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Thermal Decomposition of 2,2-Bis(*t*-butyldioxy)alkanes

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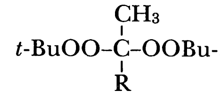
The thermal decomposition of 2,2-bis(*t*-butyldioxy)propane (**1a**) has been studied in cumene. The activation parameters obtained by the thermolysis of **1a** are $\Delta H^{\ne}=145.6$ kJ mol^{-1} and $\Delta S^{\ne}=47.3$ J K^{-1} mol^{-1}. The decomposition products of **1a** are acetone, *t*-butyl alcohol, *t*-butyl hydroperoxide, *t*-butyl peracetate, *t*-butyl 1-methyl-1-phenylethyl peroxide, and bis(1-methyl-1-phenylethyl). The peroxyacetal cleaves homolytically at one of dioxy bonds to yield an intermediate alkoxyl radical with *α*-*t*-butyldioxy group, which decomposes subsequently to *t*-butyldioxyl and methyl radicals via *β*-elimination. The thermal decomposition of 2,2-bis(*t*-butyldioxy)butane and 2,2-bis(*t*-butyldioxy)-3-methylbutane have also been examined. Relative rates of *β*-elimination of radicals from alkoxyl radicals are concluded to be isopropyl:ethyl:*t*-butyldioxyl:methyl =133:33:7:1, revealing a facile scission of dioxyl radical.

The decomposition behavior of peroxyacetals is quite interesting because of the presence of two dioxy bonds on one carbon atom, and is important as an initiator for practical polymerizations. But only a few studies have been reported on the thermal decomposition of them.[1–4] Mageli and co-workers[3] studied the thermal decomposition of butyl 4,4-bis(*t*-butyldioxy)valerate in dodecane. As decomposition products they obtained acetone, *t*-butyl alcohol, butyl propionate, and butyl levulinate. *t*-Butyl peracetate (**3**) was assumed to be an intermediate product during the decomposition, but it could not be obtained under the conditions. Previously we reported on the thermal decomposition of 2,2-bis(*t*-butyldioxy)-3-methylbutane (**1c**) in diphenylmethane.[4] The results have shown that the O–O homolysis of the acetal yields 1-(*t*-butyldioxy)-1,2-dimethylpropoxyl radical, which cleaves competitively to *t*-butyldioxyl or isopropyl radical. The *β*-elimination process was demonstrated by identifying isopropyl methyl ketone and **3** as decomposition products.

In the present paper we summarize our detailed study on the thermal decomposition of 2,2-bis(*t*-butyldioxy)alkanes (**1**) in order to elucidate the decomposition mechanism focusing on the facile *β*-elimination of *t*-butyldioxyl radical.



$$t\text{-BuOO}-\overset{\displaystyle CH_3}{\underset{\displaystyle R}{C}}-\text{OOBu-}t$$

(**1**)

(**1a**): R = CH_3, (**1b**): R = CH_2–CH_3, (**1c**): R = $CH(CH_3)_2$

Results and Discussion

Decomposition Mechanism of 1a. The thermal decomposition of 2,2-bis(*t*-butyldioxy)propane (**1a**) was carried out in cumene under nitrogen. The thermolysis rates, determined by measuring the disappearance of **1a** by GLC analyses, satisfied the first-order kinetics. For example, the first-order rate constants remained constant by changing a forty-fold increase in the initial concentration of **1a**. This means that the induced decomposition of the peroxide is negligible, if any, under these conditions. The resulting kinetic data are listed in Table 1. The activation parameters for **1a** are quite close to those for di-*t*-butyl peroxide (i.e., $\Delta H^{\ne}=153.8$ kJ mol^{-1} and $\Delta S^{\ne}=48.1$ J K^{-1} mol^{-1}),[5] indicating a non-concerted homolytic cleavage of one dioxy bond in **1a**.

Table 1. Rate Constants and Activation Parameters for the Decomposition of 2,2-Bis(*t*-butyldioxy)propane (**1a**) in Cumene[a)]

Temp	$k_1 \times 10^5$	Activation parameters	
		$\Delta H^{\ne}$	$\Delta S^{\ne}$
°C	s^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}
90	0.216±0.007		
100	0.914±0.018	145.6±3.3	47.3±8.8
110	2.97 ±0.02		
120	9.56 ±0.12		

a) The decomposition of **1a** was carried out up to about 70% conversion under nitrogen. Initial **1a** concentration: $[\mathbf{1a}]_0=0.1$ M (1 M=1 mol dm^{-3}).

The decomposition products of **1a** in cumene, as identified by GLC and/or GC-MS analyses, were acetone, *t*-butyl alcohol, *t*-butyl hydroperoxide, *t*-butyl peracetate (**3**), *t*-butyl 1-methyl-1-phenylethyl peroxide, and bis(1-methyl-1-phenylethyl) (Table 2). The dependence of products on reaction time is shown in Fig. 1. The total recovery for *t*-butyl group from **1a** was pretty high, e.g., 1.92 mol% or 96% for the decomposition at 120 °C. A likely scheme leading to major products is shown by the following equations.

Table 2. Products for Decomposition of **1a**[a)]

Temp	Time	Product yield[b)]/%							
°C	h	Me_2CO	*t*-BuOH	*t*-BuOOH	*t*-BuOOBu-*t*	$MeCO_3Bu$-*t*	*t*-BuOOR	R–R	Epoxide[c)]
		A) Decomposition in cumene							
100	24	67	107	15	<1	12	48	32	
120	2	88	110	16	<1	14	52	33	
		B) Decomposition in the presence of α-methylstyrene							
120[d)]	2	f)	f)	11	<1	13	f)	f)	8
120[e)]	2	f)	f)	8	<1	13	f)	f)	17

a) $[\mathbf{1a}]_0$=0.1 M. b) Yields of products: [(moles of products)/(moles of **1a** consumed)]×100. The conversion of **1a** was about 50%. Me=CH_3, R=$C_6H_5C(CH_3)_2$. c) α-Methylstyrene oxide. d) 0.1 M α-methylstyrene. e) 0.5 M α-methylstyrene. f) Not determined.

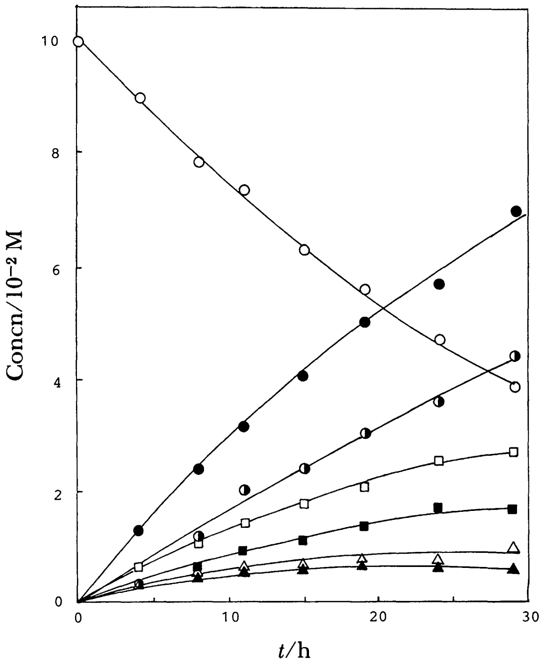
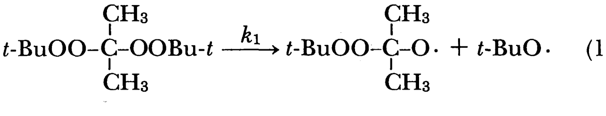
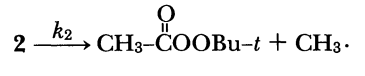


Fig. 1. Concentration change of products during the thermal decomposition of **1a** in cumene at 100 °C. $[\mathbf{1a}]_0$=0.1 M. ○: **1a**, ◑: acetone, ●: *t*-butyl alcohol, △: *t*-butyl hydroperoxide, ▲: **3**, □: *t*-butyl 1-methyl-1-phenylethyl peroxide, ■: bis(1-methyl-1-phenylethyl).

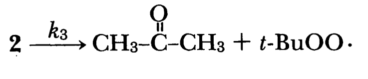


$$t\text{-BuOO-}\overset{CH_3}{\underset{CH_3}{C}}\text{-OOBu-}t \xrightarrow{k_1} t\text{-BuOO-}\overset{CH_3}{\underset{CH_3}{C}}\text{-O}\cdot + t\text{-BuO}\cdot \qquad (1)$$

(**1a**) (**2**)

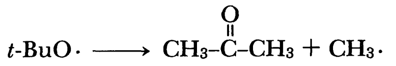


$$\mathbf{2} \xrightarrow{k_2} CH_3\text{-}\overset{O}{\overset{\|}{C}}OOBu\text{-}t + CH_3\cdot \qquad (2)$$



$$\mathbf{2} \xrightarrow{k_3} CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + t\text{-BuOO}\cdot \qquad (3)$$

$$t\text{-BuO}\cdot + RH \longrightarrow t\text{-BuOH} + R\cdot \qquad (4)$$



$$t\text{-BuO}\cdot \longrightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3 + CH_3\cdot \qquad (5)$$

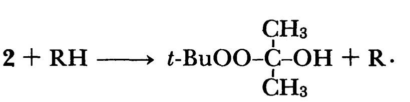
$$t\text{-BuOO}\cdot + R\cdot \longrightarrow t\text{-BuOOR} \qquad (6)$$

$$R\cdot + R\cdot \longrightarrow R\text{–}R \qquad (7)$$

Here, RH denotes cumene and R–R is bis(1-methyl-1-phenylethyl). The O–O homolysis of **1a** produces *t*-butoxyl and α-butyldioxyalkoxyl radical (**2**) (Eq. 1). The two major products, acetone and *t*-butyl alcohol, are formed by the β-elimination of *t*-BuOO· from **2** (Eq. 3), the elimination of methyl radical from *t*-BuO·(Eq. 5), and the hydrogen abstraction of *t*-BuO· from solvent cumene (Eq. 4). The following coupling reaction of relatively stable *t*-BuOO· and 1-methyl-1-phenylethyl radicals (Eqs. 6 and 7) affords *t*-butyl 1-methyl-1-phenylethyl peroxide and bis(1-methyl-1-phenylethyl) in relatively high yields (i.e., 30—50%).

The formation of *t*-butyl peracetate (**3**) is well explained by Eq. 2 as a competing fragmentation of methyl radical. An alternative route via a radical coupling is unlikely since acyl radical is not formed in the present reaction. Then, the relative yields of **3** and acetone are roughly the relative rates of Eqs. 2 and 3. The details are discussed in the next section.

t-Butyl hydroperoxide was obtained as a minor product as shown in Table 2A. Two routes are conceivable for its formation. One involves a hydrogen abstraction of **2** from cumene to yield hemiacetal **4** (Eq. 8a), which would decompose to *t*-butyl hydroperoxide and acetone (Eq. 8b). The other route is a hydrogen abstraction of *t*-BuOO· from cumene (Eq. 9). To differenciate the two routes, the decomposition of **1a** was carried out in the presence of α-methylstyrene (Table 2B). While the yield of ester **3** remained unchanged by the addition of the olefin, the



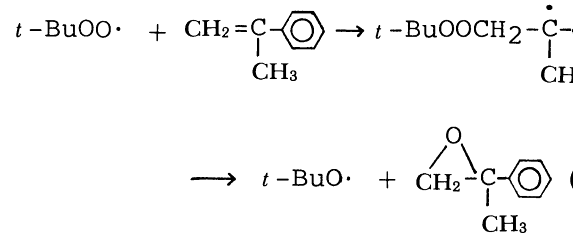
$$\mathbf{2} + RH \longrightarrow t\text{-BuOO-}\overset{CH_3}{\underset{CH_3}{C}}\text{-OH} + R\cdot \qquad (8a)$$

(**4**)

$$\mathbf{4} \longrightarrow t\text{-BuOOH} + (CH_3)_2CO \qquad (8b)$$

$$t\text{-BuOO}\cdot + RH \longrightarrow t\text{-BuOOH} + R\cdot \qquad (9)$$

amount of *t*-BuOOH decreased significantly, affording the corresponding epoxide. The radical epoxidation with alkyldioxyl radical (Eq. 10) is well known.[6]



(10)

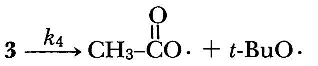
These facts suggest that *t*-BuOO· radical is clearly formed and the precursor for *t*-BuOOH in the reaction of **1a**. Moreover, the yield of *t*-BuOOH was decreased by the increasing concentration of α-methylstyrene. Judging from all of these results, *t*-BuOOH is formed mainly from Eq. 9 and not from Eq. 8. This is quite interesting since the hydrogen abstraction of *t*-BuO· is known to be faster than that of *t*-BuOO· by a factor of 10^4.[7] The unimportance of Eq. 8a in the present case is simply due to a facile scission of *t*-BuOO· from **2**; that is, the life time of **2** is too short to abstract a hydrogen atom from solvent.

Di-*t*-butyl peroxide could not be detected in the reaction mixture (less than 1%). This indicates that the coupling reaction of *t*-BuOO· to form the peroxide[8] does not occur at all and the predominant one is the hydrogen abstraction from solvent (Eq. 9).

Relative Rates of β-Elimination of Radicals. In order to obtain accurate ratios of β-elimination from alkoxyl radical **2**, the following equation was derived by applying a steady-state assumption on [**3**] in Eqs. 1, 2, and 3.[4] That is,

$$d[\mathbf{3}]/dt = \alpha k_1[\mathbf{1a}] - k_4[\mathbf{3}] \qquad (11)$$

where $\alpha = k_2/(k_2+k_3)$, and k_4 is the rate constant for the decomposition of **3** (Eq. 12).



$$\mathbf{3} \xrightarrow{k_4} CH_3\text{-}\overset{O}{\overset{\|}{C}}O\cdot + t\text{-BuO}\cdot \qquad (12)$$

Integration of Eq. 11 gives

$$[\mathbf{3}] = \alpha k_1[\mathbf{1a}]_0(e^{-k_4 t} - e^{-k_1 t})/(k_1 - k_4) \qquad (13)$$

The most appropriate values for α were obtained by computer simulation, and are listed in Table 3. A typical correlation between the observed and calculated concentration of **3** is shown in Fig. 2. The resulting α values of 0.21—0.25 mean that the rate ratio of *t*-butyldioxyl and methyl radicals is about 4 in the β-elimination from **2**.

The relative rates of ethyl and isopropyl radicals for the β-elimination in intermediate alkoxyl radicals were also investigated in the thermal decomposition of 2,2-bis(*t*-butyldioxy)butane (**1b**) and 2,2-bis(*t*-butyldioxy)-3-methylbutane (**1c**). Rate constants for the decomposition of **1b** and **1c** were $1.84\times10^{-5}\,s^{-1}$ and $3.17\times10^{-5}\,s^{-1}$, respectively, at 100 °C. Thus, the decomposition rates of 2,2-bis(*t*-butyldioxy)alkanes decrease in the order of **1c**>**1b**>**1a**, the ratios being 3.5:2.0:1.0.

Table 3. Ratios of β-Elimination of **2**

Temp[a]	$k_1\times10^5$	$k_4\times10^5$	α[b]
°C	s^{-1}	s^{-1}	
90	0.216±0.007	0.378±0.003	0.21
100	0.914±0.018	1.47 ±0.02	0.23
110	2.97 ±0.02	4.92 ±0.06	0.25
120	9.56 ±0.12	16.1 ±0.1	0.24

a) For reaction conditions see footnote a in Table 1. b) $\alpha=k_2/(k_2+k_3)$ was obtained as noted in the text and Eq. 13.

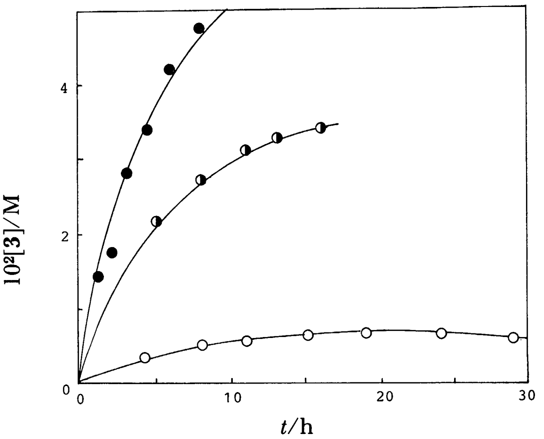


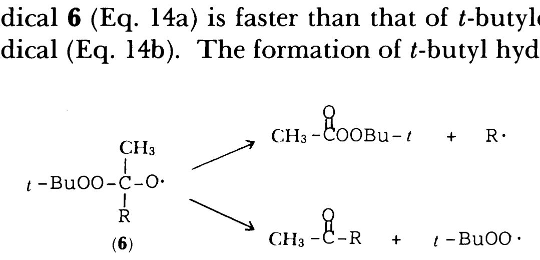
Fig. 2. Concentration change of *t*-butyl peracetate (**3**) during the thermal decomposition of **1a** (○), **1b** (◑), and **1c** (●) in cumene at 100 °C. $[\mathbf{1}]_0=0.1$ M. The curve shows a theoretical line calculated from Eq. 13.

Table 4. Products for Decomposition of **1b** and **1c**[a]

Products	Yield[b]/%	
	1b	**1c**
Acetone	15	11
Alkyl methyl ketone	16[c]	10[d]
t-Butyl alcohol	104	108
t-Butyl hydroperoxide	<1	<1
Di-*t*-butyl peroxide	<1	<1
t-Butyl peracetate	61	84
t-Butyl 1-methyl-1-phenylethyl peroxide	8	2
Bis(1-methyl-1-phenylethyl)	86	76

a) Decomposition was carried out at 100 °C. Reaction time: **1b**, 11 h; **1c**, 6 h. b) Yields of products: [(moles of products)/(moles of **1b** or **1c** consumed)]×100. The conversion of **1b** or **1c** was about 50%. c) Yield of ethyl methyl ketone. d) Yield of isopropyl methyl ketone.

The decomposition products of **1b** and **1c** are listed in Table 4. In contrast to the case of **1a**, higher yields of *t*-butyl peracetate was obtained, while *t*-butyl 1-methyl-1-phenylethyl peroxide and *t*-butyl hydroperoxide containing dioxy group were of much smaller or trace amount. These results indicate that the elimination of ethyl or isopropyl radical from alkoxyl radical **6** (Eq. 14a) is faster than that of *t*-butyldioxyl radical (Eq. 14b). The formation of *t*-butyl hydroperoxide in only trace amount is consistent with the very minor elimination of *t*-butyldioxyl radical from **6**. By the same calculation as the case of **1a**, the α values of 0.83 and 0.95 were obtained for ethyl and isopropyl radicals at 100 °C. The correlations between the observed and calculated data are shown in Fig. 2. Thus, the resulting relative rates of radicals for the elimination from *t*-alkoxyl radicals **6** are of isopropyl : ethyl : *t*-butyldioxyl : methyl=133 : 33 : 7 : 1.



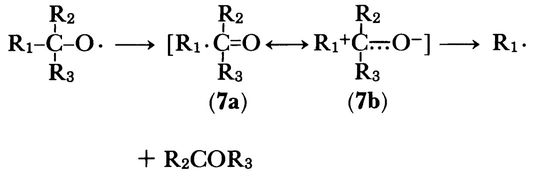
$$t\text{-BuOO-}\overset{\displaystyle CH_3}{\underset{\displaystyle R}{C}}\text{-O}\cdot \;(\mathbf{6}) \;\begin{cases} \rightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}OOBu\text{-}t + R\cdot & (14a)\\ \rightarrow CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}R + t\text{-BuOO}\cdot & (14b)\end{cases}$$

Several studies have been reported on the β-elimination from alkoxyl radicals with simple alkyl substituents.[9–12] Among them, Walling and Padwa[9] have investigated the β-elimination of *t*-alkoxyl radicals by carrying out the photodecomposition of a series of *t*-alkyl hypochlorites in the presence of cyclohexane in carbon tetrachloride. From the competitive reactions of Eqs. 15a and 15b, it was found

$$R_1R_2R_3CO\cdot \begin{cases} \xrightarrow[k_a]{C_6H_{12}} R_1R_2R_3COH + C_6H_{11}\cdot & (15a)\\ \xrightarrow[k_\beta]{} R_2R_3C{=}O + R_1\cdot & (15b)\end{cases}$$

out that the rate ratio for the β-elimination of radicals at 70 °C was isopropyl : ethyl : methyl=1300 : 40 : 1. In order to compare more precisely with our results, we calculated the k_β/k_a value at 100 °C from the reported difference in activation energies between the decomposition and abstraction (i.e., $E_\beta-E_a$) and in the frequency factor (i.e., A_β/A_a). The calculated rate ratio at 100 °C is isopropyl : ethyl : methyl=167 : 7 : 1, which is close to the present value of 133 : 33 : 1.[13]

Finally, it is interesting to note that the elimination of *t*-butyldioxyl radical is quite easy in comparison with that of methyl radical. So far, the elimination of alkyl radicals has been explained by their polar effect in the transition state, i.e., the importance of **7b** in Eq. 16.[11]



$$R_1\text{-}\overset{R_2}{\underset{R_3}{C}}\text{-O}\cdot \longrightarrow [R_1\cdot\overset{R_2}{\underset{R_3}{C}}{=}O \longleftrightarrow R_1^{+}\overset{R_2}{\underset{R_3}{C}}{\cdots}O^{-}] \longrightarrow R_1\cdot + R_2COR_3 \tag{16}$$

(**7a**) (**7b**)

However, in the present case of *t*-butyldioxyl radical, it is clearly shown that the stability of radical or the contribution of **7a** is also important for the β-elimination of radicals.

Experimental

^{1}H NMR spectra were recorded on a JEOL JNM MH-100 spectrometer. GLC analyses were performed with a Shimadzu GC-9A gas chromatograph with a flame ionization detector by using a 15 m flexible fused silica capillary column (0.53 mm in diameter) coated with silicone OV-1. A Shimadzu Chromatopac C-R6A integrator was used for quantitative analyses. Mass spectra were obtained on a JEOL JMS-DX300 mass spectrometer at 70 eV under electron impact condition.

Materials. 2,2-bis(*t*-butyldioxy)propane (**1a**) was prepared in the following procedure. To a solution of acetone (5.8 g, 0.10 mol) and 94.0% *t*-butyl hydroperoxide (24.0 g, 0.25 mol), cooled to 0 °C, was added dropwise a solution of 65% sulfuric acid (15.1 g, 0.10 mol). After stirring for 30 min at 10 °C, 50 ml of ice water was added, and the organic layer was separated, washed with 2% sodium hydroxide and distilled water, dried over anhydrous magnesium sulfate. Trace amount of di-*t*-butyl peroxide was removed in vacuo. The purity of **1a** was 98.2% by iodometric titration[1] and 98.6% by GLC analysis: MS (70 eV) *m/z* (rel intensity) 131 (2), 73 (75), 58 (32), and 43 (100). ^{1}H NMR ($CDCl_3$) δ=1.20 (18H, s, *t*-CH_3) and 1.36 (6H, s, CH_3).

2,2-Bis(*t*-butyldioxy)butane (**1b**) was similarly prepared from ethyl methyl ketone (7.2 g, 0.10 mol) with 94.0% *t*-butyl hydroperoxide (24.0 g, 0.25 mol). The purity of **1b** was 97.2% by GLC analysis: MS (70 eV) *m/z* (rel intensity) 145 (2), 73 (44), 57 (30), and 43 (100). ^{1}H NMR ($CDCl_3$) δ=0.96 (3H, d, CH_2–CH_3), 1.24 (18H, s, *t*-CH_3), 1.36 (3H, s, CH_3), and 1.76 (2H, q, CH_2–CH_3).

Likewise, 2,2-bis(*t*-butyldioxy)-3-methylbutane (**1c**) was prepared from isopropyl methyl ketone (8.6 g, 0.10 mol) with 94.0% *t*-butyl hydroperoxide (24.0 g, 0.25 mol). The purity of **1c** was 98.5% by GLC analysis: MS (70 eV) *m/z* (rel intensity) 159 (2), 73 (100), 59 (28), and 43 (44). ^{1}H NMR ($CDCl_3$) δ=0.94 (6H, d, $CH(CH_3)_2$), 1.20 (21H, m, *t*-CH_3), and 2.22 (1H, q, CH).

Cumene was purified by distillation after washing with concentrated sulfuric acid.

Typical Procedure for the Thermolysis. A 2 ml cumene solution of 0.1 M 2,2-bis(*t*-butyldioxy)alkane (**1**) was placed in a glass ampoule. The ampoule was purged with nitrogen, sealed, and immersed in a constant-temperature bath regulated ±0.1 °C. The decomposition products were analyzed by GLC and/or GC-MS in comparison with authentic samples.

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13) Here, it is not necessary that the two ratios are to be precisely identical each other. This is because that the substituents on alkoxyl radical is quite different in that the *t*-butyldioxy group is involved in the present system.