

gel, 10% ethyl acetate-hexane, 1400 psi, 60 × 13 mm column), and this mixture was used to obtain the <sup>13</sup>C NMR of 11.

**Preparation of Epoxides 12 and 13.** Compound 12, an oil, was prepared from the reaction of 2-methyl-4-*tert*-butylcyclohexanone<sup>18</sup> and 5<sup>7</sup> in 35% yield after flash chromatography<sup>19</sup> with 1% ethyl acetate-hexane. Anal. Calcd for C<sub>12</sub>H<sub>22</sub>O: 76.06; H, 12.16. Found: C, 78.82; H, 12.30. Compounds 12 and 13 were obtained as a mixture in 85% yield from the reaction of 2-methyl-4-*tert*-butylcyclohexanone with 7.<sup>7</sup> A ca. 2:1 mixture of 13 and 12 was obtained by flash chromatography with 0.75% ethyl acetate-hexane. Anal. Calcd for C<sub>12</sub>H<sub>22</sub>O: C, 79.06; H, 12.16. Found: C, 78.97; H, 12.07.

**Preparation of Oxazolidinones 16 and 17.** Compound 16 (mp 207–208 °C) was prepared in 50% yield starting with 10 and using the same procedure as outlined for 14. Anal. Calcd for C<sub>12</sub>H<sub>21</sub>NO<sub>2</sub>: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.42; H, 10.12; N, 6.44. Compounds 16 and 17 were obtained in 24% yield by starting with epoxide mixture 10/11 and using the same procedure outlined for 14. The mixture (mp 138–145 °C) resisted attempted separation by preparative chromatography, and it was judged to be a ca. 3:1 ratio of 17/16 by proton NMR (CDCl<sub>3</sub>), which showed CH<sub>2</sub>N at δ 3.27 for 16 and at δ 3.37 for 17. Anal. Calcd for C<sub>12</sub>H<sub>21</sub>NO<sub>2</sub>: C, 68.21; H, 10.02; N, 6.63. Found: C, 67.98; H, 10.28; N, 6.65.

**Acknowledgment.** We thank Joan M. Caroon for technical assistance.

**Registry No.** 3a, 83946-21-8; 3b, 83946-22-9; 4, 841-95-2; 6, 83917-83-3; 8, 83917-84-4; 9, 47136-76-5; 10, 7787-78-2; 11, 18881-26-0; 12, 53730-20-4; 13, 53698-73-0; 14, 83917-85-5; 15, 83917-86-6; 16, 83917-87-7; 17, 83917-88-8; trimethylxosulfonium iodide, 1774-47-6; trimethylsulfonium iodide, 2181-42-2; *N,N'*-carbonyldiimidazole, 530-62-1; 4-*tert*-butylcyclohexanone, 98-53-3; 2-methyl-4-*tert*-butylcyclohexanone, 5064-52-8.

(18) Conia, J.-M.; Briet, P. *Bull. Soc. Chim. Fr.* 1966, 3881.

(19) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* 1978, 43, 2923.

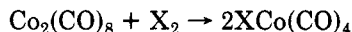
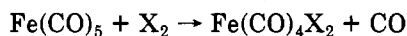
## Reaction of Alkyl Peroxides and Hydroperoxides with Iron Pentacarbonyl and Dicobalt Octacarbonyl<sup>1</sup>

Kang-Wook Lee and Joseph San Filippo, Jr.\*

Rutgers University, Department of Chemistry,  
New Brunswick, New Jersey 08903

Received April 29, 1982

Many substrates that contain simple homonuclear bonds undergo facile oxidative addition reaction with low- or zero-valent transition-metal complexes. Such reactions



are generally cited for simple diatomic systems, e.g., the halogens, oxygen, and hydrogen.<sup>2</sup> In an effort to determine if such activity is extendible to simple homonuclear bonds in general, we have examined the reactions of several organic peroxides with iron pentacarbonyl and dicobalt octacarbonyl. Here we report the results of this study and describe the products of several representative reactions.

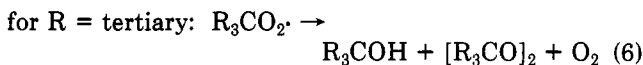
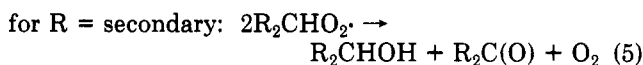
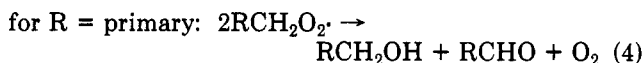
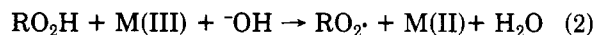
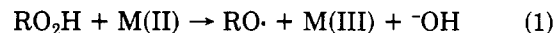
### Results and Discussion

Di-*tert*-butyl peroxide exhibits no apparent reaction with either iron pentacarbonyl or dicobalt octacarbonyl

in benzene after 1 week at ambient temperature. Similar treatment of di-*sec*-butyl peroxide results in a slow but steady reaction with a half-life of ca. 3 days. By comparison, the corresponding reaction with di-*n*-hexyl peroxide shows a half-life of ca. 3 h, leading to a reactivity order of primary > secondary > tertiary. These results are summarized in Table I.

In contrast to alkyl peroxides, alkyl hydroperoxides exhibit a much enhanced reactivity toward both iron pentacarbonyl and dicobalt octacarbonyl. Reaction with these substrates is accompanied by the immediate, vigorous evolution of carbon monoxide. The resulting product mixtures are presented in Table II. Briefly summarized, they reveal the following. First, essentially equivalent product ratios are obtained with either Fe(CO)<sub>5</sub> or Co<sub>2</sub>(CO)<sub>8</sub>. Thus, the 1:5 reaction of Fe(CO)<sub>5</sub> or Co<sub>2</sub>(CO)<sub>8</sub> with *tert*-butyl hydroperoxide produces an ~76–90% yield of *tert*-butyl alcohol, an ~3% yield of di-*tert*-butyl peroxide, and <1% acetone. The equivalent reactions with *sec*-butyl hydroperoxide results in an ~65% yield of *sec*-butyl alcohol, an ~20% yield of 2-butanone, and <1% di-*sec*-butyl peroxide while the reaction with *n*-hexyl hydroperoxide leads to the following product mixture: ~50% *n*-hexanol, ~30% *n*-hexanal, and <1% di-*n*-hexyl peroxide. Second, these product ratios remain largely unaffected by gross variations (1:1, 5:1, 10:1, 50:1) in reactant ratios.

A detailed examination of the mechanisms leading to these products has not been carried out. However, a comparison between these products and those observed from the cobalt(II)- and iron(II)-catalyzed homolytic decomposition of hydroperoxides (Table III) is informative. Indeed, the strong similarity in product distributions suggests that similar processes are involved. Thus, the variety of products formed in these reactions can be rationalized in terms of a scheme (eq 1–6) first proposed by



Hiatt.<sup>3</sup> This conclusion is sustained by the coproduction of several solvent-derived products. Thus, reaction of *tert*-butyl hydroperoxide with dicobalt octacarbonyl in *n*-heptane yields small amounts (~1–3%) of each of the following solvent-derived products: 4-heptanol and 2-, 3-, and 4-heptanones, as well as the unsymmetrical peroxide *t*-C<sub>4</sub>H<sub>9</sub>OOC<sub>7</sub>H<sub>15</sub>.

In summary, the reaction of iron pentacarbonyl and dicobalt octacarbonyl with organic peroxides falls into two distinct classes: the limited reactivity characteristic of dialkyl peroxides and the very substantial reactivity exhibited by alkyl hydroperoxides. Since the O–O bond strength is essentially the same in either substrate, the dramatic difference in their reactivities suggests that different rate-determining steps are involved. Although an oxidative addition is clearly indicated, its nature is not readily apparent and may, in fact, be a relatively minor

(1) Supported by the National Science Foundation (Grant 80-17045) and by DOE Contract DE-AS05-80-ER-1062.

(2) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Wiley-Interscience: New York, 1972; Chapter 24.

(3) Hiatt, R.; Irwin, K. C.; Gould, C. W. *J. Org. Chem.* 1968, 33, 1430.

Table I. Reaction of Di-*n*-hexyl, Di-*sec*-butyl, and Di-*tert*-butyl Peroxides with Iron Pentacarbonyl and Dicobalt Octacarbonyl<sup>a</sup>

metal carbonyl <sup>c</sup>	ROOR <sup>d</sup>	reaction time, h	products, <sup>b</sup> %			
			alcohol	aldehyde	ketone	recovd ROOR
Co <sub>2</sub> (CO) <sub>8</sub>	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	1.5	17	27		56
		3	24	12		35
		18	35	12		27
Co <sub>2</sub> (CO) <sub>8</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	6	6		3	82
		12	10		5	77
		24	15		7	72
		72	19		10	54
Co <sub>2</sub> (CO) <sub>8</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	168	~1		<1	98
Fe(CO) <sub>5</sub>	<i>n</i> -C <sub>6</sub> H <sub>13</sub>	24	44	36		10
		72	46	34		<1
Fe(CO) <sub>5</sub>	<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	24	13		11	70
Fe(CO) <sub>5</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	72	<1		0	99

<sup>a</sup> All reactions were carried out in benzene solvent at 25 °C. <sup>b</sup> Determined by HPLC. <sup>c</sup> In a 0.1 M concentration. <sup>d</sup> In a 1.0 M concentration.

Table II. Reaction of Iron Pentacarbonyl and Dicobalt Octacarbonyl with Selected Alkyl Hydroperoxides<sup>a</sup>

metal carbonyl (concn, M)	ROOH (concn, M)	reaction time, h	products, <sup>b</sup> %				
			alcohol	aldehyde	ketone	ROOR	recovd ROOH
Co <sub>2</sub> (CO) <sub>8</sub> (0.2)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> (1.0)	0.5	50	32		<1	<1
Co <sub>2</sub> (CO) <sub>8</sub> (0.1)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> (1.0)	0.5	61	34		<1	<1
Co <sub>2</sub> (CO) <sub>8</sub> (0.05)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> (1.0)	0.5	48	40		<1	<1
Co <sub>2</sub> (CO) <sub>8</sub> (0.02)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> (1.0)	0.5	44	35		<1	10
Co <sub>2</sub> (CO) <sub>8</sub> (0.2)	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	0.5	66		21	<1	<1
Co <sub>2</sub> (CO) <sub>8</sub> (0.1)	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	0.5	63		25	<1	<1
Co <sub>2</sub> (CO) <sub>8</sub> (0.05)	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	0.5	61		33	<1	<1
Co <sub>2</sub> (CO) <sub>8</sub> (0.02)	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	0.5	37		23	<1	18
Co <sub>2</sub> (CO) <sub>8</sub> (0.2)	<i>t</i> -C <sub>4</sub> H <sub>9</sub> (0.2)	0.5	81		<1	<1	<1
Co <sub>2</sub> (CO) <sub>8</sub> (0.2)	<i>t</i> -C <sub>4</sub> H <sub>9</sub> (0.4)	0.5	77		1	<1	<1
Co <sub>2</sub> (CO) <sub>8</sub> (0.2)	<i>t</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	0.5	76		2	3	<1
Co <sub>2</sub> (CO) <sub>8</sub> (0.1)	<i>t</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	0.5	84		2	5	<1
Co <sub>2</sub> (CO) <sub>8</sub> (0.05)	<i>t</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	0.5	84		4	7	<1
Co <sub>2</sub> (CO) <sub>8</sub> (0.02)	<i>t</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	0.5	88		2	10	<1
Fe(CO) <sub>5</sub> (0.2)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> (1.0)	1.0	25			<1	32
Fe(CO) <sub>5</sub> (0.2)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> (1.0)	3.0	26	37		<1	32
Fe(CO) <sub>5</sub> (0.1)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> (1.0)	1.0	11	17		<1	70
Fe(CO) <sub>5</sub> (0.05)	<i>n</i> -C <sub>6</sub> H <sub>13</sub> (1.0)	0.5	6	9		<1	84
Fe(CO) <sub>5</sub> (0.2)	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	1.0	70		20	<1	10
Fe(CO) <sub>5</sub> (0.1)	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	1.5	25		8	<1	66
Fe(CO) <sub>5</sub> (0.1)	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	3.0	26		8	<1	63
Fe(CO) <sub>5</sub> (0.1)	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	18	29		11	<1	60
Fe(CO) <sub>5</sub> (0.05)	<i>sec</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	18	30		9	<1	61
Fe(CO) <sub>5</sub> (0.2)	<i>t</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	1	90		<1	3	4
Fe(CO) <sub>5</sub> (0.1)	<i>t</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	3	84		<1	5	6
Fe(CO) <sub>5</sub> (0.05)	<i>t</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	12	52		<1	2	44
Fe(CO) <sub>5</sub> (0.05)	<i>t</i> -C <sub>4</sub> H <sub>9</sub> (1.0)	48	55		<1	3	35

<sup>a</sup> All reactions were carried out in benzene at 6–8 °C. <sup>b</sup> Determined by HPLC.

Table III. Summary of Reported Product Distributions from Selected Metal Iron- and Cobalt-Catalyzed Decomposition of Alkyl Hydroperoxides<sup>a</sup>

M <sup>n+</sup> (concn, mM)	ROOH (concn, M)	solvent (temp, °C)	products % yield
Co <sup>3+</sup> (26)	<i>t</i> -C <sub>4</sub> H <sub>9</sub> (0.1)	C <sub>6</sub> H <sub>5</sub> Cl (25)	ROH (87), (CH <sub>3</sub> ) <sub>2</sub> C(O) (<1)
Fe <sup>2+</sup> (4.7)	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> Cl (25)	ROH (86), (CH <sub>3</sub> ) <sub>2</sub> C(O) (<1), ROOR (12)
Co <sup>2+</sup> (25)	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>5</sub> H <sub>12</sub> (37)	ROH (67), C <sub>2</sub> H <sub>5</sub> CHO (33)
Co <sup>2+</sup> (25)	<i>sec</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>5</sub> H <sub>12</sub> (37)	ROH (61), C <sub>2</sub> H <sub>5</sub> C(O)CH <sub>3</sub> (36), ROOR (3)
Co <sup>2+</sup> (6)	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>n</i> -C <sub>5</sub> H <sub>12</sub> (37)	ROH (91), (CH <sub>3</sub> ) <sub>2</sub> C(O) (<1), ROOR (8) <sup>b</sup>
[MoO <sub>2</sub> ] <sup>2+</sup>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> Cl	ROH (27), (CH <sub>3</sub> ) <sub>2</sub> C(O) (<1), ROOH (83)
[VO] <sup>2+</sup>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> Cl	ROH (44), (CH <sub>3</sub> ) <sub>2</sub> C(O) (<1), ROOH (56)

<sup>a</sup> Taken from ref 3. <sup>b</sup> Product distribution in these reactions can apparently be significantly affected by the introduction of protic solvent. For example, the equivalent catalytic reduction of *tert*-butyl hydroperoxide by Fe<sup>2+</sup> in water produces a 52–45% yield of *t*-C<sub>4</sub>H<sub>9</sub>OH and a 48–55% yield of acetone (cf. ref 8).

pathway serving to initiate an alternative process, the mechanism of which has not been established in any detail but which product distributions suggest involves metal-catalyzed, homolytic decomposition.

### Experimental Section

**General Methods.** All reactions were performed in duplicate under a static head of prepurified nitrogen. Benzene was distilled from sodium benzophenone ketyl. Dicobalt octacarbonyl (Alfa

Inorganica) was recrystallized from hexane. Iron pentacarbonyl (Pressure Chemicals) was distilled under nitrogen in the dark. *tert*-Butyl peroxide and hydroperoxide were commercial samples that were purified according to literature procedures.<sup>4</sup> Di-*n*-hexyl peroxide [bp 65 °C (0.23 torr); lit.<sup>5</sup> bp 58 °C (0.5 torr)], di-*sec*-butyl peroxide [bp 43 °C (18 torr); lit.<sup>6</sup> bp 59 °C (50 torr)], *n*-hexyl hydroperoxide [bp 47 °C (2.3 torr); lit.<sup>7</sup> bp 42 °C (2 torr)], and *sec*-butyl hydroperoxide [bp 45 °C (11 torr); lit.<sup>8</sup> bp 41 °C (11 torr)] were all prepared by following literature procedures.

<sup>1</sup>H NMR spectra were recorded on a Varian T-60 spectrometer, and GLC analyses were performed on a Varian Model 90P instrument equipped with a thermal-conductivity detector and a Hewlett-Packard Model 3380A electronic integrator. Unexceptional internal standard techniques were employed for quantitation. HPLC assays were carried out on a Waters Associates Model 6000A instrument equipped with a refractive index detector. Capillary GC/MS was carried out on a Hewlett-Packard Model 5985B instrument employing 50 m × 0.25 mm fused silica columns of Carbowax 20M or methylsilicone.

**Typical Reactions between Alkyl Peroxides and Hydroperoxides and Dicobalt Octacarbonyl and Iron Pentacarbonyl.** In an inert-atmosphere drybox dicobalt octacarbonyl (0.342 g, 1.00 mmol) was placed in a 40-mL centrifuge tube equipped with a Teflon-coated stirrer bar. The vessel was capped with a rubber septum and removed to the bench top. Benzene (5 mL) was added by syringe and the vessel cooled in a temperature bath to 6–8 °C. To this solution was subsequently added by syringe, slowly and with vigorous stirring, a solution of *n*-hexyl hydroperoxide (0.591 g, 5.00 mmol) in benzene (5 mL). After an appropriate time (see Table II), the resulting mixture was filtered under nitrogen and analyzed by HPLC on a  $\mu$ -Bondapak C<sub>18</sub> column by using methanol–water (30:70).

**Reaction of Iron Pentacarbonyl with *sec*-Butyl Hydroperoxide.** A solution of *sec*-butyl hydroperoxide (451 mg, 5.00 mmol) in benzene (5 mL) was injected into a 40-mL centrifuge tube equipped with a Teflon-coated stirrer bar and capped with a rubber septum. The vessel was cooled (6–8 °C) before a solution of iron pentacarbonyl (196 mg, 1.00 mmol) in benzene was slowly added, accompanied by vigorous stirring. After a predetermined time, the contents of the vessel were filtered under nitrogen, and the product mixture was analyzed by HPLC on a  $\mu$ -Bondapak C<sub>18</sub> column by using a methanol–water (30:70) eluent.

**Reaction of *tert*-Butyl Hydroperoxide with Dicobalt Octacarbonyl in *n*-Heptane.** To a vigorously stirred solution of dicobalt octacarbonyl (0.171 g, 0.500 mmol) in olefin-free *n*-heptane (5 mL) at 0 °C was added by syringe a solution of *tert*-butyl hydroperoxide (0.901 g, 10.0 mmol) in *n*-heptane. After 1 h the mixture was filtered under nitrogen. Analysis of the resulting solution by GC/MS revealed the presence of a number of solvent-derived products, e.g., 2-heptanone, 4-heptanol, 3-heptanone, and 4-heptanone, identified by a comparison of their respective mass spectra to literature spectra. In addition, an unknown compound with the empirical formula C<sub>11</sub>H<sub>24</sub>O<sub>2</sub> was observed. On the basis of its characteristic mass spectrum [*m/e* (relative intensity) 189 (M + 1, 0.2), 188 (M<sup>+</sup>, 1.7), 131 (0.1), 115 (0.3), 99 (0.2), 98 (9.2), 73 (5.0), 57 (100), 43 (24)], this material is tentatively formulated as the unsymmetrical peroxide *t*-C<sub>4</sub>H<sub>9</sub>OOC<sub>7</sub>H<sub>15</sub>.

**Acknowledgment.** We thank Dr. Robert H. Schwartz, who carried out some of the preliminary experiments described in this work.

**Registry No.** Di-*n*-hexyl peroxide, 3903-89-7; di-*sec*-butyl peroxide, 4715-28-0; di-*tert*-butyl peroxide, 110-05-4; *n*-hexyl hydroperoxide, 4312-76-9; *sec*-butyl hydroperoxide, 13020-06-9; *tert*-butyl hydroperoxide, 75-91-2; Fe(CO)<sub>5</sub>, 13463-40-6; Co<sub>2</sub>(CO)<sub>8</sub>, 10210-68-1.

(4) Bartlett, P. D.; McBride, J. M. *J. Am. Chem. Soc.* 1965, 87, 1727.  
(5) Williams, H. R.; Mosher, H. S. *J. Am. Chem. Soc.* 1954, 76, 2984, 2987.

(6) Welch, F.; Williams, H. R.; Mosher, H. S. *J. Am. Chem. Soc.* 1955, 77, 551.

(7) Cookson, P. G.; Davies, A. G.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* 1976, 1022.

(8) Kochi, J. K. *J. Am. Chem. Soc.* 1962, 84, 1193.

## Thermolysis of Dioxetanes: Activation Parameters for *cis*-/*trans*-3,4-Dialkyl-1,2-dioxetanes

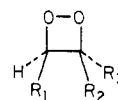
Alfons L. Baumstark,\*<sup>1</sup> Tandra Dunams, Peter C. Roskamp, and Catherine E. Wilson

Laboratory for MBS, Department of Chemistry, Georgia State University, Atlanta, Georgia 30303

Received July 7, 1982

The thermal decomposition of alkyl-substituted 1,2-dioxetanes has been shown<sup>2</sup> to produce two carbonyl fragments, one of which may be produced in an excited state (high yields of excited triplets). Historically, two mechanistic extremes have been proposed<sup>2</sup> to describe the thermal decomposition of alkyldioxetanes:<sup>3</sup> (a) diradical and (b) concerted (Scheme I).

Evidence has accumulated in favor of a diradical mechanism. Group additivity calculations have been employed<sup>4</sup> to predict activation parameters based on the thermochemistry of the dioxetane and the postulated diradical intermediate. Experimental results (lack of solvent effect,<sup>5</sup> insensitivity of  $E_a$  to phenyl for methyl substitution,<sup>6</sup> lack of deuterium isotope effect,<sup>7</sup> lack of additional ring-strain effect<sup>8</sup> on  $E_a$ ) have been interpreted to be consistent with a diradical-like mechanism. Recent results<sup>9</sup> have shown that substituent effects influence the activation parameters of the thermolysis of alkyldioxetanes in unexpected ways. Despite the considerable interest in substituent effects on dioxetane activation parameters, there has been no characterization of *cis*/*trans* pairs of dioxetanes (although several pairs have been synthesized).<sup>2,10</sup> We report the characterization of three pairs of *cis*-/*trans*-3,4-dialkyl-1,2-dioxetanes (1–6).



- 1, R<sub>1</sub> = Et; R<sub>2</sub> = Et; R<sub>3</sub> = H
- 2, R<sub>1</sub> = Et; R<sub>2</sub> = H; R<sub>3</sub> = Et
- 3, R<sub>1</sub> = *n*-propyl; R<sub>2</sub> = *n*-propyl; R<sub>3</sub> = H
- 4, R<sub>1</sub> = *n*-propyl; R<sub>2</sub> = H; R<sub>3</sub> = *n*-propyl
- 5, R<sub>1</sub> = *n*-butyl; R<sub>2</sub> = *n*-butyl; R<sub>3</sub> = H
- 6, R<sub>1</sub> = *n*-butyl; R<sub>2</sub> = H; R<sub>3</sub> = *n*-butyl

### Results and Discussion

Dioxetanes 1–6 were prepared in low yield by closure of the corresponding bromo hydroperoxides with base at

(1) Fellow of the Camille and Henry Dreyfus Foundation, 1981–1986.

(2) For reviews see: (a) Wilson, T. *Int. Rev. Sci.: Phys. Chem., Ser. Two* 1976, 9, 265. (b) Adam, W. *Adv. Heterocycl. Chem.* 1977, 21, 437. (c) Horn, K. A.; Koo, J.; Schmidt, S. P.; Schuster, G. B. *Mol. Photochem.* 1978, 9 (1), 1.

(3) The electron-transfer mechanism(s) of chemiluminescent decomposition (high yields of excited singlets) does not occur readily with alkyl-substituted 1,2-dioxetanes.

(4) O'Neal, H. E.; Richardson, W. H. *J. Am. Chem. Soc.* 1970, 92, 6553; correction, 1971, 93, 1828.

(5) Wilson, T.; Landis, M. E.; Baumstark, A. L.; Bartlett, P. D. *J. Am. Chem. Soc.* 1973, 95, 4765.

(6) Richardson, W. H.; Burns, J. H.; Price, M. E.; Crawford, R.; Foster, M.; Slusser, P.; Andergg, J. H. *J. Am. Chem. Soc.* 1978, 100, 7596 and references therein.

(7) Koo, J.; Schuster, G. B. *J. Am. Chem. Soc.* 1977, 99, 5403.

(8) Wilson, T.; Golan, D. E.; Scott, M. S.; Baumstark, A. L. *J. Am. Chem. Soc.* 1976, 98, 1086.

(9) (a) Baumstark, A. L.; Wilson, C. E. *Tetrahedron Lett.* 1981, 4363. (b) Bechara, E. J. H.; Wilson, T. *J. Org. Chem.* 1980, 45, 5261. (c) Lechtken, P.; Reissenweber, G.; Grubmueller, P. *Ibid. Tetrahedron Lett.* 1977, 2881. (d) Baumstark, A. L.; Wilson, C. E. *Ibid. Tetrahedron Lett.* 1979, 2569.

(10) (a) White, E. H.; Wildes, P. D.; Wiecko, J.; Doshan, H.; Wei, C. *J. Am. Chem. Soc.* 1973, 95, 7050. (b) Wilson, T.; Schaap, A. P. *Ibid.* 1971, 93, 4126. (c) Schaap, A. P.; Bartlett, P. D. *Ibid.* 1970, 92, 6055.