J. Org. Chem. **2001,** *66,* 66−73

Trapping of 1,8-Biradical Intermediates by Molecular Oxygen in Photocycloaddition of Naphthyl-*N*-(naphthylcarbonyl)carboxamides; Formation of Novel 1,8-Epidioxides and Evidence of Stepwise Aromatic Cycloaddition

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Received July 7, 2000

The photocycloaddition reaction of naphthyl-*N*-(naphthylcarbonyl)carboxamides (**1**) was examined under argon and oxygen atmospheres. In addition to the [2 + 2] and [4 + 4] cycloadducts, **3** and **4**, respectively, novel 1,8-epidioxides (**5**) were formed under oxygen atmosphere. The transient absorption at λ_{max} of 360 nm with the lifetime of 360 ns was observed by laser flash photolysis of **1c** and was interpreted as the absorption of biradical intermediate **2**. On the basis of the anti stereochemistry of **5**, which was different from that of the major [4 + 4] cycloadducts, *syn*-**4**, it was deduced that equilibrium between biradical intermediates *syn*-**2** and *anti*-**2** would exist. Retro [2 + 2] cycloaddition of **3** was responsible for the efficient trapping of the biradical intermediate with molecular oxygen. The photocycloaddition of the anthryl derivatives, 9-anthryl-*N*-(methylethyl)-*N*-(naphthylcarbonyl)carboxamides (**7**), afforded the [4 + 4] cycloadducts (**8**) exclusively in a quantitative yield even under oxygen atmosphere. The absence of trapping with molecular oxygen was interpreted to be due to the lack of retro [4 + 4] cycloaddition of **8**.

Introduction

Since an exciplex mechanism was first proposed by Corey[1] and later modified by de-Mayo[2] in [2 + 2] photocycloadditions of enones and alkenes, the stepwise mechanism involving a 1,4-biradical intermediate has been widely considered[3] for these cycloadditions, and numerous attempts have been made to trap the 1,4-biradical intermediates. In some successful cases, the involvement of the 1,4-biradical intermediates was shown experimentally. The cyclopropylcarbinyl radical rearrangement, a free radical clock,[4] has been applied to the [2 + 2] photocycloaddition of olefin−olefin,[5] double bonds to benzenes,[6] and olefin−carbonyl[7] to detect the existence of 1,4-biradical intermediates. A carbene was generated if the resulting 1,4-biradical was conjugated with an alkynyl group.[8] The hydrogenselenide trapping technique was demonstrated to be a useful tool for the interception of 1,4-biradical intermediates.[9] Molecular oxygen is also a trapping reagent of 1,4-biradical intermediates. In the Paterno−Büchi reaction, in particular the reaction of quinones with olefins, 1,4-biradical intermediates were trapped by it to give 1,2,4-trioxanes.[10] Despite the vast research that has been carried out on aromatic photocycloaddition[11] and also its importance, neither chemical trapping of the biradical intermediates nor the apparent elucidation of such by direct observation has been reported. A few reports mentioned involvement of a singlet biradical intermediate in photodimerization of anthracene.[12] The radical was detected by ESR spectros-

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10.1021/jo0010227 CCC: $20.00

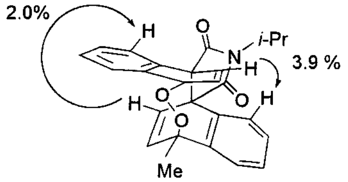
copy on irradiation of 1,2,3,4,5,6,7,8-octamethylanthracene in toluene at −100 °C. Because of lack of detail in the ESR spectrum, the nature of the radical species was only speculated, possibly as a biradical.[13] In this report, we demonstrate the first trapping of the biradical intermediate by molecular oxygen in aromatic photocycloaddition.

To generate a stable biradical intermediate for trapping, we designed the intramolecular [4 + 4] photocycloaddition of naphthyl-*N*-(naphthylcarbonyl)carboxamide derivatives **1**. The [4 + 4] photocycloadditions of extended aromatic systems, especially naphthalene[14] and anthracene,[15] are well-known. The [4 + 4] photocycloaddition of **1** should afford the syn and anti biradical intermediates *syn*-**2** and *anti*-**2**, respectively, if the cycloaddition proceeds via a stepwise process. According to a stability study of biradicals generated from azoalkanes, a phenyl substituent at the radical sites remarkably stabilizes triplet biradicals,[16] which allows their interception by molecular oxygen. The biradicals **2** should be reasonably stabilized since the radical sites are benzylic and allylic. Moreover, the distance between the two radical sites fits the distance required for the peroxy bridge.

Table 1. Isolated Yields[a] of Photocycloadducts

compd	condition[b]	**3** (%)	*syn*-**4** (%)	*anti*-**4** (%)	**5** (%)	recovd **1** (%)
1a	A (6.5)	41	27	trace	0	8
	B (4.5)	16	11	trace	26	7
1b	A (4.5)	73	0	0	0	14
	B (4.5)	10	0	0	38	11
1c	A (6.0)	29	27	13	0	7
	B (4.5)	41	15	6	11	11
1d	A (4.0)	71	0	0	0	19
	B (5.0)	14	0	0	34	8

[a] Isolated yields after HPLC purification. Due to the difficulty in separation, yields are relatively poor. [b] Irradiation was carried out with ca. 2.5×10^{-2} M of **1** in benzene under bubbling of argon (A) or under bubbling of oxygen (B). Irradiation time (h) in parentheses.



5b

Figure 1. NOE relations in **5b**.

Results and Discussion

Photocycloaddition of 1 under Argon or Oxygen Atmosphere. Intramolecular photocycloadditions of **1a**−**d** under an argon atmosphere were carried out in benzene irradiated with a 400 W high-pressure mercury lamp through Pyrex glass. The [2 + 2] (**3a** and **3c)** and the [4 + 4] cycloadducts, *syn*- and *anti*-**4a** and **4c**, were obtained from **1a** and **1c**, respectively. However, the reaction of **1b** and **1d** gave solely the [2 + 2] adduct **3b** and **3d**, respectively (yields are summarized in Table 1). The two facing benzene ring protons of *syn*-**4a** and *syn*-**4c**, and the vinylic protons of *anti*-**4a** and **4c** showed upfield shifts relative to those of the other corresponding diastereomers due to the shielding effect caused by the benzene ring. Their bridgehead methine and vinylic protons showed agreeable ^{1}H NMR chemical shifts to those of a similar system.[17,18] Syn preference of the [4 + 4] adduct originated from the effective π-orbital overlap for the exciplex formation between the two facing naphthalene rings.[19] When **1a**−**d** were irradiated under bubbling of oxygen, novel trapping products, 1,8-epidioxides **5a**−**d**, were obtained as a single diastereomer with the suppressed yield of the other cycloadducts (isolated yields are summarized in Table 1). The trapping by molecular oxygen may indicate the involvement of the triplet biradical intermediate. The result differs from the photocycloaddition of anthracene derivatives in which the singlet biradical intermediate was suggested.[12] The stereochemistry of the peroxide was unequivocally determined to be anti from the single-crystal X-ray structure analysis of **5d** and also from NOE difference experiments by ^{1}H NMR spectroscopy. Figure 1 shows the NOE enhancement observed in **5b**. The observed distance between the two oxygen atoms [1.441(5) Å] in **5d** is the typical value observed for those of hydroperoxides and monocyclic peroxides.[20] Elongated bond length of the O−O (ca. 1.50 Å) was commonly observed in bicyclic 1,4-endoperoxide which originated in their rigid structure.[21] To reduce the electron repulsion between lone pairs of electrons on the oxygen atoms in an eclipsed configuration, the O−O bond may be elongated. In contrast to those rigid cyclic peroxides, **5d** possesses a flexible

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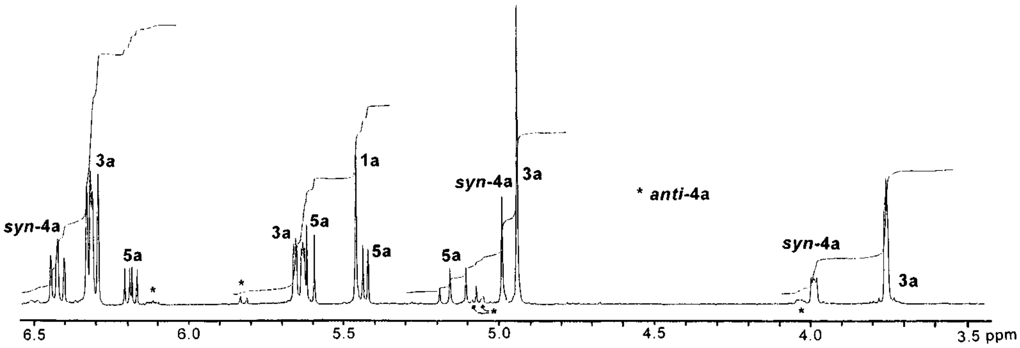

Figure 2. The ^{1}H NMR spectrum of the reaction mixture after 50 min irradiation of **1a**.

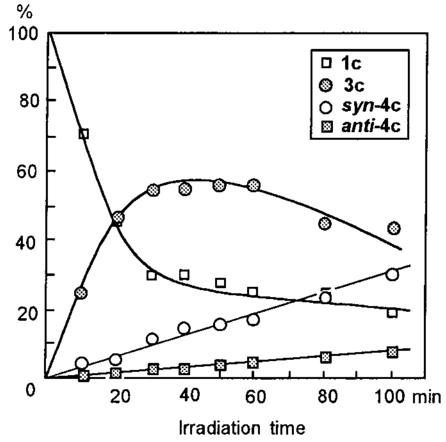

Figure 3. Irradiation time-dependent product ratios of the photocycloaddition of **1c** in benzene-d_6 under bubbling of argon monitored by ^{1}H NMR (400 MHz) spectroscopy.

structure with the dihedral angle C−O−O−C of 114.9(4)° which is larger than that of 1,4-endoperoxide (1.3°; the reported dihedral angle of C−O−O−C).[21] Interestingly, the stereochemistry of peroxides differed from that of the major [4 + 4] adducts which showed syn stereochemistry. This means that the *syn*-**2** preferentially cyclized to the [2+2] cycloadduct while the *anti*-**2** was selectively trapped by molecular oxygen under oxygen atmosphere. Inspection of the molecular model of the *syn*-peroxide **6**, which was not obtained, showed that the steric hindrance between the two facing hydrogen atoms at *peri*-position of the naphthalene rings might be severe. The AM1[22] calculation showed that the *anti*-peroxide **5a** was 1.5 kcal/mol more stable than that of the corresponding *syn*-peroxide **6a** in ΔH_f. The contradictory results, the amount of the peroxides exceeds that of *anti*-adducts formed under an argon atmosphere, can be rationalized by considering the equilibrium between *syn*-**2** and *anti*-**2** via the starting amide **1**. The retro [2 + 2] reaction results in the formation of *syn*-**2** which subsequently regenerates **1**. As reported,[17] the [2 + 2] cycloaddition of naphthalene derivatives was reversible. We observed this retro [2 + 2] reaction in our system when we irradiated the isolated **3a** and **3b** in benzene-d_6 under bubbling of argon. A similar reverse process from a 1,4-biradical intermediate to a ground state starting material was suggested in [2 + 2] photocycloaddition of *N*-acylindoles with alkenes from kinetic study.[23] From the anti stereochemistry of the peroxides, it is presumed they are not derived directly from the biradical generated in the retro [2 + 2] process which should result in the generation of *syn*-**2**. The *syn*-1,8-epidioxide **6** should be obtained from the reaction of *syn*-**2** with molecular oxygen if it was reactive enough, though **6** was not obtained. Therefore, the *anti*-epidioxide formation is the result of trapping of *anti*-**2** originated in the equilibrium between *syn*-**2** and *anti*-**2** via the starting material **1a**.

To understand the course of the reaction, the irradiation time-dependent product ratio was examined by monitoring the ^{1}H NMR spectroscopy. The reaction was clean enough to allow the ^{1}H NMR (400 MHz) analysis of the reaction mixture up to the irradiation time of 100 min (up to ca. 80% conversion). Figure 2 shows the ^{1}H NMR spectrum of the photolyzed mixture of **1c** after 50 min irradiation. The signals corresponding to four products, **3c**, *syn*-**4c**, *anti*-**4c**, and **5c**, and the unreacted starting material **1c** were assigned in comparison with those of the isolated compounds. Prolonged irradiation caused decomposition of the epidioxide. A gradual decomposition was observed when the benzene-d_6 solution of the isolated epidioxide was irradiated under bubbling of oxygen, which resulted in a dirty reaction mixture. The 1,8-epidioxides were found to be sensitive to acid. Their rapid decomposition due to acidic impurities was observed when their NMR spectrum was measured in $CDCl_3$. However, they were stable in $CDCl_3$ freshly passed through a short potassium carbonate column.

Figures 3 and 4 show the results of the reaction of **1c** in benzene-d_6 in an NMR tube under bubbling of argon and oxygen, respectively. In both figures, the [2 + 2] cycloaddduct formed rapidly in the early stage of the reaction and then gradually decreased due to the retro [2 + 2] reaction. The amounts of [4 + 4] cycloadducts were increased constantly, which indicated that the retro process was not involved in [4 + 4] cycloaddition. Figure 5 shows the results of the irradiation of **1b** in benzene-d_6 under bubbling of oxygen monitored by ^{1}H NMR (400 MHz). Due to the lack of [4 + 4] cycloaddition which was irreversible, the epidioxide formation was very efficient. Since [2 + 2] cycloaddition was reversible, a steady-state concentration of *anti*-**2** could be expected, which should be trapped with molecular oxygen to afford **5**.

Our mechanistic proposal of the biradical trapping was verified by irradiating isolated **3b** in the presence of oxygen (Figure 6). Efficient formation of **5b** suggests that the photocycloreversion of **3b** is the crucial step for the trapping.

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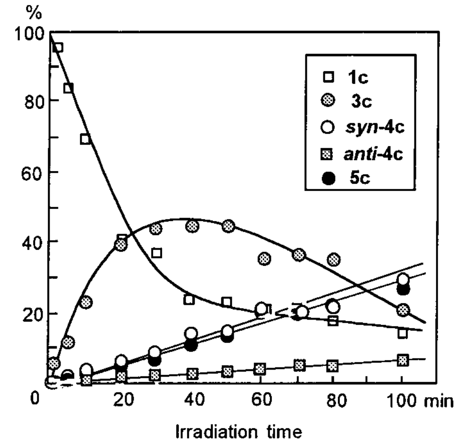


Figure 4. Irradiation time-dependent product ratios of the photocycloaddition of **1c** in benzene-d_6 under bubbling of oxygen monitored by ^{1}H NMR (400 MHz) spectroscopy.

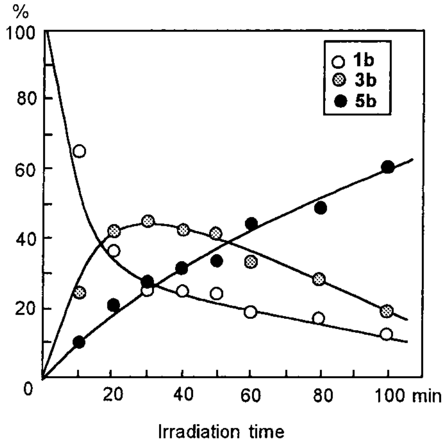


Figure 5. Irradiation time-dependent product ratios of the photocycloaddition of **1b** in benzene-d_6 under bubbling of oxygen monitored by ^{1}H NMR (400 MHz) spectroscopy.

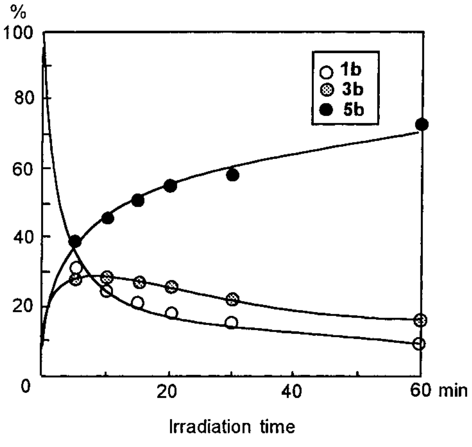


Figure 6. Irradiation time-dependent product ratios of the photocycloreversion of **3b** in benzene-d_6 under bubbling of oxygen monitored by ^{1}H NMR (400 MHz) spectroscopy.

Table 2. Calculated ΔH_f [a] and $\Delta\Delta H_f$ [b] (in parentheses) of Cycloadducts by AM1 Calculation

x	R^1	R^2	**3**	*syn*-**4**	*anti*-**4**
a	*i*-Pr	H	44.9 (0.0)	48.6 (3.7)	48.0 (3.1)
b	*i*-Pr	Me	38.7 (0.0)	47.1 (8.4)	46.5 (7.8)
c	Bn	H	80.9 (0.0)	84.7 (3.8)	84.1 (3.2)
d	Bn	Me	74.7 (0.0)	83.2 (8.5)	82.6 (7.9)

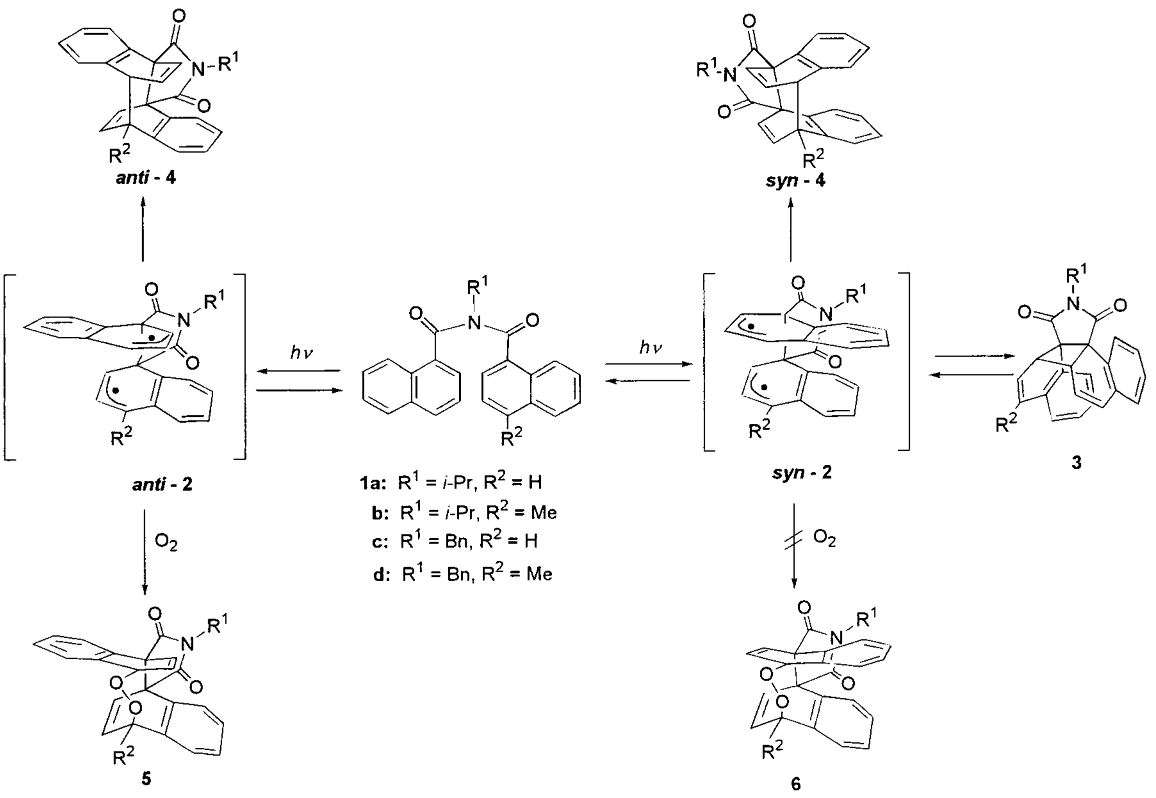
[a] Heat of formation in kcal/mol. [b] Relative energies; ΔH_f of cycloadducts minus that of **3** in kcal/mol.

The Role of Methyl Substituent at the 4-Position of Naphthalene Ring. The photochemical reaction of **1b** and **1d** resulted in the formation of the [2 + 2] cycloadducts **3b** and **3d**, respectively, and did not give the corresponding [4 + 4] cycloadducts. This substituent-dependent *peri*-selectivity may be caused by the steric effect of the methyl group substituted at the 4-position of the naphthalene ring. Another possibility, the known thermal rearrangement of [4 + 4] adducts to [2 + 2] adducts in naphthalene photodimers,[15] could be ruled out since the rearrangement of *syn*-**4a** and *syn*-**4c** to the corresponding [2 + 2] adducts required heating at 60 °C for 3 h for completion. The calculated heat of formation by AM1 calculation showed that the [2 + 2] cycloadducts were more stable than the [4 + 4] cycloaddducts in all cases. The calculated results are shown in Table 2. Introduction of a methyl group as R^2 increases $\Delta\Delta H_f$ (the difference in the heat of formation between the [4 + 4] and the [2 + 2] cycloadducts) about 4.7 kcal/mol more than the amides with R^2 = H. Since the reaction involves the retro [2 + 2] process, the [4 + 4] cycloadducts whose formation is irreversible, can be accumulated while the reaction proceeds if the difference in the heat of formation is relatively small (R^2 = H). However, the [4 + 4] cycloaddition becomes thermodynamically unfavorable, when the difference in the heat of formation becomes greater with R^2 = Me.

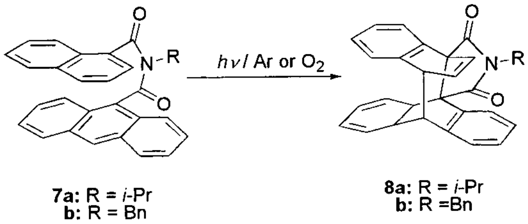
Photocycloaddition of Anthryl Derivatives 7 under Oxygen Atmosphere. By Changing the aromatic ring from naphthalene to anthracene, we might expect a more stable biradical intermediate similar to **2** in its photocycloaddition reaction since the radical site could be the doubly benzylic position. The efficacy of the oxygen trapping would be improved in this system. Thus, we explored the photochemistry of 9-anthryl-*N*-(naphthylcarbonyl)carboxamide **7** under argon and oxygen atmospheres. However, irradiation of **7** in benzene or chloroform under bubbling oxygen gave the corresponding [4 + 4] cycloadducts **8** in quantitative yields without the formation of the corresponding 1,8-epidioxide. The results were the same in the irradiation under bubbling argon (Scheme 2). Unlike electron-rich anthracene derivatives, the anthracene moiety of **7** was not sensitive to photooxidation. One reason for this unsuccessful oxygen trapping may be as follows. The anthracene derivative **7** cyclizes only in a [4 + 4] mode without its retro cycloaddition, which differs from the photocycloaddition of **1**. Thus, it is impossible to maintain steady concentration of the biradical intermediate during irradiation. The reactivity of the biradical intermediate was not sufficient toward molecular oxygen to be trapped within its lifetime, and the generated biradical collapsed to afford the [4 + 4] cycloadduct, the irreversible product. In addition, there would be the severe steric hindrance between the hydrogen atoms at peri-positions of anthracene and naphthalene moieties in the corresponding 1,8-epidioxides which was not actually obtained.

Laser Flash Photolysis. To investigate the intermediate involved in this photochemical reaction, the laser flash photolysis of **1c** and **7b** were carried out in nitrogen- or argon-purged benzene. The sample solution was excited by the 355 nm laser pulse, and the spectra were

Scheme 1



Scheme 2



monitored with xenon arc light.[24] The transient species were observed at λ_{max} of 360 and 440 nm with the lifetime (τ) of 360 and 930 ns for **1c** and **7b**, respectively (Figure 7). As we expected, the longer lifetime was observed for **7b**, the anthracene derivatives. Since both the lifetime and the λ_{max} are fairly shorter than those of the triplet–triplet absorptions of naphthyl derivatives,[25] these absorptions can be reasonably assigned to the biradical intermediates. The transient absorptions of triplet biradicals derived from Norrish I and II reactions of carbonyl compounds have been well studied, and the lifetimes of constrained diaryldiyls were reported to be in the order of 10^2 ns.[26] The observed decay rate constants k ($k = 1/\tau = 2.8 \times 10^6$ and 1.1×10^6 s^{-1} for **1c** and **7b**, respectively) might correspond to the intersystem crossing (isc) rates of the biradicals to give *anti*- or *syn*-**4c** (because a singlet biradical would cyclize in much faster time scale than the isc) for **1c** and to give **8b** for **7b** or the cycloreversion rates of the biradicals to the reactants.

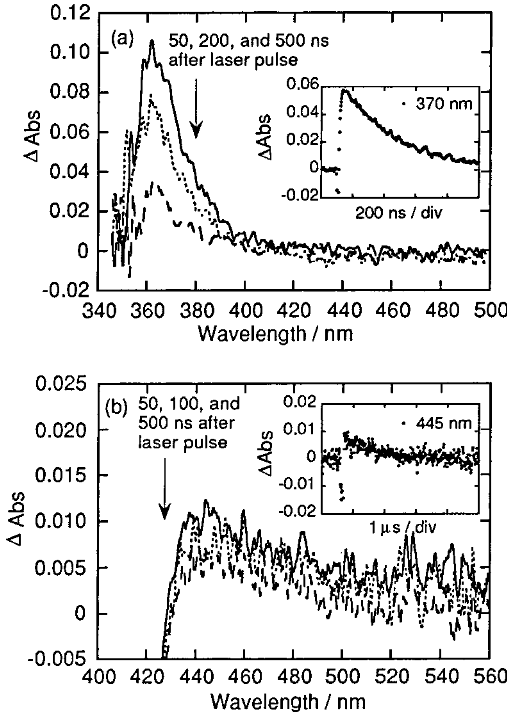


Figure 7. Transient absorption spectra measured by excitation of **1c** (a) and **7b** (b) at 355 nm in nitrogen or argon purged benzene. The insets are the time profiles monitored at 370 and 445 nm for **1c** and **7b**, respectively.

When the laser flash photolyses were carried out under air, the lifetime of the transient species became shorter (75 ns for **1c** and 340 ns for **7b**, respectively at $[O_2] = 1.9 \times 10^{-3}$ mol dm^{-3},[27] and $k_{ox} = 5.5 \times 10^9$ and 9.8×10^8 mol^{-1} dm^3 s^{-1} were obtained for **1c** and **7b**, respectively).

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The results indicated that the intermediates in these photochemical reactions must be the triplet biradicals. However, no direct evidence was obtained to enable us to distinguish *anti*-**2c** and *syn*-**2c** by a spectroscopic method at this time.

Oxygen Species for Peroxidation. It is well-known that singlet oxygen reacts with electron-rich aromatic compounds to give 1,4-epidioxides.[28] To find out whether singlet oxygen was involved in the peroxidation of **1**, **1a**, **3a**, *syn*-**4a**, and *anti*-**4a** were irradiated separately with a halogen lamp in the presence of methylene blue as a sensitizer in dichloromethane under bubbling of oxygen. All the compounds were found to be inert under this oxygenation condition. Singlet oxygen is not the reactive species for the production of peroxide **5**. Therefore, the ground state triplet oxygen should be reacted with the intermediate, possibly a triplet biradical. There are a few examples in which triplet naphthalene was involved in its photocycloaddition[29] in contrast to the large number of examples involving the intermediacy of singlet exciplexes.[30]

In the former examples, an acyl group seems to be essential for the formation of naphthalene triplet excited states. From this consideration, it is reasonable to assume that our naphthyl-*N*-(naphthylcarbonyl)carboxamide system would have the triplet excited state. We tried triplet sensitization or quenching of the cycloaddition with benzophenone, benzil, biacetyl, or piperylene; however, no sensitization or quenching was observed.

Conclusion

The intramolecular photocycloaddition of naphthyl-*N*-(naphthylcarbonyl)carboxamide was found to proceed via a stepwise mechanism involving a triplet biradical intermediate. This 1,8-biradical intermediate was trapped by ground-state molecular oxygen to give the novel 1,8-epidioxide, which was the first example of the trapping of the biradical intermediate in aromatic photocycloaddition. A retro cycloaddition reaction may be essential to maintain a steady concentration of the biradical intermediate for efficient oxygen trapping. This was confirmed in the photoreaction of 9-anthryl-*N*-(naphthylcarbonyl)carboxamide which lacked the retro cycloaddition. Though the biradical intermediate derived form **7b** has longer lifetime than that of **1c**, **7b** does not afford the corresponding 1,8-epidioxide.

We are particularly interested in knowing how the stability of this type of biradical can be controlled and thereby to establish a new generation of stable biradicals based on the photochemistry of extended aromatic systems.

Experimental Section

General Remarks. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ with Me_4Si as an internal standard on 90, 400, and 500 MHz spectrometers. Reaction mixtures were concentrated on a rotary evaporator at 10−15 mmHg. Chromatographic separations were accomplished on silica gel (150−350 mesh). Further purification of the reaction products was carried out by a preparative HPLC run with column Merck NH_2 (7 μm, 10 × 250 mm), hexane−ethyl acetate as eluent.

Procedure for Preparation of Carboxamide Derivatives (1 and 7). To a stirred solution of isopropylamine (0.356 g, 6.02 mmol) and triethylamine (4.00 mL, 28.45 mmol) in toluene (30 mL) was added a solution of 1-naththoyl chloride (3.434 g, 18.02 mmol) in toluene (30 mL) at room temperature. After being refluxed for 17 h, the resulting solution was quenched with aqueous 1 N HCl. The resulting organic layer was washed with saturated aqueous solution of $NaHCO_3$ and brine and then dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel using *n*-hexane−ethyl acetate (4:1) as eluent. Recrystallization from *n*-hexane−ethyl acetate gave **1a** (59%, 1.306 g, 3.55 mmol). In a similar manner, **1c** was prepared in 48% yield after recrystallization (*n*-hexane/ethyl acetate). Unsymmetrical carboxamides (**1b**, **1d**, **7a**, and **7b**) were prepared stepwise (two steps) in total yields of 54, 15, 48, and 25%, respectively.

***N*-Methylethyl)naphthyl-*N*-(naphthylcarbonyl)carboxamide (1a):** colorless plates; mp 169.5−171.0 °C (*n*-hexane/ethyl acetate); UV λ_{max} (ϵ) (CH_3CN) 329.0 (sh, 5600), 296.0 (10 100), 255.5 (10 900); IR (KBr) 1650 cm^{-1} (C=O); ^{1}H NMR (89.5 MHz, $CDCl_3$) δ 8.01−7.78 (m, 2H), 7.42−7.02 (m, 10H), 6.86 (d, J = 6.8 Hz, 1H), 6.77 (d, J = 6.8 Hz, 1H), 5.30 (septet, J = 6.8 Hz, 1H), 1.75 (d, J = 6.8 Hz, 6H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ 173.4 (s), 135.3 (s), 132.7 (s), 130.3 (d), 129.0 (s), 127.7 (d), 126.7 (d), 126.3 (d), 126.1 (d), 124.9 (d), 123.8 (d), 49.1 (d), 20.4 (q); MS (FAB) 368 (MH^+). Anal. Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found; C, 81.79; H, 5.66, N, 3.74.

***N*-(Methylethyl)-*N*-[(4-methylnaphthyl)carbonyl]naphthylcarboxamide (1b):** colorless needles; mp 159−160 °C (*n*-hexane/ethyl acetate); UV λ_{max} (ϵ) (CH_3CN) 328.0 (sh, 5700), 297.5 (10 400), 257.5 (9900); IR (KBr) 1650 cm^{-1} (C=O); ^{1}H NMR (89.5 MHz, $CDCl_3$) δ 8.05−7.10 (m, 11H), 6.92−6.60 (m, 2H), 5.28 (sept, J = 6.8 Hz, 1H), 2.19 (s, 3H), 1.74 (d, J = 6.8 Hz, 6H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ 173.5 (s), 173.5 (s), 137.5 (s), 135.4 (s), 134.0 (s), 132.7 (s), 131.8 (s), 129.9 (d), 129.0 (s), 128.9 (s), 127.6 (d), 126.5 (d), 126.4 (d), 126.23 (d), 125.9 (d), 125.4 (d), 125.0 (d), 124.68 (d), 123.72 (d), 123.5 (d), 49.0 (d), 20.4 (q), 19.1 (q); HRMS (FAB) calcd for $C_{26}H_{24}NO_2$ (MH^+) 382.1808, found 382.1802. Anal. Calcd for $C_{26}H_{23}NO_2$: C, 81.86; H, 6.08; N, 3.67. Found; C, 81.89; H, 6.05, N, 3.61.

Naphthyl-*N*-(naphthylcarbonyl)-*N*-benzylcarboxamide (1c): colorless crystals; mp 123−124 °C (*n*-hexane/ethyl acetate); UV λ_{max} (ϵ) (CH_3CN) 329.0 (sh, 5000), 295.5 (10 100), 255.0 (9100); IR (KBr) 1660 cm^{-1} (C=O); ^{1}H NMR (89.5 MHz, $CDCl_3$) δ 7.92−7.60 (m, 4H), 7.55−7.00 (m, 13H), 6.79−6.55 (m, 2H), 5.46 (s, 2H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ 173.1 (s), 137.3 (s), 134.1 (s), 132.5 (s), 130.1 (d), 129.5 (d), 129.0 (s), 128.6 (d), 127.8 (d), 127.7 (d), 126.7 (d), 126.0 (d), 125.9 (d), 124.7 (d), 123.5 (d), 48.6 (t); MS (FAB) 416 (MH^+). Anal. Calcd for $C_{29}H_{21}NO_2$: C, 83.83; H, 5.09; N, 3.37. Found; C, 83.57; H, 4.93, N, 3.31.

N-[(4-Methylnaphthyl)carbonyl]naphthyl-*N*-benzylcarboxamide (1d): colorless oil; UV λ_{max} (ϵ) (CH_3CN) 331.0 (sh, 4900), 296.5 (10 600), 258.0 (9100); IR (KBr) 1655 cm^{-1} (C=O); ^{1}H NMR (89.5 MHz, $CDCl_3$) δ 7.90−7.60 (m, 4H), 7.60−6.90 (m, 12H), 6.78−6.45 (m, 2H), 5.44 (s, 2H), 2.16 (s, 3H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ 173.4 (s), 173.3 (s), 137.5 (s), 137.4 (s), 134.3 (s), 132.8 (s), 132.6 (s), 131.7 (s), 129.7 (d), 129.5 (d), 129.1 (s), 128.9 (s), 128.6 (d), 127.8 (d), 127.7 (d), 126.6 (d), 126.4 (d), 126.0 (d), 126.0 (d), 125.7 (d), 125.2 (d), 124.8 (d), 124.5 (d), 123.7 (d), 123.5 (d), 48.7 (t), 19.0 (q); HRMS (EI) calcd for $C_{30}H_{23}NO_2$ (M^+) 429.1729, found 429.1738.

9-Anthryl-*N*-(methylethyl)-*N*-(naphthylcarbonyl)carboxamide (7a): yellow blocks; mp 200−202 °C (*n*-hexane/ethyl acetate); UV λ_{max} (ϵ) (CH_3CN) 400.0 (4000), 379.5 (4400), 325.5 (5900), 262.5 (37 900); IR (KBr) 1655 cm^{-1} (C=O): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.7, 2H), 7.53−7.40 (m, 5H), 7.35−7.26 (m, 3H), 7.20 (d, J = 7.2, 1H), 7.12 (td, J = 7.5, 1.0, 1H), 6.99 (d, J = 8.2, 1H), 6.73 (t, J = 7.5, 1H), 6.62 (d, J =

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8.2, 1H), 6.51 (t, *J* = 7.7, 1H), 5.45 (sept, *J* = 6.9, 1H), 1.87 (appeared as a broad peak, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 174.4 (s), 171.0 (s), 133.2 (s), 132.2 (s), 130.7 (s), 130.1 (s), 129.3 (d), 128.5 (d), 128.3 (d), 128.3 (s), 128.3 (d), 128.0 (s), 128.3 (d), 128.3 (s), 128.3 (d), 128.0 (s), 127.2 (d), 126.9 (d), 126.2 (d), 125.7 (d),125.4 (d), 125.0 (d), 123.2 (d), 123.0 (d), 49.4 (d), 20.6 (q); MS (EI, *m/z*) 417 (M$^+$, 47), 303 (5), 246 (9), 205 (100), 177 (41), 155 (73), 127(89). Anal. Calcd for $C_{29}H_{23}NO_2$: C, 83.43; H, 5.55; N, 3.35. Found; C, 83.45; H, 5.31; N, 3.43.

9-Anthryl-*N*-(naphthylcarbonyl)-*N*-benzylcarboxamide (7b): yellow crystals; mp 166−171 °C (*n*-hexane/ethyl acetate); UV λ_{max} (ϵ) (CH$_3$CN) 398.0 (4100), 380.0 (4500), 323.5 (5500), 262.5 (37 300)IR (KBr) 1655 cm^{-1} (C═O); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (d, *J* = 7.1, 2H), 7.71 (br d, *J* = 7.2, 2H), 7.56−7.21 (m, 11H), 7.11 (t, *J* = 7.0, 1H), 6.90 (d, *J* = 7.8, 1H), 6.79 (dd, *J* = 7.1, 1.0, 1H), 6.73 (td, *J* = 7.7, 1.2, 1H), 6.63 (d, *J* = 7.8, 1H), 6.37 (dd, *J* = 8.0, 7.3, 1H), 5.65 (s, 2H); ^{13}CNMR (100 MHz, CDCl$_3$) δ 173.4 (s), 172.2 (s), 137.1 (s), 132.5 (s), 131.9 (s), 130.1 (d), 129.8 (s), 129.6 (s), 128.7 (d), 128.6 (d), 128.5 (d), 128.3 (d), 128.1 (s), 128.02 (s), 127.98 (d), 127.1 (d), 126.9 (d), 126.1 (d), 125.3 (d), 124.92 (d), 124.86 (d), 124.3 (d), 123.0 (d), 122.8 (d), 48.1 (t); MS (EI, *m/z*) 465 (M$^+$, 57), 303 (6), 260 (6), 205 (94), 177 (50), 155 (90), 127 (97), 91 (100), 57(51). Anal. Calcd for $C_{33}H_{23}NO_2$: C, 85.14; H, 4.98; N, 3.01. Found; C, 85.11; H, 4.98; N 3.11.

Photocycloaddition of 1 and 7. A solution of **1** or **7** (ca. 0.25 mmol) in benzene (10 mL) in a Pyrex test tube (18 mm × 180 mm) was irradiated with a 400-W high-pressure mercury lamp (AHH400S) under bubbling argon or oxygen for 4−6.5 h. The reaction tube was cooled in a water bucket. In the case of photocycloaddition of **1**, after the evaporation of the mixture, the residue was chromatographed on silica gel and further purified by HPLC with hexanes−ethyl acetate as eluent. Photocycloaddition of **7** proceeded quantitatively and gave the pure cycloadduct **8** without purification.

The ^{1}H NMR (400 MHz) monitoring experiment of the photocycloaddition of **1** (ca. 0.02 mmol) was carried out in an NMR tube with benzene-d_6 (0.5 mL) as a solvent under bubbling of argon or oxygen without an internal standard.

Transient absorption spectra were measured on excitation at 355 nm (Continuum SL I-10, 6 ns fwhm, 20 mJ per pulse at 5 Hz repetition) with a detection system (Tokyo instruments) composed of a multichannel diode array (Princeton IRY-512G: 18 ns gate width) with a SPEX 270M monochromator (resolution: 0.3 nm/channel). Decay profiles measured by a photomultiplier (Hamamatsu Photonics SR928) were analyzed by the Marquardt nonlinear least-squares fitting method.

Data for [2 + 2] photocycloadduct (3a): colorless crystals; 190−191 °C (*n*-hexane/ethyl acetate); IR (KBr) 1700 cm^{-1} (C═O); ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.02 (td, *J* = 7.3, 1.4 Hz, 2H), 6.91 (td, *J* = 7.3, 1.4 Hz, 2H), 6.83 (dd, *J* = 7.3, 1.4 Hz, 2H), 6.44 (br d, *J* = 7.3 Hz, 2H), 6.30 (br d, *J* = 9.9 Hz, 2H), 5.67 (ddd, *J* = 9.9, 2.5, 1.5 Hz, 2H), 4.67 (sept, *J* = 6.9 Hz, 1H), 3.79 (br dd, *J* = 2.5, 1.5 Hz, 2H), 1.60 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (22.4 MHz, CDCl$_3$) δ 179.8 (s), 133.1 (s), 128.3 (d), 127.7 (d), 127.6 (d), 126.9 (s), 123.2 (d), 58.3 (s), 44.5 (d), 19.3 (q); HRMS (FAB) calcd for $C_{25}H_{22}NO_2$ (MH$^+$) 368.1651, found 368.1649. Anal. Calcd for $C_{25}H_{21}NO_2$: C, 81.72; H, 5.76; N, 3.81. Found; C, 81.45; H, 5.60, N, 3.73.

Data for [2 + 2] photocycloadduct (3b): amorphous, IR (KBr) 1705 cm^{-1} (C═O); ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.12−6.76 (m, 6H), 6.46−6.38 (m, 2H), 6.26 (br d, *J* = 10.0 Hz, 1H), 5.66 (dm, *J* = 10.0 Hz, 1H), 5.53 (br m, 1H), 4.66 (sept, *J* = 6.9 Hz, 1H), 3.74 (br m, 2H), 1.94 (s, 3H), 1.60 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (22.4 MHz, CDCl$_3$) δ 179.8 (s), 134.6 (s), 133.1 (s), 132.1 (s), 128.14 (d), 128.08 (d), 128.0 (d), 127.4 (d), 127.3 (d), 127.2 (d), 123.7 (d), 123.4 (d), 120.4 (d), 58.3 (s), 58.1 (s), 44.4 (d), 44.3 (d), 43.7 (d), 20.0 (q), 19.3 (q); HRMS (FAB) calcd for $C_{26}H_{24}NO_2$ (MH$^+$) 382.1808, found 382.1805.

Data for [2 + 2] photocycloadduct (3c): colorless crystals; mp 196.5−197.5 °C (*n*-hexane/ethyl acetate); IR (KBr) 1700 cm^{-1} (C═O); ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.54 (dd, *J* = 7.5, 1.4 Hz, 2H), 7.45−7.29 (m, 3H), 7.00 (td, *J* = 7.5, 1.4 Hz, 2H), 6.85 (td, *J* = 7.5, 1.4 Hz, 2H), 6.81 (br dd, *J* = 7.5, 1.4 Hz, 2H), 6.31 (br d, *J* = 7.5 Hz, 2H), 6.28 (br d, *J* = 10.0 Hz, 2H), 5.63 (ddd, *J* = 10.0, 2.3, 1.5 Hz, 2H), 4.94 (s, 2H), 3.75 (br dd, *J* = 2.3, 1.5 Hz, 2H); ^{13}C NMR (22.4 MHz, CDCl$_3$) δ 179.4 (s), 136.0 (s), 133.0 (s), 128.9 (d), 128.8 (d), 128.4 (d), 128.3 (d), 128.1 (d), 127.8 (d), 127.7 (d), 127.6 (d), 126.6 (s), 123.1 (d), 58.7 (s), 44.3 (d), 43.2 (t); MS (FAB) 416 (MH$^+$). Anal. Calcd for $C_{29}H_{21}NO_2$: C, 83.83; H, 5.09; N, 3.37. Found; C, 83.54; H, 5.03, N, 3.32.

Data for [2 + 2] photocycloadduct (3d): colorless crystals; mp 198−200 °C (*n*-hexane/ethyl acetate); IR (KBr) 1700 cm^{-1} (C═O); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (dd, *J* = 7.5, 1.4 Hz, 2H), 7.45−7.29 (m, 3H), 7.00 (td, *J* = 7.5, 1.4 Hz, 2H), 6.85 (td, *J* = 7.5, 1.4 Hz, 2H), 6.81 (br dd, *J* = 7.5, 1.4 Hz, 2H), 6.31 (br d, *J* = 7.5 Hz, 2H), 6.28 (br d, *J* = 10.0 Hz, 2H), 5.63 (ddd, *J* = 10.0, 2.3, 1.5 Hz, 2H), 4.94 (s, 2H), 3.75 (br dd, *J* = 2.3, 1.5 Hz, 2H), 1.92 (s, 3H); ^{13}C NMR (22.4 MHz, CDCl$_3$) δ 179.5 (s), 136.1 (s), 134.6 (s), 133.1 (s), 132.2 (s), 128.8 (d), 128.3 (d), 128.2 (d), 127.72 (d), 127.66 (d), 127.6 (d), 127.4 (d), 127.3 (d), 126.6 (s), 123.8 (d), 123.4 (d), 120.4 (d), 58.9 (s), 58.7 (s), 44.3 (d), 43.6 (d), 43.2 (t), 20.0 (q); HRMS (EI) calcd for $C_{30}H_{23}NO_2$ (M$^+$) 429.1729, found 429.1725.

Data for [4 + 4] photocycloadduct (*syn*-4a): white powder, mp 113.5−114.0 °C; IR (KBr) 1705 cm^{-1} (C═O); ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.80−6.70 (m, 6H), 6.66−6.51 (m, 4H), 6.42 (d, *J* = 8.3 Hz, 2H), 4.74 (septet, *J* = 6.9 Hz, 1H), 4.00 (m, 2H), 1.62 (d, *J* = 6.9 Hz, 6H); HRMS (FAB) calcd for $C_{25}H_{22}NO_2$ (MH$^+$) 368.1651, found 368.1648.

Data for [4 + 4] photocycloadduct (*syn*-4c): white powder, mp 194.8−195.5 °C; IR (KBr) 1710 cm^{-1} (C═O); ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.59−7.51 (m, 2H), 7.46−7.31 (m, 3H), 6.79−6.59 (m, 8H), 6.43 (d, *J* = 6.9 Hz, 2H), 6.40 (d, *J* = 6.9 Hz, 2H), 4.99 (s, 2H), 3.98 (m, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 177.7 (s), 143.7 (s), 141.2 (s), 139.2 (d), 135.9 (s), 135.5 (d), 128.8 (d), 128.6 (d), 127.2 (d), 125.9 (d), 125.3 (d), 124.4 (d), 123.1 (d); HRMS (FAB) calcd for $C_{29}H_{22}NO_2$ (MH$^+$) 416.1651, found 416.1653.

Data for [4 + 4] photocycloadduct (*anti*-4a): ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.20−7.10 (m, 6H), 6.88 (d, *J* = 6.9 Hz, 2H), 6.12 (ddd, *J* = 8.2, 4.7, 2.5 Hz, 2H), 5.83 (d, *J* = 8.2 Hz, 2H), 4.77 (sept, *J* = 6.9 Hz, 1H), 4.05 (m, 2H), 1.68 (d, *J* = 6.9 Hz, 3H), 1.62 (d, *J* = 6.9 Hz, 3H); HRMS (FAB) calcd for $C_{25}H_{22}NO_2$ (MH$^+$) 368.1651, found 368.1655.

Data for [4 + 4] photocycloadduct (*anti*-4c): colorless crystals; mp 144.0−144.2 °C; IR (KBr) 1710 cm^{-1} (C═O); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.57 (m, 2H), 7.45−7.35 (m, 3H), 7.13 (m, 4H), 7.08−7.02 (m, 2H), 6.72 (d, *J* = 7.4 Hz, 2H), 6.12 (ddd, *J* = 8.2, 4.7, 2.5 Hz, 2H), 5.82 (d, *J* = 8.2 Hz, 2H), 5.06 (dd, *J* = 13.9 Hz, 1H), 4.97 (d, *J* = 13.9 Hz, 1H), 4.02 (m, 2H); ^{13}C NMR (22.4 MHz, CDCl$_3$) δ 177.9 (s), 144.3 (s), 142.1 (s), 138.3 (d), 135.9 (s), 134.0 (d), 128.9 (d), 128.7 (d), 128.2 (d), 126.7 (d), 126.6 (d), 126.0 (d), 123.5 (d), 63.8 (s), 47.7 (d), 43.1 (t); HRMS (FAB) calcd for $C_{29}H_{22}NO_2$ (MH$^+$) 416.1651, found 416.1649.

Data for 1,8-epidioxide (5a): colorless crystals; mp 168.5−169.0 °C (*n*-hexane/ethyl acetate); IR (KBr) 1705 cm^{-1} (C═O); ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.32−7.24 (m, 4H), 7.22−7.12 (m, 2H), 7.05−6.95 (m, 2H), 6.20 (dd, *J* = 9.6, 6.5 Hz, 2H), 5.65 (d, *J* = 9.6 Hz, 2H), 5.45 (d, *J* = 6.5 Hz, 2H), 4.89 (sept, *J* = 6.9 Hz, 1H), 1.76 (d, *J* = 6.9 Hz, 3H), 1.75 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (22.4 MHz, CDCl$_3$) δ 178.3 (s), 137.4 (s), 135.1 (s), 133.4 (d), 130.3 (d), 128.6 (d), 128.3 (d), 127.2 (d), 123.5 (d), 77.5 (d), 60.4 (s), 45.3 (d), 20.2 (q), 19.0 (q); HRMS (FAB) calcd for $C_{25}H_{22}NO_4$ (MH$^+$) 400.1533, found 400.1541. Anal. Calcd for $C_{25}H_{21}NO_4$: C, 75.17; H, 5.30; N, 3.51. Found; C, 75.42; H, 5.33, N, 3.49.

Data for 1,8-epidioxide (5b): white powder; mp 160.0−161.0 °C; IR (KBr) 1710 cm^{-1} (C═O); ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.44−7.38 (m, 1H), 7.35−7.24 (m, 4H), 7.22−7.14 (m, 1H), 7.05−6.96 (m, 2H), 6.16 (dd, *J* = 9.6, 6.8 Hz, 1H), 5.92 (d, *J* = 9.6 Hz, 1H), 5.69 (d, *J* = 9.6 Hz, 1H), 5.48 (d, *J* = 9.6 Hz, 1H), 5.40 (d, *J* = 6.8 Hz, 1H), 4.89 (sept, *J* = 6.9 Hz, 1H), 1.76 (d, *J* = 6.9 Hz, 3H), 1.76 (s, 3H), 1.75 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (22.4 MHz, CDCl$_3$) δ 178.6 (s), 138.3 (s), 137.8 (s), 136.2 (s), 135.6 (s), 133.6 (d), 133.3 (d), 130.8 (d), 130.3 (d), 128.6 (d), 128.4 (d), 128.3 (d), 128.2 (d), 127.1 (d), 126.2 (d), 123.8 (d), 123.5 (d), 79,1 (s), 77.7 (d), 60.6 (s), 60.4 (s), 45.3 (d), 26.1 (q), 20.2 (q), 19.0 (q); HRMS (FAB) calcd for $C_{26}H_{24}NO_4$ (MH^+) 414.1706, found 414.1712, calcd for $C_{26}H_{24}NO_2$ (MH^+ - O_2) 382.1807, found 382,1807.

Data for 1,8-epidioxide (5c): white powder; mp 161.5−162.5 °C; IR (KBr) 1710 cm^{-1} (C═O); ^1H NMR (270 MHz, $CDCl_3$) δ 7.74−7.68 (m, 2H), 7.49−7.42 (m, 3H), 7.22 (td, J = 7.6, 1.5 Hz, 2H), 7.13 (dd, J = 7.6, 1.5 Hz, 2H), 7.07 (td, J = 7.6, 1.5 Hz, 2H), 6.58 (br d, J = 7.6 Hz, 2H), 6.19 (dd, J = 9.6, 6.5 Hz, 2H), 5.61 (d, J = 9.6 Hz, 2H), 5.44 (d, J = 6.5 Hz, 2H), 5.18 (d, J = 13.5 Hz, 1H), 5.08 (d, J = 13.5 Hz, 1H); HRMS (FAB) calcd for $C_{29}H_{22}NO_4$ (MH^+) 448.1549, found 448.1551.

Data for 1,8-epidioxide (5d): colorless prisms; mp 153−155 °C (*n*-hexane/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (m, 2H), 7.43−7.34 (m, 3H), 7.35 (dd, J = 8.0, 1.2 Hz, 2H), 7.21 (dd, J = 7.7, 1.4 Hz, 1H), 7.18(dd, J = 7.5, 1.2 Hz, 1H), 7.12 (dd, J = 7.5, 1.4, 1H), 7.06−7.01 (m, 2H), 6.58 (dd, J = 7.7, 0.9 Hz, 1H), 6.54 (d, J = 7.7 Hz, 1H), 6.11 (dd, J = 9.7, 6.5 Hz, 1H), 5.93 (d, J = 9.7 Hz, 1H), 5.63 (d, J = 9.7 Hz, 1H), 5.42 (d, J = 9.7 Hz, 1H), 5.38 (d, J = 6.5 Hz, 1H), 5.15 (d, J = 13.4 Hz, 1H), 5.07 (d, J = 13.4 Hz, 1H), 1.71 (s, 3H); ^{13}C NMR (22.4 MHz, $CDCl_3$) δ 178.3 (s), 138.2 (s), 137.5 (s), 135.9 (s), 135.5 (s), 135.2 (s), 133.7 (d), 132.9 (d), 130.4 (d), 130.2 (d), 129.9 (d), 129.0 (d), 128.7 (d), 128.5 (d), 128.3 (d), 128.2 (d), 128.1 (d), 127.2 (d), 126.1 (d), 123.9 (d), 123.7 (d), 79.1 (s), 77.6 (d), 61.1 (s), 60.9 (s), 43.6 (t), 26.0 (q); MS (EI, *m*/*z*) 461 (M^+, 26), 300 (27), 239 (26), 185 (38), 171 (75), 155 (100), 127 (86), 91 (59); HRMS (EI) calcd for $C_{30}H_{23}NO_4$ (M^+) 461.1637, found 461.1652.

Data for [4 + 4] photocycloadduct (8a): colorless crystals; mp 205−206 °C (*n*-hexane/ethyl acetate); IR (KBr) 1705 cm^{-1} (C═O); ^1H NMR (400 MHz, $CDCl_3$) δ 7.28−7.12 (m, 3H), 7.05 (dd, J = 7.2, 1.3, 1H), 6.88−6.74 (m, 6H), 6.71 (dd, J = 7.2, 1.2, 1H), 6.61 (m, 1H), 6.21 (t, J = 7.7, 1H), 5.91 (dd, J = 8.0, 1.2, 1H), 4.88 (sept, J = 7.0, 1H), 4.53 (d, J = 10.9, 1H), 4.14 (dd, J = 10.9, 7.0, 1H), 1.73 (d, J = 7.0, 3H), 1.70 (d, J = 7.0, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.8 (s), 176.7 (s), 143.9 (s), 143.2 (s), 143.1 (s), 141.2 (s), 141.0 (s) 139.9 (s), 137.8 (d), 134.1 (d), 127.4 (d), 127.33 (d), 127.28 (d), 127.1 (d), 126.60 (d), 126.56 (d), 126.2 (d), 125.8 (d), 125.7 (d), 125.5 (d), 124.4 (d), 124.2 (d), 66.9 (s), 63.4 (s), 53.1 (d), 48.1 (d), 45.0 (d), 20.1 (q), 19.7 (q); MS (EI, *m*/*z*) 417 (M^+, 48), 303 (5), 246 (9), 205 (100), 155 (63), 127 (56). Anal. Calcd for $C_{29}H_{23}NO_2$: C, 83.43; H, 5.55; N, 3.35. Found; C, 83.09; H, 5.49; N, 3.35.

Data for [4 + 4] photocycloadduct (8b): colorless crystals; mp 175−178 °C (*n*-hexane/ethyl acetate); IR (KBr) 1710 cm^{-1} (C═O); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.1, 2H), 7.49−7.37 (m, 3H), 7.25 (m, 2H), 7.18 (td, J = 7.5, 1.3, 1H), 7.05 (td, J = 7.6, 1.5, 1H), 6.94 (d, J = 7.6, 1H), 6.89−6.71 (m, 5H), 6.64 (d, J = 7.3, 1H), 6.48 (d, J = 7.5, 1H), 6.22 (dd, J = 8.3, 7.3, 1H), 5.92 (dd, J = 8.3, 1.2, 1H), 5.34 (d, J = 13.9, 1H), 5.17 (d, J = 13.9, 1H), 4.56 (d, J = 10.9, 1H), 4.15 (ddd, J = 10.9, 7.2, 1.2, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.6 (s), 176.5 (s), 143.7 (s), 143.1 (s), 143.0 (s), 141.0 (s), 140.7 (s), 139.6 (s), 138.0 (d), 136.0 (s), 133.9 (d), 129.0 (d), 128.8 (d), 128.3 (d), 127.40 (d), 127.36 (d), 127.3 (d), 127.1 (d), 126.7 (d), 126.6 (d), 126.3 (d), 125.9 (d), 125.7 (d), 125.6 (d), 124.6 (d), 124.3 (d), 67.6 (s), 63.9 (s), 53.1 (d), 48.1 (d), 43.3 (t); MS (EI, *m*/*z*) 465 (M^+, 59), 303 (5), 205 (100), 177 (43), 155 (47), 127 (34), 91 (77). Anal. Calcd for $C_{33}H_{23}NO_2$: C, 85.14; H, 4.98; N 3.01. Found C, 85.00; H 4.88; N, 2.98.

X-ray Crystal Structure Determination of 5d. A crystal of **5d** from ethyl acetate-*n*-hexane, with approximate dimensions of 0.40 × 0.24 × 0.18 mm was mounted on a glass fiber and used for the X-ray study.

Crystal Data. $C_{30}H_{23}NO_4$, M = 461.52. Monoclinic, space group $P2_1/n$, a = 8.759(4), b = 18.604(2), c = 14.692(2) Å, β = 104.98(2)°, V = 2312.7(9) Å^3, Z = 4, D_c = 1.325 g cm^{-3}. Colorless prism. $F(000)$ = 968, μ(Mo−Kα) 0.7 cm^{-1}.

Data Collection, Structure Solution, and Refinement. Intensity data were collected on a Rigaku RAXIS−II imaging plate area detector with graphite-monochromated Mo−Kα radiation. The data were collected at a temperature of 15 ± 1 °C. A total of 2535 reflections was collected, and 1834 observed reflections with $|F_o| > 4.5\sigma(|F_o|)$ were used for further calculations after Lorentz and polarization corrections. The structure was solved by direct methods (SHELX86) and expanded using Fourier techniques (DIRDIF92). Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. A total of 408 parameters was refined to final residuals R = 0.068 and R_w = 0.079. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Cooperation.

Supporting Information Available: Copies of ^1H NMR spectra for compounds **1d**, **3b**, **3d**, *syn*-**4a**, *anti*-**4a**, *syn*-**4c**, *anti*-**4c**, **5b**, **5c**, and **5d**; tables of crystal data, atomic coordinates, bond lengths and angles, anisotropic thermal parameters for **5d**, and ORTEP diagram of **5d**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0010227