Reactions of *tert*-Butylperoxy Esters. XV Decomposition of Dialkyl *tert*-Butylperoxy Phosphates^{1a}

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(Z. Naturforsch. **31b**, 820-831 [1976]; received November 20, 1975)

Dialkyl *tert*-Butylperoxy Phosphates, Tetraalkyl Pyrophosphates, Dialkyl Phosphates, Trialkyl Phosphates, Free Radicals

The thermal decomposition of dialkyl *tert*-butylperoxy phosphates, in the presence and absence of solvents, yields the corresponding dialkyl phosphate, acetone, methanol, 2,2-dimethoxypropane, and methyl isopropenyl ether as the primary products. Prolonged heating of the product mixture produces trialkyl phosphates, (RO)₃P(O), which arise from the thermal decomposition of dialkyl phosphates. Data are presented to support a mechanism involving the heterolytic cleavage of the peroxide linkage.

Introduction

The synthesis of the first peroxyester of a phosphorus acid was reported in 1959 by RIECHE, HILGETAG, and SCHRAMM². At that time RIECHE and coworkers reported the difficulty of preparation of peroxyester (1) and noted their thermal instability but did not examine the products of the thermal decomposition².

In 1964, a detailed investigation of the chemistry of dialkyl *tert*-butylperoxy phosphates was begun in our laboratory. On the basis of the reports by RIECHE and coworkers, we began our investigation with the synthesis of diethyl-, diisopropyl-, and di-*n*-butyl *tert*-butylperoxy phosphates (1, R = C₂H₅, *i*-C₃H₇, *n*-C₄H₉) from the reaction of the corresponding dialkyl phosphorochloridates (2) with *tert*-butyl hydroperoxide in the presence of pyridine.

These syntheses yielded oils which were identified as peroxyesters on the basis of the following observations: (a) their active oxygen content was 70-80% of the theoretical active oxygen content of

pure peroxyesters, (b) their infrared spectra were consistent with what was expected from crude peroxyesters, and (c) their purification by distillation was extremely difficult as had been reported.

Distillation of these oils was successful only on a very small scale. These distillations followed a consistent pattern. They proceeded without difficulty during the initial phases and excess of the unreacted dialkyl phosphorochloridates, *tert*-butyl hydroperoxide (3), and pyridine were recovered. The temperature of the distillate then rose as a small amount of peroxyester distilled. The distillations were then interrupted by a rapid exothermic darkening of the material in the distillation flask and the concomitant evolution of gases.

We have reported the distillation of the residue of the decomposition of 1 (R = C₂H₅) to yield tetraethyl pyrophosphate (4, R = C₂H₅), while the analogous treatment of crude diisopropyl- and di-*n*-butyl *tert*-butylperoxy phosphates (1, R = *i*-C₃H₇, *n*-C₄H₉) yielded products which were identified as tetraiso-propyl pyrophosphate (4, R = *i*-C₃H₇) and di-*n*-butyl *tert*-butyl phosphate (5, R = *n*-C₄H₉, R' = *tert*-C₄H₉), respectively³.

These results were communicated³ but have subsequently proven to be unreproducible.

The investigation reported herein was instituted in an effort to more completely examine the products

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of the thermal decomposition of peroxyesters (1, R = C₂H₅, *i*-C₃H₇, *n*-C₄H₉).

Results

The products of the decomposition, in vacuum, of peroxyesters (1, R = C₂H₅, *i*-C₃H₇, *n*-C₄H₉) are quite variable. The primary phosphorus-containing product in each case is the corresponding dialkyl phosphate (6). However, if the pyrolysis is prolonged, trialkyl phosphates (5, R = R') which arise from the thermal degradation of acids (6) are obtained

Thus, a sample of diethyl *tert*-butylperoxy phosphate (1, R = C₂H₅) which was decomposed at room temperature during a two week period yielded only diethyl phosphate (6, R = C₂H₅).

The distillation of small batches of di-*n*-butyl *tert*-butylperoxy phosphate (1, R = *n*-C₄H₉) at 0.1 mm has not been achieved. In every attempt, the decomposition of the peroxyester has produced either tri-*n*-butyl phosphate (5, R = *n*-C₄H₉) or a mixture of tri-*n*-butyl phosphate and di-*n*-butyl phosphate (6, R = *n*-C₄H₉) in addition to an undistillable residue. Analogous results were obtained during the attempted distillations of peroxyesters (1, R = C₂H₅, *n*-C₃H₇, *i*-C₃H₇) even though peroxyesters (1, R = C₂H₅, *i*-C₃H₇) are usually distillable in small quantity. The results of the distillative decomposition of peroxyesters (1) are extremely variable and all efforts to devise decomposition procedures which would yield more consistent results were unsuccessful. The composition of the phosphorus-containing products of the thermal decomposition of peroxyesters (1) is shown in Table I. The results shown in Table I indicate that the thermal decomposition of peroxyesters (1) produces either the corresponding dialkyl phosphate (6) or the corresponding trialkyl phosphate (5). This result can be explained on the basis of the thermal decomposition of the dialkyl phosphate (6).

The thermal instability of diethyl phosphate (6, R = C₂H₅) was recognized by Toy⁴ who reported that distillation of 6 (R = C₂H₅) *in vacuo* was possible only if samples of 95% purity or better were taken for distillation. If samples of lower purity were used, the distillate was contaminated with triethyl phosphate (5, R = C₂H₅). Experimental

Table I. Phosphorus-containing products obtained from the thermal decomposition of dialkyl *tert*-butylperoxy phosphates (1).

	(RO) ₂ P(O)OOC(CH ₃) ₃ 1		(RO) ₂ P(O)OH + (RO) ₃ P(O) 6 5		
Peroxy- ester (1)	Tem- perature [°C]	Pressure [mm]	Pyrolysis Time [h]	Yield (6)	% ^a (5)
R =					
C ₂ H ₅	80	0.2	0.17	19	b
C ₂ H ₅	100	0.04	1.0	79	b
C ₂ H ₅	70	0.05	0.5	74	b
C ₂ H ₅ ^c	70	0.1	1.0	80	b
<i>n</i> -C ₃ H ₇	102	0.05	2	39	b
<i>i</i> -C ₃ H ₇	72-80	0.2	24	33	b
<i>i</i> -C ₃ H ₇	80	0.1	19.5	4	20
<i>i</i> -C ₃ H ₇	90-100	0.1-1.0	4	52	9
<i>n</i> -C ₄ H ₉	68-72	0.1	8	a	72
<i>n</i> -C ₄ H ₉ ^d	62-68	0.1	8	trace	59
<i>n</i> -C ₄ H ₉	122-125	0.1	0.5	a	74

^a Not including intractable tar. ^b Not isolated or detected spectroscopically. ^c Plus 8 mole percent diethyl pyridinium phosphate. ^d Plus 20 mole percent *tert*-butyl hydroperoxide.

evidence in this laboratory is in agreement with that report, and additional support has been obtained using other dialkyl phosphates (6, R = *i*-C₃H₇, *n*-C₃H₇, *n*-C₄H₉). In all cases, vacuum distillation of impure samples of dialkyl phosphates (6, R = C₂H₅, *n*-C₃H₇, *n*-C₄H₉) yielded the corresponding trialkyl phosphates (5); however, the amount of 5 obtained was variable and depended on the purity of the sample being distilled and on the size of the alkyl substituents. Thus, distillation of 6 (R = *n*-C₄H₉) could not be accomplished. Distillation of 6 (R = *n*-C₃H₇, *i*-C₃H₇) could be achieved only with spectroscopically pure (NMR) samples of less than 10 g. Distillation of 6 (R = C₂H₅) was more readily achieved and from a practical preparative point of view only 6 (R = C₂H₅) should be considered distillable. Pure samples of the other dialkyl phosphates are best obtained without distillation from the alkaline hydrolysis of the corresponding trialkyl phosphate (5)⁵.

The pyrolysis at 111 °C of diethyl phosphate (6, R = C₂H₅) has been studied in some detail⁶. The major products are reported to be water, ethanol, triethyl phosphate (5, R = C₂H₅), ethyl phosphate, orthophosphoric acid, and diethyl pyrophosphate; no polyphosphates were found⁶. These results, combined with the experimental data obtained in this laboratory, clearly demonstrate that the trialkyl

phosphates (5) obtained from the prolonged thermal decomposition of peroxyesters (1) are secondary products. This conclusion is buttressed by the observation that the decomposition of 1 ($R = C_2H_5$) at room temperature over a period of two weeks produces diethyl phosphate (6, $R = C_2H_5$) and that rapid decomposition of peroxyphosphates (1) at temperatures between 60 and 120 °C also produced the corresponding dialkyl phosphates (6).

In addition to the phosphorus-containing products the thermal decomposition of peroxyesters (1) also produces methanol, acetone, 2,2-dimethoxy propane (7), methyl isopropenyl ether (8), and possibly water.

Although water is a product of the reaction sequence proposed below, the experimental techniques utilized preclude positively identifying it as a reaction product and not as a contaminant caused by the

handling of the cold (−78 °C) product mixture during work-up.

No typical free-radical products, such as *tert*-butanol, methane, or ethane, which are found in the decomposition of carboxylic acid *tert*-butylperoxy esters, have been detected, in this laboratory, in the decompositions of dialkyl *tert*-butylperoxy phosphates (1). The yields of the non-phosphorus-containing products of the decomposition of peroxyesters (1) are shown in Table II.

The decomposition of neat diisopropyl *tert*-butylperoxy phosphate (1, $R = i-C_3H_7$) at 83° under nitrogen gas was studied in the presence of diethyl phosphate (6, $R = C_2H_5$) and in the presence of pyridine. The decomposition of the peroxyester, as shown in Table III, is accelerated by the added acid and retarded by the added base.

The results in Table III show that the decomposition of peroxyesters (1) is autocatalytic in dialkyl phosphate (6) since 6 is the primary decomposition product.

Our initial observations³ that the decomposition of diethyl- and diisopropyl *tert*-butylperoxy phosphates (1, $R = C_2H_5$, $i-C_3H_7$) proceeds smoothly below 100° to produce high yields of the corres-

Table II. Nonphosphorus-containing products of the thermal decomposition of dialkyl *tert*-butylperoxy phosphates (1).

Peroxyester (1)	Temp. [°C]	Recovered Me ₃ CO as products [% yield]	Nonphosphorus-containing products percent composition			
			CH ₃ OH	CH ₃ C(O)CH ₃	7	8
R =						
<i>i</i> -C ₃ H ₇	90–100	92	22	37	22	2
<i>i</i> -C ₃ H ₇	58–62	^a	28	3	28	28
<i>n</i> -C ₄ H ₉	68–72	90	4	10	67	19
<i>n</i> -C ₄ H ₉ ^b	62–68		5	4	68	23

^a Incomplete decomposition. ^b In the presence of 20 mole percent *tert*-butyl hydroperoxide.

Table III. Effect of acid and base on the decomposition of diisopropyl *tert*-butylperoxy phosphate (1, $R = i-C_3H_7$) at 83 °C.

Reaction time [min]	peroxyester (1) neat	Percent peroxyester remaining	
		peroxyester (1) plus 10 mole % pyridine	peroxyester (1) plus 10 mole% Diethyl phosphate (6, $R = C_2H_5$)
0	100	100	100
55	78	96	61
85	47	85	0

ponding tetraalkyl pyrophosphates (4) have proven to be unreproducible. As was shown in our previous paper⁷, the pyrophosphates probably arose as side products during the synthesis of the peroxyesters. In more recent experiments the decomposition products of peroxyesters (1) occasionally and randomly exhibited weak IR absorptions at 950 cm⁻¹ that are attributable to P-O-P linkages. However, in no case was isolation of the tetraalkyl pyrophosphates (4) achieved and the IR absorptions are ascribed to the presence of small amounts of polymeric polyphosphates.

The decomposition of dialkyl *tert*-butylperoxy phosphates (1, R = C₂H₅, *i*-C₃H₇) in benzene, ethanol, chloroform, and thiophenol solution resulted in the formation of products (Table IV) which are the same as those obtained from the thermal decomposition of neat peroxyesters, namely dialkyl phosphate (6), trialkyl phosphate (5), methanol, acetone, 2,2-dimethoxy propane (7), and methyl isopropenyl ether (8). The results of Table IV show that below 100° the composition of products is essentially independent of the solvent. The solvent, however, does effect the rate of disappearance of the peroxyester (Table V). Thus, the peroxyester is completely decomposed after refluxing a solution of diisopropyl *tert*-butylperoxy phosphate (1, R = *i*-C₃H₇) in absolute ethanol for 17 h, whereas, after 22 h at reflux a solution of 1 (R = *i*-C₃H₇) in benzene contains 81% of the peroxyester. The data in Table V indicate that in benzene solution the decomposition of the peroxyesters is accelerated by

Discussion

Our observations seem to exclude the homolytic decomposition pattern commonly found in the series of peroxyesters of carbon. The results are not consistent with the normal behavior of **9**, **10**, **11**, and **12** in free-radical reactions. Diphenylpicrylhydrazyl (**10**) and the stable nitroxyl radical (**9**) are usually free-radical inhibitors and their accelerating effect on the decomposition of peroxyesters (**1**) is best explained on the basis of the nucleophilicity of the nitrogen atoms in **9** and **10**. Galvinoxyl (**11**) is usually an inhibitor of free-radical reactions and azobisisobutyronitrile (**12**) is a commonly used initiator of free-radical reactions. The lack of effect on the rate of decomposition of peroxyesters (**1**) by **11** and **12** is still further evidence that the primary reaction in the decomposition of **1** is not free-radical.

Table IV. Thermal decomposition of dialkyl *tert*-butylperoxy phosphates (1) in solution.

Peroxyster (1)	Solvent	Temp. [°C]	Time [h]	6	5	Yield [%] ^a		7	8
						CH ₃ OH	CH ₃ C(O)CH ₃		
R =									
C ₂ H ₅	C ₆ H ₆	77	24	90	4				
C ₂ H ₅	C ₆ H ₆	80	7	53					
C ₂ H ₅	C ₆ H ₆	80	22	66		27	18	26	4
<i>i</i> -C ₃ H ₇	C ₆ H ₆	80	4		9 ^b	c	c	c	
<i>i</i> -C ₃ H ₇	C ₂ H ₅ OH	78	3.5	59		c	c	c	c
<i>i</i> -C ₃ H ₇	CHCl ₃	61	5			c	c		c
<i>i</i> -C ₃ H ₇	C ₆ H ₅ SH	110–115	2	trace ^d	trace ^d				
<i>i</i> -C ₃ H ₇ ^e	C ₆ H ₆	80	47	19 ^f					
<i>i</i> -C ₃ H ₇	C ₆ H ₆	80	42.5	66					

^a The decompositions always produced intractable tar. ^b 24% peroxyester recovered. ^c Determined qualitatively. ^d Plus 10% diphenyl disulfide. ^e Plus 20 mole% pyridinium hydrochloride. ^f 8% peroxyester recovered. ^g Plus 20 mole% pyridine.

^g Plus 20 mole% pyridine.

Table V. Thermal decomposition of dialkyl *tert*-butylperoxy phosphates (1) at 80° in benzene.

Peroxyester (1)	Percent peroxyester (1) remaining											
	Elapsed time [h]											
	0	3	4	7	9	17	20	22	25	28	44	52
R =												
<i>i</i> -C ₃ H ₇	100							81		69	38	27
<i>i</i> -C ₃ H ₇ plus 11	100					82			65			
<i>i</i> -C ₃ H ₇ plus 9	100	96		21								
<i>i</i> -C ₃ H ₇ plus 10	100			82								
C ₂ H ₅	100	77			35		0					
C ₂ H ₅ plus 12	100	72			34							
C ₂ H ₅ plus 10	100		70		20							
<i>n</i> -C ₄ H ₉	100						10					
<i>i</i> -C ₄ H ₉	100						14					

Nevertheless, polymerization of styrene is induced by dialkyl *tert*-butylperoxy phosphates (1, R = C₂H₅, *i*-C₃H₇, *n*-C₄H₉), and polymerization of methyl methacrylate has been achieved with 1 (R = *i*-C₃H₇). However, the peroxyphosphates (1) are not as efficient as polymerization catalysts as is benzoyl peroxide.

It is difficult to interpret these polymerizations in light of the previous observations. The lack of significant effect on the decomposition of peroxyesters (1) by azobisisobutyronitrile (12), a typical free-radical initiator, or by galvinoxyl (11), a typical free-radical inhibitor, coupled with the acceleration of the decomposition by 9 and 10, which are usually free-radical inhibitors, would seem to indicate that free-radicals do not play a significant role in the decomposition of peroxyesters (1). The polymerization of styrene and methyl methacrylate is usually accomplished with free-radical initiators although these compounds can also undergo ionic polymerizations. Our results do not allow a determination to be made of the path followed during the polymerizations since we have shown that, under the conditions of our experiment, styrene is not polymerized by diethyl phosphate (6, R = C₂H₅), a strong acid and the primary thermal decomposition product of 1 (R = C₂H₅).

Unlike the uncatalyzed thermal decomposition of *tert*-butyl peroxyesters of carbon, the reaction of dialkyl *tert*-butylperoxy phosphates (1) produces no detectable *tert*-butanol or gaseous products. The decomposition is also unaffected by the addition of small amounts of *tert*-butyl hydroperoxide and 12.

It is, however, accelerated by polar solvents and by traces of dialkyl phosphates (6) and it is retarded by bases such as pyridine. In addition, prolonged storage of diisopropyl *tert*-butylperoxy phosphate (1, R = *i*-C₃H₇) at 5° under anhydrous conditions produces diisopropyl phosphate (6, R = *i*-C₃H₇), methanol, acetone, 7, and 8. The presence of undecomposed peroxyester may be demonstrated after 48 months at 5 °C.

On the basis of the product analysis the following mechanistic sequence which is compatible with existing literature⁸⁻¹⁴ is proposed.

In light of the lack of evidence suggesting a homolytic cleavage of the peroxide linkage, an ionic mechanism is most plausible. Thus, the peroxyester degrades into a dialkyl phosphate anion and the *tert*-butyloxonium ion (step 1). The oxonium ion can be expected to undergo rapid Criegee-type rearrangement (step 2) to yield a tertiary carbonium ion which then eliminates a proton (step 3) to form methyl isopropenyl ether (8).

The reaction at room temperature of ethyl vinyl ether (13) with diethyl phosphate (6, R = C₂H₅) has been reported to produce high yields of tetraethyl pyrophosphate (4, R = C₂H₅)¹⁵.

In an analogous manner, the interaction of dialkyl phosphates (6) with methyl isopropenyl ether (8) might be expected to yield the corresponding tetraalkyl pyrophosphates (4). In our hands, the reaction of carefully purified diethyl phosphate (6, R = C₂H₅) with ethyl vinyl ether (13) yielded (a) small amounts of triethyl phosphate (5, R = C₂H₅) if the reaction mixture was worked up by distillation, and (b) recovered starting materials if the acid was isolated by extraction with aqueous sodium hydroxide solution. Similarly, reactions of dialkyl phosphates (6) with methyl isopropenyl ether (8) yielded the corresponding trialkyl phosphates (5) if the reaction mixture was distilled and only starting materials were obtained by extraction. In no case was the tetraalkyl pyrophosphate (4) isolated or even detected by IR.

The preliminary results of our investigations of the thermal decomposition of neat dialkyl *tert*-butylperoxy phosphates (1) and the mechanistic sequence to explain these results were presented as early as 1966³. Shortly after these presentations the results of a study of the decomposition of diethyl *tert*-butylperoxy phosphate (2, R = C₂H₅) in nonane were published¹⁶. This report¹⁶ indicates that at 140 °C in nonane solution the decomposition of peroxyester (1, R = C₂H₅) produces mainly diethyl phosphate (6, R = C₂H₅), acetone, *tert*-butanol, and small amounts of tetraethyl pyrophosphate (4, R = C₂H₅), methane, isobutane, isopropenyl methyl

ether (8), methanol, and a mixture of octadecane isomers. The authors postulate the decomposition to proceed simultaneously by heterolytic and homolytic mechanisms as shown below.

No evidence was presented to indicate that compounds 4, 14, and 15 were isolated or that evidence of their existence as intermediates had been obtained.

The same group of investigators has also studied the decomposition of 1 (R = C₂H₅) in polar solvents¹⁷. Thus, the decomposition of diethyl *tert*-butylperoxy phosphate (1, R = C₂H₅) in a series of solvents of high dielectric constant yielded the following products, diethyl phosphate (6, R = C₂H₅), methanol, and acetone, which were independent of the solvent and which appear to arise from the heterolytic degradation of the peroxyester. The following mechanism was proposed:

The decomposition of di-*n*-butyl *tert*-butylperoxy phosphate (1, R = *n*-C₄H₉) in *n*-nonane is similar to the analogous decomposition of diethyl *tert*-butylperoxy phosphate (1, R = C₂H₅)¹⁸. In fact, on the basis of a series of investigations of the decompositions in *n*-nonane of dialkyl *tert*-butylperoxy phosphates (1) and alkyl *tert*-butylperoxy alkylphosphonates, (R)ROP(O)OOC(CH₃)₃, the decomposition of peroxyesters of phosphoric and phosphonic acids has been postulated¹⁸ to be essentially independent of the nature of the substituents attached to the phosphorus atom.

It appears, therefore, that, on the basis of the results obtained in this laboratory as well as those reported in the literature, the decomposition of dialkyl *tert*-butylperoxy phosphates (1) is primarily an ionic process which is not very dependent on the alkyl substituents. It further is clear that the primary phosphorus-containing product is the dialkyl phosphate (6) which may, depending upon the conditions, react further. The data available, to date, indicate that, although it is possible that free radicals are involved, especially at elevated temperatures, the thermal decompositions of dialkyl *tert*-butylperoxy phosphates (1) in the absence of catalysts proceed preferentially by ionic processes.

Experimental

Boiling points and melting points are uncorrected. NMR spectra were obtained on a Varian HA-100 or a T-60 spectrometer using an internal TMS standard; unless otherwise noted, the spectra were obtained on 10% (v/v) samples in carbon tetrachloride. IR spectra were obtained on a Perkin-Elmer model 137 spectrophotometer. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Illinois, or on an F&M Carbon Hydrogen Nitrogen Analyzer, model 185. Molecular weights were determined cryoscopically in benzene or isopiastically on a Hitachi Perkin-Elmer model 115 Molecular Weight Apparatus. Gas chromatographic analyses were performed on Varian Aerograph instruments models 1700 and A-90P3 equipped with thermal conductivity detectors using wx filaments and linear temperature programmers. The conditions were varied as required to achieve separation of the mixtures being analyzed; the

column used was a 10 ft × 1/8 in. stainless steel column, Porapak Q 100–200 mesh. Unless otherwise noted, materials were concentrated at less than 50° on a rotating evaporator at 10–15 mm Hg.

Procedures for the preparation of dialkyl phosphorochloridates (1) and sodium *tert*-butylperoxide have been previously described¹⁹. Benzene was dried azeotropically. The residue was distilled from sodium and was stored over sodium. Carbon tetrachloride was stored over calcium chloride. All other materials were the best commercial grade. With the exceptions of the solvents and inorganic reagents, all materials were purified by suitable techniques of distillation, recrystallization, sublimation, or chromatography before use. Unless otherwise noted, the petroleum ether used had b. p. 20–40 °C.

Determination of active oxygen content of peroxyesters

A: Neat dialkyl *tert*-butylperoxy esters were analyzed by the addition of a weighed sample of the peroxyester (approx. 0.1 g) to a nitrogen-saturated reagent consisting of excess sodium iodide in glacial acetic acid. The liberated iodine was titrated after 5 min at ambient temperature with 0.1 N sodium thiosulfate solution to a colorless end point²⁰.

B: The peroxide content of solutions of dialkyl *tert*-butylperoxy phosphates was determined in analogy with the method of SILBERT and SWERN²¹. Thus, 15 ml glacial acetic acid containing 0.1% ferric chloride hexahydrate was purged with dry nitrogen for 5 min and 2 ml of a saturated aqueous solution of sodium iodide was added. The sample was added and the flask was stoppered and stored at ambient temperature for 5 min. Water (50 ml) was added followed by 5 ml of a stable starch solution (Fisher Chemicals, Inc.). The solution was titrated to a colorless end point with 0.1 N sodium thiosulfate solution. The procedure typically required a titration blank of 0.5 ml sodium thiosulfate.

Preparation of diethyl phosphate (6, R = C₂H₅)

A:²² A mixture of 5.4 g (0.3 mole) water, 1.46 g (0.02 mole) N,N-dimethyl formamide, and 34.5 g (0.2 mole) diethyl phosphorochloridate was heated gently to start the very exothermic reaction. The mixture was cooled intermittently to maintain the temperature below 80 °C. When the exothermicity had dissipated, the mixture was heated at 60–65 °C for 30 min and then at 60 °C (1 mm) for 1 h. This procedure gave an essentially pure diethyl phosphate which was distilled before use, b. p. 138–140 °C (0.4 mm).

B: A mixture of 10 g (0.25 mole) sodium hydroxide, 45.5 g (0.25 mole) triethyl phosphate (5, R = C₂H₅), 25 ml water, and 100 ml ethanol was stirred overnight at ambient temperature and was then concentrated to a white solid. The solid was dissolved in a minimal amount of water and the resulting solution was extracted with ether and then was acidified with concentrated hydrochloric acid. The aqueous acid solution was extracted repeatedly

with ether. The ether extracts were dried (MgSO_4) and concentrated. The residual oil was pure diethyl phosphate (6, $R = \text{C}_2\text{H}_5$) (36.0 g, 93%).

Analysis for $\text{C}_4\text{H}_{11}\text{O}_4\text{P}$

Calcd C 31.20 H 7.19,
Found C 31.09 H 7.11.

Preparation of diisopropyl phosphate

(6, $R = i\text{-C}_3\text{H}_7$)

A:²² A mixture of 40.1 g (0.2 mole) diisopropyl phosphorochloridate, 5.4 g (0.3 mole) water, and 1.74 g (0.02 mole) N,N-dimethyl formamide was heated gently to start the very exothermic reaction. The heating was discontinued and the reaction mixture was cooled as necessary to maintain the temperature between 90 °C and 100 °C. When the exothermicity had subsided, the mixture was heated at 80 °C for 30 min. Concentration of the mixture at 80 °C (15 mm) for 1 h and then at 80 °C (0.1 mm) for 1 h yielded 32 g (88%) diisopropyl phosphate.

B:²³ A mixture of 20.5 g (0.10 mole) diisopropyl phosphorochloridate and 10 ml water was boiled for 10 min. After cooling the mixture was extracted repeatedly with benzene and the combined benzene extracts were washed with ice cold water until free of chloride ion. The organic layer was dried (Na_2SO_4) and concentrated. Distillation of the residual oil gave 5 g (27%) diisopropyl phosphate: b.p. 114 °C (0.1 mm); n_D^{25} 1.4132. This compound was characterized as the cyclohexylammonium salt, m.p. 198 °C [lit.²⁴ m.p. 193 °C].

*Preparation of di-*n*-propyl phosphate*

(6, $R = n\text{-C}_3\text{H}_7$)

A mixture of 10 g (0.25 mole) sodium hydroxide, 56 g (0.25 mole) tri-*n*-propyl phosphate (5, $R = n\text{-C}_3\text{H}_7$), 100 ml ethanol, and 25 ml water was stirred overnight at room temperature. The resulting clear solution was concentrated to a moist solid which was dissolved in a minimal amount of water. The resulting solution was extracted with ether and was then acidified with concentrated hydrochloric acid. The acid solution was extracted vigorously with ether several times. The ethereal extracts were dried (MgSO_4) and concentrated. The residual oil was di-*n*-propyl phosphate (20.6 g, 45%).

Preparation of tetraethyl pyrophosphate

(4, $R = \text{C}_2\text{H}_5$)

A: Crude diethyl *tert*-butylperoxy phosphate (45 g, 0.2 mole) prepared using pyridine was heated at 0.1 mm. The pressure dropped with rising temperature and the residue gave, after repeated distillation, 24 g (83%) tetraethyl pyrophosphate: b.p. 104 °C (0.1 mm); n_D^{25} 1.4166; NMR (CCl_4) δ 1.33 (t, 3, $\text{CH}_3\text{CH}_2\text{O}$), 4.15 (m, 2, $\text{CH}_3\text{CH}_2\text{O}$).

Analysis for $\text{C}_8\text{H}_{20}\text{O}_7\text{P}_2$

Calcd C 33.00 H 6.93,
Found C 32.96 H 6.84.

B:⁴ A mixture of 17.2 g (0.1 mole) diethyl phosphorochloridate, 8.61 g (0.102 mole) sodium bicarbonate, and 1 ml water was stirred at room temperature. After a short induction period the temperature rose rapidly to 45 °C. The organic layer was separated and distilled giving 10 g (69%) tetraethyl pyrophosphate: b.p. 106–108 °C (0.1 mm); n_D^{25} 1.4162.

Preparation of tetraisopropyl pyrophosphate

(4, $R = i\text{-C}_3\text{H}_7$)

A: Crude diisopropyl *tert*-butylperoxy phosphate (25 g, 0.1 mole) prepared using pyridine was distilled yielding 15 g (60%) diisopropyl *tert*-butylperoxy phosphate and a residue which, upon further distillation, gave 5 g tetraisopropyl pyrophosphate: b.p. 104 °C (0.2 mm); n_D^{25} 1.4163 [lit.⁴ b.p. 92 °C (0.01 mm); n_D^{25} 1.4170].

Analysis for $\text{C}_{12}\text{H}_{28}\text{O}_7\text{P}_2$

Calcd C 41.67 H 8.20,
Found C 41.93 H 8.37.

B:⁴ To a solution of 26.5 g (0.336 mole) pyridine and 3 g (0.167 mole) water was added slowly without cooling 64 g (0.319 mole) diisopropyl phosphorochloridate. The temperature was maintained below 50 °C during the addition and when heat evolution had ceased, 50 ml cracked ice was added. The organic layer was separated, washed with water (2 × 50 ml), and distilled giving 22 g (40%) tetraisopropyl pyrophosphate: b.p. 120–125 °C (0.3 mm); n_D^{52} 1.4174; NMR δ 1.33 [d, 6, $(\text{CH}_3)_2\text{CHO}$], 4.73 (m, 2, $>\text{CHO}$).

*Decomposition of neat diethyl *tert*-butylperoxy phosphate (1, $R = \text{C}_2\text{H}_5$)*

A: At room temperature in air: A sample of diethyl *tert*-butylperoxy phosphate was stored at room temperature for 2 weeks. Analysis of the NMR spectrum of the resulting black oil indicated the presence of diethyl phosphate, δ 13 (s, 1, POH), and traces of 2,2-dimethoxypropane (7).

B: At 70 °C *in vacuo*: Diethyl *tert*-butylperoxy phosphate (8 g, 0.035 mole) at 0.05 mm was heated in a 70 °C oil bath for 30 min. Distillation of the resulting black oil yielded 0.5 g (6%) undecomposed peroxyester, b.p. 75–82 °C (0.3 mm), 4 g (74%) diethyl phosphate, b.p. 122–125 °C (0.2 mm), and 0.7 g of an intractable residue.

C: At 80 °C *in vacuo*: Diethyl *tert*-butylperoxy phosphate (8.7 g, 0.04 mole) was heated at 80 °C (0.2 mm) for 10 min. Distillation of the resulting oil was accompanied by gassing and yielded 1.1 g (19%) diethyl phosphate: b.p. 138 °C (1.2 mm), 118–122 °C (0.5 mm); NMR δ 1.28 (t, 6, CH_3CH_2), 6.05 (m, 4, $\text{CH}_3\text{CH}_2\text{O}$), 13 (s, 1, POH); and an intractable residue.

D: At 100 °C *in vacuo*: Diethyl *tert*-butylperoxy phosphate (6.3 g, 0.03 mole) at 0.04 mm was heated in a 100 °C oil bath for 1 h. During this period the peroxyester refluxed. Distillation of the resulting

brown oil yielded 3.4 g (79%) diethyl phosphate, b.p. 126–129 °C (0.2 mm).

Decomposition of diethyl tert-butylperoxy phosphate (1, R = C₂H₅) in the presence of diethyl pyridinium phosphate

A solution of 6.0 g (0.027 mole) diethyl *tert*-butylperoxy phosphate and 0.5 g (0.002 mole) diethyl pyridinium phosphate which had been prepared from the reaction of equimolar amounts of pyridine and diethyl phosphate (6, R = C₂H₅) was heated at 70 °C (0.1 mm) for 1 h. Distillation of the resulting brown oil yielded 3.3 g (80%) diethyl phosphate: b.p. 123–127 °C (0.2 mm) n_D^{25} 1.4160; and 0.5 g of an intractable residue.

Decomposition of neat diisopropyl tert-butylperoxy phosphate (1, R = C₃H₇)

A: Diisopropyl *tert*-butylperoxy phosphate (6.9 g, 0.027 mole) was heated at 58–62 °C (0.1 mm) for 24 h. During this time approximately 2 g of the perester distilled. The residual yellow oil, 3.5 g, was found by titration to contain 78% of the theoretical peroxide content. Storage of this oil at 5 °C for 26 months yielded a brown oil and a colorless solid. Analysis of the NMR spectrum of the oil indicated the oil to contain peroxyester, acetone, methanol, diisopropyl phosphate (6, R = *i*-C₃H₇), and 2,2-dimethoxypropane. The solid material was identified by NMR analysis as diisopropyl phosphate.

The thermal decomposition of the oil yielded 1 ml of a mixture of water (13%), methanol (28%), acetone (3%), methyl isopropenyl ether (28%), and 2,2-dimethoxypropane (28%).

B: Diisopropyl *tert*-butylperoxy phosphate (12.7 g, 0.05 mole) was heated at 72–80 °C (0.2 mm) for 24 h. Distillation of the resulting brown oil, 7.7 g, afforded 3.0 g (33%) diisopropyl phosphate, b.p. 122–126 °C, 0.1 mm) n_D^{25} 1.4120, and an intractable residue.

C: Diisopropyl *tert*-butylperoxy phosphate (12.7 g, 0.05 mole) was heated at 0.1 mm in a 77–83 °C oil bath for 19.5 h. During this time the peroxyester refluxed. The volatile products, 2.1 g, were collected in a trap at –78 °C and were identified by glc as water, methanol, acetone, methyl isopropenyl ether, and 2,2-dimethoxypropane. No gas was evolved during the decomposition. Distillation of the residual oil, 8.90 g, yielded, as a yellow oil, 4.3 g (47%) diisopropyl phosphate (6, R = *i*-C₃H₇): b.p. 110–115 °C (0.14 mm), and 4.5 g of an intractable black tar. Redistillation of the impure diisopropyl phosphate gave 1.09 g (20%) triisopropyl phosphate: b.p. 44–45 °C (0.1 mm), n_D^{25} 1.4076, and 0.35 g diisopropyl phosphate: b.p. 118–121 °C (0.25 mm), n_D^{25} 1.4109.

D: Diisopropyl *tert*-butylperoxy phosphate (12.7 g, 0.05 mole) was heated at 0.1 mm to 1.0 mm in a 90–100 °C oil bath for 4 h. During this time the peroxyester refluxed. The volatile products of the decomposition, 3.4 g (92%), were collected in a trap

at –78 °C. Repeated distillation of the dark residue afforded 0.5 g (9%) triisopropyl phosphate: b.p. 65–67 °C (0.4 mm), n_D^{25} 1.4045; and 4.7 g (52%) diisopropyl phosphate: b.p. 126–128 °C (0.3 mm), n_D^{25} 1.4126; which were analyzed by NMR and IR. The IR spectra contained no P–O–P absorption.

The volatile products were analyzed by glc and were identified as water (0.008 mole), methanol (0.02 mole), 2,2-dimethoxypropane (0.007 mole), methyl isopropenyl ether (0.001 mole), acetone (0.02 mole), and four unidentified trace components.

Decomposition of neat di-n-butyl tert-butylperoxy phosphate (1, R = n-C₄H₉)

A: Di-*n*-butyl *tert*-butylperoxy phosphate (5.0 g) was heated at 100 °C (0.3 mm) for 0.5 h. A rapid exothermic decomposition occurred giving an unidentified white gas and a black oil. The oil was distilled giving 1.4 g of a colorless oil: b.p. 106 °C (0.2 mm); n_D^{25} 1.4238. This material was analyzed by NMR to be a 70:30 w/w mixture of tri-*n*-butyl phosphate and di-*n*-butyl phosphate.

Analysis for 70:30 (w/w) tri-*n*-butyl phosphate to di-*n*-butyl phosphate:

Calcd	C 51.61	H 9.89,
Found	C 51.81	H 9.91.

B: Di-*n*-butyl *tert*-butylperoxy phosphate (15.00 g, 0.053 mole) was heated at 0.1 mm in a 68–72 °C oil bath for 8 h. The volatile products, 3.5 g (90%), were collected in a trap at –78 °C, and analyzed by glc on Porapak Q. They were identified as methanol (0.0046 mole), acetone (0.0058 mole), methyl isopropenyl ether (8) (0.0094 mole) and 2,2-dimethoxypropane (7) (0.026 mole). Distillation of the high-boiling residue was accompanied by gassing and yielded 5 g (72%) tri-*n*-butyl phosphate (5, R = *n*-C₄H₉): b.p. 84–86 °C (0.03 mm), n_D^{25} 1.4224.

C: A solution of 0.90 g (0.01 mole) *tert*-butyl hydroperoxide and 14.1 g (0.05 mole) di-*n*-butyl *tert*-butylperoxy phosphate was heated at 0.1 mm to 2.0 mm in a 62–68 °C oil bath for 8 h. The volatile products, 4 g (89%), were analyzed by glc and were found to contain methanol, acetone, methyl isopropenyl ether, and 2,2-dimethoxypropane. Distillation of the high-boiling residue yielded 3.9 g (59%) tri-*n*-butyl phosphate: b.p. 98 °C (0.1 mm), n_D^{25} 1.4215; and di-*n*-butyl phosphate: b.p. 138 °C (0.02 mm); n_D^{25} 1.4238; NMR δ 4.6 (m, 4, –CH₂O), 12.8 (s, 1, P(O)OH).

D: Di-*n*-butyl *tert*-butylperoxy phosphate (10 g, 0.035 mole) was added dropwise at 0.1 mm over a period of 33 min to a flask which was heated in a 122–125 °C oil bath. The volatile products, 2 g, were collected and analyzed by glc and were found to contain methanol, acetone, methyl isopropenyl ether, 2,2-dimethoxypropane, and *tert*-butanol. Distillation of the high-boiling residue, 6.8 g, yielded 3.5 g (74%) tri-*n*-butyl phosphate and an intractable tar.

Decomposition of diisopropyl tert-butylperoxy phosphate (1, R = i-C₃H₇) in the presence of diethyl phosphate (6, R = C₂H₅) and in the presence of pyridine

A: Freshly distilled diisopropyl *tert*-butylperoxy phosphate (2.55 g, 0.01 mole) was heated under dry nitrogen in an 83 ± 1 °C oil bath for 115 min. During the heating, 0.1 ml aliquots were titrated for active oxygen content (Table III) distillation of the residual oil yielded 0.8 g (44%) diisopropyl phosphate: b.p. 124–128 °C (0.4 mm), n_D^{25} 1.4150.

B: An identical experiment using a solution of 0.079 g (0.001 mole) pyridine and 2.55 g (0.01 mole) diisopropyl *tert*-butylperoxy phosphate was run simultaneously. Distillation of the residual oil yielded 1 g (39%) unreacted peroxyester: b.p. 66–68 °C (0.1 mm), n_D^{25} 1.4148; traces of diisopropyl phosphate: b.p. 114–118 °C (0.1 mm), n_D^{25} 1.4140; and 0.4 g of an intractable oil.

C: An identical experiment reacting a solution of 0.159 g (0.001 mole) diethyl phosphate and 2.55 g (0.01 mole) diisopropyl *tert*-butylperoxy phosphate was run simultaneously. Aliquots were removed periodically for titration of the peroxide content (Table III).

Decomposition of diethyl tert-butylperoxy phosphate (1, R = C₂H₅) in benzene solution

A: Diethyl *tert*-butylperoxy phosphate (22.6 g, 0.1 mole) was added over a period of 11 min at 77 °C under nitrogen to 150 ml benzene. The reaction mixture was heated at 77 °C for 24 h after the addition was completed. Aliquots taken periodically were analyzed by tlc and IR, and none were found to contain any tetraethyl pyrophosphate. The mixture was concentrated to 18.1 g of a black oil which was dissolved in ether. The ethereal solution was extracted with 10% aqueous sodium hydroxide solution (2 × 50 ml), dried (Na₂SO₄), and concentrated to a brown oil. Distillation of the oil yielded 0.4 g (4%) triethyl phosphate: b.p. 38–40 °C (0.5 mm), and 1.8 g of an intractable residue.

The sodium hydroxide extracts were concentrated to approximately one-half the original volume, were acidified with concentrated hydrochloric acid, and then were extracted with ether (2 × 100 ml). The ether extracts were dried (Na₂SO₄) and concentrated to yield 14 g (90%) diethyl phosphate which was identified by IR and NMR.

B: A solution of 11.3 g (0.05 mole) diethyl *tert*-butylperoxy phosphate in benzene (35 ml) was refluxed for 7 h after which time no peroxyester remained. The solution was concentrated. Repeated distillation of the residual oil yielded 4.1 g (53%) diethyl phosphate: b.p. 120–122 °C (0.1 mm). During the reaction aliquots were periodically titrated to follow the decomposition of the peroxyester (Table VI).

C: A solution of 22.6 g (0.1 mole) diethyl *tert*-butylperoxy phosphate in 125 ml benzene was refluxed for 22 h. During this time 22 ml of an

Table VI. Decomposition of diethyl *tert*-butylperoxy phosphate in benzene solution at 77–80 °C.

Elapsed time [h]	Percent peroxyester
0	100
1	67
3	60
4	44
7	0

Table VII. Decomposition of diisopropyl *tert*-butylperoxy phosphate in solution at 78 °C.

Elapsed time [h]	Percent peroxyester	
	In ethanol	In chloroform
0	100	100
20		99
40		96
46	61	
70	40	
94	38	
124	35	
140		93
180	27	88
220		74
280		70

uninvestigated gas was evolved. The solvent was distilled to b.p. 80 °C (760 mm). The distillate was analyzed by glc and was found to contain mostly benzene in addition to methanol (0.027 mole), methyl isopropenyl ether (0.004 mole), acetone (0.018 mole), and 2,2-dimethoxypropane (0.026 mole). The glc analysis eliminated the possibility of the presence of water or *tert*-butanol. The residual oil was concentrated to a black oil which was diluted with benzene. The resulting solution was extracted with 10% aqueous sodium hydroxide solution. The extracts were acidified and extracted with ether. The ethereal extracts were dried (Na₂SO₄). Concentration of the solution yielded 10 g (66%) diethyl phosphate which was identified by IR and NMR.

Decomposition of diisopropyl tert-butylperoxy phosphate (1, R = i-C₃H₇) in benzene solution

A: A solution of 12.7 g (0.05 mole) diisopropyl *tert*-butylperoxy phosphate in 30 ml benzene was refluxed for 4 h and was then kept at ambient temperature for 20 h. The volatile products were analyzed by glc and were identified as water, methanol, acetone, and 2,2-dimethoxypropane in addition to benzene. Distillation of the residual oil gave 0.5 g (9%) triisopropyl phosphate: b.p. 69–71 °C (0.1 mm), n_D^{25} 1.4140; and 3.0 g (24%) undecomposed peroxyester: b.p. 81–83 °C (0.1 mm), n_D^{27} 1.4152.

B: A solution of 12.7 g (0.05 mole) diisopropyl *tert*-butylperoxy phosphate, 0.8 g (0.01 mole) pyridine, and 35 ml benzene was heated in an 80 ± 1 °C oil bath for 42.5 h. The solution was concentrated. Distillation of the residual oil yielded 1 g (8%)

undecomposed peroxyester: 6 g (66%) diisopropyl phosphate: b.p. 118–120 °C (0.1 mm); and 1.3 g of an intractable tar.

C: A mixture of 12.7 g (0.05 mole) diisopropyl *tert*-butylperoxy phosphate, 1.15 g (0.01 mole) pyridinium hydrochloride, and 35 ml benzene was heated in an 80 ± 1 °C oil bath for 46.75 h. The mixture was concentrated. Distillation of the residual oil, 11 g, yielded 1 g (8%) undecomposed peroxyester; 1.7 g (19%) diisopropyl phosphate: b.p. 140–142 °C (1.0 mm), n_D^{25} 1.4142; pyridinium hydrochloride; and an intractable residue.

Decomposition of diisopropyl tert-butylperoxy phosphate (1, R = i-C₃H₇) in ethanol

A solution of 12 g (0.047 mole) diisopropyl *tert*-butylperoxy phosphate and 15.8 g (0.34 mole) absolute ethanol was refluxed under nitrogen for 3.5 h. Aliquots (1.0 ml) of the reaction mixture were periodically titrated to follow the peroxyester decomposition (Table VII). No gas was evolved during the decomposition. The reaction mixture was kept at room temperature for 9 h and was then concentrated at 10 mm on a rotating evaporator. The volatile products, 16 g, were collected in a trap at –78 °C and were shown by glc to contain mostly ethanol in addition to water, methanol, acetone, 2,2-dimethoxypropane, methyl isopropenyl ether, and traces of two unidentified components. Distillation of the residual oil gave 3.5 g (59%) diisopropyl phosphate: b.p. 115–118 °C (0.1 mm), n_D^{25} 1.4121.

Decomposition of diisopropyl tert-butylperoxy phosphate (1, R = i-C₃H₇) in chloroform

Diisopropyl *tert*-butylperoxy phosphate (12.7 g, 0.05 mole) was added in one portion under nitrogen to 28 ml refluxing chloroform. Aliquots (1.0 ml) of the reaction mixture were titrated to follow the decomposition of the peroxyester (Table VII). No gas was evolved during the decomposition. The volatile products were shown by glc to be water, methanol, acetone, and methyl isopropenyl ether.

Decomposition of diisopropyl tert-butylperoxy phosphate (1, R = i-C₃H₇) in thiophenol

Diisopropyl *tert*-butylperoxy phosphate (12.7 g, 0.05 mole) was added over 1 h under nitrogen at 110–115 °C to 49.6 g (0.45 mole) thiophenol and the reaction mixture was heated at 110–115 °C for 2 h after the addition was completed. No gas was evolved during the reaction. The cooled mixture was concentrated and the volatiles were collected in a trap at –78 °C. The residue was crystallized from acetone. Recrystallization from isopropanol yielded 5 g (10%) diphenyl disulfide, m.p. 56–58 °C. When no more crystalline material could be recovered, distillation of the mother liquor yielded traces of triisopropyl phosphate: b.p. 50–55 °C (0.1 mm), and diisopropyl phosphate; b.p. 101–109 °C (0.1 mm) which were identified by NMR, and an intractable

residue. Distillation of the material in the trap yielded 0.7 g (19%) *tert*-butanol: b.p. 88–91 °C (760 mm), n_D^{25} 1.3931; 27.5 g (55%) thiophenol: b.p. 166–169 °C (760 mm); and 2.7 g of an intractable residue.

The effect of various additives on the decomposition of dialkyl tert-butylperoxy phosphates (1) in solution at 82 °C (Table V)

General procedure: A solution of 0.02 mole peroxyphosphate, 0.002 mole additive, and 25 ml of solvent was purged with nitrogen for at least 5 min and was then immersed in a preheated 82 °C oil bath. Aliquots (1.0 ml) were titrated to follow the peroxyester decomposition.

Polymerization of styrene using dialkyl tert-butylperoxy phosphates (1) as initiator (Table VIII)

A solution of 0.001 mole dialkyl *tert*-butylperoxy phosphate in 20 g (0.192 mole) freshly distilled styrene was heated in a boiling water bath for 2 h. The unreacted monomer was dissolved in methanol. The polymer was collected by filtration and heated at 30 °C (10 mm) until constant weight was achieved.

Polymerization of methyl methacrylate using diisopropyl tert-butylperoxy phosphate (1, R = i-C₃H₇) as initiator

Methyl methacrylate was distilled under nitrogen immediately before use collecting the fraction b.p. 99–100 °C (760 mm).

A: Blank Experiment: Methyl methacrylate (10 g) was heated in a boiling water bath for 2 h. No polymerization was observed.

B: Polymerization with benzoyl peroxide: A solution of 10 mg benzoyl peroxide in 10 g methyl methacrylate was heated in a boiling water bath for 20 min to form a solid white mass.

C: Polymerization with diisopropyl *tert*-butylperoxy phosphate (1, R = i-C₃H₇): A solution of 0.1 ml diisopropyl *tert*-butylperoxy phosphate in 10 g methyl methacrylate was heated in a boiling water bath for 45 min to form a viscous jelly-like colorless oil.

Preparation of methyl isopropenyl ethyl (8)²⁵

Into a 3-necked, 500-ml, round bottom flask fitted with a strong mechanical stirrer, thermometer, and 2 × 30 cm distillation column packed with 8 mm

Table VIII. Polymerization of styrene at 100 °C.

Initiator	Percent polymerization
(C ₂ H ₅ O) ₂ P(O)OOCMe ₃	33
(i-C ₃ H ₇ O) ₂ P(O)OOCMe ₃	19.5
(n-C ₄ H ₉ O) ₂ P(O)OOCMe ₃	39
(C ₂ H ₅ O) ₂ P(O)OH	5.5
(C ₆ H ₅ C(O)OOC(O)C ₆ H ₅	99
None	6.5

glass helices and fitted with a variable takeoff distillation head was added 156 g (1.1 mole) phosphorus pentoxide, 156 g (1.1 mole) quinoline, and 104 g (1 mole) 2,2-dimethoxypropane. The very viscous mixture was stirred and heated until reflux began. Distillate was removed at as low a boiling point as possible collecting a colorless liquid, b.p. 42–60 °C. The distillate was redistilled through the above column collecting 31 g (43%) methyl isopropenyl ether, b.p. 34 °C, which is stable indefinitely when stored at –5 °C over anhydrous potassium carbonate.

Reaction of diethyl phosphate (6, R = C₂H₅) with methyl isopropenyl ether (8)

A solution of 4.62 g (0.03 mole) diethyl phosphate in 10 ml ether was added over 3 min at 28–35 °C to a solution of methyl isopropenyl ether in 10 ml ether. The solution was stirred at room temperature 4 h and was concentrated at 10 °C to a dark oil. Distillation of this oil yielded 1.2 g triethyl phosphate: b.p. 50–55 °C (0.2 mm); and 2.5 g (54%) diethyl phosphate: b.p. 105–130 °C (0.05 mm) which was identified by IR and NMR.

Reaction of diethyl phosphate (6, R = C₂H₅) with ethyl vinyl ether (13)

A: A solution of 5.1 g (0.033 mole) freshly distilled diethyl phosphate (pure on the basis of NMR

analysis) in 5 ml ether was added at 26.5–27 °C over a period of 4 min to a solution of 2.4 g (0.033 mole) ethyl vinyl ether in 10 ml ethyl ether. The reaction mixture was stirred at ambient temperature for 3 h after the addition was completed and was then concentrated to a dark red oil whose IR spectrum, neat and in benzene solution, showed no pyrophosphate absorption at $\nu_{\max} = 950 \text{ cm}^{-1}$. Distillation of the red oil yielded 1.1 g (37%) triethyl phosphate: b.p. 43–45 °C (0.2 mm), $n_D^{27} 1.4020$; and 2.7 g (52%) diethyl phosphate: b.p. 135–145 °C (0.4 mm).

Analysis: Calcd for C₆H₁₅O₄P MW, 182: Found: MW, 188.

B: A solution of 10.2 g (0.066 mole) diethyl phosphate in 10 ml ether was added over a period of 6 min at 23–26 °C to a solution of 4.8 g (0.066 mole) ethyl vinyl ether in 20 ml ethyl ether. The reaction mixture was stirred at ambient temperature for 6 h and was concentrated to a yellow oil whose IR spectrum showed no pyrophosphate adsorption. The oil was dissolved in ether and the resulting solution was extracted with 10% aqueous sodium hydroxide solution. The alkaline extracts were concentrated and acidified with concentrated hydrochloric acid. The resulting acid solution was extracted with ether. The ether extracts were dried (Na₂SO₄) and concentrated. This procedure yielded 7 g (69%) diethyl phosphate which was identified by analysis of its NMR and IR spectra.

¹ a This investigation was supported by grants from the Public Health Service, U. S. Department of Health, Education, and Welfare (GM 16741), and from the Graduate School of the University of Wisconsin-Milwaukee.
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