Reactions of tert-Butyl Peroxy Esters, XIV. Further Observations on the Preparation of Dialkyl tert-Butylperoxy Phosphates\textsuperscript{1b}

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\textit{tert-Butylperoxy Esters, tert-Butylperoxy Phosphates, Dialkyl tert-Butylperoxy Phosphates, Tetraalkyl Pyrophosphates, Dialkyl Phosphates}

The preparation of dialkyl \textit{tert}-butylperoxy phosphates (2, \(R = \text{alkyl}\)) has been achieved by the reaction of the corresponding dialkyl phosphorochloridates (1, \(R = \text{alkyl}\)) with \textit{tert}-butyl hydroperoxide either in the presence of pyridine or in the presence of aqueous potassium hydroxide solution. Neither of these routes is suitable for the preparation of dialkyl \textit{tert}-butylperoxy phosphates in quantity since they yield peroxyphosphates which are contaminated either with the corresponding tetraalkyl pyrophosphates or dialkyl phosphates; the contaminants cannot easily be removed by conventional means from the peroxyphosphates. The method of choice for the preparation in high yield of large quantities of pure dialkyl \textit{tert}-butylperoxy phosphates involves the interaction of the corresponding dialkyl phosphorochloridate with sodium \textit{tert}-butyl peroxide which has been prepared \textit{in situ} from the reaction of \textit{tert}-butyl hydroperoxide with sodium hydride.

\textbf{Introduction}

The preparation of dialkyl \textit{tert}-butylperoxy phosphates (2) was first accomplished by Rieche, Hilgetag, and Schramm\textsuperscript{2-5}, who synthesized dimethyl- and diethyl \textit{tert}-butylperoxy phosphate via the reaction of the corresponding dialkyl phosphorochloridates (1) with \textit{tert}-butyl hydroperoxide in the presence of pyridine.

\[
\begin{align*}
(R\text{O})_2\text{P(O)Cl} + \text{Me}_3\text{COOH} & \xrightarrow{\text{pyridine}} (R\text{O})_2\text{P(O)}\text{OMe}_3 \\
2 & \\
R & = \text{CH}_3, \text{C}_2\text{H}_5
\end{align*}
\]

Rieche \textit{et al.}\textsuperscript{2} reported that peroxyesters (2) (\(R = \text{CH}_3, \text{C}_2\text{H}_5\)) showed extreme thermal lability and that distillation of the crude materials often resulted in decomposition accompanied by formation of intractable black tars. Our early work substantiated these reports; however, we found that the tars were not intractable. Rather, it was shown that after carefully performed distillations, they gave good yields of the corresponding tetraalkyl pyrophosphate (3). In each case the distillation of the crude peroxyester was interrupted by a sudden exothermic, vigorous outgassing and darkening of the distillation mixture. When the decomposition had subsided, distillation of the dark residue yielded the pyrophosphate. At the time these results were obtained we were unaware that pyrophosphates (3) could form during the synthesis of dialkyl \textit{tert}-butylperoxy phosphates and incorrectly reported\textsuperscript{6} the pyrophosphates to be thermal decomposition products of the peroxyesters\textsuperscript{7}.

In our hands the peroxyesters obtained from exact replications of the procedures reported by Rieche \textit{et al.} were always contaminated with small amounts of the corresponding tetraalkyl pyrophosphates (3) which could not be separated by distillation or by repeated washing of the product. The contamination of the peroxyester by the pyrophosphate is evidenced by a broadening of the \(R-O-P\) band at 950-980 cm\(^{-1}\) (10.2-10.5 \(\mu\)) in the infrared spectrum and by slight errors in the integration and line shape of the NMR spectrum.
The synthesis of diisopropyl tert-butylperoxy phosphate (2, R = i-C₃H₇) from the reaction of diisopropyl phosphorochloridate (1, R = i-C₃H₇) with tert-butyl hydroperoxide in the presence of pyridine was slightly more successful than the synthesis by the same route of diethyl tert-butylperoxy phosphate (2, R = C₂H₅). The crude peroxyster was contaminated by pyrophosphate but the greater stability of diisopropyl tert-butylperoxy ester allowed it to be obtained pure by distillation of the reaction mixture.

When Rieche's procedure was scaled-up three fold, the peroxyesters were obtained in lower yield and lower purity. This observation and the requisite purification of the thermally labile peroxyesters by distillation make this route unsuitable for the routine preparation of pure dialkyl tert-butylperoxy phosphates in large quantity (1 mole or more).

After the study of the decomposition of peroxyesters (2) prepared by a synthetic route not involving pyridine as the condensing agent we realized that the pyrophosphates (3) are not produced by the thermal decomposition of the peroxy phosphates, and examined the synthesis involving pyridine in some detail.

Results and Discussion

In our hands, the mixing of pyridine and tert-butyl hydroperoxide, even in the cold, was always exothermic. However, no attempt was made to determine whether this exothermicity resulted from a simple acid-base reaction or from some more involved interaction of the reagents.

The esterification of tertiary alkyl or aralkyl hydroperoxides with acid chlorides in the presence of pyridine has been used to prepare a large number of tert-butylperoxy esters. Such reactions are carried out in the presence of an inert organic solvent. The analogous reaction of diisopropyl phosphorochloridate (1, R = i-C₃H₇) with tert-butyl hydroperoxide in the presence of pyridine in petroleum ether solution yielded the corresponding peroxyester (2) (R = i-C₃H₇), and pyrophosphate (3) (R = i-C₃H₇). However, reaction of 1 (R = i-C₃H₇) with tert-butyl hydroperoxide in the presence of triethylamine in ether solution yielded only peroxyester (2) (R = i-C₃H₇) and no pyrophosphate was formed. The reaction of phosphorochloridates (1) (R = alkyl) with tert-butyl hydroperoxide in the presence of pyridine always resulted in pyrophosphate formation; the order of addition and addition temperatures ranging from —20 °C to +20 °C had no decisive effect.

\[
\begin{align*}
(RO)₂P(O)Cl + Me₃COOH & \rightarrow pyridine \\
(RO)₂P(O)OOCMe₃ + (RO)₂P(O)OP(0)(OR)₂ & \rightarrow 3
\end{align*}
\]

Tetraalkyl pyrophosphates (3) have been prepared by the controlled hydrolysis of the corresponding dialkyl phosphorochloridates (1) in the presence of a tertiary amine such as pyridine. The dialkyl phosphorochloridates utilized in this study were synthesized in our laboratory and were shown by physical methods to be free of water and dialkyl phosphates which are intermediates in the conversion of the phosphorochloridates into pyrophosphates. We then examined other potential sources of water.

The most obvious sources of water are the reagents themselves. Contamination of the starting materials by water was minimized by the appropriate techniques of distillation, and care in storage, handling and transfer. The probability that the dialkyl phosphorochloridates, the solvents, or the pyridine are the sources of water is minimized by the observation that our use of these materials in other reactions, e.g., with alcohols to yield trialkyl phosphates and with amines to yield dialkyl N-alkyl-phosphoramidates did not produce tetraalkyl pyrophosphates in amounts detectable by IR.

Peroxyester (2) (R = i-C₃H₇) is not converted to the corresponding pyrophosphate (3) (R = i-C₃H₇) either by a mixture of pyridine and tert-butyl hydroperoxide or by pyridine alone. Periodic investigation, by IR, of the reaction mixtures during a week at room temperature did not demonstrate the presence of pyrophosphate.

Little is known about the reaction of tert-butyl hydroperoxide with pyridine. The reaction of pyridine and tert-butyl hydroperoxide in the presence of metal catalysts has been shown to produce quantitative yields of pyridine N-oxide and tert-butyl alcohol. In the absence of metal catalysts, radicals have been detected as intermediates, and the following process was proposed.

\[
Me₃COOH + \overset{\bigcirc}{\bigcirc} \rightarrow \overset{\bigcirc}{\bigcirc} \rightarrow \overset{\bigcirc}{\bigcirc} \rightarrow Me₃CO^- + \cdot OH
\]
The production of water can be envisioned as resulting from the following two reactions.

\[ 2 \text{HO} \rightarrow \text{H}_2\text{O} + 1/2 \text{O}_2 \]
\[ \text{HO} + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R} \cdot \]

RH = solvent.

The reaction of diethyl phosphorochloridate (1, \( R = C_2H_5 \)) with water in the presence of pyridine is apparently much faster than the analogous reaction of diethyl phosphorochloridate (1, \( R = C_2H_5 \)) with tert-butyl hydroperoxide. Thus, reaction of tert-butyl hydroperoxide containing ten percent water with diethyl phosphorochloridate (1, \( R = C_2H_5 \)) in the presence of pyridine produced only tetraethyl pyrophosphate (3, \( R = C_2H_5 \)). This result implies that, given the reaction of pyridine with tert-butyl hydroperoxide to form water, peroxyesters (2) synthesized by this route will always be contaminated with tetraalkyl pyrophosphates. The reactions may be summarized as follows.

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{COOH} & \xrightarrow{\text{pyridine}} \text{(CH}_3\text{)}_2\text{COH} + \text{H}_2\text{O} \\
2 \text{(RO)}_2\text{P(O)}\text{Cl} + \text{H}_2\text{O} & \xrightarrow{\text{pyridine}} \text{(CH}_3\text{)}_2\text{COH} + \text{H}_2\text{O} \\
\text{(RO)}_2\text{P(O)}\text{OP(O)}\text{(OR)}_2 & \xrightarrow{\text{pyridine}} \text{(RO)}_2\text{P(O)}\text{OP(O)}\text{(OR)}_2 \\
\text{(RO)}_2\text{P(O)}\text{Cl} + \text{(CH}_3\text{)}_2\text{COOH} & \xrightarrow{\text{pyridine}} \text{(RO)}_2\text{P(O)}\text{Cl} + \text{(CH}_3\text{)}_2\text{COOH} \\
\text{(RO)}_2\text{P(O)}\text{OOC(CH}_3\text{)}_2 & \xrightarrow{\text{pyridine}} \text{(RO)}_2\text{P(O)}\text{OOC(CH}_3\text{)}_2
\end{align*}
\]

The preparation of dialkyl tert-butylperoxy phosphates (2, \( R = CH_3, C_3H_7, n-C_4H_9, i-C_4H_9, n-C_5H_11, C_6H_5CH_2 \)) by the reaction of the corresponding dialkyl phosphorochloridates with tert-butyl hydroperoxide in the presence of a mixture of twenty percent aqueous potassium hydroxide solution and petroleum ether (b.p. 20–40 °C) has been reported. However, the methods reported are unsuitable for the large scale preparation of the peroxyesters.

The problems encountered with the procedures involving pyridine and aqueous potassium hydroxide solution indicated the need for another route to peroxyphosphates (2). The synthesis of alkyl tert-butylperoxy alkylphosphonates from the reaction of the corresponding alkyl alkylphosphonochloridates with sodium tert-butyl peroxide has been reported. Although our initial attempts to prepare peroxyester (2) (\( R = i-C_3H_7 \)) by means of the reaction with sodium tert-butyl peroxide had been unsuccessful, the route still seemed potentially useful.

Vacuum distillation of dialkyl tert-butylperoxy phosphates (2) is inefficient, laborious, and time consuming. Only peroxyesters (2) (\( R = C_4H_9, i-C_4H_9 \)) can be distilled in batches as large as 25 g. The practical limits of the batch size for distillation of these peroxyesters are 25 g for diisopropyl tert-butylperoxy phosphate (2, \( R = i-C_3H_7 \)) and 10 g for diethyl tert-butylperoxy phosphate (2, \( R = C_4H_9 \)). Since the efficient purification of large quantities of peroxyesters (2) is difficult, it is requisite that they be obtained of such a high quality as to require no further purification by distillation or chromatography. In an effort to effect this high quality of the crude peroxyesters the proportions of the reagents were varied (Table I). For optimum results the reaction seems to require a slight excess of sodium hydride and equimolar amounts of tert-butyl hydroperoxide and dialkyl phosphorochloridate (1).

The scope of the reaction was investigated briefly. In addition to the peroxyesters listed in Table I, attempts were made to prepare peroxyesters (2) (\( R = C_6H_5 \)), 4, 5, and 6. Diphenyl tert-butylperoxy phosphate (2, \( R = C_6H_5 \)) is extremely unstable when prepared by other routes. An ethereal solution of 2 (\( R = C_6H_5 \)) produced by this method is, however, stable for several days at 5 °C whereas ethereal solutions of 2 (\( R = C_6H_5 \)) obtained by other routes are not stable even at —10 °C. The added stability of peroxyester (2) (\( R = C_6H_5 \)) produced by the route utilizing sodium hydride is apparently due to the lack of even traces of diphenyl phosphate, \( (C_6H_5O)_2P(O)OH \), as an impurity.

Peroxyesters 4 and 5 are obtained as very viscous colorless oils that decompose at room temperature to yield polymeric dark tars and large amounts of volatile products. No attempt was made to characterize these products. All attempts to prepare peroxyester (6) failed and the starting material, \( [(C_6H_5)_2N]_2P(O)Cl \), was recovered. Preparation of peroxyester (6) by the reaction of the
Table I. Preparation of dialkyl tert-butylperoxy phosphates (2) by the reaction of the corresponding dialkyl phosphorochloridates (1) with sodium tert-butyl peroxide.

\[
\text{Me}_3\text{COOH} + \text{NaH} \rightarrow \text{Me}_3\text{COONa} (\text{RO})_2\text{P(O)}0\text{OCMe}_3 + \text{NaCl}
\]

<table>
<thead>
<tr>
<th>R =</th>
<th>(RO)_2P(O)Cl</th>
<th>Me_3COOH</th>
<th>NaH</th>
<th>(RO)_2P(O)OOCMe_3</th>
<th>n_H</th>
<th>n_H, lit.</th>
<th>Molecular weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_3H_7</td>
<td>0.18</td>
<td>0.22</td>
<td>0.2</td>
<td>71</td>
<td>1.4166</td>
<td>1.4169</td>
<td>226</td>
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<tr>
<td>C_4H_9</td>
<td>1.0</td>
<td>1.0</td>
<td>1.1</td>
<td>75</td>
<td>1.4171</td>
<td>1.4169</td>
<td>228</td>
</tr>
<tr>
<td>C_5H_11</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>69</td>
<td>1.4175</td>
<td>1.4169</td>
<td>226</td>
</tr>
<tr>
<td>n-C_5H_11</td>
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<td>0.27</td>
<td>0.25</td>
<td>81</td>
<td>1.4225</td>
<td>1.4219</td>
<td>236</td>
</tr>
<tr>
<td>i-C_5H_11</td>
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<td>0.1</td>
<td>0.1</td>
<td>66</td>
<td>1.4225</td>
<td>1.4219</td>
<td>234</td>
</tr>
<tr>
<td>C_6H_5</td>
<td>0.09</td>
<td>0.11</td>
<td>0.1</td>
<td>81</td>
<td>1.4212</td>
<td>1.4215</td>
<td>230</td>
</tr>
<tr>
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<td>0.45</td>
<td>0.55</td>
<td>0.5</td>
<td>77</td>
<td>1.4215</td>
<td>1.4214</td>
<td>244</td>
</tr>
<tr>
<td>C_7H_15</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>67</td>
<td>1.4216</td>
<td>1.4214</td>
<td>236</td>
</tr>
<tr>
<td>n-C_7H_15</td>
<td>0.4</td>
<td>0.48</td>
<td>0.44</td>
<td>86</td>
<td>1.4216</td>
<td>1.4215</td>
<td>232</td>
</tr>
<tr>
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<td>0.09</td>
<td>0.093</td>
<td>0.1</td>
<td>65</td>
<td>1.4216</td>
<td>1.4215</td>
<td>272</td>
</tr>
<tr>
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<td>0.09</td>
<td>0.093</td>
<td>0.1</td>
<td>60</td>
<td>1.4612</td>
<td>—</td>
<td>318</td>
</tr>
</tbody>
</table>

a Satisfactory spectra were obtained on all samples. b Satisfactory analyses for active oxygen were obtained.

Attempts to extend the method to phosphate esters of \(a, a\)-dimethylbenzyl hydroperoxide (cumyl hydroperoxide, \((7)\)) have been unsuccessful. Thus, reaction of anhydrous distilled cumyl hydroperoxide with sodium and then diisopropyl phosphorochloridate did not yield the expected peroxyester \((8)\).

Rather, an unidentified peroxide-containing oil was obtained. The NMR spectrum of this oil was very complex and no conclusions about structure could be drawn.

This result is in agreement with a recent report\(^{15}\) that the reaction of di-\(n\)-butyl phosphorochloridate \((1, \text{ R} = \text{n-C}_4\text{H}_9)\) with cumyl hydroperoxide hydrate at 20 °C yields a mixture of di-\(n\)-butyl phosphate, isopropenyl phenyl ether, and an unidentified resinous product.

**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 isopiestically on a Hitachi Perkin-Elmer model 115 Molecular Weight Apparatus.

**Determination of active oxygen content of peroxyphosphate esters**

Neat dialkyl tert-butylperoxypophosphate 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 point\(^{16}\).
Preparation of diethyl tert-butylperoxy phosphate 
\((2, R = C_2H_5)\) by the method of Rieche et al.\(^2\)

A. On the reported\(^2\) scale: Diethyl phosphoro-
chloridate (8.63 g, 0.05 mol) was added at \(-10^\circ C\) to 20 ml pyridine. Then a solution of 6.75 g (0.075 mol) tert-butyl hydroperoxide in 8 ml pyridine, which had been prepared by adding tert-butyl hydroperoxide to frozen pyridine, was added drop-
wise at \(-8\) to \(-12^\circ C\). The reaction mixture was
stirred for 5 h at 33 \(^\circ C\) and exhibited a distinct
pyrophosphate absorption in the IR spectrum. At
no time during the reaction was any pyrophosphate
detectable by IR.

B. On three-fold scale \((2, R = C_2H_5)\):
Diethyl phosphoro-
chloridate (25.9 g, 0.15 mol) was added over 8 min at \(-20\) to \(-12^\circ C\) to 60 ml pyridine. A solution of 20.25 g (0.225 mol) tert-butyl hydroperoxide in 24 ml pyridine, which had been pre-
pared by adding cold tert-butyl hydroperoxide to cold pyridine, was then added over 5 min at \(-12\) to \(-10^\circ C\). The reaction mixture was stirred at 33 \(^\circ C\) for 5 h, was diluted with 180 ml benzene, and
was filtered. The precipitate was washed on the
filter with benzene \((2 \times 45 \text{ ml})\). The combined
filtrates were washed successively with ice cold
2 N sulfuric acid \((3 \times 100 \text{ ml})\), ice cold water \((1 \times 100 \text{ ml})\), cold 5% sodium bicarbonate solution
\((1 \times 100 \text{ ml})\); and then with 100 ml ice water; were
dried \((\text{Na}_2\text{SO}_4)\); and were concentrated to a color-
less oil \((9 \text{ g})\) whose IR spectrum showed a diminished
phosporochloridate absorption. Distillation of the crude perester in 2 g portions through a short path
distillation head yielded 6.8 g (60%) diethyl tert-
butylperoxy phosphate: b.p. 83-86 \(^\circ C\) (0.3 mm), \(\nu_{\text{max}}^{\text{IR}} 1640\text{ cm}^{-1}\).

Distillation of this oil through a short path distilla-
tion head yielded 4.8 g (94%) diisopropyl tert-
butylperoxy phosphate: b.p. 83-86 \(^\circ C\) (0.3 mm), \(n^\circ_\text{D} 1.4169\). Periodic examination of the IR
spectrum of the reaction mixture did not indicate
the formation of any pyrophosphate.

Reaction of diisopropyl tert-butylperoxy phosphate
\((2, R = i-C_3H_7)\) with pyridine

A solution of 6.35 g (0.025 mol) pure diisopropyl
tert-butylperoxy phosphate and 2.4 g (0.03 mol) pyridine was stirred at ambient temperature for
72 h and was then distilled yielding 5.5 g \((87\%)\) diisopropyl tert-butylperoxy phosphate: b.p. 75-85 \(^\circ C\) (0.1 mm), \(n^\circ_\text{D} 1.4145\), which evidenced no pyrophosphate absorption in the IR spectrum. At

Preparation of diisopropyl tert-butylperoxy phosphate
\((2, R = i-C_3H_7)\) in the presence of pyridine

A. Pyridine \((4.74 \text{ g}, 0.06 \text{ mol})\) was added over 2 min at 2 \(^\circ C\) to a solution of 10.03 g (0.05 mol) disisopropyl phosphoro-
chloridate in 100 ml petroleum ether and then 4.95 g (0.055 mol) tert-butyl hydroperoxide was added at 3-5 \(^\circ C\) during 2 min. The resulting mixture was stirred at 5 \(^\circ C\) for 0.5 h and then at room temperature for 24 h and was then filtered. The filtrate was concentrated, stored at \(-10^\circ C\) overnight, and filtered again. The
filtrate was stored at \(-10^\circ C\) for 7 days and then was
filtered. Distillation of the filtrate, which exhibited a pyrophosphate absorption in the IR spectrum, through a short path distillation head yielded 4.2 g \((33\%)\) disisopropyl tert-butylperoxy phosphate: b.p. 84-86 \(^\circ C\) (0.1 mm), \(n^\circ_\text{D} 1.4135\); 2.0 g \((23\%)\) tetraisopropyl pyrophosphate: b.p. 124-126 \(^\circ C\) (0.3 mm), \(n^\circ_\text{D} 1.4145\); and 1.2 g of an intractable residue.

B. Anhydrous tert-butyl hydroperoxide \((9.9 \text{ g}, 0.11 \text{ mol})\) was added at 0-2 \(^\circ C\) to a solution of 9.5 g (0.12 mol) pyridine and 100 ml petroleum ether. Diisopropyl phosphoro-
chloridate \((20.05 \text{ g}, 0.10 \text{ mol})\) was added to the resulting solution at \(-10\) to
-13 \(^\circ C\) and the mixture was warmed to 25 \(^\circ C\) over 0.5 h, stirred at 25 \(^\circ C\) for 1 h, filtered, concen-
trated, and filtered again. The filtrate was stored at room temperature for 36 h and was then filtered. The filtrate \((21 \text{ g})\) was a straw colored oil which contained 92\% of the theoretical peroxyde content of pure peroxyester. NMR analysis indicated the crude peroxyester to contain 9 mol percent of tert-
butyl hydroperoxide and IR analysis indicated the presence of some pyrophosphate. Distillation of a
15 g portion of the crude perester yielded 5 g \((27\%)\) disisopropyl tert-butylperoxy phosphate, b.p. 82-85 \(^\circ C\) (0.4 mm) and 3 g tetraisopropyl pyrophos-
phosphate \((3, R = i-C_3H_7)\), b.p. 108-110 \(^\circ C\) (0.1 mm) which was shown by IR analysis to contain traces of diisopropyl phosphate as evidenced by the
P-OH absorption, \(\nu_{\text{max}}^{\text{IR}} = 1640\text{ cm}^{-1}\).
Preparation of diisopropyl tert-butylperoxy phosphate \((2, R = \text{t}-\text{C}_3\text{H}_7)\) in the presence of triethylamine

Tert-butyl hydroperoxide (9.9 g, 0.11 mol) was added at 8–10 °C to a solution of 11.1 g (0.11 mol) triethylamine and 100 ml ether. Diisopropyl phosphorochloridate (20.05 g, 0.1 mol) was then added at 8–10 °C. The resulting mixture was stirred at 10 °C for 30 min and then at room temperature for 2.5 h, filtered, concentrated, and filtered again. The filtrate was stored at 5 °C overnight and was again filtered. The filtrate was analyzed by IR and was found to contain the peroxyester and tert-butyl hydroperoxide. No peroxophosphate absorption, \(v_{\text{max}} = 950 \text{ cm}^{-1}\), was observed. Distillation of a portion of the crude peroxyester, b.p. 135–136 °C (0.2 mm), afforded an almost quantitative yield of tetraethyl pyrophosphate: b.p. 108–110 °C (0.2 mm), \(\alpha\beta 1.4172\).

Preparation of diisopropyl tert-butylperoxy phosphate \((2, R = \text{t}-\text{C}_3\text{H}_7)\) in the presence of pyridine and anhydrous magnesium sulfate

A solution of 4.74 g (0.06 mol) pyridine and 30 ml petroleum ether was added over 6 min at —10 to —15 °C to a solution of 10.6 g (0.05 mol) diisopropyl phosphorochloridate in 5.0 ml petroleum ether. The separatory funnel which had been used during the addition was rinsed with 25 ml petroleum ether which was then added to the reaction mixture. A solution of 4.95 g (0.055 mol) tert-butyl hydroperoxide and 25 ml petroleum ether was added over 7 min at —15 to —5 °C. The reaction mixture was stirred at 0 °C for 1 h and then at room temperature for 20 h. At this point the IR spectrum of the reaction mixture evidenced a pyrophosphate band at \(v_{\text{max}} = 950 \text{ cm}^{-1}\). The reaction mixture was filtered and concentrated to yield a mixture of diisopropyl tert-butylperoxy phosphate and tetraisopropyl pyrophosphate which was analyzed by IR.

Reaction of diethyl phosphorochloridate with tert-butyl hydroperoxide and water in the presence of pyridine to produce tetraethyl pyrophosphate \((3, R = \text{C}_3\text{H}_8)\)

A solution of 30.6 (0.34 mol) tert-butyl hydroperoxide, 3.4 g (0.19 mol) water, and 24 g (0.3 mol) pyridine was added over 20 min at —30 to —20 °C to a solution of 35 g (0.2 mol) diethyl phosphorochloridate in 100 ml petroleum ether. The mixture was warmed to room temperature over 1 h and was filtered. The filtrate was concentrated and the residual oil was dissolved in 100 ml benzene. The resulting mixture was washed with 50 ml cold water, dried (\(\text{Na}_2\text{SO}_4\)), and concentrated first at 10 mm and then overnight at 0.1 mm. The resulting oil, 23 g (79%), evidenced no peroxyester absorption in the IR, \(v_{\text{max}} = 910 \text{ cm}^{-1}\). Distillation afforded an almost quantitative yield of tetraethyl pyrophosphate: b.p. 73.1–73.4 °C (0.2 mm), \(\alpha\beta 1.4172\).

Preparation of diisopropyl tert-butylperoxy phosphate \((2, R = \text{i}-\text{C}_3\text{H}_7)\) in the presence of pyridine and tert-butyl hydroperoxide

A solution of 30.6 (0.34 mol) tert-butyl hydroperoxide was added over 6 min at —10 to —15 °C to a solution of 11.1 g (0.11 mol) diisopropyl phosphorochloridate in 5.0 ml petroleum ether. The mixture was stirred until a thick white paste had formed. The mixture was stirred at 0 °C for 1 h and then at room temperature for 20 h. At this point the IR spectrum of the reaction mixture evidenced a pyrophosphate band at \(v_{\text{max}} = 950 \text{ cm}^{-1}\). The reaction mixture was filtered and concentrated to yield a mixture of diisopropyl tert-butylperoxy phosphate and tetraisopropyl pyrophosphate which was analyzed by IR.

Reaction of tetraisopropyl pyrophosphate \((3, R = \text{i}-\text{C}_3\text{H}_7)\) with tert-butyl hydroperoxide

A solution of 17.3 g (0.05 mol) tetraisopropyl pyrophosphate and 9 g (0.1 mol) tert-butyl hydroperoxide was stirred at room temperature for 20 h. Distillation of the resulting solution yielded 8.4 g (93%) tert-butyl hydroperoxide, b.p. 73.1–73.4 °C (0.1 mm), and 15 g (87%) tetraisopropyl pyrophosphate, b.p. 124–126 °C (0.1 mm).

Preparation of diethyl tert-butylperoxy phosphate \((2, R = \text{C}_3\text{H}_8)\) in the presence of sodium tert-butyl hydroperoxide

A. tert-Butyl hydroperoxide (19.8 g, 0.22 mol) was added dropwise at room temperature to a slurry of 8.4 g (0.2 mol) sodium hydride (57% dispersion in oil) in 250 ml anhydrous ether. The mixture was stirred until a thick white paste had formed.
formed and then 100 ml ether was added. Diethyl phosphorochloridate (31.06 g, 0.18 mol) was added at 10 °C. The resulting mixture was stirred at 10 °C for 10 min and then at room temperature for 1 h. The mixture was filtered several times through diatomaceous filter aid and the filtrate was concentrated yielding a faintly yellow oil. The oil was dissolved in 50 ml absolute ethanol and the resulting solution was stored at —10 °C overnight. The layers which had formed were separated and the lower layer was centrifuged to remove the last traces of mineral oil from the peroxyester. The crude peroxyester was held on a rotary evaporator at room temperature (0.2 mm) for 16 h. This procedure yielded 28.7 g (71%) diethyl tert-butylperoxy phosphate, \( \text{W} \frac{\text{d}}{\text{f}} 1.4215 \).

Analysis: Caled for \( \text{C}_{10}\text{H}_{19}\text{O}_5\text{P} \): \( \text{MW} \), 226; Found: \( \text{MW} \), 224.

B. A similar procedure reacting 46.4 g (1.10 mol) sodium hydride from which the oil had been removed by washing with benzene, 90 g (1.0 mol) tert-butyl hydroperoxide, 172.6 g (1.0 mol) diethyl phosphorochloridate, and 1600 ml absolute ether which was stirred for 3 h at 10 °C yielded, after filtration and removal of the solvent, 170 g (75%) diethyl tert-butylperoxy phosphate, \( \text{W} \frac{\text{d}}{\text{f}} 1.4175 \).

Analysis: Caled for \( \text{C}_{10}\text{H}_{19}\text{O}_5\text{P} \): \( \text{MW} \), 226; Found: \( \text{MW} \), 228.

Preparation of di-n-propyl tert-butylperoxy phosphate (2, \( R = \text{n}-\text{C}_3\text{H}_7 \)) in the presence of sodium tert-butyl peroxide

Sodium hydride (10.52 g, 0.25 mol) (57% dispersion in oil) was washed with benzene to remove the oil and was then slurried with 400 ml absolute ether. tert-Butyl hydroperoxide (24.3 g, 0.27 mol) was added at 30 °C and the mixture was stirred at room temperature for 1 h. Di-n-propyl phosphorochloridate (46.5 g, 0.23 mol) was added at 10 °C and the mixture was stirred at 10 °C for 1 h and then overnight at room temperature. The mixture was filtered and the filtrate was centrifuged to remove the last traces of the precipitate. The clear supernatent liquid was concentrated. The residual oil was dissolved in benzene (200 ml), washed with 10% aqueous sodium bicarbonate solution (2×100 ml), then with 100 ml saturated sodium chloride solution, and was dried (\( \text{Na}_2\text{SO}_4 \)). Concentration of the solution first at 10 mm and then overnight at room temperature (0.2 mm) yielded 48 g (81%) di-n-propyl tert-butylperoxy phosphate, \( \text{W} \frac{\text{d}}{\text{f}} 1.4212 \).

Analysis: Caled for \( \text{C}_{10}\text{H}_{13}\text{O}_5\text{P} \): \( \text{MW} \), 254; Found: \( \text{MW} \), 236.

Preparation of diisopropyl tert-butylperoxy phosphate (2, \( R = \text{i-C}_3\text{H}_7 \)) in the presence of sodium tert-butyl peroxide

A. A suspension of 4.2 g (0.1 mol) sodium hydride (57% dispersion in oil) in 25 ml benzene was stirred and the solvent was removed by decantation. The solid was washed into the reaction flask with absolute ether (150 ml) and 9.9 g (0.11 mol) tert-butyl hydroperoxide was added. The mixture was stirred at ambient temperature for 1 h. An additional 50 ml ether was added to facilitate stirring of the resultant thick white paste. Diisopropyl phosphorochloridate (18.05 g, 0.09 mol) was added over 1 h at 10 °C. The reaction mixture was stirred at room temperature for 16 h and was then filtered through filter-aid. The filtrate was concentrated. Distillation of the resulting oil through a short path distillation head afforded 13.2 g (66%) diisopropyl tert-butylperoxy phosphate, b.p. 78–81 °C (0.2 mm), \( \text{W} \frac{\text{d}}{\text{f}} 1.4142 \).

Analysis: Caled for \( \text{C}_{10}\text{H}_{15}\text{O}_5\text{P} \): \( \text{MW} \), 254; Found: \( \text{MW} \), 260.

B. A similar procedure using 49.5 g (0.55 mol) tert-butyl hydroperoxide, 21.0 g (0.5 mol) sodium hydride (used without removing the oil), 800 ml ether, and 90.2 g (0.45 mol) diisopropyl phosphorochloridate, yielded, after distillation, 88 g (77%) diisopropyl tert-butylperoxy phosphate: b.p. 82–85 °C (0.3 mm), \( \text{W} \frac{\text{d}}{\text{f}} 1.4150 \).

Analysis: Caled for \( \text{C}_{10}\text{H}_{15}\text{O}_5\text{P} \): \( \text{MW} \), 254; Found: \( \text{MW} \), 244.

Preparation of diisobutyl tert-butylperoxy phosphate (2, \( R = \text{i-C}_4\text{H}_9 \)) in the presence of sodium tert-butyl peroxide

Sodium hydride (4.21 g, 0.1 mol) (57% dispersion in oil) was washed with benzene to remove the oil and was then slurried with 150 ml absolute ether. tert-Butyl hydroperoxide (8.4 g, 0.093 mol) was added at 30 °C and the mixture was stirred at 10 °C for 1 h and then overnight at room temperature. The mixture was filtered through diatomaceous filter aid and the filtrate was concentrated yielding a yellow oil. The oil was dissolved in absolute ether, washed with 10% sodium bicarbonate solution (2×100 ml), then 100 ml saturated sodium chloride solution, and with dried (\( \text{Na}_2\text{SO}_4 \)). Concentration of the resulting solution first at 10 mm and then overnight at room temperature (0.2 mm) yielded 16.5 g (65%) diisobutyl tert-butylperoxy phosphate, \( \text{W} \frac{\text{d}}{\text{f}} 1.4226 \).

Analysis: Caled for \( \text{C}_{12}\text{H}_{25}\text{O}_5\text{P} \): \( \text{MW} \), 282; Found: \( \text{MW} \), 272.

Preparation of di-n-butylperoxy phosphate (2, \( R = \text{n-C}_4\text{H}_9 \)) in the presence of sodium tert-butyl peroxide

An identical procedure involving 18.5 g (0.44 mol) sodium hydride (57% dispersion in oil), 43.2 g (0.48 mol) tert-butyl hydroperoxide, 91.4 g (0.4 mol) di-n-butyl phosphorochloridate, and 500 ml absolute ether yielded 97 g (86%) di-n-butyl tert-butylperoxy phosphate, \( \text{W} \frac{\text{d}}{\text{f}} 1.4251 \).
Analysis: Caled for C_{12}H_{27}O_5P: MW, 282; Found: MW, 295.

Preparation of dicyclohexyl tert-butylperoxy phosphate (2, \(R = \text{cyclo-C}_6\text{H}_{11}\)) in the presence of sodium tert-butyl peroxide

An identical procedure using 4.21 g (0.1 mol) sodium hydride (57\% dispersion in oil), 8.4 g (0.093 mol) tert-butyl hydroperoxide, 25.2 g (0.09 mol) dicyclohexyl phosphorochloridate, and 150 ml absolute ether yielded 18 g (60\%) dicyclohexyl tert-butylperoxy phosphate, \(n_{\text{d}}^2 1.4612.

Analysis: Caled for C_{16}H_{31}O_5P: MW, 334; Found: MW, 318.

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7 The details of our investigation of the Thermal Decomposition of Peroxyesters 2 will be presented in a forthcoming paper.


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