Reactions of *tert*-Butylperoxy Esters, XIII

Reactions of Dialkyl *tert*-Butylperoxy Phosphates with Amines^{a, b, c}

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(Z. Naturforsch. **30b**, 724-731 [1975]; received February 17, 1975)

tert-Butylperoxy Esters, Dialkyl Cycloalkylammonium Phosphates,
tert-Butylperoxy Phosphates, Dialkyl Phosphates, Amines

The interaction of dialkyl *tert*-butylperoxy phosphates, $(RO)_2P(O)OOCMe_3$ (**1**) with primary and secondary cycloalkylamines, $R'R''NH$, $R' = \text{cyclo-C}_6\text{H}_{11}$, $R'' = H$; $R' = R'' = \text{cyclo-C}_6\text{H}_{11}$ (**2**) in the presence and absence of water, produces the corresponding dialkyl cycloalkyl ammonium phosphates, $(RO)_2P(O)O-N^+H_2R'R'$ (**3**), and *tert*-butanol. In carbon tetrachloride the reaction produces in addition to **3** the corresponding cyclohexylammonium chloride. Possible mechanisms of the reaction are discussed.

Introduction

The reaction of organophosphorus compounds with hydrogen peroxide in the presence of amines to produce colored products is known as the SCHONEMANN reaction and it forms the basis of a sensitive method for the determination of phosphorus-containing nerve gases¹⁻³. The reactions of isopropyl methylphosphono-fluoridate (SARIN)⁴⁻⁶ and diethyl *p*-nitrophenyl phosphate^{1-3, 7} with hydrogen peroxide in aqueous alkaline solution in the absence of amines involve rapid nucleophilic attack by the hydroperoxy anion on the phosphorus ester. The peroxyacid then slowly undergoes either a bimole-

cular reaction⁴ or a unimolecular decomposition followed by rapid formation of oxygen⁶.

To date, no esters of monoperoxy phosphoric acid are known, and a recent attempt to synthesize them was unsuccessful⁸. It is, therefore, not possible to study their reactions with amines. However, in the presence of acetone or other carbonyl compounds the interaction of aromatic amines with inorganic peroxyphosphoric acid has been reported⁹ to produce phenolic derivatives of the amines.

Although organophosphate esters are found in all living systems many organophosphorus compounds are extremely toxic and have been used as insecticides and war gases. The toxicity of such compounds, *e.g.* SARIN, is ascribed to their ability to inhibit, through phosphorylation of histidine or serine or both, cholinesterase-type enzymes.

Diisopropyl *tert*-butylperoxy phosphate (**1**, $R = i\text{-C}_3\text{H}_7$) was shown in our laboratory¹⁰ to be a mild cholinesterase inhibitor in rats. Therefore, it was of interest to investigate the interaction of peroxyesters (**1**) with imidazole and histidine. Such a study is complicated by the extreme instability of dialkyl phosphorylated imidazole¹¹ and histidine derivatives. Thus, the reactions of peroxyesters (**1**) with cyclo-alkyl amines were chosen as model systems.

^a This paper is dedicated to Professor Dr. EUGEN MÜLLER in honor of his 70th birthday.

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

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The mechanism by which peroxyesters (**1**) react with amines to produce the corresponding dialkyl N-alkylammonium phosphates remains unclear. Nucleophilic attack on phosphorus by the amine can be expected to yield the corresponding dialkyl N-alkylphosphoramidate (**4**) and *tert*-butyl hydroperoxide.

Reaction of *tert*-butyl hydroperoxide with the amine might then yield the corresponding imine and *tert*-butanol¹⁴.

Our results indicate that, although *tert*-butanol is a major product, the reaction of peroxyester (**1**) ($\text{R} = i\text{-C}_3\text{H}_7$) with cyclohexylamine produces only traces of diisopropyl N-cyclohexylphosphoramidate (**4**, $\text{R} = i\text{-C}_3\text{H}_7$; $\text{R}' = \text{cyclo-C}_6\text{H}_{11}$) and cyclohexanone oxime.

Although phosphoramidates (**4**) are difficult to crystallize they are readily purified by sublimation as was shown using a synthetic mixture of a dialkyl cyclohexylammonium phosphate and the corresponding dialkyl N-cyclohexylphosphoramidate. Moreover, if **1** is interacted with cyclohexylamine in the presence of phosphoramidate (**4**) the reaction proceeds normally to yield salt **3**, and **4** is recovered without difficulty. These observations, coupled with the evidence, lead us to believe that if phosphoramidates (**4**) had been formed in more than trace amounts we would have been able to isolate them.

There is evidence that nitrogen compounds will participate in nucleophilic displacements on oxygen even though the picture is often clouded by data which could be just as readily explained on the basis of a free radical interaction¹⁵. Nucleophilic attack by the amine on the peroxide linkage can be envisioned as follows.

Intermediate **5** might then decompose by two different routes as shown in schemes (a) and (b).

(a) A proton transfer

(b) A cleavage to give radicals

An alternative mechanism (c) involving nucleophilic attack on the peroxide in a concerted manner can also be envisioned.

(c) A nucleophilic displacement

Our results do not permit a choice to be made between these or any other theoretically possible routes. On the basis of the product analysis, none of the routes shown is satisfactory since each involves some intermediates which were not intercepted. However, the reactions always produce

intractable tars and, therefore, product analysis is not a sufficient criterion for determination of the mechanism. Routes (a) and (c) are intriguing in that they explain the production of salt **3** without involving water. However, failure to isolate either methyl isopropenyl ether (**8**) or the *O-tert*-butyl hydroxylamine derivative (**7**) is disappointing. Methyl isopropenyl ether (**8**) is a product of the thermal decomposition of peroxyesters¹⁰ and although it is very reactive under the present reaction conditions probably would have been detected. *O-tert*-Butyl *N*-cyclohexyl hydroxylamine (**7**, R' = cyclo-C₆H₁₁) has not been reported. However, an analogous compound, *O,N*-di-*tert*-butyl hydroxylamine (**7**, R' = (CH₃)₃C), has been prepared and isolated either as the hydrobromide or hydrochloride and has been shown to survive treatment with aqueous acid solution¹⁶. Under the relatively mild reaction conditions employed in our experiments, it might be expected that **7** (R' = cyclo-C₆H₁₁) would have survived. The major fault with the sequences is that they do not explain the production of *tert*-butanol as a primary reaction product.

A mechanistic explanation of the products of the reactions of peroxyesters (**1**) with amines is made even more difficult by the following observations.

(1) The reaction of peroxyester (**1**, R = C₂H₅) in benzene in the presence of cyclohexylamine is much faster than is the disappearance of the peroxyester in benzene alone and the rate appears to be dependent on the amine concentration. The amine thus appears to be inducing the decomposition of the peroxyester.

(2) The reaction of peroxyesters (**1**) with cyclohexylamine is faster in ethanol than in benzene. This could imply an ionic intermediate in the rate determining step.

(3) The reaction of peroxyesters (**1**) with cyclohexylamine is accelerated by the addition of galvinoxyl [2,6-di-*tert*-butyl- α -(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)] (**9**), a free radical trap which usually retards free radical reactions.

(4) The reaction of peroxyesters (**1**) with cyclohexylamine is accelerated by the addition of 2,6-di-*tert*-butyl phenol, a compound which usually retards free radical reactions.

(5) The reaction of peroxyesters (**1**) with cyclohexylamine is inhibited by the addition of azobisisobutyronitrile which usually serves as an initiator of free radical reactions. The inhibition, in this case,

can be explained by a reaction sequence involving the oxidation of the amine by peroxyesters to a nitroxyl radical followed by the formation of an adduct arising from the combination of the nitroxyl with radicals derived from the azobisisobutyronitrile¹⁷.

Observations 1, 2, and 4 point to an ionic reaction as the rate determining step. If the rate determining step is indeed ionic, then the acceleration of the amine-peroxyester interaction by galvinoxyl points to the formation of free radicals at some point in the process. This conclusion is based (a) upon the production of phenol (**10**) and aldehyde (**11**) from the interaction of galvinoxyl with *tert*-butoxy radicals¹⁸, (b) upon the previously discussed interaction of inorganic peroxyphosphates with aromatic amines in the presence of carbonyl compounds⁹, and (c) upon our observation that 2,6-di-*tert*-butyl phenol accelerates the amine-peroxyester interaction.

The results of this investigation, therefore, are not amenable to interpretation by either simple ionic or free radical mechanisms.

Experimental

Boiling points and melting points are uncorrected. 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. Gas chromatography

graphic analyses were performed on Varian Aerograph instruments models 1700 and A-90 P3 equipped with thermal conductivity detectors using wx filaments on a 10 ft × 1/8 in steel column packed with 100–200 mesh Porapak Q. Unless otherwise noted, materials were concentrated at less than 50 °C on a rotating evaporator at 10–15 mm Hg.

Dialkyl phosphoric acids were prepared by the method of ZWIERZAK¹⁹ and we have previously reported methods for the preparation of dialkyl *tert*-butylperoxy phosphates^{20, 21}. Cyclohexylamine and the other amines were distilled over zinc under nitrogen and were stored over sodium hydroxide under nitrogen. 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.

Preparation of dialkyl ammonium phosphates (3). General procedure (Table II)

Equimolar amounts of the dialkyl phosphoric acid (6) and the amine were stirred at ambient temperature in the solvent indicated. The reaction mixture was concentrated on a rotating evaporator and the residual oils were crystallized and recrystallized as indicated.

Determination of active oxygen content of peroxyesters

The peroxide content of solutions of dialkyl *tert*-butylperoxy phosphates was determined in analogy with the method of SILBERT and SWERN²². 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.

Thin layer chromatography

Peroxyphosphates and *tert*-butyl hydroperoxide were visualized by spraying the dried developed plate with a solution of sodium iodide in nitrogen-saturated glacial acetic acid. They appeared as brown spots on a white background. All phosphorus esters could be visualized by spraying the dried developed plates with concentrated hydrochloric acid followed by exposure to iodine vapor and appeared as brown spots on a white background. This procedure is capable of detecting 5 µg of phosphorus compound in a spot. The phosphoramidates were visualized by exposing the dried developed plates to iodine vapor, and they appeared as brown spots on a white background.

Reaction of diethyl *tert*-butylperoxy phosphate (1, R = C₂H₅) with cyclohexylamine

Diethyl *tert*-butylperoxy phosphate (11.31 g, 0.05 mol) was added in one portion to a solution of 9.92 g (0.10 mol) cyclohexylamine and 25 ml benzene and the resulting mixture was stored at room temperature for 16 h. Filtration of the precipitate which had formed yielded a hygroscopic solid, m.p. 78–80 °C. Repeated recrystallization of the solid from benzene yielded 7.2 g (53%) diethyl cyclohexylammonium phosphate monohydrate.

Analysis: Calcd for C₁₀H₂₄NO₄P · H₂O: C 46.50; H 9.65. Found: C 46.44; H 9.55.

Table II. Dialkyl cycloalkylammonium phosphates (3) prepared from dialkyl phosphates (6).

Dialkyl phosphate (6) R	Amine 2 R' = C ₆ H ₁₁ R''	Solvent	Reaction time [h]	Salt 3* m.p. [°C]	Recrys. solvent
CH ₃	H	CHCl ₃	1	77.5–78.5	Ether-Pentane
<i>i</i> -Pr	H	C ₆ H ₆	1	198–199	Acetone
<i>n</i> -Pr	H	C ₆ H ₆	6	81.5–83	Ligroin or Ether
<i>n</i> -Bu	H	CHCl ₃	1	81–82	Ether Pentane
<i>i</i> -Bu	H	C ₆ H ₆	1	200–201.5	Ligroin-Acetone
Me	C ₆ H ₁₁	CHCl ₃	24	159.5–160.5	Acetone
Et	C ₆ H ₁₁	CHCl ₃	24	133.5–134.5	Ligroin
<i>i</i> -Pr	C ₆ H ₁₁	C ₆ H ₆	19	172–173	Acetone
<i>n</i> -Pr	C ₆ H ₁₁	C ₆ H ₆	3	133–134	Acetone
<i>n</i> -Bu	C ₆ H ₁₁	CCl ₄	60	106–107	Ligroin
<i>i</i> -Bu	C ₆ H ₁₁	C ₆ H ₆	3	165.0–165.5	Acetone
<i>i</i> -Bu	-CMe ₃	C ₆ H ₆	1	181.0–181.5	Benzene

* C, H, N analyses were within 0.3% of the theoretical values.

Reaction of diisopropyl tert-butylperoxy phosphate (1, R = i-C₃H₇) with cyclohexylamine in the absence of solvent

Cyclohexylamine (1.98 g, 0.02 mol) was added in one portion without cooling to 5.08 g (0.02 mol) diisopropyl *tert*-butylperoxy phosphate. The resulting mixture was stirred at room temperature for 12 h during which time it slowly solidified. Repeated recrystallization of the resulting brown solid from acetone yielded 3.1 g (55%) diisopropyl cyclohexylammonium phosphate: m.p. 192–196 °C.

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

I. At ambient temperature

A. A solution of 10.2 g of (0.04 mol) diisopropyl *tert*-butylperoxy phosphate, 5 g (0.05 mol) cyclohexylamine, and 15 ml benzene was stirred at ambient temperature for 14 h. The mixture was concentrated. Crystallization of the residual oil from acetone yielded 6.0 g (54%) diisopropyl cyclohexylammonium phosphate.

B. A solution of 5.08 g (0.02 mol) diisopropyl *tert*-butylperoxy phosphate, 1.98 g (0.02 mol) cyclohexylamine, and 25 ml benzene was stirred at room temperature for 3 weeks and was then concentrated to an orange oil. Crystallization of this oil under 20–40 °C petroleum ether yielded 4.7 g (84%) of a tan solid. Recrystallization of this solid produced 1.5 g diisopropyl cyclohexylammonium phosphate: m.p. 184–187 °C; and an uncrystallizable oil whose IR spectrum was essentially superimposable with the IR spectrum of pure diisopropyl cyclohexylammonium phosphate.

II. At 70 °C

A. Into a 100 ml, 3-necked, round bottom flask equipped with thermometer, reflux condenser, drying tube, a –78 °C trap, magnetic stirrer, and gas buret filled with saturated sodium chloride solution, and the entire system purged with nitrogen gas, was added a solution of 12.7 g (0.05 mol) diisopropyl *tert*-butylperoxy phosphate and 25 ml benzene. To this solution was added a solution of 9.9 g (0.10 mol) cyclohexylamine in 25 ml benzene and the reaction flask was immersed in a 70 °C oil bath. When thermal equilibrium had been achieved (15 min) the flow of nitrogen gas was stopped and the gas buret opened. Gas evolution occurred for the first hour and 59 ml (5.3%) of unidentified gas was collected. The mixture was heated at 70 °C for 4 h more and was then kept overnight at room temperature. Concentration by distillation of the benzene at atmospheric pressure under nitrogen gave a black residue. Crystallization of the residue from acetone yielded 11 g (79%) diisopropyl cyclohexylammonium phosphate, m.p. 194–196 °C; and 7.4 g of a black uncrystallizable oil which was analyzed by tlc on alumina using benzene, ether, and ethyl

acetate as eluants and was found to be comprised of at least five components of which diisopropyl N-cyclohexylphosphoramidate, cyclohexanone oxime, and diisopropyl cyclohexylammonium phosphate were identified by comparison with authentic samples. The tlc investigation eliminated the possibility of the oil containing cyclohexylamine or cyclohexanone. The benzene distillate was shown by glc to contain *tert*-butanol (41%) with traces of methanol, water and acetone.

B. A solution of 5.08 g (0.02 mol) diisopropyl *tert*-butylperoxy phosphate in 15 ml benzene was purged at room temperature with nitrogen. A solution of 3.96 g (0.04 mol) cyclohexylamine in 10 ml benzene was added in one portion and the reaction flask was immersed in a 40 °C oil bath. The reaction mixture was then concentrated. Repeated recrystallization of the residue from acetone yielded 3.8 g (68%) diisopropyl cyclohexylammonium phosphate. Aliquots (0.05 ml) of the reaction mixture were periodically titrated for peroxide content.

Elapsed time [h]:	0	1	3	6	10.
Percent peroxide:	100	96	96	78	54.

A duplicate experiment was performed simultaneously; however, the amine solution also contained 0.84 g (0.002 mol) galvinoxyl. Analogous work-up after 1 h yielded 3.1 g (55%) diisopropyl cyclohexylammonium phosphate. Titration of the reaction mixture after 1 h was not possible because the mixture had almost solidified.

Reaction of diisopropyl tert-butylperoxy phosphate (1, R = i-C₃H₇) with cyclohexylamine in carbon tetrachloride

A. In the presence of water

A mixture of 6.35 g (0.025 mol) diisopropyl *tert*-butylperoxy phosphate, 4.95 g (0.05 mol) cyclohexylamine, 0.9 ml water, and 50 ml carbon tetrachloride was stirred at room temperature for 7 days. The reaction mixture was filtered to remove a small amount of cyclohexylammonium chloride. Recrystallization of the filtrate from ligroin yielded in several crops, 4 g (57%) diisopropyl cyclohexylammonium phosphate: m.p. 191–193 °C.

B. In the absence of water

1. A solution of 4.95 g (0.05 mol) cyclohexylamine, 6.35 g (0.025 mol) diisopropyl *tert*-butylperoxy phosphate, and 50 ml carbon tetrachloride was stirred at ambient temperature for 7 days. The solution was filtered to remove 2 g (30%) cyclohexylammonium chloride. The filtrate was concentrated. Crystallization of the residue from acetone yielded 2.1 g (30%) diisopropyl cyclohexylammonium phosphate.

2. Cyclohexylamine (4.95 g, 0.05 mol) was added over 9 min at 22–25 °C to a solution of 6.35 g (0.025 mol) diisopropyl *tert*-butylperoxy phosphate and 50 ml carbon tetrachloride. The resulting

mixture was stirred at 25 °C for 2 h and was filtered to remove 1.1 g (16%) cyclohexylamine hydrochloride. The filtrate was concentrated. Crystallization of the residue from acetone yielded 1.5 g (21%) diisopropyl cyclohexylammonium phosphate: m.p. 186 °C.

3. A glove box was purged with dried (H_2SO_4) nitrogen and at intervals during the reaction the chamber's drying-train was activated. The carbon tetrachloride (reagent grade) was dried over calcium chloride. The diisopropyl *tert*-butylperoxy phosphate was doubly distilled and was stored at -10 °C but was warmed to ambient temperature and opened in the glove box. A solution of 10.08 g (0.0394 mol) peroxyester in 25 ml carbon tetrachloride was dried over sodium sulfate and was decanted into the reaction flask. Carbon tetrachloride (25 ml) was added and then 3.9 g (0.0394 mol) cyclohexylamine (dried over sodium hydroxide pellets) was added in one portion. The reaction mixture was stirred at ambient temperature in the glove box for 20 h and was then removed from the glove box. Cyclohexylammonium chloride, 1.5 g (28%), was removed by filtration and the filtrate was concentrated. Crystallization of the residual oil from acetone yielded 2.9 g (26%) diisopropyl cyclohexylammonium phosphate. Distillation of the residual oil yielded 4.7 g (46%) diisopropyl *tert*-butylperoxy phosphate and an intractable black tar.

Reaction of diisopropyl tert-butylperoxy phosphate (1, R = i-C₃H₇) with cyclohexylamine in methanol

A solution of 1.98 g (0.02 mol) cyclohexylamine, 5.01 g (0.02 mol) diisopropyl *tert*-butylperoxy phosphate, and 25 ml methanol was stirred at ambient temperature for 9 h and was then concentrated to a yellow solid. Recrystallization of the solid from acetone yielded 1.8 g (32%) diisopropyl cyclohexylammonium phosphate, m.p. 195–196 °C.

Reaction of diisopropyl tert-butylperoxy phosphate (1, R = i-C₃H₇) with cyclohexylamine in the presence of sodium methoxide

A mixture of 0.54 g (0.01 mol) sodium methoxide, 1.98 g (0.02 mol) cyclohexylamine, 5.01 g (0.02 mol) diisopropyl *tert*-butylperoxy phosphate, and 25 ml methanol was stirred at 40 °C for 17.5 h and was concentrated to a yellow oil. Repeated recrystallization from acetone gave 1.8 g (32%) diisopropyl cyclohexylammonium phosphate, m.p. 194–196 °C; and 1.9 g of an intractable brown oil, n_D^{25} 1.4300.

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

To a solution of 5.08 g (0.02 mol) diisopropyl *tert*-butylperoxy phosphate in 15 ml absolute ethanol which had been purged with dry nitrogen was added in one portion a solution of 3.96 g (0.04 mol) cyclohexylamine in 10 ml absolute ethanol. The reaction mixture was immediately immersed in a preheated

40 °C oil bath and 0.5 ml aliquots were periodically removed for titration of the peroxide content.

Elapsed time [h]:	0	3	7	17.
Percent peroxide:	100	98	20	0.

After 17 h the reaction mixture was concentrated. Repeated recrystallization of the residue from acetone yielded 3.1 g (56%) cyclohexylammonium phosphate, m.p. 186–192 °C.

An identical experiment was carried out in which the reaction residue was sublimated in an unsuccessful effort to isolate diisopropyl *N*-cyclohexylphosphoramidate had it been formed.

Reaction of diethyl tert-butylperoxy phosphate (1, R = C₂H₅) with dicyclohexylamine in benzene

A. Diethyl *tert*-butylperoxy phosphate (4.52 g, 0.02 mol) was added to 3.62 g (0.02 mol) dicyclohexylamine. The mixture was diluted with 10 ml benzene and was stirred in a stoppered flask for 2 days at ambient temperature. The mixture was filtered to remove 0.2 g dicyclohexylammonium chloride. The filtrate was concentrated leaving a dark brown solid. Recrystallization of the solid from skellysolve B yielded 4.0 g (59%) diethyl dicyclohexylammonium phosphate, m.p. 138–139 °C, which was identified by comparison with an authentic sample by tlc on silica gel G plates using acetone-ethanol (1:1) and benzene-ethyl acetate (4:1) solutions as eluants and iodine to visualize the spots.

B. A solution of 6.50 g (0.029 mol) diethyl *tert*-butylperoxy phosphate, 10.5 g (0.048 mol) dicyclohexylamine, and 20 ml benzene was stored at room temperature for 39 h and was concentrated to a thick oil. Crystallization of the oil from petroleum ether yielded 5.27 g (54%) diethyl dicyclohexylammonium phosphate, m.p. 131–133 °C, a portion of which was recrystallized from cyclohexane yielding white crystals, m.p. 140–140.5 °C.

Analysis: Calcd for $\text{C}_{16}\text{H}_{34}\text{NO}_4\text{P}$: C 57.29; H 10.22; N 4.18. Found: C 57.47; H 10.41; N 4.32.

Reaction of di-n-butyl tert-butylperoxy phosphate (1, R = n-C₄H₉) with cyclohexylamine and galvinoxyl. Determination of the volatile products

A solution of 7.05 g (0.025 mol) di-*n*-butyl *tert*-butylperoxy phosphate, 1.05 g (0.0025 mol) galvinoxyl, 4.92 g (0.05 mol) cyclohexylamine, and 25 ml benzene was heated under nitrogen at 65 °C for 4 h. Nitrogen was gently bubbled through the reaction mixture for 1 h and 1.2 g of a benzene solution of the volatile products was collected in a tap at -78 °C. Analysis of this solution by glc on Porapak Q showed it to contain (% yield) water (1.6%), methanol (4%), acetone (0.8%), *tert*-butanol (9%), and an unidentified component in trace amounts.

The analogous reaction of a solution of 14.1 g (0.05 mol) di-*n*-butyl *tert*-butylperoxy phosphate, 4.95 g (0.05 mol) cyclohexylamine, and 50 ml

benzene at 65 °C for 24 h yielded as identified by glc analysis (% yield) water (0.7%), methanol (1.5%), acetone (0.7%), and *tert*-butanol (1.4%).

Reaction of diisopropyl phosphate (6, R = i-C₃H₇) with diisopropyl N-cyclohexylphosphoramidate (4, R = i-C₃H₇; R' = cyclo-C₆H₁₁)

A mixture of 2.73 g (0.015 mol) diisopropyl phosphate, 3.96 g (0.015 mol) diisopropyl N-cyclohexylphosphoramidate, 4 ml water, and 30 ml benzene was stirred at 60 °C for 24 h and was concentrated. Sublimation of the residual oil at 50 °C (0.1 mm) yielded 3.6 g (99%) diisopropyl N-cyclohexylphosphoramidate and extraction of the sublimation residue with ether yielded 2.73 g (100%) diisopropyl phosphate.

Reaction of diisopropyl tert-butylperoxy phosphate (1, R = i-C₃H₇) with cyclohexylamine in the presence of diisopropyl N-cyclohexylphosphoramidate (4, R = i-C₃H₇; R' = cyclo-C₆H₁₁) in benzene at 60 °C

A solution of 4.57 g (0.018 mol) diisopropyl *tert*-butylperoxy phosphate, 4.7 g (0.018 mol) diisopropyl N-cyclohexylphosphoramidate, 1.86 g (0.018 mol) cyclohexylamine, and 30 ml benzene was stirred at 60 °C for 24 h and was then concentrated.

Crystallization of the residual oil from acetone yielded 3.2 g (63%) diisopropyl cyclohexylammonium phosphate. The mother liquor was concentrated. Crystallization of the residue from a minimal amount of ether at -70 °C yielded 1.8 g (38%) diisopropyl N-cyclohexylphosphoramidate.

*Effect of galvinoxyl, azobisisobutyronitrile (AIBN), and 2,6-di-*tert*-butyl phenol on the reactions of dialkyl tert-butylperoxy phosphates (1, R = C₂H₅, i-C₃H₇) with cyclohexylamine. General procedure*

A. Solutions of 2.26 g (0.01 mol) diethyl *tert*-butylperoxy phosphate, 10 ml benzene, and

0.002 mol of the additive, where required, were stirred at the temperature specified for 20 min under nitrogen. Then 1.98 g (0.02 mol) cyclohexylamine was injected and heat was applied. Aliquots (0.5 ml) were titrated for peroxide content periodically.

a. At 73 °C a solution of peroxyester (1) in benzene contained 96% of the peroxide after 3 h.

b. At 73 °C a solution of peroxyester (1) and the amine in benzene contained no titratable peroxide after 1 h.

c. At 73 °C a solution of peroxyester (1), the amine, AIBN, and benzene contained 95% of the peroxide after 3 h.

d. At 73 °C a solution of peroxyester (1), the amine, galvinoxyl, and benzene contained no peroxide after 0.25 h.

e. At 30 °C a solution of peroxyester (1), the amine, and benzene contained 85% of the peroxide after 1 h.

f. At 30 °C a solution of peroxyester (1), the amine, galvinoxyl, and benzene contained 33% of the peroxide after 1 h.

B. Analogous reactions using diisopropyl *tert*-butylperoxy phosphate (1, R = i-C₃H₇), the additive, and benzene were performed at 73 °C.

a. A solution of 0.005 mol peroxyester (1), 0.005 mol amine, and 10 ml benzene contained 68% of the peroxide after 40 min.

b. A solution of 0.005 mol peroxyester (1), 0.01 mol amine, 0.0006 mol AIBN, and 10 ml benzene contained 75% of the peroxide after 40 min.

c. A solution of 0.005 mol peroxyester (1), 0.108 mol amine, 0.0013 mol 2,6-di-*tert*-butyl phenol, and 10 ml benzene contained 37% of the peroxide after 40 min.

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