Reactions of t-Butyl Peresters, XVII
The Photochemical Reaction of Dialkyl t-Butylperoxy Phosphates and Alkyl t-Butylperoxy Alkylphosphonates with Cyclohexene and Cyclopentene in the Presence of Copper Ions

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t-Butylperoxy Phosphates, t-Butylperoxy Phosphonates, Copper Ion Catalysis, Triplet Sensitizers, Photochemistry

The photochemical reaction of dialkyl t-butylperoxy phosphates (1) and alkyl t-butylperoxy alkylphosphonates (2) with cyclohexene in benzene in the presence

\[
\begin{align*}
(R'O_2P(=O)OCCH_3)_2 & \rightarrow \quad (R'O_2P(=O)OCCH_3)_2 \\
& \quad \text{1} \\
& \quad \text{2}
\end{align*}
\]

of a catalytic amount of copper(I) bromide produced the corresponding phosphates (3) and phosphonates (4) in 50–70% yield. The analogous reaction of 1

\[
\begin{align*}
(R'O_2P(=O)OCCH_3)_2 & \quad \text{3} \\
& \quad \text{4} \\
& \quad \text{5}
\end{align*}
\]

(R = t-CsH5) with cyclopentene gave a 36% yield of cyclopent-1-en-3-yl di-isopropyl phosphate (3), which could not be obtained by the thermal copper ion catalyzed reaction. Benzene, benzophenone, and acetone were effective as triplet photosensitizers in the phosphorylation reaction. Typical free radical inhibitors, such as, galvinoxyl (6), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (7), and DPPH (8) retarded the photosensitized reaction. The reaction was not affected by the singlet sensitizer Eosin-Y.

In the past two decades, the photochemical reactions of peroxides of carbon have been studied to some extent [1–3]. However, very little information is available on the photochemical reactions of peroxides in the presence of metal ions undergoing redox reactions [1–4]. The photochemistry of organophosphorus peroxides is also virtually unknown. Thus, to our knowledge, the decomposition of only two compounds, diethyl t-butylperoxy phosphate (1; R = C6H5) and bis-diphenylphosphinic peroxide were studied [5, 6].

Now, we report our studies on the photochemical reactions of dialkyl t-butylperoxy phosphates (1) and alkyl t-butylperoxy alkylphosphonates (2) in the presence of copper ions. Recently, we found [7, 8] that the copper ion catalyzed thermal reactions of t-butylperoxy phosphates (1) and phosphonates (2) with cyclohexene proceed to give the cyclohex-1-en-3-yl dialkyl phosphates (3) and cyclohex-1-en-3-yl alkyl alkylphosphonates (4), respectively. It was now found that the same products can be obtained in comparable yields by the copper ion catalyzed photochemical reaction of 1 and 2 in the presence of photosensitizers, such as, benzene, acetone, and benzophenone. Thus, the photochemical reaction of 1 produced phosphates 3,

\[
\begin{align*}
(R'O_2P(=O)OCCH_3)_2 & \quad \text{3} \\
& \quad \text{CuBr/C6H5} \\
& \quad \text{h/5-10°C} \\
& \quad \text{ICl} \text{3} \text{CHOH}
\end{align*}
\]

and the photochemical reaction of 2 produced phosphonates 4 in 52 to 69% yields. In the absence of the copper ions, no phosphate (3) or phosphonates (4) was formed.

The thermal reaction is more rapid, i.e., complete within fifteen minutes, as compared to the four to five hours necessary for the photochemical reaction.
However, the photochemical reaction can be conducted under much milder conditions, i.e., at 5–10 °C, considerably lower than the elevated temperature of 80 °C which is required for the thermal reaction. The advantage of the reaction at a lower temperature is especially evident during the preparation of the thermally unstable cyclopent-1-en-3-yl di-isopropyl phosphate (5).

\[
\begin{align*}
\text{(i-C}_3\text{H}_7\text{O)}_2\text{P(O)}(\text{O})\text{CICH}_3 + 5 \rightarrow \text{CuBr/C}_6\text{H}_6 \rightarrow & \text{OP(O)(OR)}_2 \cdot (\text{CH}_3)_2\text{COH} \\
1 & \rightarrow 5
\end{align*}
\]

As it was reported [8], the attempted preparation of 5 via the thermal copper ion catalyzed phosphorylation reaction afforded only 1,3-cyclopentadiene, the decomposition product of phosphate 5, whereas 5 could be isolated and identified when prepared by the milder photochemical reaction. Although 5 could not be purified by distillation under vacuum due to extensive decomposition, the results of microanalysis and molecular weight determination of the undistilled product confirm its identity. The results of the photochemical reaction of dialkyl t-butyl phosphates (1) and alkyl t-butylperoxy alkylphosphonates (2) with cyclohexene in the presence of copper ions are shown in Tables I and II, respectively.

During the photochemical reaction, it was noted that if benzene was omitted as solvent, the reaction was retarded considerably. Thus, in cyclohexene alone, after four hours, a 30% yield of cyclohex-1-en-3-yl di-isopropyl phosphate (3; R = i-C$_3$H$_7$) was obtained and 43% of the unreacted perester 1 (R = i-C$_3$H$_7$) was recovered, and only after eight hours could no trace of the perester 1 be detected, and a 53% yield of phosphate 3 (R = i-C$_3$H$_7$) was obtained. Thus, it appeared that benzene used here as a solvent was also acting as a photosensitizer. In order to ascertain the role of benzene as a triplet sensitizer [9, 10] in the reaction, the copper ion catalyzed photochemical phosphorylation was conducted in the presence of only a ten mol percent of benzene. Under these conditions, the reaction was faster and more efficient, giving a 55% yield of phosphate 3 (R = i-C$_3$H$_7$) after eight hours.

### Table I. Photochemical preparation of cyclohex-1-en-3-yl dialkyl phosphates (3).

<table>
<thead>
<tr>
<th>R</th>
<th>Yield [%]</th>
<th>b.p. [°C/torr]</th>
<th>$n_D^2$</th>
<th>Microanalysis</th>
<th>IR [v, cm$^{-1}$]</th>
<th>$^1$H NMR [δ, ppm]$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C$_3$H$_7$</td>
<td>61</td>
<td>99–101/0.1</td>
<td>1.4537</td>
<td>262.89</td>
<td>3.4–4.2 (m, 1H)</td>
<td>5.7 (s, N-H, 2H)</td>
</tr>
<tr>
<td>n-C$_4$H$_9$</td>
<td>52</td>
<td>110–115/0.1b</td>
<td>1.4536</td>
<td>290.34</td>
<td>4.3–4.9 (m, 1H)</td>
<td>5.8 (s, s, 2H)</td>
</tr>
<tr>
<td>C$_3$H$_7$</td>
<td>53</td>
<td>90–92/0.05</td>
<td>1.4427</td>
<td>262.29</td>
<td>4.3–4.9 (m, 1H)</td>
<td>5.8 (s, s, 2H)</td>
</tr>
<tr>
<td>C$_5$H$_9$</td>
<td>69</td>
<td>90–92/0.1</td>
<td>1.4523</td>
<td>234.23</td>
<td>3.4–4.2 (m, 1H)</td>
<td>5.7 (s, s, 2H)</td>
</tr>
<tr>
<td>C$_7$H$_9$</td>
<td>52</td>
<td>110–115/0.1b</td>
<td>1.4536</td>
<td>290.34</td>
<td>4.3–4.9 (m, 1H)</td>
<td>5.8 (s, s, 2H)</td>
</tr>
</tbody>
</table>

$^a$ Mol. wt. found. $^b$ Kugelrohr distillation. $^c$ The integrations were in accordance with the expected structures. The three band P–H coupling constants were virtually identical to the vicinal H–H coupling constants leading in some cases to simple first order multiplet structures.
Table II. Photochemical preparation of cyclohex-1-en-3-yl alkyl alkylphosphonates (4).

<table>
<thead>
<tr>
<th>R</th>
<th>R¹</th>
<th>Yield [%]</th>
<th>b.p. [°C/torr]</th>
<th>ν&lt;sup&gt;®&lt;/sup&gt;</th>
<th>Microanalysis</th>
<th>IR [ν, cm&lt;sup&gt;-1&lt;/sup&gt;]</th>
<th>&lt;sup&gt;1&lt;/sup&gt;H NMR [δ, ppm]&lt;sup&gt;c&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>56</td>
<td>87–89/0.05</td>
<td>1.4625</td>
<td>Found C 55.10, H 8.43</td>
<td>P = O (1250–1280)</td>
<td>3.8–4.4 (m, 6 H)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.6–2.2 (m, 6 H)</td>
<td>4.7–5.0 (m, 1 H)</td>
</tr>
<tr>
<td>i-C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>55</td>
<td>90–92/0.1</td>
<td>1.4600</td>
<td>Found C 54.89, H 9.02</td>
<td>P = O (1240–1270)</td>
<td>5.8 (s, b, 2 H)</td>
</tr>
<tr>
<td>n-C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;9&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>52</td>
<td>110–115/0.1&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.4539</td>
<td>Found C 56.88, H 8.99</td>
<td>P = O (1240–1260)</td>
<td>4.7–5.2 (m, 2 H)</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>55</td>
<td>90–92/0.1</td>
<td>1.4588</td>
<td>Found C 55.15, H 9.01</td>
<td>P = O (1240–1260)</td>
<td>5.7 (s, b, 2 H)</td>
</tr>
<tr>
<td>i-C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;7&lt;/sub&gt;</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>51</td>
<td>93–95/0.1</td>
<td>1.4508</td>
<td>Found C 56.93, H 9.13</td>
<td>P = O (1240–1260)</td>
<td>4.3–5.0 (m, 2 H)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Kugelrohr distillation. <sup>b</sup> Mol. wt. found. <sup>c</sup> The integrations were in accordance with the expected structures. The three band P–H coupling constants were virtually identical to the vicinal H–H coupling constants leading in some cases to simple first order multiplet structures.
Table III. Photochemical reaction of di-isopropyl t-butyperoxy phosphate (1, R = i-C₃H₇) with cyclohexene in the presence of copper(I) bromide and photosensitizer.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.010</td>
<td>none</td>
<td>4</td>
<td>3</td>
<td>30</td>
<td>92-94/0.05</td>
<td>1.4430</td>
</tr>
<tr>
<td>50</td>
<td>0.010</td>
<td>none</td>
<td>8</td>
<td>5</td>
<td>53</td>
<td>88-90/0.1</td>
<td>1.4427</td>
</tr>
<tr>
<td>50</td>
<td>0.010</td>
<td>benzene</td>
<td>0.0010</td>
<td>4</td>
<td>53</td>
<td>88-90/0.05</td>
<td>1.4430</td>
</tr>
<tr>
<td>50</td>
<td>0.010</td>
<td>benzophenone</td>
<td>0.0010</td>
<td>41/2</td>
<td>66</td>
<td>88-91/0.1</td>
<td>1.4424</td>
</tr>
<tr>
<td>50</td>
<td>0.010</td>
<td>acetone</td>
<td>0.0010</td>
<td>5</td>
<td>58</td>
<td>92-93/0.1</td>
<td>1.4421</td>
</tr>
<tr>
<td>50</td>
<td>0.010</td>
<td>Eosin-Y</td>
<td>0.0010</td>
<td>8</td>
<td>60</td>
<td>92-95/0.1</td>
<td>1.4430</td>
</tr>
</tbody>
</table>

a Reaction was terminated after 4 h. Unreacted perester 1 (52%) was determined by titration [8, 12].
b Perester 1 was recovered in 43% yield.
c In the presence of 18-Crown-6 (0.0031 mol) to solubilize Eosin-Y [14].

benzene and other triplet sensitizers, such as, acetone and benzophenone. In all cases, the reaction was accelerated by these additives. However, no effect was observed by the addition of the singlet sensitizer, Eosin-Y [9, 10, 14] (Table III).

Since the photosensitized reaction seems to proceed through radical-type intermediates, it was expected that the reaction would be inhibited by typical radical scavengers, such as, 2,6-di-t-butyl-α(3,5-di-t-butyl-4-oxo-2,5-cyclohexadiene-1-ylidene)-p-tolylmethoxy (galvinoxyl, 6), 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (7), and 2,2-diphenyl-1-picryl hydrazyl (DPPH, 8).

Indeed, it was found that the addition of a ten mol percent of any one of these inhibitors to a mixture of the perester 1 (R = i-C₃H₇), cyclohexene, copper ions, and benzophenone effectively retarded the photochemical reaction. On the basis of these results, it can be assumed that the mechanism of the copper ion catalyzed photophosphorylation reaction is analogous to that of the photochemical reaction of peroxyesters of carbon [2, 3], and that the main steps probably involve species proposed for the thermal reaction [8]. However, the finer delineation of the individual steps seems to be very complex, and beyond the scope of the present work.

**Experimental**

*Photochemical apparatus:* All photochemical experiments were performed in a cylindrical water-jacketed reaction vessel made entirely of quartz glass. The reaction vessel was fitted with a magnetic stirrer, immersion thermometer, condenser, and nitrogen inlet. The vessel was placed in a Rayonet® Srinivasan-Griffin photochemical reactor equipped with sixteen ultraviolet lamps, which completely surrounded the reactor, emitting radiation at 2537 Å. The reaction vessel was placed approximately 10 cm from the lamps.

*Materials:* Cyclohexene and cyclopentene were distilled from sodium. The benzene used as solvent and photosensitizer was distilled from and stored over sodium. Nitrogen was dried by passing it through a tube filled with calcium chloride. Aluminum oxide (activity 4 according to Brockmann. 100-200 mesh) was obtained from Mallinckrodt, Inc. All other reagents were of the best grade commercially available. Peroxy phosphates (1) and peroxy phosphonates (2) were prepared by a known method [11].

*Analytical procedures:* A Varian Aerograph 1700 thermal conductivity gas chromatograph equipped with a 20% Carbowax 20M on Chromasorb P (20 ft by 3/8 in) column was used for all G.L.C. procedures. The following conditions were maintained: column temperature 82 °C, injector temperature 175 °C, detector temperature 210 °C, bridge current 150 ma, flow rate 50 ml He/min. Identification of products was made by peak enhancement ("spiking") with authentic samples. Infrared spectra were obtained on a Perkin Elmer Infrared Spectrophotometer, Model 137. NMR spectra were obtained on a Varian T-60 spectrometer, using TMS as the internal standard. Molecular weight analyses were performed isopiestically in benzene on a Hitachi Perkin-Elmer Model 115 Molecular Weight Apparatus.
lysation were performed on a F&M Scientific Corporation Carbon, Hydrogen, Nitrogen Analyzer, Model 185. All melting points and boiling points are uncorrected. Distillations of phosphates (3) and phosphonates (4) were performed repeatedly until a constant refractive index was obtained. The progress of the photochemical phosphorylation reactions was followed by titration [8, 12].

Photochemical reaction of dialkyl \(\text{t-butylperoxy phosphates (1)}\) with cyclohexene in the presence of copper(1) bromide

General procedure A. The reaction vessel was purged with nitrogen for 5 min. Cyclohexene (4.1 g, 0.050 mol), copper(I) bromide (0.1 g), and benzene (50 ml) were then introduced. Purring with nitrogen was continued for an additional 5 min, then the dialkyl \(\text{t-butylperoxy phosphate (1)}\) (0.010 mol) was added in one portion. The stirred reaction mixture was irradiated at 5–10 °C under a slight flow of nitrogen for 4 h. The solvent and excess of cyclohexene were removed on a rotating evaporator at 25–30 °C/12 torr. Benzene (30–40 ml) was added to the concentrate, and the resulting solution was passed through 2.5 cm \(\times\) 2–3 cm packing of aluminum oxide. The aluminum oxide was washed with benzene (10–15 ml) and the combined eluates were concentrated on a rotating evaporator at 25–30 °C/12 torr. The remaining liquid was distilled using a Kugelrohr apparatus to give the cyclohex-1-en-3-yl dialkyl phosphates (3) shown in Table I.

Photochemical reaction of alkyl \(\text{t-butylperoxy alkylphosphonates (2)}\) with cyclohexene in the presence of copper(1) bromide

As described in the general procedure A, alkyl \(\text{t-butylperoxy alkylphosphonates (2)}\) (0.010 mol) were reacted with cyclohexene (4.1 g, 0.050 mol) in benzene (50 ml) in the presence of copper(I) bromide (0.1 g) to give cyclohex-1-en-3-yl alkyl alkylphosphonates (4) shown in Table II.

Photochemical reaction of di-isopropyl \(\text{t-butylperoxy phosphate (1, R = \text{i-C}_3\text{H}_7)}\) with cyclohexene in the presence of copper(1) bromide

As described in the general procedure A, a solution of di-isopropyl \(\text{t-butylperoxy phosphate (1, R = \text{i-C}_3\text{H}_7; 2.54 g, 0.010 mol)}\), cyclopentene (3.40 g, 0.050 mol), benzene (50 ml), and copper(I) bromide (0.1 g) was irradiated at 5–10 °C for 4 h. The solvent and other low boiling materials were removed by distillation below 20 °C/0.1 torr through a short unpacked column, and collected in several traps cooled with dry ice-acetone baths. The distillate consisted of a mixture of cyclopentene, \(t\)-butanol, and benzene as determined by G.L.C. The residue from the distillation was combined with benzene (5 ml), and the solution was passed through a 2.5 \(\times\) 10 cm packing of aluminum oxide. The aluminum oxide was washed with benzene (25–30 ml) and the combined eluates were concentrated on a rotating evaporator at 25–30 °C/12 torr to give cyclopent-1-en-3-yl di-isopropyl phosphinate (5; 0.45 g, 36%), \(n_H^*\) 1.4661.

Analysis for \(\text{C}_{11}\text{H}_{21}\text{O}_4\text{P}\)

Calcd C 53.22 H 8.53 mol wt: 248.36, Found C 52.71 H 7.92 mol wt: 236.

Photochemical reaction of di-isopropyl \(\text{t-butylperoxy phosphate (1, R = \text{i-C}_3\text{H}_7)}\) with cyclohexene in the presence of copper(1) bromide. A four hour reaction

As described in the general procedure A, a solution of di-isopropyl \(\text{t-butylperoxy phosphate (1, R = \text{i-C}_3\text{H}_7; 2.54 g, 0.010 mol)}\) in cyclohexene (50 ml) in the presence of copper(I) bromide (0.1 g) was irradiated at 5–10 °C. After 4 h, titration indicated 52% of peroxyphosphate (1, R = \text{i-C}_3\text{H}_7) still to be present. Following the workup as described in the general procedure A and distillation using a short path distillation head, there was obtained di-isopropyl \(\text{t-butylperoxy phosphate (1, R = \text{i-C}_3\text{H}_7; 2.54 g, 0.010 mol)}\).
Table IV. Photochemical reaction of di-isopropyl t-butylperoxy phosphate (1, \( R = i-C_3H_7 \)) with cyclohexene in the presence of copper(1) bromide, benzophenone as photosensitizer, and radical inhibitors.

<table>
<thead>
<tr>
<th>Cyclohexene [ml]</th>
<th>Benzophenone [mol]</th>
<th>Inhibitor</th>
<th>Inhibitor [mol]</th>
<th>Reaction time [h]</th>
<th>Perester consumed(^a) [%]</th>
<th>Recovered 1 [%]</th>
<th>Yield 3 [%]</th>
<th>b.p. [°C/0.05 torr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.0010</td>
<td>galvinoxyl</td>
<td>0.0010</td>
<td>7</td>
<td>62</td>
<td>31</td>
<td>38</td>
<td>88-90/0.05</td>
</tr>
<tr>
<td>50</td>
<td>0.0010</td>
<td>ROH(b)</td>
<td>0.0010</td>
<td>11</td>
<td>75</td>
<td>16</td>
<td>19</td>
<td>89-91/0.1</td>
</tr>
<tr>
<td>50</td>
<td>0.0010</td>
<td>DPPH</td>
<td>0.0010</td>
<td>11</td>
<td>57</td>
<td>16</td>
<td>23</td>
<td>90-92/0.05</td>
</tr>
</tbody>
</table>

\( ^a \) Determined by titration.

\( ^b \) ROH = 7

1.10 g, 43% recovery b.p. 63-66 °C/0.05 torr; \( n_\text{D}^\circ \) 1.4143, lit\(^3\) b.p. 64-67 °C/0.1 torr; \( n_\text{D}^\circ \) 1.4148, and cyclohex-1-en-3-yl di-isopropyl phosphate (3, \( R = i-C_3H_7; 0.80 \text{ g}, 30\% \)), b.p. 81-83 °C/0.05 torr.

**Analysis for \( C_{12}H_{23}O_4P \)**

Calcd C 54.95 H 8.84 molwt: 262.29, Found C 55.15 H 8.93 molwt: 250.

Photochemical reaction of di-isopropyl t-butylperoxy phosphate (1, \( R = i-C_3H_7 \)) with cyclohexene in the presence of benzophenone as photosensitizer, copper(1) bromide, and a radical inhibitor

As described in the general procedure A, a solution of di-isopropyl t-butylperoxy phosphate (1, \( R = i-C_3H_7; 2.54 \text{ g}, 0.010 \text{ mol} \)) in cyclohexene (50 ml) in the presence of benzophenone (0.1 g) and a radical inhibitor (0.001 mol, 10 mol percent) was irradiated at 5-10 °C for 4-8 h. After the workup as described in the general procedure A, and distillation using a Kugelrohr apparatus, there was obtained cyclohex-1-en-3-yl di-isopropyl phosphate (3, \( R = i-C_3H_7 \)) in the yields shown in Table III.

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