m/e (rel intensity) 258 (M^+, 85), 214 (39), 213 (41), 205 (100), 204 (66), 196 (68), 161 (52), 160 (82), 149 (53), 148 (96), 77 (45), and 63 (43).

A solution of 1.30 g (5.0 mmol) of the crude ketal **30** and 12 mL of aqueous 6 M HCl in 28 mL of THF was stirred at 26 °C for 24 h and then partitioned between Et_2O and H_2O. After the organic extract had been washed with aqueous $NaHCO_3$, dried, and concentrated, the residual liquid was distilled (ca. 130 °C at 0.2 mm) in a short-path still to separate 913 mg (85%) of the crude ketone **31**, $n^{25}{}_D$ 1.5825. The product contained (GLC, Apiezon M on Chromosorb P) mainly the ketone **31** (retention time 16.9 min) accompanied by several minor, unidentified impurities (2.6, 8.7, and 22.9 min). The ketone **31** was collected (GLC) as a yellow liquid that solidified on standing, mp 37–38.1 °C. Recrystallization from pentane afforded the pure ketone **31** as colorless prisms: mp 41–42.1 °C; IR (CCl_4) 1720, 1710 (C=O), and 1618 cm^{-1} (C=C); UV max (95% EtOH) 219 nm (ϵ 26 300), 249 (8400), and 322 (3500); NMR (CCl_4) δ 7.0–7.5 (3 H, m, aryl CH), 5.6–6.0 (2 H, m, vinyl CH), 3.77 (3 H, s, OCH_3), 3.3–3.7 (1 H, m, benzylic CH), and 1.8–3.0 (5 H, m, aliphatic CH); mass spectrum m/e (rel intensity) 214 (M^+, 39), 161 (12), 160 (100), 145 (15), and 51 (14).

Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.38; H, 6.59.

To estimate the relative rates of reaction of the methoxyindenes **18b** and **21d** with butadiene, 0.92–0.98-mmol samples of these indenes were dissolved in 7.76-g (143 mmol) portions of cold (−5 °C) liquid butadiene and heated to 130 °C in sealed tubes for 8.5 or 12 h. After the tubes had been cooled and opened the crude product was dissolved in $CHCl_3$, concentrated, and extracted with several portions of boiling EtOH to separate the reactants **18b** and **21d** and products **28** and **30** from polymeric butadiene that was insoluble in EtOH. The EtOH extracts were diluted with EtOH to a known volume and subjected to UV analysis to measure the proportions of **18b** to **30** (using UV absorption at 317 nm) or **21d** to **28** (using UV absorption at 343 nm). After a reaction period of 8.5 h, the amounts of unchanged indenes remaining were 62% of **18b** and 40% of **21d**; after 12 h, the values were 40% of **18b** and 23% of **21d**. Consequently, we estimate that indene ester **21d** reacts with butadiene at 130 °C about twice as fast as the indene **18b**.

Registry No.—**7a**, 83-33-0; **7b**, 13623-25-1; **8a**, 1929-29-9; **8b**, 15893-42-2; **11**, 6768-23-6; **12**, 6335-37-1; **13**, 6099-04-3; **14a**, 1775-27-5; **14b**, 62015-79-6; **15a**, 58521-74-7; **15b**, 62015-80-9; **16a**, 7749-02-2; **16b**, 62015-81-0; **17a**, 62015-78-5; **17b**, 62046-07-5; **18a**, 6710-43-6; **18b**, 62015-82-1; **19a**, 62015-83-2; **19b**, 62015-84-3; **21a**, 62015-85-4; **21b**, 62015-86-5; **21c**, 62015-87-6; **21d**, 62015-88-7; **24a**, 62015-89-8; **25**, 62015-90-1; **27**, 62015-91-2; **28**, 62015-92-3; **29**, 62015-93-4; **30**, 62015-94-5; **31**, 62015-95-6; anisaldehyde, 123-11-5; malonic acid, 141-82-2; hydrocinnamic acid, 501-52-0; 1,2-ethanediol, 107-21-1; butadiene, 106-99-0.

References and Notes

(1) This research has been supported by Public Health Service Grant RO1-GM-20197 from the National Institute of General Medical Science. The execution of this research was also assisted by Institution Research Grants from the National Science Foundation for the purchase of a mass spectrometer and a Fourier transform NMR spectrometer.
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Thermal Decomposition of Bifunctional Peroxides[1]

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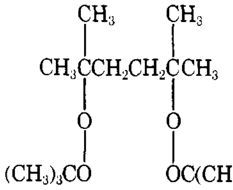
Quantitative determination of the products resulting from the thermal decomposition of 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane (**1**) in *m*-xylene and 2-octanol indicates extensive fragmentation of the 2,5-dimethylhexane moiety of **1**. A mechanism is proposed to account for the observed amounts of these fragmentation products in these solvents and the extent of self-induced decomposition of **1**. In contrast to **1**, 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)-3-hexyne (**2**) undergoes thermal decomposition in *m*-xylene and in 2-butanol with no detectable amounts of fragmentation of the 2,5-dimethyl-3-hexyne moiety.

The bifunctional peroxide 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane (**1**)[2] is used as an initiator for free radical polymerizations and, presumably owing to its bifunctional character, for crosslinking of polyethylene and other polymers. Its value in this latter capacity depends at least in part on the ability of the two peroxide functionalities to react independently of each other when **1** undergoes thermal decomposition. Our investigations of the decomposition products of **1** in *m*-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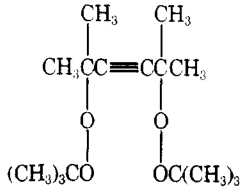
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Table I. Decomposition Products of 1 in *m*-Xylene at 125 °C

	Time[a]				
	205	530	840	1500	2940
1 consumed[b]	0.50	0.82	1.00	1.12	1.21
Products					
Acetone	0.54	0.99	1.31	1.90	2.00
tert-Butyl alcohol	0.46	0.80	1.07	1.54	1.64
tert-Amyl alcohol	0.04	0.08	0.15	0.71	0.82
tert-Amyl-*tert*-butyl peroxide (8)	0.28	0.37	0.31	0.15	0.00
2,5-Dimethyl-2-hydroxy-5-(*tert*-butylperoxy)hexane (5)	0.12	0.22	0.18	0.04	0.00
2,5-Dimethyl-2,5-dihydroxyhexane (11)	0.00	0.07	0.12	0.25	0.28

[a] Minutes. [b] Amounts in millimoles.

Table II. Product Distribution for Decomposition of 1 in *m*-Xylene at 125 °C

	Run 1	Run 2
Initial amount of 1[a]	12.76	12.60
Amount of 1 reacted	4.17	5.38
Products		
Acetone	4.21	6.13
tert-Butyl alcohol	3.66	5.24
tert-Amyl alcohol	0.32	0.49
tert-Amyl-*tert*-butyl peroxide (8)	2.30	2.70
Methane	1.05	1.62
Ethylene	0.10	0.16
Ethane	0.31	0.61
2,5-Dimethyl-2-hydroxy-5-*tert*-butylperoxyhexane (5)	0.98	1.09

[a] Amounts in millimoles.

xylene and in 2-octanol indicate that while there is extensive unimolecular fragmentation of the 2,5-dimethylhexane moiety of 1 there is little self-induced decomposition of one peroxide moiety by the other. Decomposition of 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)-3-hexyne (2) in similar solvents yields radicals less prone to unimolecular fragmentation.

Results and Discussion

The nongaseous products resulting from the decomposition of 1 at 125 °C in *m*-xylene are listed in Table I. The presence of these products and the qualitative identification of methane, ethane, and ethylene as the gaseous decomposition products led to the proposed decomposition path for 1 shown in reaction Scheme I (RH = *m*-xylene, R· = 3-methylbenzyl). Support for this reaction scheme is found in the observed stoichiometric relationships among the decomposition products of 1. Table II lists both the gaseous and nongaseous decomposition products found after 1 has been allowed to undergo partial decomposition in *m*-xylene at 125 °C. The amount of 1 that has reacted in each run should equal the sum of the amounts of 2,5-dimethyl-2-hydroxy-5-(*tert*-butylperoxy)hexane (5), *tert*-amyl-*tert*-butyl peroxide (8), *tert*-amyl alcohol, ethane, and ethylene produced in the reaction (4.01 and 5.05 mmol for runs 1 and 2, respectively). Also, the amounts of acetone formed should equal the sum of the amounts of methane, 2 × ethane, 2 × ethylene, 8, and *tert*-

Scheme I

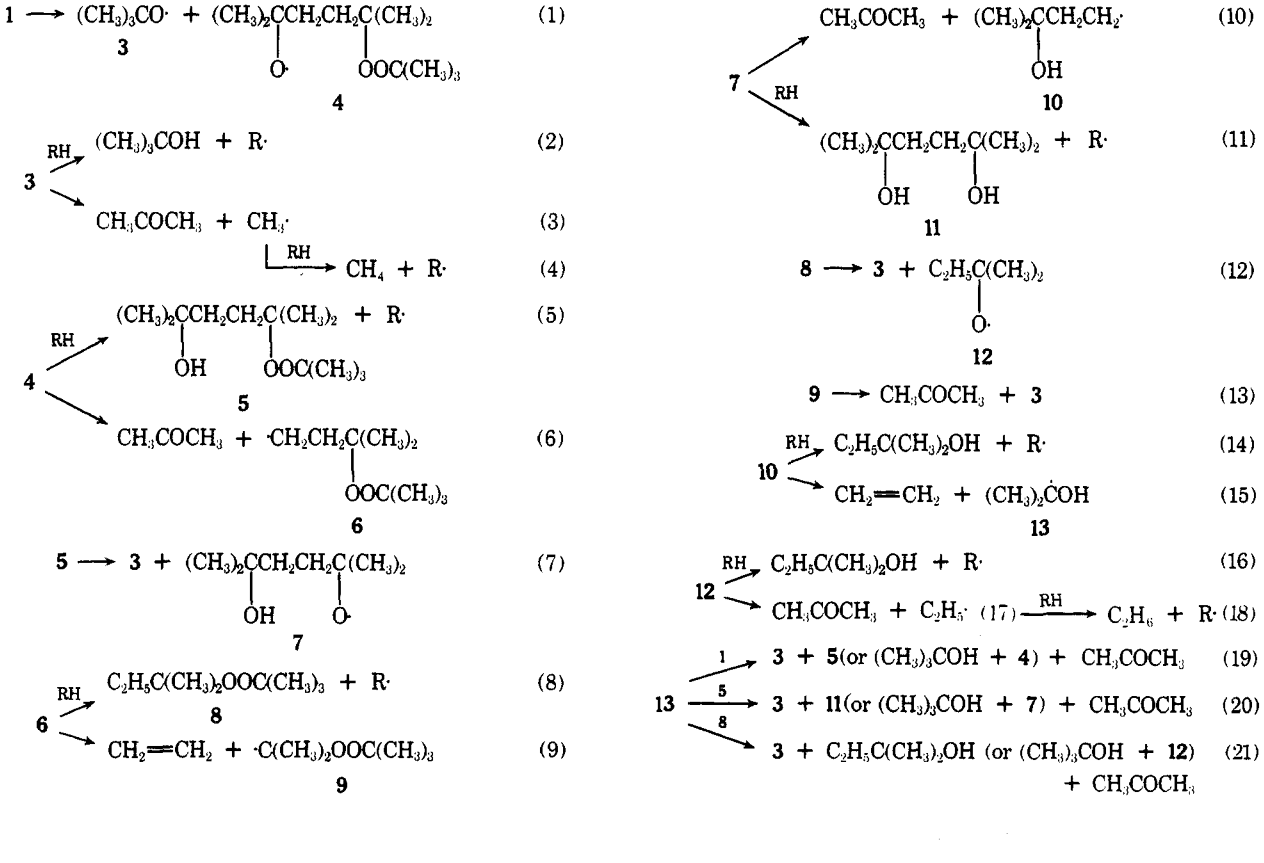


Table III. Product Distribution for Decomposition of 1 in 2-Octanol

	Run 3	Run 4
Initial amount of 1	10.48	12.65
Amount of 1 reacted	4.67	6.95
Products		
Acetone	5.09	9.05
tert-Butyl alcohol	4.74	8.07
tert-Amyl alcohol	0.71	1.59
8	1.61	2.31
Methane	1.44	2.18
Ethylene	0.16	0.20
Ethane	0.69	1.52
5	1.46	1.24
2-Octanone (**14**)	6.34	10.42

Table IV. Products of the Decomposition of 2 in *m*-Xylene and 2-Butanol

	m-Xylene (62.6 mmol)	2-Butanol (65.1 mmol)
Initial amount of **2**	13.83	13.10
Amount of **2** reacted	5.33	9.48
Products		
Acetone	0.99	2.70
tert-Butyl alcohol	6.05	14.31
Methane	0.99	2.74
16	2.97	1.60
18	2.09	7.76
2-Butanone		17.56

amyl alcohol (4.49 and 6.35 mmol for runs 1 and 2, respectively). A further relationship is that the sum of the amounts of *tert*-butoxyl-derived products, namely, *tert*-butyl alcohol, methane, **5**, and **8** (7.99 mmol for run 1 and 10.65 mmol for run 2) should equal twice the amount of **1** that has reacted (8.34 and 10.76 mmol for runs 1 and 2, respectively). The agreement between these predicted and observed stoichiometric relationships is well within the experimental reliabilities of the gas chromatographic techniques employed for the quantitative determinations and support the unimolecular decomposition path for **1** outlined in reaction Scheme I.

The appearance of each of these products with the exception of acetone and ethylene results from hydrogen abstraction from the *m*-xylene by the radical precursor of the decomposition product (reactions 2, 4, 5, 8, 11, 14, 16, and 18), yielding in each case the 3-methylbenzyl radical (R·) along with the observed decomposition product. The 3-methylbenzyl radicals likely couple

$$2R\cdot \rightarrow R_2 \qquad (22)$$

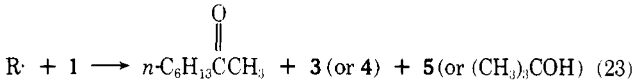
and do not interact in any significant manner with either **1** or its decomposition products. This is not the case when **1** is allowed to decompose in 2-octanol (RH = n-$C_6H_{13}CHOHCH_3$). The hydrogen atom abstraction from 2-octanol yields an α-hydroxyalkyl radical (R· = n-$C_6H_{13}\dot{C}OHCH_3$), a species that reacts with the dialkyl peroxide functionalities as shown in reactions 23–25 in reaction Scheme II. That induced decompositions of the dialkyl peroxide functionalities do occur is supported by the observation that the half-life of **1** at 125 °C in 2-octanol at 125 °C is about 90 min, in contrast to a half-life of about 300 min in toluene at 125 °C. The involvement of the α-hydroxyalkyl radical is also evidenced by the formation of 2-octanone as a reaction product. Not only should the stoichiometric relationships observed in the decompositions of **1** in *m*-xylene be observed in the decompositions of **1** in 2-octanol, but the amount of 2-octanone produced should be dependent on the extent of reduction of the peroxidic functionalities available (Table III). The amount of **1** that has reacted should equal the sum of the amounts of **5**, **8**, *tert*-amyl alcohol, ethane, and ethylene formed (4.63 and 6.86 mmol for runs 1 and 2, respectively). The calculated amounts of acetone formed should equal the sum of the amounts of methane, 2 × ethane, 2 × ethylene, *tert*-amyl alcohol, and **8** produced (5.46 and 9.52 mmol for runs 3 and 4, respectively); the calculated *tert*-butoxyl moieties involved in reaction based on the amounts of **1** that have reacted (9.34 mmol for run 3 and 13.9 mmol for run 4) correspond with the amounts of *tert*-butyl alcohol, methane, **5**, and **8** found as reaction products (9.25 mmol for run 3 and 13.8 mmol for run 4). The amount of 2-octanone produced should equal the sum of 2 × **1** that has reacted minus the amounts of **5**, **8**, and ethylene found as reaction products (6.11 and 10.15 mmol for runs 3 and 4, respectively). Again, the agreement between the predicted and observed stoichiometric relationships is within the experimental reliability expected for the number of quantitative gas chromatographic determinations involved.

Scheme II

(RH = n-$C_6H_{13}CHOHCH_3$ and R· = n-$C_6H_{13}\dot{C}OHCH_3$)

(all reactions of Scheme I)

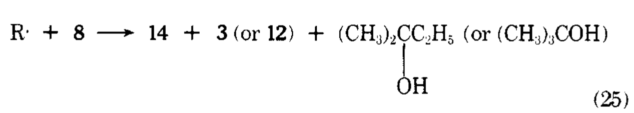
and



$$R\cdot + \mathbf{1} \longrightarrow n\text{-}C_6H_{13}\overset{\overset{\displaystyle O}{\|}}{C}CH_3 + \mathbf{3}\,(\text{or }\mathbf{4}) + \mathbf{5}\,(\text{or }(CH_3)_3COH) \qquad (23)$$

14

$$R\cdot + \mathbf{5} \longrightarrow \mathbf{14} + \mathbf{11}\,(\text{or }CH_3)_3COH) + \mathbf{3}\,(\text{or }\mathbf{7}) \qquad (24)$$



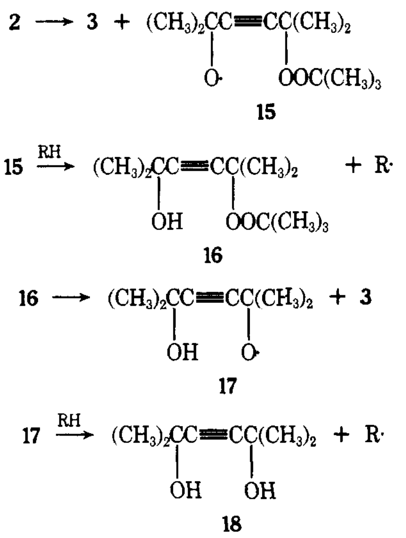
$$R\cdot + \mathbf{8} \longrightarrow \mathbf{14} + \mathbf{3}\,(\text{or }\mathbf{12}) + (CH_3)_2\underset{\underset{\displaystyle OH}{|}}{C}C_2H_5\;(\text{or }(CH_3)_3COH) \qquad (25)$$

In marked contrast to the thermal decompositions of **1**, the thermolysis of **2** in *m*-xylene shows no evidence of fragmentation of the main carbon skeleton of the molecule, namely the 2,5-dimethyl-3-hexyne moiety (Table IV). The amounts of methane, acetone, *tert*-butyl alcohol, 2,5-dimethyl-2-hydroxy-5-(*tert*-butylperoxy)-3-hexyne (**16**) and 2,5-dimethyl-2,5-dihydroxy-3-hexyne (**18**) found in the decomposition in both *m*-xylene and 2-butanol correspond to the stoichiometry expected on the basis of reaction Scheme III, namely, methane and acetone are formed in equal amounts, the sum of acetone, *tert*-butyl alcohol, and **16** equal 2 × **2** that has reacted and the sum of **16** and **18** equal the amount of **2** that has reacted. Furthermore, the amount of 2-butanone, the oxidation product of the secondary alcohol, corresponds to the extent of reduction of the available peroxide functionality.

The reactions outlined in Schemes I, II, and III are, for the most part, not unexpected for either the radical intermediates and the substrates available for reaction with these radicals. The fragmentation reactions of the alkoxyl radicals (reactions 3, 6, 10, and 17) follow the expected course in that the most stable radical is eliminated.[3] The interactions of the α-hydroxyalkyl radicals with dialkyl peroxide functions (reactions 19, 20, 21, 23, 24, 25, 30, and 31) are also known to occur with concurrent oxidation of the α-hydroxyalkyl radical to the corresponding carbonyl-containing compound.[4] Fragmentations similar to that encountered in the reaction of the α-(alkylperoxy)alkyl radical (reaction 13) have been proposed as chain propagating reactions in the self-induced decompositions of primary and secondary alkyl peroxides.[5]

The β-elimination of either the α-(alkylperoxy)alkyl radical **9** from radical **6** (reaction 9) or the α-hydroxyalkyl radical **13**

Scheme III



$$2 \longrightarrow 3 + (CH_3)_2\underset{\displaystyle O\cdot}{C}C\equiv C\underset{\displaystyle OOC(CH_3)_3}{C}(CH_3)_2 \qquad (26)$$

15

$$15 \xrightarrow{RH} (CH_3)_2\underset{\displaystyle OH}{C}C\equiv C\underset{\displaystyle OOC(CH_3)_3}{C}(CH_3)_2 + R\cdot \qquad (27)$$

16

$$16 \longrightarrow (CH_3)_2\underset{\displaystyle OH}{C}C\equiv C\underset{\displaystyle O\cdot}{C}(CH_3)_2 + 3 \qquad (28)$$

17

$$17 \xrightarrow{RH} (CH_3)_2\underset{\displaystyle OH}{C}C\equiv C\underset{\displaystyle OH}{C}(CH_3)_2 + R\cdot \qquad (29)$$

18

If RH = *m*-xylene,

$$2R\cdot \longrightarrow R_2 \qquad (22)$$

If $RH = C_2H_5CHOHCH_3$ and $R\cdot = C_2H_5COHCH_3$,

$$R\cdot + 2 \longrightarrow C_2H_5COCH_3 + 16 + 3(\text{or } 15 + (CH_3)_3COH) \qquad (30)$$

$$R\cdot + 16 \longrightarrow C_2H_5COCH_3 + 18 + 3(\text{or } 17 + (CH_3)_3COH) \qquad (31)$$

from radical **10** (reaction 15) are the only sources of ethylene in the decompositions of **1**. The radicals formed along with ethylene in reactions 9 and 15, namely the 2-(*tert*-butylperoxy)propyl radical **9** and the 2-hydroxypropyl radical **13**, respectively, are the only radicals derived from **1** capable of effecting the induced decomposition of a peroxide functionality (reactions 13, 19, 20, and 21). The induced decomposition of a peroxide function by reaction 13 is an intramolecular route for the self-induced decomposition of **1**, whereas the reactions of radical **13** would be an intermolecular route for self-induced decomposition. The contributions of each route might possibly be ascertained by kinetic analysis of the rate of ethylene formation (the intramolecular route would be independent of the concentration of **1**, whereas the intermolecular route could show a kinetic order of 1 greater than unity).[6] The extent of the self-induced decomposition in both *m*-xylene and 2-octanol, however, was too small (~3%) to allow for such kinetic analysis.

Experimental Section

2,5-Dimethyl-2,5-bis(*tert*-butylperoxy)hexane (**1**) and 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)-3-hexyne (**2**) were obtained from the Lucidol Division of Pennwalt Corp. The materials were redistilled [bp of **1** 87–90 °C (30 mm) and bp of **2** 81–83 °C (30 mm)] and gave a single peak on gas chromatographic analysis. An authentic sample of *tert*-amyl-*tert*-butyl peroxide [bp 40 °C (40 mm)] was prepared by interaction of *tert*-amyl alcohol and *tert*-butyl hydroperoxide (Lucidol) in the presence of sulfuric acid. Authentic samples of 2,5-dimethyl-2,5-dihydroxyhexane (**11**) and 2,5-dimethyl-2,5-dihydroxy-3-hexyne (**18**) were obtained from Aldrich. *m*-Xylene (Matheson, Coleman and Bell), 2-octanol (Fisher Scientific), and 2-butanol (Baker Analyzed) were distilled before using. All other liquid reagents used for gas chromatographic retention time comparisons were reagent grade materials, and, when necessary, redistilled until gas chromatographic analysis showed a single peak. The gaseous compounds were commercial materials (Matheson) and used without further purification.

Qualitative Identification of Decomposition Products of 1 and 2. All liquid and gaseous products with the exception of 2,5-dimethyl-2-hydroxy-5-(*tert*-butylperoxy)hexane (**5**) and 2,5-dimethyl-2-hydroxy-5-(*tert*-butylperoxy)-3-hexyne (**16**) were identified by comparison of their gas chromatographic retention time on two or more different columns with those of authentic samples. Attempts to prepare authentic samples of **5** and **16** by the acid-catalyzed reaction of *tert*-butyl hydroperoxide in excess of the corresponding diols **11** and **18**, respectively, led only to formation of the diperoxides **1** and **2**. The assignment of the structures **5** and **16** to the gas chromatographic peaks used to calculate the amounts of these materials as decomposition products **1** and **2**, respectively, was based on the facts that the retention times were between those of the diperoxide and the diol in each case and, as in the case of *tert*-amyl-*tert*-butyl peroxide, the peak areas decreased with time.

Quantitative Determinations. A reaction mixture consisting of the diperoxide in the appropriate solvent in a 1:5 molar ratio was heated in a 250-mL flask equipped with an efficient condenser by immersing the flask in an oil bath set at 125 °C. The gases evolved were collected in a gas buret that was connected to the end of the condenser. The composition of the gaseous products was determined by gas chromatographic analysis of a sample of the gas on a 6-ft column packed with Poropak Q. The amounts of diperoxides **1** and **2**, the hydroxymonoperoxides **5** and **16**,[7] and the diols **11** and **18** were determined by gas chromatographic analysis using a 5-ft column packed with DC-200 on Chromosorb W of a sample of the reaction mixture using dodecane as an internal standard. The amounts of 2-octanone formed in the reactions of **1** in 2-octanol were determined by gas chromatographic analysis of a sample of the reaction mixture on a 10-ft column packed with polyethyleneglycol succinate on Chromosorb W using isoamyl acetate as an internal standard. All other products were determined by gas chromatographic analysis on a 10-ft column packed with 10% dodecyl phthalate on Chromosorb W using either isoamyl acetate or ethyl propionate as the internal standards.

Kinetic Measurements. The rates of the decompositions of **1** and **2** were determined in toluene and in 2-octanol by the following general procedure: A master solution of the solvent and the peroxide in a molar ratio of approximately 10:1 was divided into seven 9-mm Pyrex tubes which were cooled to −80 °C and sealed. The tubes were warmed to room temperature and then immersed in a 125 °C oil bath. Tubes were removed periodically and the peroxide remaining determined by gas chromatographic analysis of a weighed portion of the reaction mixture with a weighed amount of dodecane, which served as the internal standard. The first-order rate constants for the decompositions of **1** and **2** in toluene were 2.41×10^{-3} ($t_{1/2} = 288$ min) and 1.19×10^{-3} min^{-1} ($t_{1/2} = 583$ min), respectively. The pseudo-first-order rate constants for the induced decompositions[4] of **1** and **2** in 2-octanol were 7.67×10^{-3} ($t_{1/2} = 90.3$ min) and 2.73×10^{-3} min^{-1} ($t_{1/2} = 254$ min), respectively.

Registry No.—**1**, 78-63-7; **2**, 1068-27-5.

References and Notes

(1) This work was supported in part by a Grant (GM AM18191) from the Department of Health, Education, and Welfare.

(2) The difunctional peroxides **1** and **2** are commercially available materials. The samples used in this work were supplied to us by the Lucidol Division of Pennwalt Corp. and the receipt of these materials is gratefully acknowledged.

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(4) E. S. Huyser and C. J. Bredeweg, *J. Am. Chem. Soc.*, **86**, 2401 (1964).

(5) For example, see R. Hiatt, D. J. LeBlanc, and C. Thankachan, *Can. J. Chem.*, **52**, 4090 (1974); also R. Hiatt, "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N.Y., 1971, p 91.

(6) K. Nozaki and P. D. Bartlett, *J. Am. Chem. Soc.*, **68**, 1686 (1946).

(7) Since authentic samples of the hydroxymonoperoxides **5** and **16** were not available, the correction factor required to relate their gas chromatographic peak areas and that of the internal standard to the amounts of **5** and **16** in the reaction mixtures were assumed in each case to be intermediate between those of the diperoxides **1** and **2** and the diols **11** and **18**, respectively.