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Photolysis of Dibenzoyl Peroxide under Direct and Singlet Sensitized Irradiations. Mechanism for the Formation of the Geminate Product

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Attempts have been made to elucidate the mechanism for the efficient production of phenyl benzoate, the geminate product, from direct and singlet sensitized irradiations of dibenzoyl peroxide in solution. It is concluded that these irradiations produce a reactive state of the peroxide which can undergo two-bond cleavage of the O–O and C(α)–C(carbonyl) bonds to give a phenyl–benzoyloxy radical pair in a solvent cage, followed by the recombination of the component radicals to give the geminate product or by their diffusion out of the solvent cage to give diffusion products.

Although direct or aromatic hydrocarbon-sensitized photolysis[1-8] of dibenzoyl peroxide (BPO) has been shown to proceed through the singlet excited pathway,[9-15] some aspects of the reaction remain uncertain. Previously we reported[10] that direct photolysis and singlet sensitized decomposition of BPO give a noticeable amount of phenyl benzoate in contrast with triplet sensitization[4,8,16] and thermal decomposition[17,18] which give only a low yield of the ester. It has been shown that phenyl benzoate arises from the geminate recombination of benzoyloxy radicals and phenyl radicals on the basis of its noticeable formation from photolysis of BPO in toluene, *p*-xylene, and chlorobenzene[5] as well as CIDNP results.[11-15]

The efficient formation of the geminate product in the photolysis of BPO cannot be accounted for by the usual cleavage of the peroxide bond to give a pair of benzoyloxy radicals as results from thermolysis,[17,18] because benzoyloxy radicals decarboxylate too slowly[19] to afford a benzoyloxy–phenyl radical pair within the lifetime of the primary solvent-cage. The noticeable formation of the geminate product can be explained by a mechanism in which a significant fraction of excited peroxide molecules decomposes by either concerted or unusually rapid stepwise cleavage of the O–O and C(α)–C(carbonyl) bonds to give benzoyloxy–phenyl radical pairs followed by the cage recombination (Eq. 1).[3,8,20]

$$(PhCO_2)_2 \xrightarrow{h\nu} \overline{PhCO_2\cdot + \cdot OCOPh} \quad \overline{PhCO_2\cdot + Ph\cdot + CO_2} \rightarrow PhCO_2Ph \qquad (1)$$

Lemaire's group[8] investigated direct photolysis of BPO in solution, particularly in view of wavelength dependence of its quantum yield, and postulated that benzoyloxy radicals would be formed in the vibrationally excited state on 313-nm light irradiation, and that irradiation with shorter wavelength light would directly generate phenyl radicals which, in high concentrations of BPO, might attack the peroxide to give phenyl benzoate and benzoyloxy radicals.

On the other hand, McBride *et al.*,[21] by ESR spectroscopic investigation, reported that UV-irradiation of crystalline acetyl benzoyl peroxide at 64 K gave benzoyloxy–methyl radical pairs, and that subsequent irradiation with visible light led to the decarboxylation of the benzoyloxy radicals to give phenyl–methyl radical pairs, with the highest efficiency on irradiation with 750-nm light. The photo-induced decarboxylation of benzoyloxy radicals could explain the noticeable formation of phenyl benzoate in the photolysis of BPO.

In the present paper we report some features of the photolysis of BPO and attempts to elucidate the mechanisms for the formation of the geminate product. The present results will show that the simultaneous two-bond cleavage plays an important role in the noticeable formation of the geminate product, and that concurrent irradiation of visible light does not remarkably contribute to the formation of the geminate product.

Results

Thermal and Photochemical Decomposition of Substituted Dibenzoyl Peroxides. Dibenzoyl, bis(4-methoxybenzoyl), bis(4-methylbenzoyl), and bis(4-chlorobenzoyl) peroxides ($ArCO_2OCOAr$, 0.03 M) were thermally decomposed at 80, 90, and 100 °C and photolyzed at room temperature without any sensitizer in benzene and with chrysene (0.002 M) as a singlet sensitizer in benzene until the peroxides were completely decomposed. The resulting geminate products, $ArCO_2Ar$, were determined by GLPC analysis. The results are summarized in Table 1.[22]

CIDNP in Photolysis of BPO. In order to clearly observe a CIDNP spectrum due to the geminate product, deuterated BPO was employed to eliminate

Table 1. Yield of substituted phenyl benzoates in thermal and photochemical decompositions of bis(4-substituted benzoyl) peroxides

Mode of decomposition	Yield of substituted phenyl benzoate, $ArCO_2Ar$ (mol/mol-peroxide)			
	Ar = $MeOC_6H_4$	MeC_6H_4	C_6H_5	ClC_6H_4
Direct photolysis	0.047	0.072	0.13	0.074
Chrysene sensitized photolysis	0.037	0.056	0.12	0.044
Thermolysis at 80 °C	0.011	0.006	0.022	0.005
Thermolysis at 90 °C	0.011	0.006	0.023	0.004
Thermolysis at 100 °C	0.010	0.007	0.025	0.006

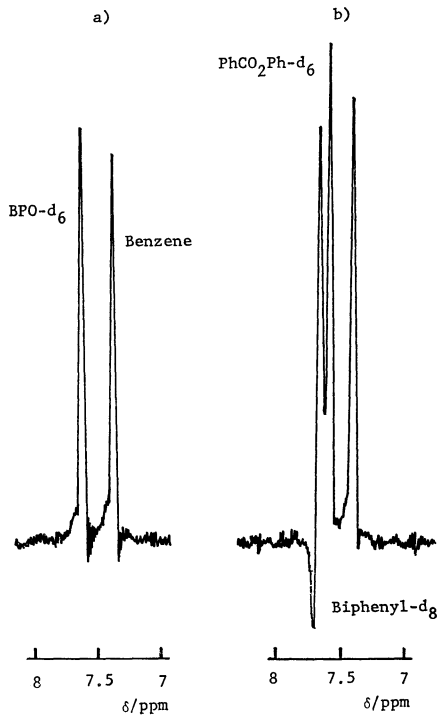

Fig. 1. CIDNP spectrum of BPO-d_6 in benzene-d_6 before irradiation (a) and during irradiation (b).

nuclear spin-spin couplings between aromatic ring protons and lengthen spin-lattice relaxation times of the products. When BPO-2,2′,4,4′,6,6′-d_6 was photolyzed in benzene-d_6 at room temperature with a 1 kW high pressure mercury lamp in the probe of an NMR spectrometer, a very clear polarized spectrum was observed as shown in Fig. 1. The enhanced absorption represents the meta protons on the phenoxyl segment of the geminate product, phenyl-2,4,6-d_3 benzoate-2,4,6-d_3, and the emission is assigned to biphenyl-2,2′,3,4,4′,5,6,6′-d_8. Irradiation of a solution of BPO-d_6 in the presence of naphthalene or chrysene in benzene-d_6 gave the same polarized NMR spectrum as the direct irradiation.

Sensitized Decomposition of BPO in the Presence of a Radical Scavenger. BPO (0.02 M) was irradiated with 366-nm light at room temperature in a mixed solvent consisting of varying fractions of styrene and benzene in the presence of chrysene (0.002 M) as a singlet sensitizer until the peroxide was completely decomposed (3.75 h). The yields of phenyl benzoate were determined by GLPC analysis to be 0.10, 0.10, 0.07, and 0.09 mol per 1 mol of the peroxide at the concentrations of styrene in 0, 1.74, 4.35, and 6.09 M, respectively.

Trapping of Carbon Dioxide in Thermal and Photochemical Decompositions of BPO in the Presence of a Radical Scavenger. In a mixture of varying fractions of benzene and styrene, BPO (0.02 M) was thermally decomposed at 80 °C and photolyzed at room temperature with a 400 W high pressure mercury lamp through a Pyrex wall. The resulting carbon dioxide was absorbed with an Ascarite tube and determined by gravimetry. The results are depicted in Fig. 2. The yields of carbon dioxide were suppressed to approach limiting values

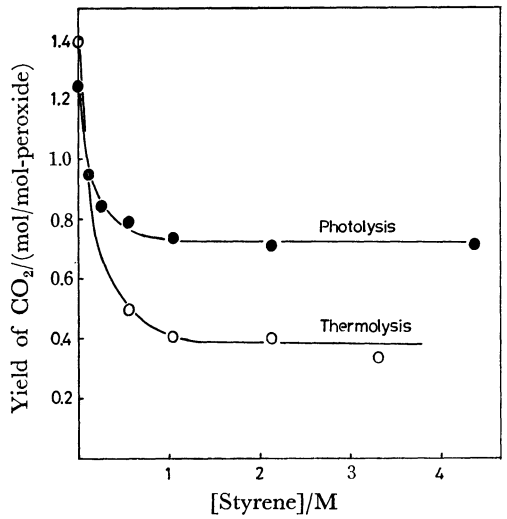

Fig. 2. Change of carbon dioxide yield in thermolysis and photolysis of BPO with concentration of styrene in benzene.

as the fraction of styrene increased in both photolysis and thermolysis. The limiting yields, however, are different between the photolysis (*ca.* 0.7 mol per 1 mol of the peroxide) and the thermolysis (*ca.* 0.3 mol).

Spin Trapping in Decomposition of BPO. When a solution of BPO (0.01 M) in benzene containing *N*-benzylidene-*t*-butylamine oxide (0.1 M) was irradiated in the cavity of an ESR spectrometer at room temperature with a 400 W high pressure mercury lamp for several minutes, signals due to both of the benzoyloxy spin adduct, *N*-*t*-butyl-α-benzoyloxybenzylaminyloxyl ($PhCO_2$–SA, a_N=14.0 G),[23] and the phenyl spin adduct, *N*-*t*-butyldiphenylmethanaminyloxyl (Ph-SA, a_N=15.5 G),[23] were observed in the ESR spectrum. The ratio of these spin adducts, $PhCO_2$–SA/Ph–SA, was determined to be *ca.* 5.6. This value was not varied with irradiation time (5—10 min). On the other hand, heating of a benzene solution of the same composition as above at 40 °C for 8 min gave only the signals due to the benzoyloxy spin adduct.

Effects of Singlet Excitation Energy of Sensitizers on the Geminate Product Yield. BPO (0.03 M) was irradiated in benzene at room temperature in the presence of aromatic hydrocarbons (1.3×10^{-4}—1.8×10^{-2} M) as sensitizers with a 1 kW high pressure mercury lamp through a Pyrex wall. The concentrations of the sensitizers were chosen so that the sensitizers absorbed more than 95% of incident light at 313 nm. Table 2 summarizes the yields of the products determined by GLPC analysis. The yield of phenyl benzoate tends to increase with increasing singlet excitation energy of the sensitizers.

Effects of Longer Wavelength Light on the Product Yields. In order to explore the contribution of the light-induced decarboxylation of benzoyloxy radicals to the formation of the geminate and diffusion products, in the course of the thermal decomposition, UV-irradiation, and nitrogen laser irradiation of BPO (0.03 M) in benzene, the solutions were concurrently irradiated with light of wavelengths longer than 400 nm. In this wavelength region neither BPO nor chrysene has

Table 2. Yields of products in hydrocarbon-sensitized photolysis of dibenzoyl peroxide (0.03 M) in benzene[a)]

Sensitizer	Singlet excitation energy of sensitizer[b)] /kcal mol^{-1}	Concentration of sensitizer /M	Yield (mol/mol-peroxide)		
			$PhCO_2Ph$	$PhCO_2H$	Ph-Ph
Naphthalene	91	1.8×10^{-2}	0.16	0.35	0.22
Triphenylene	83	6.7×10^{-3}	0.15	0.33	0.22
Fluoranthene	80	5.0×10^{-4}	0.10	0.31	0.22
Chrysene[c)]	79	2.0×10^{-3}	0.12		
Pyrene	77	1.3×10^{-4}	0.10	0.44	0.29
Anthracene	75	1.7×10^{-3}	0.091	0.46	0.27
9,10-Diphenylanthracene	70	1.2×10^{-3}	0.096	0.41	0.24
Perylene	65	3.2×10^{-3}	0.063	1.5	0.16

a) Irradiation was carried out through a Pyrex wall unless otherwise noted. b) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, Inc., New York, N. Y. (1973). c) Irradiated at 366 nm.

Table 3. Yields of products in thermal and photochemical decomposition of BPO (0.03 M) in benzene with concurrent irradiation of a tungsten-bromine lamp

Light source	Yield (mol/mol-peroxide)		
	$PhCO_2Ph$	$PhCO_2H$	Ph-Ph
HPML[a)]	0.13	0.45	0.23
HPML[a)] + BL[b)]	0.11	0.44	0.30
Thermal (80 °C)	0.02	0.31	0.26
Thermal (80 °C) + BL[b)]	0.02	0.22	0.33
N_2 Laser[c)]	0.16	0.45	0.30
N_2 Laser[c)] + BL[b)]	0.16	0.45	0.35

a) HPML stands for a high pressure mercury lamp. b) BL stands for a tungsten-bromine lamp. c) Sensitized with chrysene (6×10^{-3} M).

Table 4. Yields of products in photolysis of BPO with 313-nm light of varying intensity

Relative light intensity	Yield (mol/mol-peroxide)		
	$PhCO_2Ph$	$PhCO_2H$	Ph-Ph
0.23	0.21	0.51	0.33
0.37	0.17	0.48	0.42
0.58	0.17	0.48	0.44
0.61	0.08	0.47	0.29
0.68	0.17	0.45	0.37
1	0.14	0.45	0.30

any absorption band. Table 3 summarizes the yields of the products determined by GLPC analysis. The yield of biphenyl seems to be increased by irradiation of the longer wavelength light; however, no remarkable effects on the yield of phenyl benzoate are observed.

Effects of Light Intensity on the Product Yields. BPO (0.03 M) in benzene was irradiated with 313-nm light of varying intensity. The yields of the products determined by GLPC analysis are summarized in Table 4, which shows that the increase of light intensity in nearly five times does not remarkably affect the distribution of the products, although the yields of phenyl benzoate and benzoic acid tend to be slightly reduced with increasing light intensity.

In order to investigate the effect of strong laser pulses on the geminate product formation, an equimolar mixture of BPO (0.015 M) and deuterated BPO, $(C_6D_5CO_2)_2$, (0.015 M) was irradiated in toluene with chrysene with a nitrogen laser at room temperature. Mass spectrometric examination of the resulting ester showed that only the undeuterated ester, $C_6H_5CO_2C_6H_5$, and the ester deuterated on both of the aromatic rings, $C_6D_5CO_2C_6D_5$, were produced but even a trace amount of the ester with one deuterated aromatic ring, $C_6D_5CO_2C_6H_5$ or $C_6H_5CO_2C_6D_5$, was not produced.

Discussion

Production of phenyl benzoate from decomposition of dibenzoyl peroxide (BPO) in solutions under nitrogen remains in a low yield from thermolysis[17,18)] but is noticeable from direct and singlet sensitized photolyses.[2,5,7,10)] As Table 1 indicates, substituted dibenzoyl peroxides behave like unsubstituted BPO. Thus, the former peroxides also gave geminate products in higher yields in photolyses than in thermolyses. These findings suggest that the direct and singlet sensitized photolyses effectively produce benzoyloxy–phenyl radical pairs to give phenyl benzoate.

Formation of phenyl benzoate as the geminate product is further confirmed by the effect of styrene and CIDNP. As described above, increasing fractions of styrene added in the photolyzing system did not show any significant effect on the yield of phenyl benzoate. In addition, in CIDNP (Fig. 1), the sharp enhanced absorption due to the meta protons on the phenoxyl segment of the resulting phenyl-d_3 benzoate-d_3 indicates that the polarization must be due to phenyl-d_3 radicals which have escaped from the initial polarizing cage and retained some polarization through their recombination with benzoyloxy radicals.[13)] This observation accords well with the prediction by Kaptein's[24)] and Closs's[25)] rules applied to the polarizing pair of benzoyloxy and phenyl radicals.

The effect of styrene and a spin trap revealed the effective decarboxylation taking place during the pho-

tolysis. Figure 2 indicates that as the fraction of styrene increases, the production of carbon dioxide is rapidly suppressed to approach limiting yields in both photolysis and thermolysis. The limiting yield is much higher in the photolysis (*ca.* 0.7 mol per 1 mol of the peroxide) than in the thermolysis (*ca.* 0.3 mol).

On decomposition of BPO in the presence of the spin trap, *N*-benzylidene-*t*-butylamine oxide, both phenyl spin adduct and benzoyloxy spin adduct were obtained in the photolysis in a ratio of 1:5.6, whereas only the benzoyloxy spin adduct was obtained in the thermolysis. The extent of the decarboxylation under spin trapping conditions is estimated to be $1/(1+5.6)=15\%$ and this figure is lower than that estimated from scavenging by styrene to measure carbon dioxide, $0.71/2=35\%$. This difference probably reflects the different ability between styrene and the nitrone to trap benzoyloxy radicals.

From the results mentioned above, it is obvious that the photolysis of BPO produces certain amounts of phenyl radicals and carbon dioxide without the intervention of benzoyloxy radicals of usual lifetimes which would be effectively scavenged by styrene or the spin trap. For the efficient formation of the benzoyloxy–phenyl radical pairs the following three possibilities can be envisaged.

The first possibility is a simultaneous two-bond cleavage of the peroxide in which the singlet excitation energy will be converted to vibrational energy enough to break both the oxygen-oxygen and carbon(α)-carbon(carbonyl) bonds giving simultaneously a benzoyloxy radical, a phenyl radical, and a carbon dioxide molecule (one-photon simultaneous process, Eq. 2). Direct excitation and excited singlet sensitizers seem to provide sufficient energies for the peroxide bond cleavage and the decarboxylation of benzoyloxy radicals in the thermal processes, *ca.* 31[26] and 13[19] kcal mol^{-1}, respectively.

The second possibility is a rapid successive two-bond cleavage in which the photolysis gives vibrationally[8] or electronically excited benzoyloxy radicals followed by their rapid decarboxylation within the lifetime of the solvent cage (one-photon successive process, Eq. 3).

A two-photon process is the third possibility where benzoyloxy radicals once formed are excited by continuing irradiation and decarboxylate within the lifetime of the solvent cage (two-photon successive process, Eq. 4).

$$PhCO_2OCOPh \xrightarrow{h\nu} \overline{PhCO_2 + CO_2 + Ph\cdot} \quad (2)$$

$$PhCO_2OCOPh \xrightarrow{h\nu} \overline{(PhCO_2\cdot)^* + PhCO_2\cdot} \longrightarrow \overline{Ph\cdot + CO_2 + PhCO_2\cdot} \quad (3)$$

$$PhCO_2OCOPh \xrightarrow{h\nu} \overline{PhCO_2\cdot + PhCO_2\cdot} \xrightarrow{h\nu} \overline{(PhCO_2\cdot)^* + PhCO_2\cdot} \longrightarrow \overline{Ph\cdot + CO_2 + PhCO_2\cdot} \quad (4)$$

In the singlet sensitization, the singlet excited hydrocarbon molecule will interact with the peroxide molecule to give a reactive exciplex.[9,10] In this exciplex the singlet excitation energy of the hydrocarbon moiety would be converted to the vibrational energy of the complex to cause the cleavage of the peroxide moiety into free radicals. Table 2 shows that the yield of phenyl benzoate tends to increase with increasing singlet excitation energy of the sensitizers. This result suggests that, on formation of the reactive exciplex, the higher the singlet excitation energy of the sensitizer, the more efficient the cleavage of both of the oxygen-oxygen and carbon-carbon bonds of BPO to give the geminate product.

Table 3 indicates that the concurrent irradiation with a tungsten-bromine lamp, which was used to increase light intensity in the visible region, gives no pronounced effect on the product distribution, although it seemingly enhances the formation of biphenyl in both photolysis and thermolysis. Consequently, under the present experimental conditions, the visible light illumination does not significantly accelerate the decomposition of benzoyloxy radicals in contrast with the reported results for crystalline acetyl benzoyl peroxide.[21]

Concurrent illumination of a tungsten-bromine lamp on the samples irradiated by a nitrogen laser was undertaken for the following intention. Thus, under laser irradiation, the excited peroxide molecules undergo decomposition almost during the nanosecond duration of the pulse, and the resulting benzoyloxy radicals would decarboxylate during the "dark period" of nearly 10 ms before the next pulse irradiation. Accordingly, the concurrent irradiation with a tungsten-bromine lamp could act during the "dark period" on the free radicals. However, as Table 3 indicates, the tungsten-bromine lamp was not effective to induce the decarboxylation of benzoyloxy radicals.

Furthermore, Table 4 shows that on irradiation at 313 nm the increase of light intensity in nearly five times does not remarkably affect the distribution of the products, although the yields of phenyl benzoate and benzoic acid tend to be slightly reduced with increasing light intensity. This finding suggests that 313-nm light also does not significantly induce the decarboxylation of benzoyloxy radicals.

On laser irradiation, it would be expected that the laser pulses, which supply 10^6—10^7 times as many photons as a 1 kW high pressure mercury lamp in a unit time, would transiently generate high concentrations of free radicals, and hence benzoyloxy and phenyl radicals diffused from the different initial solvent cages would combine to give phenyl benzoate as a diffusion product in addition to the geminate product. However, chrysene-sensitized laser irradiation of an equimolar mixture of BPO and BPO-d_{10} in toluene gave no diffusion products, $C_6H_5CO_2C_6D_5$ and $C_6D_5CO_2C_6H_5$, but gave only a mixture of the geminate products, $C_6H_5CO_2C_6H_5$ and $C_6D_5CO_2C_6D_5$. This result shows that even on irradiation with light of strong intensity benzoyloxy–phenyl radical pairs effectively result in the geminate product, and that the radicals escaped from the solvent cage undergo decomposition or reactions with the solvent before they would randomly combine to give phenyl benzoate.

Therefore it is reasonable to conclude that in the decomposition of BPO from its excited singlet state,

the one-photon simultaneous (Eq. 2) or successive two-bond cleavage (Eq. 3) mainly contributes to the efficient formation of the benzoyloxy–phenyl radical pairs leading to the noticeable formation of the geminate product, and that the contribution of the two-photon process involving the light-induced decarboxylation of benzoyloxy radicals (Eq. 4) would be negligible.

Finally, it should be mentioned that both of the direct irradiation and singlet sensitized irradiation of BPO give nearly the same distribution of the products, suggesting that both photolytic reactions will proceed through the same reactive state of the peroxide. On direct photolysis, the initially produced (Franck-Condon-state), electronically excited peroxide molecule would relax into a reactive state which can dissociate at both of the O–O and C–C bonds. In the singlet sensitization, however, the singlet excited sensitizers do not have sufficient energies to be transferred to give electronically excited peroxide molecules as produced on direct photolysis. Consequently, the excited sensitizer molecules would complex with ground-state peroxide molecules to give reactive exciplexes, in which the electronic excitation energy would be relaxed through vibrational energy probably leading the peroxide moiety to the same reactive state as produced on direct photolysis.

Experimental

Materials. Dibenzoyl peroxide-2,2′,4,4′,6,6′-d_6, dibenzoyl peroxide-2,2′,3,3′,4,4′,5,5′,6,6′-d_{10}, bis(4-chlorobenzoyl), bis(4-methylbenzoyl), and bis(4-methoxybenzoyl) peroxides were prepared from the corresponding acyl chlorides and sodium peroxide, and recrystallized from dichloromethane–methanol. Dibenzoyl peroxide commercially obtained was purified similarly. Benzoyl-2,4,6-d_3 chloride was prepared in the following manner. A mixture of anilinium chloride and deuterated water was refluxed, and the anilinium salt was recovered. This process was repeated three times. Anilinium-2,4,6-d_3 chloride obtained was converted to benzonitrile-2,4,6-d_3 by the Sandmeyer reaction, and its hydrolysis and chlorination gave benzoyl-2,4,6-d_3 chloride. Other substituted benzoyl chlorides were prepared from the corresponding, commercially purchased acids in a usual manner. Aromatic hydrocarbons used as singlet sensitizers were purified by column chromatography and crystallization. Benzene and styrene were purified by distillation. Phenyl-2,4,6-d_3 benzoate-2,4,6-d_3 was prepared by irradiation of BPO-d_6 in carbon tetrachloride in the presence of naphthalene.

Photolysis. A solution of a peroxide (0.03 M) in benzene (3 ml) in a Pyrex tube was degassed by the usual freeze-thaw cycles or deaerated by bubbling of nitrogen, and irradiated by a 400 W or a 1 kW high pressure mercury lamp immersed in a Pyrex cooling well or furthermore surrounded by Toshiba UV-D36B glass filters when chrysene (0.002 M) was used as a sensitizer using a merry-go-round type Riko Rotary Photochemical Reactor, Model RH400-10W. Irradiation was continued for five times the half-life periods of the peroxide determined by iodometric analysis under the same conditions.

Thermolysis. A solution of a peroxide (0.03 M) in benzene (3 ml) in a Pyrex tube was degassed by the usual freeze-thaw cycles and heated in an air bath constantly maintained at 80, 90, and 100 °C for five times the half-life periods. The reaction times were chosen according to the reported decomposition rate constants of peroxides.[27]

Product Analyses. Phenyl benzoate, substituted phenyl benzoates, biphenyl, and benzoic acid were determined by GLPC analysis on a Shimadzu GC 4CM gas chromatograph equipped with a flame ionization detector. The following columns were used for quantitative analyses: Diethylene glycol succinate (5%) with H_3PO_4 (2%), Polyethylene Glycol 20 M (5%), and Silicone GE SE-30 (2%). Carbon dioxide was determined gravimetrically using an Ascarite tube.

Irradiation by a Tungsten-bromine Lamp during Thermolysis and Photolysis. A solution of BPO (0.03 M) in benzene (10 ml) was irradiated under nitrogen atmosphere at room temperature for 3 h by two lamps at the same time, a 1 kW high pressure mercury lamp immersed in a Pyrex cooling well and a 650 W tungsten-bromine lamp (Ushio, Type JCD) through a Toshiba Y-43 glass filter which transmits light longer wavelength than 400 nm.

Thermolysis under illumination of visible light was performed in a water bath kept at 80 °C for 23.75 h, during which the reacting solution was irradiated by the 650 W tungsten-bromine lamp through a water layer and a Toshiba Y-43 glass filter.

Irradiation of 313-nm Light of Varying Intensity. A solution of BPO (0.03 M) in benzene (10 ml) was irradiated under nitrogen atmosphere at room temperature for 11.5—51 h through a filter solution ($NiSO_4 \cdot 7H_2O$, 0.5 g/ml; transmittance, *ca.* 70% at 313 nm) and a Pyrex wall using a 1 kW high pressure mercury lamp. Light intensity was reduced by inserting piled silk cloth between a sample tube and the filter solution. Relative light intensity was calculated from half-life periods determined by iodometry.

CIDNP Measurements and ESR Spectra. CIDNP measurements were performed on a JEOL JNM-PX-100 NMR spectrometer and ESR spectra were recorded on a JEOL JES-ME-1X ESR spectrometer. A 1 kW and a 400 W high pressure mercury lamp were used as light sources in the CIDNP and ESR measurements, respectively.

Laser Photolysis. Nitrogen laser pulses were supplied from a 1 MW (3.5 mJ) Lambda Physik laser pulse generator. A solution of BPO (0.03 M) in benzene (2 ml) containing chrysene (0.006 M) was irradiated by the laser (100 pulses per second). Irradiation was continued for five times the half-life periods determined by iodometry in advance.

Mass Spectrometry. A solution of BPO and BPO-d_{10} (0.015 M, respectively) in toluene (2 ml) containing chrysene (0.006 M) was irradiated by the nitrogen laser. The photolyzed sample was examined by gas chromatography/mass spectrometry (Hitachi RMU-6M GC/MS). The relative intensities of the parent peaks of phenyl benzoate and phenyl-d_5 benzoate-d_5 were found to be different between the ascending part and descending part of the gas chromatographic peak (*e.g.*, 0.7 and 1.6, respectively), but in neither case a peak was detected at *m/e* 203 attributable to phenyl benzoate-d_5 or phenyl-d_5 benzoate.

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References

1) F. Fichter and A. Schnider, *Helv. Chim. Acta*, **13**, 1428 (1930).
2) Y. Ikeda, *Nippon Kagaku Zasshi*, **79**, 354 (1958).

3) J. C. Bevington and T. D. Lewis, *Trans. Faraday Soc.*, **54**, 1340 (1958).
4) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3413 (1965).
5) T. Nakata, K. Tokumaru, and O. Simamura, *Tetrahedron Lett.*, **1967**, 3303.
6) H. C. Box, E. E. Sudzinski, and H. G. Freund, *J. Am. Chem. Soc.*, **92**, 5305 (1970).
7) J. D. Bradley and A. P. Roth, *Tetrahedron Lett.*, **1971**, 3907.
8) P. Lebourgeois, R. Arnaud, and J. Lemaire, *J. Chim. Phys.*, **1972**, 1633, 1643.
9) T. Nakata and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **43**, 3315 (1970).
10) K. Tokumaru, A. Ohshima, T. Nakata, H. Sakuragi, and T. Mishima, *Chem. Lett.*, **1974**, 571.
11) R. Kaptein, J. A. den Hollander, D. Antheunis, and L. J. Oostehoff, *J. Chem. Soc., Chem. Commun.*, **1970**, 1687.
12) S. R. Fahrenholtz and A. M. Trozzolo, *J. Am. Chem. Soc.*, **93**, 251 (1971).
13) S. R. Fahrenholtz and A. M. Trozzolo, *J. Am. Chem. Soc.*, **94**, 282 (1972).
14) H. D. Roth and M. L. Kaplan, *J. Am. Chem. Soc.*, **95**, 262 (1973).
15) C. F. Poranski, Jr., W. B. Moniz, and S. A. Sojka, *J. Am. Chem. Soc.*, **97**, 4275 (1975).
16) W. F. Smith, Jr., *Tetrahedron*, **25**, 2071 (1969).
17) D. H. Hey, M. J. Perkins, and G. H. Williams, *J. Chem. Soc.*, **1964**, 3412.
18) K. Tokumaru, *Nippon Kagaku Zasshi*, **92**, 887 (1971).
19) T. Suehiro and M. Ishida, *Bull. Chem. Soc. Jpn.*, **44**, 1692 (1971).
20) J. Saltiel and H. C. Curtis, *J. Am. Chem. Soc.*, **93**, 2056 (1971).
21) N. J. Karch, E. T. Koh, B. L. Whitsel, and J. M. McBride, *J. Am. Chem. Soc.*, **97**, 6729 (1975).
22) Bradley and Roth[7] reported that direct photolysis of bis(4-chlorobenzoyl) and bis(4-methylbenzoyl) peroxide gave the corresponding geminate products in the yields of 0.04 and 0.16 mol/mol-peroxide, respectively.
23) E. G. Janzen, C. A. Evans, and Y. Nishi, *J. Am. Chem. Soc.*, **94**, 8236 (1972).
24) R. Kaptein, "Chemically Induced Magnetic Polarization," ed by A. Leply and G. L. Closs, Wiley, New York, N. Y. (1973), Chap. 4.
25) G. L. Closs and M. S. Czerpski, *J. Am. Chem. Soc.*, **99**, 6127 (1977).
26) I. Jaffe, E. J. Prosen, and M. Szwarc, *J. Chem. Phys.*, **27** 416 (1957).
27) C. G. Swin, W. H, Stockmayer, and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950); A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951); W. Cooper, *J. Chem. Soc.*, **1951**, 3106.