, R = PhCH₂) was prepared according to the method of Atherton, *et al.*[9] Thus a solution of 14 g (0.094 mol) of sulfuryl chloride in 50 ml of CCl_4 was added under nitrogen at 16–19° to a solution of 26.2 g (0.1 mol) of dibenzyl hydrogen phosphite in 300 ml of CCl_4. After the addition, nitrogen was bubbled rapidly through the mixture for 90 min. The solution was concentrated giving 28.33 g (96%) of dibenzyl chlorophosphate (**2**, R = $PhCH_2$): nmr (CCl_4) δ 4.22 (s, 10, $\mathbf{C_6H_5}CH_2O$), 3.0 (d, 4, J = 8 Hz, $C_6H_5\mathbf{CH_2}O$).

Dibenzyl *t*-Butylperoxy Phosphate (1, R = PhCH₂).—To a solution of 12.32 g (0.1 mol) of sodium *t*-butyl hydroperoxide in 300 ml of absolute ether was added at 5–7° 26.85 g (0.097 mol) of **2** (R = $PhCH_2$). The mixture was stirred at 6° for 1 hr and then the temperature was raised to 25° over 40 min. The mixture was filtered and the filtrate concentrated leaving dibenzyl *t*-butylperoxy phosphate (**1**, R = $PhCH_2$): nmr (CCl_4) δ 4.26 (m, 10, $\mathbf{C_6H_5}CH_2O$), 3.08 (d, 4, J = 8 Hz, $C_6H_5\mathbf{CH_2}O$), 1.24 [s, 9, $(CH_3)_3COO$].

This compound decomposes rapidly at ambient temperature and was identified by nmr.

Registry No.—**1** (R = Me), 18963-64-9; **1** (R = Et), 10160-45-9; **1** (R = *n*-Pr), 18963-66-1; **1** (R = *i*-Pr), 10160-46-0; **1** (R = *n*-Bu), 10160-47-1; **1** (R = *i*-Bu), 18963-69-4; **1** (R = *n*-octyl), 18963-70-7; **1** (R = $PhCH_2$), 18963-71-8; **1** (R = Ph), 20194-03-0; **2** (R = $PhCH_2$), 538-37-4; **2** (R = Ph), 2524-64-3; **2** (R = Me), 813-77-4; **2** (R = Et), 814-49-3; **2** (R = *n*-Pr), 2510-89-6; **2** (R = *i*-Pr), 2574-25-6; **2** (R = *n*-Bu), 819-43-2; **4** (R = *i*-Bu), 17158-87-1.

Acknowledgments.—We gratefully acknowledge Mr. K. Schmitt for technical assistance. Victor Division, Stauffer Chemical Co., New York, N. Y., and Hooker Chemical Corp., Niagara Falls, N. Y., supplied various phosphorus compounds used in this investigation.

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(7) P. Brigl and H. Müller, *Chem. Ber.*, **72**, 2121 (1939).

(8) E. N. Walsh, *J. Amer. Chem. Soc.*, **81**, 3023 (1959).

(9) F. R. Atherton, H. T. Howard, and A. R. Todd, *J. Chem. Soc.*, 1106 (1948).