

# Effects of methylene chains on photoreactions of diphenylalkane-diones and phenylalkenones

Mitsunobu Nakamura,<sup>\*a</sup> Masamichi Miki<sup>a</sup> and Tetsuro Majima<sup>\*b</sup>

<sup>a</sup> Department of Engineering Science, Himeji Institute of Technology, Shosha 2167, Himeji, Hyogo 671-2201, Japan

<sup>b</sup> The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

Received (in Cambridge, UK) 16th August 1999, Accepted 11th November 1999

Upon conventional UV-irradiation of 1,ω-diphenylalkane-1,ω-dione (PhC(O)–(CH<sub>2</sub>)<sub>n</sub>–C(O)Ph, *n* = 5, 6, 7, 8, and 10) in acetonitrile using a medium-pressure Hg lamp, an intramolecular γ-hydrogen abstraction of the triplet ketone (type II photoreaction) occurred to give acetophenone and 1-phenylalk-*n*-en-1-one (PhC(O)–(CH<sub>2</sub>)<sub>n–3</sub>–CH=CH<sub>2</sub>), respectively, in a 1 : 1 product ratio. Type II photoreaction occurred in all the 1,ω-diphenylalkane-1,ω-diones. The product 1-phenylalk-*n*-en-1-one also underwent a photoreaction to give secondary products under prolonged photoirradiation. The secondary products obtained from 1-phenylalk-*n*-en-1-one varied with the number of the methylene group *n*. For instance, no reaction occurred on the photolysis of 1-phenylbut-4-en-1-one obtained from type II photoreaction of 1,7-diphenylheptane-1,7-dione (*n* = 5). On the other hand, 1-phenylhex-5-en-1-one from the photoreaction of 1,8-diphenyloctane-1,8-dione (*n* = 6) gave acetophenone, buta-1,3-diene, 1-phenylhex-4-en-1-one, 2-vinyl-1-phenylcyclobutan-1-ol, and 1-phenylcyclohex-3-en-1-ol. Photolyses of other 1,ω-diphenylalkane-1,ω-dione (*n* = 7, 8, and 10) gave similar secondary products. Consequently, type II photoreaction of 1,ω-diphenylalkane-1,ω-dione occurs in which the number of methylenes between the two benzoyl groups does not affect the products. On the other hand, the length of the methylene group influences the photoreaction of 1-phenylalk-*n*-en-1-ones.

## Introduction

It is well known that an intramolecular γ-hydrogen abstraction occurs to form a 1,4-biradical through triplet excited states of benzoyl compounds.<sup>1,2</sup> The 1,4-biradical produces acetophenone and olefin *via* radical β-fission, and cyclobutanol *via* radical coupling.<sup>3</sup> Photoreactions of 1,ω-diphenylalkane-1,ω-diones (PhC(O)(CH<sub>2</sub>)<sub>n</sub>C(O)Ph) such as 1,5-diphenylpentane-1,5-dione (*n* = 3) and 1,6-diphenylhexane-1,6-dione (*n* = 4) have been investigated, although there are no reports on the photoreaction of 1,ω-diphenylalkane-1,ω-diones having longer methylene-chain spacers than *n* = 4.<sup>4</sup> On the photoirradiation of 1,5-diphenylpentane-1,5-dione (*n* = 3), acetophenone, 1-phenylprop-2-en-1-one, and 2-hydroxy-2-phenylcyclobutyl phenyl ketone are produced through the 1,4-biradical generated by the intramolecular hydrogen abstraction by the carbonyl group in the triplet excited state.<sup>4e</sup> The photoirradiation of 1,6-diphenylhexane-1,6-dione (*n* = 4) also gives acetophenone, 1-phenylbut-3-en-1-one, and 2,5-diphenylfuran from the 1,4-biradical.<sup>4c</sup>

No intramolecular interaction between the two benzoyl chromophores exists in the ground states. On the other hand, a weak intramolecular interaction between the two benzoyl chromophores of 1,5-diphenylpentane-1,5-dione (*n* = 3) occurs in the triplet excited state because of the longer wavelength shift of the phosphorescence.<sup>4e</sup> The photoreactivity of 1,ω-diphenylalkane-1,ω-diones is similar to that of alkyl phenyl ketones with no effect of *n*.

Since intramolecular interaction between the benzoyl chromophores hardly occurs in the ground and excited states, it is possible that a high power photoirradiation using a laser pulse could simultaneously or consecutively excite two benzoyl groups at both ends of the methylene spacer. Butcher and co-workers have reported that photochemistry of 1,12-bis[4-(2-oxo-3-phenylpropyl)phenyl]dodecane gives a macrocyclic compound *via* an intramolecular coupling of the biradical

generated from α-bond fission of two carbonyl groups at a high photon density using a XeCl excimer laser.<sup>5</sup>

There are many studies of two photon reactions,<sup>6</sup> for example, Ouchi and co-workers have reported that the formation of acenaphthene from 1,8-bis(bromomethyl)naphthalene with irradiation using a KrF or ArF excimer laser occurs *via* the intramolecular radical coupling of naphthalene-1,8-diylbismethyl which is generated through the two photon absorption of 1,8-bis(bromomethyl)naphthalene.<sup>6d</sup>

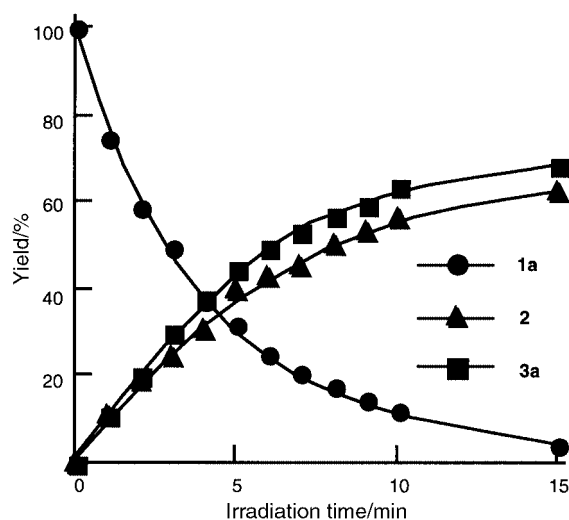
The simultaneous or consecutive excitation of the 1,ω-diphenylalkane-1,ω-diones can be assumed to occur *via* two photon excitation. Two photon absorption of the bichromophoric molecules is able to generate a short-lived active species having more than one active centre in the molecule, resulting in the characteristic products. Therefore, two photon reactions of the bichromophoric molecule are interesting from the mechanistic and synthetic points of view.

In the photoirradiation of 1,ω-diphenylalkane-1,ω-diones at a high photon density using a laser, it is assumed that a tetra-radical (quadraradical) is generated from intramolecular γ-hydrogen abstractions at both benzoyl groups, and probably gives the characteristic product. We have started to investigate the photoreactions of 1,ω-diphenylalkane-1,ω-diones (*n* = 5, 6, 8, and 10) on photoirradiation using a medium-pressure Hg lamp (one photon absorption process) and on high density photoirradiation using a laser (two photon absorption process). In this paper, we report the products and effects of the methylene-chain spacer on conventional photoirradiation of 1,ω-diphenylalkane-1,ω-diones and 1-phenylalk-*n*-en-1-one which is the photoreaction product of 1,ω-diphenylalkane-1,ω-diones.

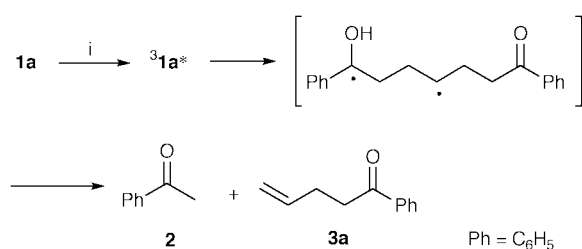
## Results

### UV-Irradiation of 1,ω-diphenylalkane-1,ω-diones

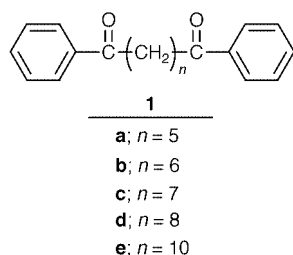
Upon photoirradiation of 1,7-diphenylheptane-1,7-dione **1a**



**Fig. 1** The time-courses of the conversion and product yields on the photoirradiation of  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  of **1a** in acetonitrile.



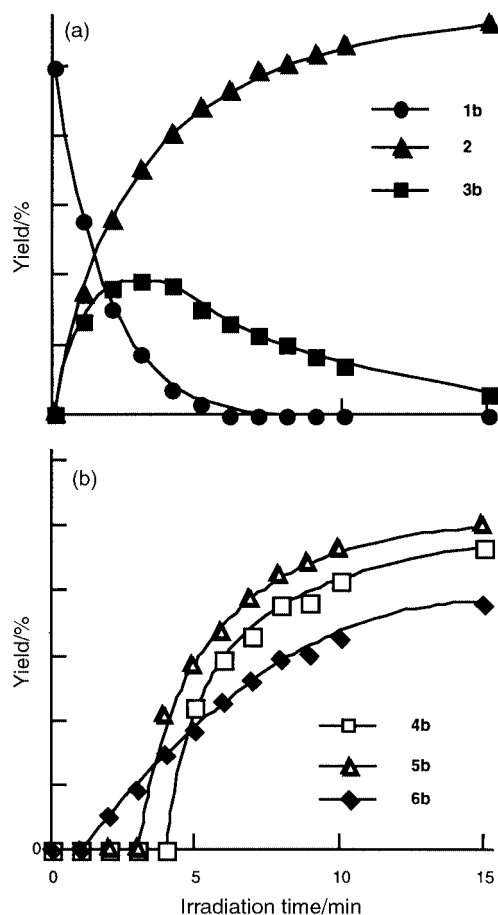
**Scheme 1** Reagents and conditions: i, hv, MeCN.



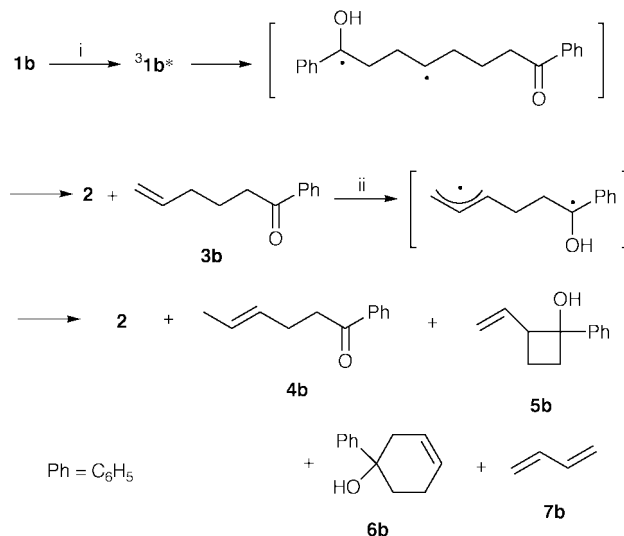
in acetonitrile for 1 min using a 350 W medium-pressure Hg lamp, type II photoreaction occurred to give acetophenone **2** (quantum yield  $\phi_2 = 0.23$ ) and 1-phenylpent-4-en-1-one **3a** ( $\phi_{3a} = 0.33$ ) in a 1:1 ratio (Scheme 1). The yields of **2** and **3a** increased with an increase of the irradiation time (Fig. 1).

On the other hand, the photoirradiation of 1,8-diphenyloctane-1,8-dione **1b** in the same manner described above gave **2** ( $\phi_2 = 0.34$ ) and 1-phenylhex-5-en-1-one **3b** ( $\phi_{3b} = 0.37$ ) in an approximately 1:1 ratio. Trace amounts of another product of which the mass number was equal to that of **1b** also formed. This product is probably a cyclobutanol derivative. The yield of **3b** decreased with prolonged photoirradiation and 1-phenylhex-4-en-1-one **4b**, 1-phenyl-2-vinylcyclobutan-1-ol **5b**, 1-phenylcyclohex-3-en-1-ol **6b**, and buta-1,3-diene **7b** were produced in the place of **3b** (Scheme 2). Fig. 2 shows the time-courses of the conversion and product yields during the photoirradiation of **1b** in acetonitrile. The formation of **4b**, **5b**, and **6b** was hardly observed during photoirradiation for 3 min. In contrast, the yield of **3b** reached a maximum at 3 min and decreased with prolonged irradiation. These results show that **4b**, **5b**, and **6b** formed from the photoreaction of **3b**. The yields of **2–6** were determined at various irradiation times, and the yield of **7b** was measured to be 20% after 5 min photoirradiation.

The photoirradiations of other 1, $\omega$ -diphenylalkane-1, $\omega$ -diones **1c–e** in acetonitrile caused the type II reaction to give **2** and the corresponding **3c–e** in a 1:1 ratio after 1 min photo-



**Fig. 2** The time-courses of the conversion of **1b** and yields of **2** and **3b** (a), and the time-courses of yields of **4b**, **5b**, and **6b** (b) on the photoirradiation of  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  of **1b** in acetonitrile.



**Scheme 2** Reagents and conditions: i, hv, MeCN; ii, hv.

irradiation. Similar secondary products **2**, **5c–e**, and **7c–e** were obtained. However, the secondary products corresponding to **4** and **6** were not produced in the photolyses of **1c–e** (Scheme 3). The yields of **7c–e** were determined to be 11%, 12%, and 3% after 5 min irradiation of **1c–e**, respectively. Trace amounts of other products which were considered to be the corresponding cyclobutanols also formed in these cases. Fig. 3 shows the product distribution depending on the irradiation time during the photoirradiation of **3c**. Similar changes in product distribution were also observed during the photoirradiation of **1d** and **1e**.

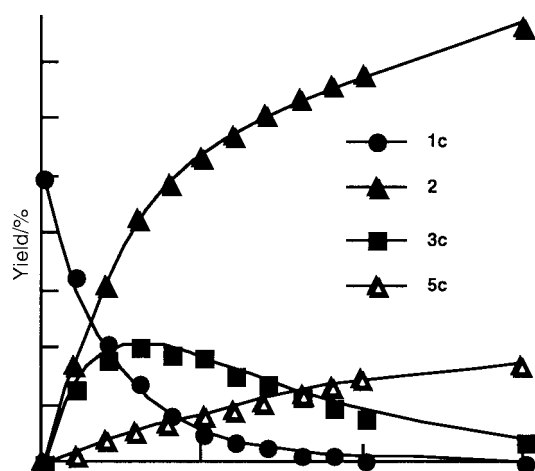
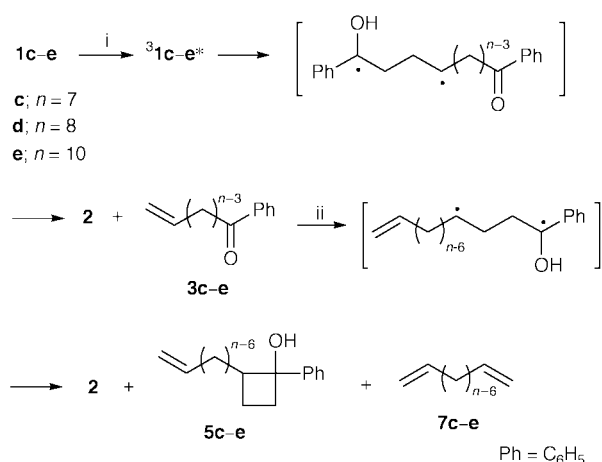


Fig. 3 The time-courses of the conversion and product yields on the photoirradiation of  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  of **1c** in acetonitrile.



Scheme 3 Reagents and conditions: i,  $h\nu$ , MeCN; ii,  $h\nu$ .

The quantum yields of **2** and **3** during the photoirradiation of **1** in acetonitrile were nearly equal to each other and to those in the photolysis of 1,5-diphenylpentane-1,5-dione which was previously reported by Bays *et al.* (Table 1).<sup>4e</sup> No effect of the methylene-chain spacer was found in the photolysis of **1**.

### Solvent effect

A solvent effect on the photolysis of **1** was observed. Photoirradiation of **1a**, **1b**, **1c**, and **1e** in several solvents was performed. In the case of **1a**, the yields of **2** and **3a** changed with solvent for 5 min photoirradiation, however the effect of the solvent polarity on the product yields was not clear (Table 2). On the contrary, the yields of **2** and **3b** decreased with a decrease of the solvent polarity on the photolyses of **1b** (Table 3). A similar solvent effect was also observed on the photoirradiations of **1c** and **1e** (Tables 4 and 5). Furthermore, **4b–6b**, which were the secondary products from **3b**, hardly formed on the photolyses of **1b** in THF, benzene, and cyclohexane. The conversions of **1** in non-polar solvents were generally smaller than those in polar solvents. These results are similar to the solvent effect on the type II reaction of benzoyl compounds.<sup>2</sup>

### Transient absorption by laser flash photolyses

Transient absorption spectra of triplet excited **1b** ( $^3\text{1b}^*$ ) in acetonitrile were measured during 266 nm laser flash photolysis (Fig. 4). A strong absorption band around 300 nm and a weak absorption band around 420 nm were observed immediately after the laser flash. These absorption bands disappeared without formation of a new absorption band. There have been

Table 1 Quantum yields of **2** and **3**<sup>a</sup>

	$\phi_2$	$\phi_3$
<b>1a</b>	0.23	0.33
<b>1b</b>	0.34	0.37
<b>1c</b>	0.32	0.30
<b>1d</b>	0.32	0.32
<b>1e</b>	0.30	0.29

<sup>a</sup> The quantum yields were determined within the 10% conversion of **1**.

Table 2 Photolyses of **1a** in several solvents<sup>a</sup>

Solvent	Conv./%	Yield/%	
		<b>2</b>	<b>3a</b>
CH <sub>3</sub> CN	68	40	45
C <sub>2</sub> H <sub>5</sub> OH	52	36	40
THF	54	25	31
Benzene	59	40	42
Cyclohexane	55	34	36

<sup>a</sup> Irradiated for 5 min (10 mM).

Table 3 Photolyses of **1b** in several solvents<sup>a</sup>

Solvent	Conv./%	Yield/%				
		<b>2</b>	<b>3b</b>	<b>4b</b>	<b>5b</b>	<b>6b</b>
CH <sub>3</sub> CN	87	83	30	4.4	3.7	4.7
C <sub>2</sub> H <sub>5</sub> OH	75	62	35	0	2.5	3.9
THF	69	62	33	0	0	0
Benzene	65	51	32	0	0	0
Cyclohexane	67	55	27	0	0	0

<sup>a</sup> Irradiated for 5 min (10 mM).

Table 4 Photolyses of **1c** in several solvents<sup>a</sup>

Solvent	Conv./%	Yield/%		
		<b>2</b>	<b>3c</b>	<b>5c</b>
CH <sub>3</sub> CN	87	105	37	16
C <sub>2</sub> H <sub>5</sub> OH	78	83	37	10
THF	62	61	31	4.5
Benzene	74	50	25	8.5
Cyclohexane	64	47	28	7.8

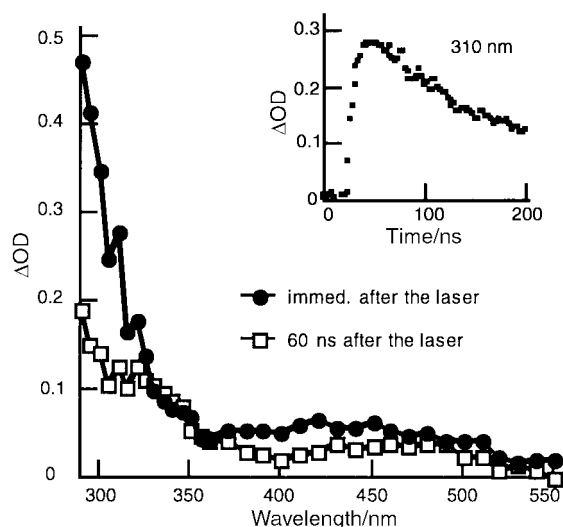
<sup>a</sup> Irradiated for 5 min (10 mM).

Table 5 Photolyses of **1e** in several solvents<sup>a</sup>

Solvent	Conv./%	Yield/%		
		<b>2</b>	<b>3e</b>	<b>5e</b>
CH <sub>3</sub> CN	85	74	28	8.3
C <sub>2</sub> H <sub>5</sub> OH	54	43	19	4.1
THF	63	38	24	2.1
Benzene	47	33	21	2.8
Cyclohexane	43	23	16	1.8

<sup>a</sup> Irradiated for 5 min (10 mM).

many reports on transient absorption spectra in the photolysis of benzoyl compounds.<sup>7</sup> The ketyl radicals have absorption maxima at 300 and 400–500 nm, respectively. Therefore, the observed absorption bands around 300 and 420 nm are assigned to the ketyl radical of **1b**. The lifetime of the ketyl radical of **1b** was determined to be 136 ns from the decay profile at 310 nm (inset Fig. 4). The lifetimes of ketyl radicals of **1a** and



**Fig. 4** Transient absorption spectra observed after a flash during 266 nm-laser flash photolysis of  $1.0 \times 10^{-3}$  mol dm $^{-3}$  of **1b** in acetonitrile, immediately after the flash (solid circle) and 60 ns after the flash (open square). Inset is the time profile of transient absorptions at 310 nm.

**1c–e** measured by the 266 nm laser flash photolysis were nearly equal to that of **1b**.

## Discussion

### Reaction mechanism of photoreaction of **1**

On the photoirradiation of **1** using a medium-pressure Hg lamp, type II reaction occurred to give **2** and **3** through the triplet excited state. The radical  $\beta$ -fission predominantly took place from the 1,4-biradical generated through intramolecular hydrogen abstraction. The intramolecular radical coupling hardly occurred. The photoreactivity of **1** was found to be almost independent of the methylene-chain length  $n$  and **1** behaves like the corresponding alkyl phenyl ketone.

The yields of **2** and **3** on the photoirradiation of **1** decreased with a decrease in the solvent polarity. It is known that a polar solvent enhances intramolecular hydrogen bonding between the carbonyl oxygen and hydrogen at the  $\gamma$ -carbon and stabilizes the 1,4-biradical, forming a hydrogen bond with the OH group of the 1,4-biradical.<sup>2</sup> In the present system, the yields of **2** and **3** were larger in acetonitrile than in other solvents.

### Mechanism of photoreaction of **3**

The photoreactivity of **3** varied with  $n$ . In this study, no reaction occurred from **3a**. This result shows that intramolecular hydrogen abstraction on the vinyl carbon, which is the  $\gamma$ -position from the carbonyl group of **3a**, hardly takes place in the triplet excited state.<sup>1b</sup> On the other hand, **3b–e** underwent photolysis (Schemes 2 and 3). In the case of **3b**, the radical on the  $\gamma$ -position from the benzoyl group in the 1,4-biradical obtained from **3b** can interact with the neighboring C=C double bond to form a 1,6-biradical shown in Scheme 2. As a result, a double bond migration and an intramolecular 1,6-radical coupling occurred through the 1,6-biradical to form **4b** and **6b**, respectively.<sup>8</sup> Therefore, an intramolecular interaction between the radical on the  $\gamma$ -position and the C=C double bond is observed. The intramolecular interaction between the radical center on the  $\gamma$ -position and C=C double bond cannot occur in the 1,4-biradical obtained from **3c–e**. The radical  $\beta$ -fission and intramolecular 1,4-radical coupling occur to form **2**, **5c–e**, and **7c–e** in the cases of **3c–e**.

### Effect of the methylene-chain length

The formation of **2** and **3** from **1** occurs independently of the methylene-chain length  $n$ . The quantum yields of **2** and **3a–e** on

photoirradiation of **1a–e** were nearly equal. These results indicate that the two benzoyl chromophores of **1** do not interact intramolecularly in the triplet excited state. On the other hand, the photoreactivity of **3** is affected by  $n$ . The type of products changes with the methylene-chain length. The interaction between the radical on the  $\gamma$ -position and neighboring double bond occurs in the 1,4-biradical generated from **3b** and enables the formation of **4b** and **6b**. No interaction between the radical on the  $\gamma$ -position and the neighboring double bond occurs in the cases of **3c–e**. It has been reported that there is a weak intramolecular interaction between the two benzoyl chromophores of 1,5-diphenylpentane-1,5-dione on the phosphorescence spectrum at 77 K. The 0–0 band of the phosphorescence of 1,5-diphenylpentane-1,5-dione shifts slightly to a longer wavelength than that of valerophenone.<sup>4e</sup> Although a similar intramolecular interaction between the two benzoyl chromophores of **1** may occur, it is difficult to discuss the existence of the intramolecular interaction in the triplet excited state with respect to the quantum yields of reaction products. The simultaneous or consecutive excitation did not occur on the conventional photoirradiation of **1** in present conditions. On the high density photoirradiation using a high power laser pulse, it is expected that **1** forms a tetraradical by the simultaneous or consecutive excitation of the two benzoyl groups. The tetraradical may give a bicyclic compound, which is a reasonable photoreaction product on high density photoirradiation, *via* a radical cross coupling. In fact, on KrF excimer laser irradiation ( $300 \text{ mJ cm}^{-2}$ ) of an acetonitrile solution containing  $0.5 \times 10^{-3}$  mol dm $^{-3}$  of **1c**, a few new products besides **2–7** were produced. The identification of the new products, probably obtained through a two photon absorption process, is now being carried out.

## Conclusion

The photolysis of **1** in acetonitrile using conventional light occurred to give **2** and **3** independently of the methylene-chain length  $n$ . It was indicated that no intramolecular interaction between the two benzoyl chromophores of **1** occurred in the triplet excited state because the quantum yields of **2** and **3** were not affected by  $n$ . On prolonged photoirradiation, **3** underwent photolysis to form secondary products. The secondary products depended on  $n$ . The photoreactivity of **3** changed with the efficiency of the hydrogen abstraction or the interaction between the radical on the  $\gamma$ -position and C=C double bond occurred through the triplet excited **3**.

## Experimental

### Apparatus

All of the compounds reported gave satisfactory CH microanalyses with a Perkin-Elmer Model 240 analyzer.  $^1\text{H}$  NMR spectra were determined in  $\text{CDCl}_3$  with tetramethylsilane as an internal standard on a JEOL JNM-EX270 spectrometer. GLC analyses were carried out on Shimadzu Model 12A with a 2% Silicone OV-17 on Chrom, WAW DMCS (60–80 mesh) and a 10% polyethylene glycol 20M on Uniport B (60–80 mesh). GC/MS spectra were recorded with a JNS-DX300 instrument. Accurate mass was recorded with a JMS-01SG-2 instrument. Laser flash photolyses were carried out using fourth-harmonic oscillation from a Nd:YAG laser (Quintel Model Brilliant).

### Syntheses

Compound **1** was prepared by Friedel–Crafts acylation of benzene with the corresponding dicarboxylic acid dichloride using  $\text{AlCl}_3$ .<sup>9</sup>

**1,7-Diphenylheptane-1,7-dione 1a.** Anal. Found: C, 81.27; H, 7.31. Calcd for  $\text{C}_{19}\text{H}_{20}\text{O}_2$ : C, 81.40; H, 7.19%.  $^1\text{H}$  NMR( $\text{CDCl}_3$ )



$\delta$  7.96 (4H, d,  $J$  7.2), 7.48 (2H, d,  $J$  7.6), 7.41 (4H, dd,  $J$  7.2 and 7.6), 2.98 (4H, t,  $J$  7.2), 1.69 (4H, tt,  $J$  6.9 and 7.2) and 1.46 (2H, quintet,  $J$  6.9). GC/MS (EI)  $m/z$  (rel. int.) 280 ( $M^+$ , 5), 262 (41), 161 (29), 133 (6), 120 (41), 105 (100), 77 (35).

**1,8-Diphenyloctane-1,8-dione 1b.** Anal. Found: C, 81.88; H, 7.29. Calcd for  $C_{20}H_{22}O_2$ : C, 81.60; H, 7.53%.  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.95 (4H, d,  $J$  6.9), 7.54 (2H, d,  $J$  7.3), 7.46 (4H, dd,  $J$  7.3 and 6.9), 2.98 (4H, t,  $J$  7.3), 1.66 (4H, tt,  $J$  5.0 and 7.3) and 1.44 (4H, quintet,  $J$  5.0). GC/MS (EI)  $m/z$  (rel. int.) 294 ( $M^+$ , 12), 276 (7), 156 (33), 120 (38), 105 (100), 77 (29).

**1,9-Diphenylnonane-1,9-dione 1c.** Anal. Found: C, 81.73; H, 7.68. Calcd for  $C_{21}H_{24}O_2$ : C, 81.78; H, 7.84%.  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.96 (4H, d,  $J$  7.9), 7.54 (2H, d,  $J$  6.4), 7.48 (4H, dd,  $J$  6.4 and 7.9), 2.97 (4H, t,  $J$  6.6), 1.73 (4H, tt,  $J$  6.6 and 6.9), 1.57 (2H, quintet,  $J$  6.6) and 1.40 (4H, quintet,  $J$  6.6). GC/MS (EI)  $m/z$  (rel. int.) 308 ( $M^+$ , 11), 290 (44), 189 (41), 133 (19), 120 (48), 105 (100), 77 (33).

**1,10-Diphenyldecane-1,10-dione 1d.** Anal. Found: C, 81.78; H, 8.25. Calcd for  $C_{22}H_{26}O_2$ : C, 81.95; H, 8.13%.  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.96 (4H, d,  $J$  8.3), 7.55 (2H, d,  $J$  6.9), 7.45 (4H, dd,  $J$  6.9 and 8.3), 2.96 (4H, t,  $J$  7.3), 1.71 (4H, tt,  $J$  6.9 and 7.3), 1.57 (4H, quintet,  $J$  6.9) and 1.36 (4H, quintet,  $J$  6.9). GC/MS (EI)  $m/z$  (rel. int.) 322 ( $M^+$ , 7), 304 (48), 203 (40), 133 (11), 120 (48), 105 (100), 77 (33).

**1,12-Diphenyldodecane-1,12-dione 1e.** Anal. Found: C, 82.41; H, 8.59. Calcd for  $C_{24}H_{30}O_2$ : C, 82.24; H, 8.63%.  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.96 (4H, d,  $J$  7.2), 7.46 (2H, d,  $J$  7.9), 7.44 (4H, dd,  $J$  7.2 and 7.9), 2.96 (4H, t,  $J$  7.4), 1.71 (4H, tt,  $J$  6.9 and 7.4), 1.58 (4H, quintet,  $J$  6.9) and 1.32 (8H, quintet,  $J$  6.9). GC/MS (EI)  $m/z$  (rel. int.) 350 ( $M^+$ , 46), 332 (11), 314 (16), 244 (12), 231 (46), 133 (14), 120 (59), 105 (100), 77 (28).

#### General photolysis procedure for isolation of products

A 200  $cm^3$  acetonitrile solution of **1** ( $1.0 \times 10^{-2}$  mol  $dm^{-3}$ ) was charged in a doughnut type cell 10 mm thick (quartz), and argon was bubbled through the solution to purge off dissolved air. After irradiation with a medium-pressure Hg lamp (350 W) at ambient temperature, the reaction mixtures were analyzed by GLC or GC/MS. The products **2** and **7** were identified by comparison of the retention times with those of the purchased authentic samples using 2% Silicone OV-17 on Chrom and 10% polyethylene glycol 20M on Uniport B columns, respectively. The reaction products **3–6** were isolated with column chromatography on silica gel, and the isolated products were identified with  $^1H$  NMR spectroscopy. The product yields were determined by GLC using eicosane as an internal standard.

#### Product analyses

**1-Phenylpent-4-en-1-one 3a.**  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.96 (2H, d,  $J$  6.9), 7.57 (1H, d,  $J$  7.2), 7.44 (2H, dd,  $J$  7.2 and 6.9), 5.85 (1H, ddt,  $J$  2.9, 3.6 and 6.6), 5.12 (1H, d,  $J$  2.9), 5.04 (1H, d,  $J$  3.6), 3.07 (2H, t,  $J$  7.2) and 2.51 (2H, dt,  $J$  6.6 and 7.2). GC/MS (EI)  $m/z$  (rel. int.) 160 ( $M^+$ , 68), 145 (48), 131 (30), 105 (100), 77 (30).

**1-Phenylhex-5-en-1-one 3b.**  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.96 (2H, d,  $J$  6.9), 7.57 (1H, d,  $J$  7.6), 7.40 (2H, dd,  $J$  6.9 and 7.6), 5.83 (1H, ddt,  $J$  3.3, 3.6 and 6.8), 5.08 (1H, d,  $J$  3.6), 4.98 (1H, d,  $J$  3.3), 3.0 (2H, t,  $J$  7.6), 2.16 (2H, dt,  $J$  6.8 and 7.3) and 1.85 (2H, tt,  $J$  7.3 and 7.6). GC/MS (EI)  $m/z$  (rel. int.) 174 ( $M^+$ , 45), 133 (6), 120 (75), 105 (100).

**1-Phenylhept-6-en-1-one 3c.**  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.95 (2H, d,  $J$  6.9), 7.57 (1H, d,  $J$  7.3), 7.46 (2H, dd,  $J$  6.9 and 7.3), 5.82 (1H, ddt,  $J$  3.0, 3.6 and 6.6), 4.99 (2H, dd,  $J$  3.0 and 3.6),

3.00 (3H, t,  $J$  7.6), 2.12 (2H, dt,  $J$  6.6 and 7.3), 1.74 (2H, tt,  $J$  7.6 and 7.6) and 1.50 (2H, tt,  $J$  7.3 and 7.6). GC/MS (EI)  $m/z$  (rel. int.) 188 ( $M^+$ , 20), 146 (24), 120 (60), 105 (100).

**1-Phenyloct-7-en-1-one 3d.**  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.96 (2H, d,  $J$  7.3), 7.56 (1H, d,  $J$  7.6), 7.46 (2H, dd,  $J$  7.3 and 7.6), 5.81 (1H, ddt,  $J$  2.9, 3.6 and 7.0), 4.98 (2H, dd,  $J$  3.0 and 3.6), 2.97 (2H, t,  $J$  7.3), 2.07 (2H, dt,  $J$  6.9 and 7.0), 1.78 (2H, tt,  $J$  6.9 and 7.3) and 1.42 (4H, tt,  $J$  6.9 and 6.9). GC/MS (EI)  $m/z$  (rel. int.) 202 ( $M^+$ , 48), 184 (8), 173 (16), 146 (8), 133 (8), 120 (76), 105 (100).

**1-Phenylnon-8-en-1-one 3e.**  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.95 (2H, d,  $J$  7.2), 7.52 (2H, dd,  $J$  6.2 and 7.2), 7.46 (1H, d,  $J$  6.2), 5.77 (1H, ddt,  $J$  3.3, 3.6 and 6.6), 5.01 (1H, d,  $J$  3.6), 4.95 (1H, d,  $J$  3.3), 2.95 (2H, t,  $J$  7.2), 2.02 (2H, dt,  $J$  6.6 and 7.2), 1.74 (2H, tt,  $J$  7.2 and 7.2) and 1.41 (8H, tt,  $J$  7.2 and 7.2). GC/MS (EI)  $m/z$  (rel. int.) 230 ( $M^+$ , 71), 187 (18), 173 (9), 159 (23), 146 (52), 133 (13), 120 (100), 105 (92), 77 (30).

**1-Phenylhex-4-en-1-one 4b.**  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.97 (2H, d,  $J$  5.0), 7.55 (1H, d,  $J$  4.6), 7.46 (2H, dd,  $J$  4.6 and 5.0), 5.53 (1H, dt,  $J$  5.6 and 6.2), 5.43 (1H, dq,  $J$  2.6 and 5.6), 2.98 (2H, t,  $J$  7.3), 2.50 (2H, dt,  $J$  6.3 and 7.3) and 1.65 (3H, d,  $J$  5.3). GC/MS (EI)  $m/z$  (rel. int.) 174 ( $M^+$ , 4), 120 (8), 105 (100).

**1-Phenyl-2-vinylcyclobutan-1-ol 5b.**  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.38 (2H, d,  $J$  6.9), 7.31 (1H, d,  $J$  6.9), 7.19 (2H, dd,  $J$  6.9 and 6.9), 5.40 (1H, ddd,  $J$  2.6, 7.3 and 7.6), 4.78 (2H, dd,  $J$  7.3 and 7.6), 2.64 (1H, dt,  $J$  2.6 and 9.2), 2.18 (2H, t,  $J$  9.9) and 1.53 (2H, dt,  $J$  9.2 and 9.9). GC/MS (EI)  $m/z$  (rel. int.) 174 ( $M^+$ , 8), 145 (10), 120 (100), 105 (96).

**2-Allyl-1-phenylcyclobutan-1-ol 5c.**  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.47 (2H, d,  $J$  5.3), 7.38 (1H, d,  $J$  6.7), 7.31 (2H, dd,  $J$  5.3 and 6.7), 5.79 (1H, ddt,  $J$  3.3, 3.4 and 6.9), 5.02 (2H, dd,  $J$  3.3 and 3.4), 2.72 (1H, tt,  $J$  7.3 and 8.2), 2.48 (2H, t,  $J$  3.0), 2.29 (2H, dd,  $J$  6.9 and 7.3) and 1.89 (2H, dt,  $J$  3.0 and 8.2). GC/MS (EI)  $m/z$  (rel. int.) 188 ( $M^+$ , 4), 160 (32), 146 (24), 120 (100).

**2-But-3-enyl-1-phenylcyclobutan-1-ol 5d.**  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.44 (2H, d,  $J$  6.9), 7.35 (1H, d,  $J$  7.3), 7.24 (2H, dd,  $J$  6.9 and 7.3), 5.79 (1H, ddt,  $J$  3.0, 3.6 and 6.4), 4.93 (2H, dd,  $J$  3.0 and 3.6), 2.67 (1H, tt,  $J$  6.3 and 8.6), 2.29 (1H, dt,  $J$  6.3 and 6.6), 2.00 (2H, t,  $J$  2.3), 1.83 (2H, dt,  $J$  6.4 and 6.6) and 1.69 (2H, tt,  $J$  2.3 and 8.6). GC/MS (EI)  $m/z$  (rel. int.) 202 ( $M^+$ , 12), 174 (48), 133 (28), 120 (100), 105 (28).

**2-Hex-5-enyl-1-phenylcyclobutan-1-ol 5e.**  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  7.46 (2H, d,  $J$  7.5), 7.26 (1H, d,  $J$  6.9), 7.12 (2H, dd,  $J$  6.9 and 7.5), 5.75 (1H, ddt,  $J$  3.3, 3.6 and 6.9), 4.89 (2H, dd,  $J$  3.3 and 3.6), 2.67 (1H, tt,  $J$  6.3 and 8.8), 2.44 (2H, t,  $J$  2.5), 1.85 (2H, dt,  $J$  2.5 and 6.3), 1.92 (2H, dt,  $J$  5.3 and 6.9), 1.27 (2H, dt,  $J$  8.5 and 8.8) and 1.25 (4H, tt,  $J$  5.3 and 8.5). GC/MS (EI)  $m/z$  (rel. int.) 230 ( $M^+$ , 15), 202 (18), 159 (18), 146 (28), 120 (100), 105 (34).

**1-Phenylcyclohex-3-en-1-ol 6b.**  $^1H$  NMR ( $CDCl_3$ ;  $Me_4Si$ )  $\delta$  8.04 (2H, d,  $J$  7.3), 7.56 (1H, d,  $J$  7.3), 7.49 (2H, dd,  $J$  7.3 and 7.3), 7.34 (2H, t,  $J$  5.3), 7.25 (2H, d,  $J$  6.9), 5.79 (2H, dt,  $J$  6.3 and 5.3), 2.28 (1H, dt,  $J$  6.3 and 6.9) and 2.05 (1H, dt,  $J$  6.3 and 5.3). GC/MS (EI)  $m/z$  (rel. int.) 174 ( $M^+$ , 28), 120 (100), 105 (56), 92 (8).

#### Measurement of quantum yield

The quantum yields were measured as follows: A 3  $cm^3$  methanol solution of the substrate ( $1.0 \times 10^{-2}$  mol  $dm^{-3}$ ) saturated with argon gas in a quartz cell (10 mm  $\times$  10 mm) was irradiated using a low-pressure Hg lamp (60 W). Photolysis was carried out to less than 10% conversion. Actinometry was carried out

using benzophenone and benzhydrol solution.<sup>10</sup> The product yield was determined by GLC.

## Acknowledgements

We thank the late Professor Reizo Dohno for helpful discussions and Dr Akito Ishida, Ms Sachiko Tojo, Mr Hisauki Utsumi, and Mr Akihiro Tomada for their help in the experiments. This work was partly supported by a Grant-in-Aid for Scientific Research (Nos. 09226223, 10132237, 09450319, and 09875209) from the Ministry of Education, Science, Sport and Culture of Japan.

## References

- For example, see; (a) P. J. Wagner, P. A. Kelso and R. Zepp, *J. Am. Chem. Soc.*, 1972, **94**, 7480; (b) P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, 1972, **94**, 7495; (c) P. J. Wagner, P. A. Kelso, A. E. Kemppainen and R. G. Zepp, *J. Am. Chem. Soc.*, 1972, **94**, 7500; (d) P. J. Wagner, P. A. Kelso, A. E. Kemppainen, J. M. McGrath, H. N. Schott and R. G. Zepp, *J. Am. Chem. Soc.*, 1972, **94**, 7506; (e) P. J. Wagner, A. E. Kemppainen and T. Jellinek, *J. Am. Chem. Soc.*, 1972, **94**, 7512; (f) J. C. Scaiano, *J. Am. Chem. Soc.*, 1977, **99**, 1494; (g) P. J. Wagner and B. J. Scheve, *J. Am. Chem. Soc.*, 1979, **101**, 378; (h) P. J. Wagner, K. C. Liu and Y. Noguchi, *J. Am. Chem. Soc.*, 1981, **103**, 3837; (i) S. Hu and D. C. Neckers, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1751; (j) N. J. Turro and D. S. Weiss, *J. Am. Chem. Soc.*, 1968, **90**, 2185; (k) F. D. Lewis, R. W. Johnson and D. E. Johnson, *J. Am. Chem. Soc.*, 1974, **96**, 6090; (l) F. D. Lewis, R. W. Johnson and D. R. Kory, *J. Am. Chem. Soc.*, 1974, **96**, 6100.
- P. J. Wagner, *J. Am. Chem. Soc.*, 1967, **89**, 5898; P. J. Wagner, I. E. Kochervar and A. E. Kemppainen, *J. Am. Chem. Soc.*, 1972, **94**, 7489.
- C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1935, 1504; R. G. W. Norrish, *Trans. Faraday Soc.*, 1939, **33**, 1521; P. J. Wagner, *Acc. Chem. Res.*, 1972, **4**, 168; N. C. Yang and D. H. Yang, *J. Am. Chem. Soc.*, 1958, **80**, 2913; P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, 1966, **88**, 1245; P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, 1965, **87**, 4009.
- (a) R. Salvin, J. Meybeck and J. Faure, *J. Photochem.*, 1976, **6**, 9; (b) P. J. Wagner and T. Nakahira, *J. Am. Chem. Soc.*, 1973, **95**, 8474; (c) Y. Okumura, K. Fuke and S. Furukawa, *Rep. Fac. Sci., Shizuoka Univ.*, 1973, **8**, 37; (d) P. F. Casals, J. Ferard, R. Ropert and M. Keravec, *Tetrahedron Lett.*, 1975, 3909; (e) J. P. Bays, M. V. Encinas, R. D. Small and J. C. Scaiano, *J. Am. Chem. Soc.*, 1980, **102**, 727.
- J. B. Butcher Jr., H. R. Hinz, N. Tsou and S. Shah, *Tetrahedron Lett.*, 1984, **25**, 5483.
- For example, see; (a) D. J. Smith, K. W. Ledingham, H. S. Kilic, T. McCanny, W. X. Peng, R. P. Sinhal, A. J. Langley, P. F. Taday and C. Kosmidis, *J. Phys. Chem. A*, 1998, **102**, 2519; (b) L. J. Mart'nez and J. C. Scaiano, *J. Am. Chem. Soc.*, 1997, **119**, 11066; (c) W. Adam, K. Schneider, M. Stapper and S. Steenken, *J. Am. Chem. Soc.*, 1997, **119**, 3280; (d) A. Ouchi, Y. Koga and W. Adam, *J. Am. Chem. Soc.*, 1997, **119**, 592.
- J. Kiwi and W. Schnabel, *Macromolecules*, 1975, **8**, 430; J. Kiwi and W. Schnabel, *Macromolecules*, 1976, **9**, 468; G. Porter and M. R. Topp, *Proc. R. Soc. London A*, 1970, **315**, 163; A. Banerjee and D. E. Falvey, *J. Am. Chem. Soc.*, 1998, **120**, 2965.
- A. Padwa and D. Eastman, *J. Am. Chem. Soc.*, 1969, **91**, 462.
- R. C. Fuson and J. T. Walker, *Org. Synth.*, 1943, **Coll. Vol. 2**, 264.
- W. M. Moore, G. S. Hammond and R. P. Foss, *J. Am. Chem. Soc.*, 1961, **83**, 2789; W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, 1962, **84**, 1368.

Paper a906631d