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# Synthesis and Properties of Peroxy Esters Having a Benzophenone Chromophore

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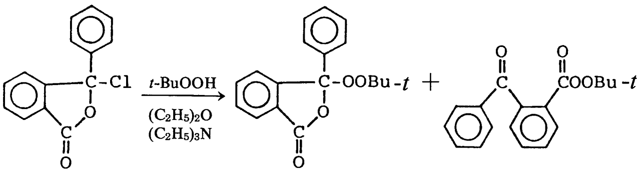
Diperoxy esters having a benzophenone chromophore have been successfully synthesized from the reaction of 3-chloro-3-phenylphthalide (**1**) with 2,5-dihydroperoxy-2,5-dimethyl-3-hexyne (**4a**) or 2,5-dihydroperoxy-2,5-dimethylhexane (**4b**). The corresponding diperoxy esters had a UV absorption above 300 nm. The free radicals produced during the photolysis of these compounds initiated the radical polymerization of methyl methacrylate at room temperature under UV light.

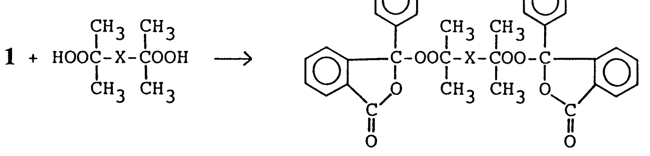
The isomerism of the various derivatives of 3-chloro-3-phenylphthalide (**1**), the pseudo-chloride of *o*-benzoylbenzoic acid, has been reported. Neckers[1] obtained a mixture of the pseudo-type peroxy ester (**2**) and the normal type peroxy ester (**3**) from the reaction of **1** with *t*-butyl hydroperoxide, and isolated **2** and **3** by means of column chromatography.



**1** **2** **3**

(1)

Rüchardt[2,3] and Chang[4] reported the synthesis of the pseudo-type diperoxy esters from the reaction of **1** with dihydroperoxides in the presence of amines in organic solvent. They obtained a viscous liquid as the reaction mixture of **1** with **4a** or **4b** and isolated the corresponding pseudo-type peroxy esters, 2,5-bis[(1-phenyl-3-oxo-1,3-dihydro-1-isobenzofuranyl)dioxy]-2,5-dimethyl-3-hexyne (**5a**) or 2,5-bis[(1-phenyl-3-oxo-1,3-dihydro-1-isobenzofuranyl)dioxy]-2,5-dimethylhexane (**5b**) by chromatography in poor yields.



**4a** (X=–C≡C–)
**4b** (X=–CH$_2$CH$_2$–)

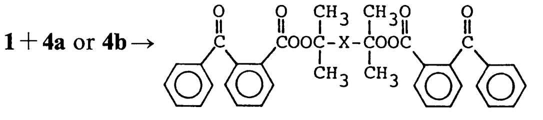
**5a** (X=–C≡C–)
**5b** (X=–CH$_2$CH$_2$–)

(2)

However, no reports concerning the synthesis of the normal type diperoxy esters have been published. If the normal type peroxy esters can be obtained, they will be useful as photoinitiators because they have a UV absorption above 300 nm.[1,5] In the present paper, we report the successful synthesis and the properties of diperoxy esters having a benzophenone chromophore from the reaction of **1** with dihydroperoxides in 40% NaOH aqueous solution.

## Results and Discussion

**Synthesis in Aq NaOH Solution.** When a benzene-dioxane solution of **1** and **4a** was treated with aq 40% NaOH solution at 0—5 °C for 4 h, a white slurry was formed. This was filtrated and washed with water and diethyl ether. After evaporation of the solvent under vacuum, a white powder was obtained. Its structure was ascertained by means of $^1$H NMR, $^{13}$C NMR and other spectral measurements. The $^1$H NMR spectrum showed this product had twelve methyl and eighteen phenyl protons. The $^{13}$C NMR spectrum showed a characteristic absorption at 163.6 (C=O of peroxy ester)[6] and 196.0 (C=O of benzophenone)[7] and the IR spectrum showed absorptions at 1760 (C=O of peroxy ester) and 1680 cm$^{-1}$ (C=O of benzophenone). These data showed that this product was the normal type peroxy ester, 2,5-bis(*o*-benzoylbenzoyldioxy)-2,5-dimethyl-3-hexyne (**6a**) (Eq.3). Compound **6a** contained 5.24% active oxygen measured by iodometric titration and it was shown to be 96.7% pure. The yield of **6a** based on **1** was 62%.



**6a** (X=–C≡C–)
**6b** (X=–CH$_2$CH$_2$–)

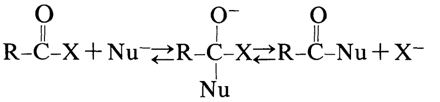
(3)

The similar treatment of **1** with **4b** gave a white powder of 2,5-bis(*o*-benzoylbenzoyldioxy)-2,5-dimethylhexane (**6b**) in a 68.4% yield (Eq.3). The structure was also ascertained by means of spectroscopic measurements. The $^1$H NMR spectrum indicated this product had twelve methyl, four methylene and eighteen phenyl protons. The IR and $^{13}$C NMR spectra showed the presence of a benzoyl group and a peroxy ester carbonyl group. This product contained 4.34% active oxygen and it was shown to be 80.7% pure. This was the first example of the synthesis of peroxy esters having a benzophenone chromophore in good yields.

**Synthesis in Pyridine/Dioxane.** In order to confirm the difference between the work of Rüchardt[2,3] and Chang[4] and the present study, we reinvestigated the reaction of **1** with **4a** under the same conditions used by Chang.[4] Thus, **1** was allowed to react with a solution of **4a** and pyridine in dioxane. The reaction mixture was diluted with water and then extracted with diethyl ether. The ether solution was treated as described in the experimental section and white crystals were obtained. The structure of this product was ascertained by means of IR, NMR, and other spectral measurements. The IR spectrum of this compound indicated absorptions at 1780 (C=O of phthalide) and 1100 cm$^{-1}$ (cyclic C–O–C) and the $^{13}$C NMR spectrum indicated characteristic absorption at 168.2 (C=O of phthalide). The mass spectrum of this compound showed the molecular weight to be 590. The lack of the absorption of a benzoyl group in the IR and $^{13}$C NMR spectra apparently showed that this compound differed from the diperoxy ester **6a**. These data indicated that this compound was the pseudo-type peroxy ester **5a**. It contained 5.30% active oxygen determined by iodometric titration and it was shown to be 97.8% pure. The yield of **5a** was only 3%.

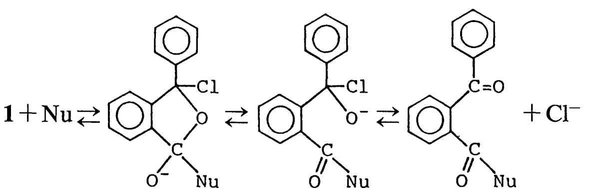
It was found that the peroxy ester **6a** was also formed under these reaction conditions. This was confirmed by HPLC analysis with an authentic sample of **6a**. However, the isolation of **6a** from this reaction mixture was unsuccessful, because only a trace amount of **6a** was formed.

**Reaction Mechanism.** It is known that **1** is susceptible to attack by nucleophiles at two centers. Displacement at the tetrahedral center leads to the pseudo-type derivatives, whereas an addition-elimination sequence at the phthalide carbonyl group results in opening of the phthalide ring.[8] The formation mechanism of the normal type peroxy ester in aq NaOH solution may be explained as follows. In nucleophilic displacement of esters, it has been shown that the addition-elimination reaction involves a tetrahedral intermediate.[9] The feasibility of the forward reaction depends on whether



$$\mathrm{R{-}\overset{O}{\overset{\|}{C}}{-}X + Nu^- \rightleftarrows R{-}\underset{Nu}{\overset{O^-}{C}}{-}X \rightleftarrows R{-}\overset{O}{\overset{\|}{C}}{-}Nu + X^-} \qquad (4)$$

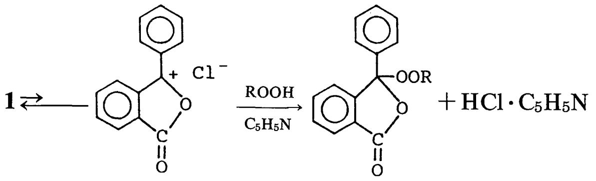
Nu$^-$ is a stronger nucleophile than X$^-$. A similar situation may exist in the case of the pseudo acid chloride derivatives. Nucleophiles stronger than the PhC(O$^-$)Cl group in **7** may be able to bring about displacement at the phthalide carbonyl group (Eq. 5).



(5)

**7**

In aq NaOH solution, a certain amount of alkyl hydroperoxide dissociates into alkylperoxide anion (ROO$^-$). This ROO$^-$ is known to be a very strong nucleophile because of its $\alpha$-effect[10] and seems to be a stronger one than the PhC(O$^-$)Cl group. On the other hand, the above-mentioned reaction will not occur in pyridine-dioxane solution because of the low concentration of ROO$^-$. It has been reported[9] that the weaker nucleophiles like organic amines bring about displacement at the tetrahedral center to form the pseudo-type derivatives. Then, in pyridine–dioxane solution, it is expected that the reaction shown in the following scheme would occur by an S$_N$1 mechanism.



(6)

**UV Absorption Spectra.** The UV absorption spectra of **5a**, **6a** and benzophenone are shown in Fig. 1. Compound **6a** behaved like benzophenone with respect to the absorption, that is, a maxima in the range 300—380 nm and a typical n-$\pi^*$ extinction coefficient of 2.29×10$^2$ dm$^3$ mol$^{-1}$ cm$^{-1}$. On the other hand, **5a** showed a dif-

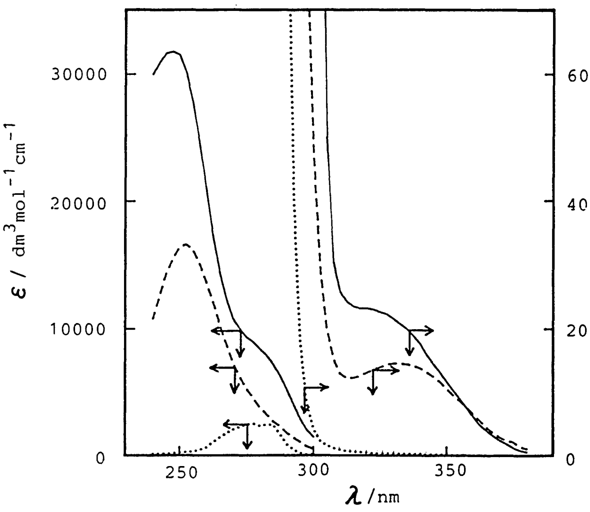


Fig. 1. UV absorption spectra of the peroxy esters and benzophenone in CH$_3$OH. ······; **5a**, ——; **6a**, – – –; benzophenone.

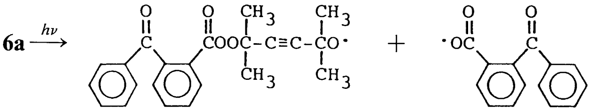
Table 1. Photodecomposition Products of **6a**[a)]

| Products | Yield[b)]/% |
|---|---|
| **10** | 100 |
| *o*-Benzoylbenzoic acid | 61 |
| Benzophenone | 20 |
| 1,2-Diphenylethane | 18 |

a) Photodecomposition was carried out in toluene at 25 °C. Initial concentration of **6a**: 0.026 mol dm$^{-3}$. b) Yields of products: [(moles of products)/(moles of **6a** consumed)]×100. The conversion of **6a** was 21.5%.

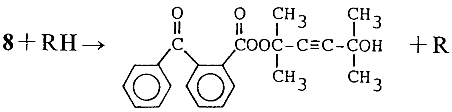
ferently shaped spectra than that of **6a**. Compound **5a** had a less intense absorption in the range 300—380 nm, which reflected the substituent in the phthalide.

**Photodecomposition.** Photodecomposition studies of **6a** were carried out in aromatic solvents at 25 °C by irradiating with 366 nm light. The decomposition products in toluene, analyzed by HPLC, were 2-(*o*-benzoylbenzoyldioxy)-5-hydroxy-2,5-dimethyl-3-hexyne (**10**), *o*-benzoylbenzoic acid and benzophenone (Table 1). The total recovery of the benzophenone moiety was 90%. The quantitative formation of **10** indicated that the photolysis of **6a** proceeded stepwise. A likely scheme leading to the products is shown by the following equations.



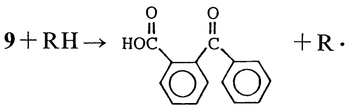
**8** **9**

(7)

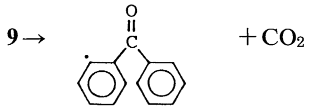


**10**

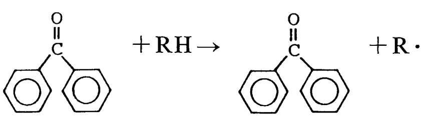
(8)



(9)



(10)



(11)

$$2\,\mathrm{R}\cdot \rightarrow \mathrm{R{-}R} \qquad (12)$$

The quantum yield of photolysis of **6a** in benzene was observed to be 0.97. Values of $\Phi$ for other peroxides in benzene have been reported by Neckers and Leffler and are 0.94 and 0.97 for *t*-butyl peroxy *p*-benzoylbenzoate (**11**)[1)] and *p*-benzoylbenzoyl peroxide (**12**),[5)] respectively. The value for **6a** was comparable to these data and it was significantly higher than that of the benzophenone-sensitized decomposition of benzoyl peroxide ($\Phi$=0.25 in benzene).[11)] This result clearly indicated the efficacy of the intramolecular energy transfer in **6a** in contrast to the bimolecular process.

Compound **6a** gave linear Stern–Volmer plots when naphthalene was used as a triplet quencher (Fig. 2), which meant the photodecomposition of **6a** proceeded via the excited triplet state.

The resulting value of $k_q\tau$ for **6a** was 4.7 dm$^3$ mol$^{-1}$. If the rate constant $k_q$ was assumed to be equal to the diffusion-controlled rate constant ($k_q$=9×10$^9$ dm$^3$ mol$^{-1}$ s$^{-1}$), the lifetime of the excited triplet, $\tau$, of **6a** was estimated to be 0.5×10$^{-9}$ s. The present $\tau$ value for **6a**

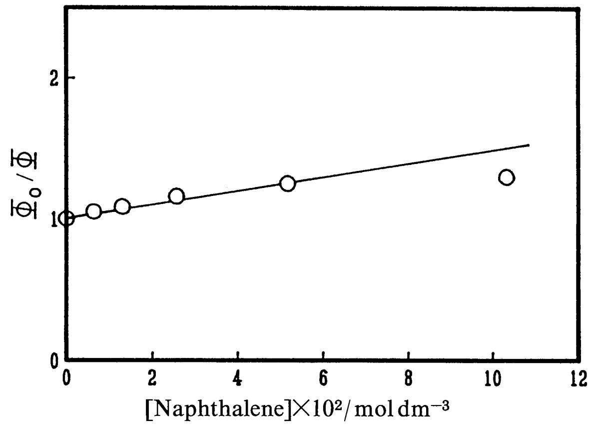


Fig. 2. Stern–Volmer plots for quenching of **6a** by naphthalene in benzene.

Table 2. Rate Constants and Activation Parameters for Thermal Decomposition of Various Peroxy Esters[a)]

| Peroxy ester | Temp | Rate const. | Activation parameters | |
|---|---|---|---|---|
| | °C | 10$^5$ $k_d$/s$^{-1}$ | $\Delta H^{\ne}$/kJ mol$^{-1}$ | $\Delta S^{\ne}$/J K$^{-1}$ mol$^{-1}$ |
| **2** | 110 | 0.83±0.03 | 164.1±4.6 | 84.1±11.7 |
| | 120 | 3.15±0.14 | | |
| | 130 | 11.24±0.82 | | |
| **5a** | 120 | 1.09±0.18 | 173.0±1.4 | 98.0±3.4 |
| | 130 | 4.26±0.16 | | |
| | 140 | 14.9 ±1.1 | | |
| **6a** | 110 | 1.49±0.11 | 149.4±0.1 | 51.0±0.14 |
| | 120 | 5.06±0.27 | | |
| | 130 | 16.13±0.21 | | |
| **6b** | 120 | 19.6 ±0.72 | | |
| **13a** | 110 | 1.69±0.14 | 167.0±3.2 | 97.8±8.2 |
| | 120 | 6.90±0.35 | | |
| | 130 | 24.8 ±1.0 | | |
| **13b** | 120 | 24.15±0.30 | | |

a) Initial concentration of peroxy esters was 0.05 mol dm$^{-3}$.

Table 3. Photopolymerization of MMA (at 25 °C 30 min)[a]

| Peroxy ester | Concn | Conv. | Molecular weight | | $M_w/M_n$ |
|---|---|---|---|---|---|
| | mol dm$^{-3}$ | % | $M_n/10^4$ | $M_w/10^4$ | |
| Blank | — | 0.05 | 194 | 358 | 1.84 |
| **2** | 0.010 | 3.9 | 9.35 | 20.1 | 2.15 |
| **5a** | 0.005 | 4.8 | 8.96 | 16.5 | 1.84 |
| **6a** | 0.010 | 14.4 | 1.99 | 5.94 | 2.98 |
| | 0.005 | 10.7 | 2.61 | 7.00 | 2.68 |
| | 0.0025 | 9.1 | 3.20 | 8.10 | 2.53 |
| **13a**+Benzophenone | 0.005 | 1.4 | 19.9 | 51.1 | 2.56 |

a) Light intensity $I_0=7.61\times10^{-4}$ Einstein min$^{-1}$.

was very close to those for **11** and **12**, that is, $\tau$ values of $4\times10^{-9}$ s[1] and $0.87\times10^{-9}$ s,[12] respectively. The lifetime of the benzophenone triplet in benzene has been reported to be $8.4\times10^{-6}$ s,[13] and $\tau$ of **6a** was $2\times10^4$ times shorter than that of benzophenone. Thus, the rates of energy transfer from the excited triplet state of benzophenone having a peroxide group to the O–O bond were about the same in these three peroxides and it was shown that the energy transfer rate was almost independent of the structure of the peroxides.

**Thermal Decompositon.** The thermal decomposition of the peroxy esters was also investigated to test the effect of the structure of the peroxy esters in the ground state. The thermolysis was carried out in cumene under nitrogen. The rates for the thermolysis were measured by iodometric titration and good first-order plots were obtained in all cases. The results are given in Table 2 together with the calculated activation parameters. The activation parameters for these peroxides indicate a nonconcerted homolytic cleavage of one peroxy bond.

The decomposition of the normal type peroxy ester **6a** occured 4—5 times faster than that of the pseudo-type peroxy ester **5a**. The rate constants and activation parameters of **6a** were comparable to those of *t*-butyl peroxybenzoate (i.e. $\Delta H^{\neq}=156.8$ kJ mol$^{-1}$ and $\Delta S^{\neq}=66.0$ J K$^{-1}$ mol$^{-1}$).[14] The activation parameters of **5a** were similar to those of **2**.

In order to clarify the effect of a benzoyl group on the thermal decomposition rate of **6a** and **6b**, the thermolysis of 2,5-bis(benzoyldioxy)-2,5-dimethyl-3-hexyne (**13a**) and 2,5-bis(benzoyldioxy)-2,5-dimethylhexane (**13b**) were carried out. The rate constants of the thermal decomposition of **6a** and **6b** having an *o*-benzoyl group were a little smaller than those of the corresponding **13a** and **13b**, respectively. This could be predicted from the electron-attractive effect of the *o*-carbonyl group.[15]

**Photopolymerization.** Some polymerization studies were carried out using the newly developed peroxy ester and methyl methacrylate (MMA) as a monomer. The results are given in Table 3.

Table 3 shows that MMA did not polymerize photochemically in the absence of any initiator under these conditions. Normal type peroxy ester **6a** initiated the photopolymerization of MMA effectively and the pseudo-type peroxy esters **2** and **5a** also initiated it. The rate of photopolymerization with **6a** was two times higher than **5a**. The photopolymerization with equimolar amounts of **13a** and benzophenone was also carried out and the result showed the polymerization rate with the benzophenone-sensitized **13a** was lower than that of **6a**.

In conclusion, the initiation of photopolymerization with **6a** occurred via the intramolecular energy-transfer mechanism from the n–π* excited state of a benzoyl group to an O–O bond.

These results showed that the peroxy esters having a benzophenone functionality provided an efficient photochemical source of free radicals.

## Experimental

$^1$H and $^{13}$C NMR spectra were recorded on a JEOL GSX 270 FT-NMR spectrometer using $CDCl_3$ as a solvent and TMS as an internal standard. HPLC analyses were performed with a Shimadzu LC-5A liquid chromatograph by using a 6.0 mm×15 cm Shimpack CLC-ODS column. GPC analyses were performed with a Shimadzu LC-6A liquid chromatograph with a Shimadzu RID-6A refractive index detector, by using two 30 cm Shodex KF-80M columns, a 30 cm Shimadzu HSG-10S, and a 30 cm Shimadzu HSG-15SH column. Infrared spectra were obtained on a JASCO A-3 infrared spectrophotometer; peaks were reported in units of cm$^{-1}$. UV spectra were measured on a Shimadzu UV-2200 UV-vis spectrophotometer. Melting points were measured with a Yanaco micro melting point apparatus. Mass spectra were obtained on a JEOL JMS-D300 mass spectrometer at 200 eV under chemical ionization conditions and on a JEOL JMS-DX300 mass spectrometer at 70 eV under electron impact conditions.

**Materials.** Cumene was purified by distillation after washing with concentrated sulfuric acid. Methyl methacrylate was purified by distillation after washing with 5% NaOH aqueous solution. 3-(*t*-Butyldioxy)-3-phenylphthalide (**2**), 2,5-bis(benzoyldioxy)-2,5-dimethyl-3-hexyne (**13a**), and 2,5-bis(benzoyldioxy)-2,5-dimethylhexane (**13b**) were the products of Nippon Oil & Fats Co., Ltd. 3-Chloro-3-phenylphthalide (**1**) was prepared by the reaction of *o*-benzoylbenzoic acid (22.6 g, 1.0 mol) with thionyl chloride (18 g, 1.5 mol in benzene (50 ml)) for 24 h under reflux. After evaporation of the thionyl chloride, the remaining oil proved to be almost pure 3-chloro-3-phenylphthalide (Cl 14.4%, purity 99.4%, no C=O absorption around 1650 cm$^{-1}$, strong C=O absorption at 1790 cm$^{-1}$).

**Preparation of 2,5-Bis[(1-phenyl-3-oxo-1,3-dihydro-1-isobenzofuranyl)dioxy]-2,5-dimethyl-3-hexyne (5a).** Compound **1** (12.2 g, 0.05 mol) was added with stirring to a solution of **4a** (4.4 g, 0.025 mol) and pyridine (4.2 g, 0.052 mol) in 13 ml of dioxane at 20—25 °C. The reaction mixture was stirred at 25—35 °C for 4 h and then allowed to stand at room temperature for about 12 h. It was diluted with 25 ml of water and then extracted five times with 25 ml of diethyl ether. The ether solution was washed five times with 10 ml portions of 5% $NaHCO_3$ aqueous solution and five times with 10 ml portions of water, and dried over anhydrous $MgSO_4$. After filtration, the diethyl ether solution was allowed to stand at −23 °C overnight. A white crystalline substance was separated. Filtration and removal of solvent in a vacuum gave a white powder. Active oxygen 5.30% (calculated 5.42%); Mp 160 °C; IR($CHCl_3$) 2975, 1780, 1610, 1475, 1460, 1290, 1160, 1100, 1060, 1000, 940, 890, and 830 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=1.37—1.52 ($CH_3$, 12H, q) and 7.32—7.80 (aromatic, 18H, m); $^{13}$C NMR ($CDCl_3$) $\delta$=26.9, 27.2 (each $CH_3$), 77.9 (acetylenic C), 85.1 (tert C), 110.1 (tert C), 123.9, 125.1, 126.2, 126.5, 126.9, 128.7, 129.8, 130.1 , 130.4, 134.2, 135.3, 146.7 (each Ph) and 168.2 (carbonyl C of phthalide); UV(MeOH) $\lambda_{max}$ nm ($\varepsilon$) 277(2490) and 284 (2410); MS(CI), Found: *m*/*z* 608; Calcd for $C_{36}H_{34}O_8N$:(M+$NH_4$), 608.

**Preparation of 2,5-Bis(*o*-benzoylbenzoyldioxy)-2,5-dimethyl-3-hexyne (6a).** Finely divided **1** (31 g, 0.127 mol) was added with stirring to a mixture of **4a** (10. 3 g, 0.058 mol) and 40% NaOH aqueous solution (12.3 g, 0.124 mol) in benzene-dioxane (20 ml, 40 ml) at 5—10 °C. The reaction mixture was stirred at 0—5 °C for 4 h. A white slurry was obtained and it was filtered and then washed three times with 60 ml of water and twice with 20 ml of diethyl ether. Vacuum drying of the solvent gave a white powder (23 g) in a 62% yield, based on the amount of **1** used; it contained 5.24% active oxygen as determined by iodometric titration. This compound gave one peak on HPLC analysis. Mp 129—130 °C; IR ($CHCl_3$) 2950, 1760, 1680, 1600, 1460, 1320, 1280, 1160, 1120, 1040, 940, 880, and 820 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=1.42 ($CH_3$, 12H, s) and 7.38—7.93 (aromatic, 18H, m); $^{13}$C NMR ($CDCl_3$) $\delta$=26.4 ($CH_3$), 78.9 (acetylenic C), 84.7 (tert C), 126.7, 128.3, 128.5, 129.7, 129.8, 129.9, 132.7, 133.3, 136.7, 141 .6 (each Ph C), 163.6 (carbonyl C of peroxy ester), and 196.0 (carbonyl C of benzophenone); UV(MeOH) $\lambda_{max}$ nm ($\varepsilon$) 203 (60800), 247 (31800), 280 (8400), and 320 (sh 230).

**Preparation of 2,5-Bis(*o*-benzoylbenzoyldioxy)-2,5-dimethylhexane (6b).** Compound **1** (12.2 g, 0.05 mol) was added with stirring to a mixture of **4b** (5.8 g, 0.025 mol) and 40% NaOH aqueous solution (5.0 g, 0.05 mol) in benzene–dioxane (5 ml, 18 ml) at 5—10 °C. The reaction mixture was stirred at 0—5 °C for 4 h and worked up as for **1a**. A white powder (15.8 g) was obtained (yield 68.4%). Active oxygen 4.34% (calculated 5.38%); Mp 154—157 °C; IR ($CHCl_3$) 2950, 1760, 1680, 1600, 1460, 1320, 1280, 1130, 1110, 940, and 880 $cm^{-1}$ $^1$H NMR ($CDCl_3$) $\delta$=1.13 ($CH_3$, 12H, s), 1.57 ($CH_2$, 4H, s), and 7.36—7.92 (aromatic, 18H, m); $^{13}$C NMR ($CDCl_3$) $\delta$=24.2 ($CH_3$), 32.6 ($CH_2$), 85.8 (tert C), 127.1, 128.2, 128.6, 129.8, 129.9, 130.0, 132.4, 133.4, 136.6, 141.3 (each Ph C), 164.3 (carbonyl C of peroxy ester), and 196.0 (carbonyl C of benzophenone).

**Photodecomposition Products.** A 10 ml toluene solution of 0.026 mol $dm^{-3}$ of **6a** was placed in Pyrex tubes (15 mm diameter), degassed by three cycles of freeze-thawing, and sealed under vacuum. The tubes were placed in a merry-go-round around a filtered UV source of 366 nm and the temperature of the tubes was controlled at 25 °C by a water-cooled bath. The light source was a TAIKA 400 W high-pressure mercury lamp combined with a Toshiba UV-D36A filter. The tubes were taken out at different predetermined intervals, and kept frozen in a freezer in the dark until analyses were done. The photolyzed solutions were analyzed by HPLC and compared with the authentic samples. The identification of 2-(*o*-benzoylbenzoyldioxy)-5-hydroxy-2,5-dimethyl-3-hexyne (**10**) was carried out by isolation from the mixture of decomposion products by means of HPLC. The fraction was collected and the removal of solvent in vacuum gave a viscous liquid. The structure was ascertained by means of IR, $^1$H NMR and $^{13}$C NMR spectroscopy. IR ($CHCl_3$) 2950, 1760, 1670, 1600, 1455, 1320, 1280, 1150, 1130, 1040, 940, 900, and 840 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$=1.46 ($CH_3$, 12H, s) and 7.45—7.98 (aromatic, 9H, m); $^{13}$C NMR ($CDCl_3$) $\delta$=26.4, 31.0 ($CH_3$), 79.2, 81.7 (acetylenic C), 64.6, 89.7 (tert C) , 126.9, 128.1 , 128.3, 128.6, 129.9, 130.1, 132.5, 133.7, 136.5, 141.4 (each Ph C), 163.8 (carbonyl C of peroxy ester), and 196.6 (carbonyl C of benzophenone); MS(EI) *m*/*z* 366($M^+$).

**Quantum Yield.** A 10 ml benzene solution of **6a** was irradiated at 25 °C. The irradiation conditions were the same as those in the decomposition products study. After irradiation, the remaining amount of peroxide was determined by iodometric titration. A tube containing an actinometric solution (benzophenone (0.1 mol $dm^{-3}$) and benzhydrol (0.1 mol $dm^{-3}$) in benzene) was irradiated in parallel with every run and light intensity was determined actinometrically.

**Thermal Decomposition.** A 10 ml cumene solution of 0. 05 mol $dm^{-3}$ peroxide was placed in a glass ampule. The ampule was purged with nitrogen, sealed, and immersed in a constant-temperature bath regulated ±0.1 °C. At successive time intervals, tubes were removed from the bath and immersed in a Dry Ice–acetone bath. The concentration of peroxide in the solution was then measured by iodometric titration. The reaction was followed up to 75—80% decomposition and exhibited first order kinetics.

**Iodometric Titration.** 10 ml of a 0.2 mol $dm^{-3}$ KOH–methanol solution was added to the solution of peroxide, then the mixture stood for 5 min in the dark, followed by iodometric titration. The titration procedure involved the use of a mixture (20 : 4 ml) of isopropyl alcohol and acetic acid as the solvent, and saturated potassium iodide aqueous solution as the source of iodine. After boiling for 3 min to liberate the iodide, the iodine was titrated to the end point with 0.01 mol $dm^{-3}$ sodium thiosulfate solution. The values for the observed first-order rate constants and their standard deviations were calculated from the first-order rate equation using the least-squares method. The values for the activation parameters and their standard deviation were calculated from the absolute rate equation of Eying using the least-squares method.

**Polymerization Studies.** The irradiation of monomer solutions was carried out in degassed sealed Pyrex tubes of 15 mm diameter that were placed in a merry-go-round with a filtered UV source of 366 nm at the center. The light source was the same as that used in the photodecomposition studies. The temperature of the tubes was maintained at 25 °C by a water-cooled bath. The yield of the polymer was measured (below 20% conversion) gravimetrically. The average molecular weight of the purified polymers was determined by GPC.

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