A Study on the Photochemistry of α,β-Unsaturated γ-Lactones. III. Photodimerization of 2-Penten-4-olide[1]

Kazuya Ohga* and Taku Matsuo**

Departmnt of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812

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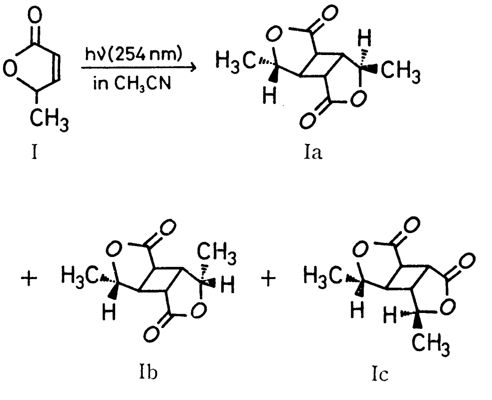
Irradiation of 2-pentene-4-olide (I) with 254 nm light afforded three anti dimers; two *head-to-tail* isomers and one *head-to-head* isomer. The photodimerization proceeds *via* the lowest triplet state. The quantum yields for the formation of the photodimers were determined as a function of the concentrations of I. Addition of I in the excited state to cyclopentene gave two isomeric cyclobutane derivatives. The photocycloaddition took place more rapidly than the photodimerization of I. The photodimerization was also quenched by anisole, probably through formation of an exciplex between I and anisole.

In a previous paper,[2] we reported an interesting photochemical behavior of α,β-unsaturated γ-lactones with a carbon-carbon double bond exocyclic to the lactone ring: the *cis-trans* isomerization proceeds *via* the lowest π,π^* triplet, while the β,γ-isomer arises from the second n,π^* triplet. On the other hand, no mechanistic detail of the photochemical behavior of an α,β-unsaturated γ-lactone with an endocyclic carbon-carbon double bond has been available partly due to experimental difficulties.[3] We have succeeded, for the first time, in obtaining the kinetic parameters by the use of 2-pentene-4-olide as a typical α,β-unsaturated γ-lactone with an endocyclic carbon-carbon double bond.

Results and Discussion

Structures of Photodimers. Irradiation of 2-penten-4-olide (I) in acetonitrile with 254 nm light afforded three products, Ia, Ib, and Ic (relative yields, 1 : 0.9 : 3). Each product was isolated by the use of both column chromatography on silica-gel and preparative VPC. The molecular weights, results of elementary analyses, characteristic IR bands, and the NMR spectroscopic data indicate that the isolated products are isomeric cycloadducts of I as in the case of 2-buten-4-olide[3] (Table 1).



Since no *trans*-fused photodimer with a five-four ring junction has been reported, the photodimers of I also are assumed to have a *cis*-fused structure. The proposed structures of the photodimers are supported by the NMR spectra. Each one doublet was observed for the methyl protons of Ia and Ic indicating that the two methyl groups in the respective dimer are at equivalent positions. Thus the signals due to the methine protons on the cyclobutane ring can be analyzed as a AA'BB'-system. The results of simulation are compared with the observed spectra (Fig. 1). The coupling constants obtained are summarized in Table 2.

In the case of cyclobutane ring protons, the *cis* vicinal coupling constants are generally larger than the *trans* couplings.[4] In the case of coumarine and carbostyryl photodimers, the long range coupling constants are positive in the *syn* configuration, while they are negative in the *anti* configuration.[4a] We thus conclude that Ia is an *anti, head-to-tail* dimer, while Ic is an *anti, head-to-head* dimer.

In the VPC (N_2, 55 ml/min) of the photodimers, the retention time of Ia (12.9 min) is shorter than that of Ic (18.1 min). This is in good agreement with the deduced structures, since it is suggested that a *head-to-tail* dimer has a shorter retention time than the corresponding *head-to-head* isomer due to the smaller dipole moment of the former.[5]

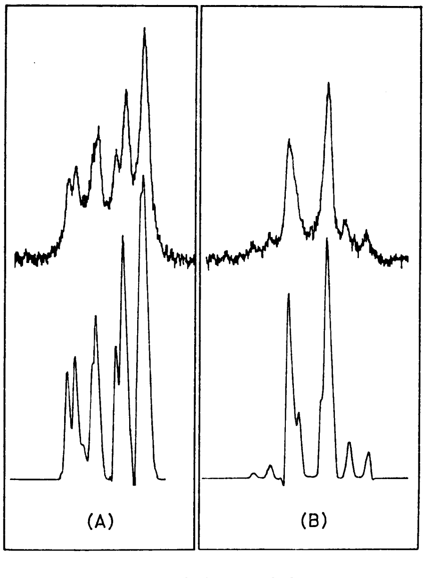


Fig. 1. NMR spectra of the cyclobutane protons: (A) Ia, (B) Ic. The simulated spectra are shown below the actually observed spectra.

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* Present address: Department of Environmental Chemistry and Engineering, Faculty of Engineering, Oita University, Dannoharu, Oita 870-11.

** To whom inquiries should be addressed.

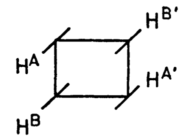
Table 1. Analytical data of photodimers

Isomer	Molecular weight[a]	Elementary analyses[b] C, %	Elementary analyses[b] H, %	Characteristic IR bands,[c] cm^{-1}	NMR Data[d] δ, ppm
Ia	196	61.04	6.10	1752(C=O) 1170(C-O-C)	1.37(d, J=6.3 Hz, 6H) 2.87(m, 2H)[e] 3.26(m, 2H)[e] 4.82(quartet-d, J=6.3 and 1.8 Hz, 2H)
Ib	196	61.26	6.15	1764(C=O) 1180(C-O-C)	1.41(d, J=6.3 Hz, 3H) 1.53(d, J=6.3 Hz, 3H) 2.6−3.5(m, 4H) 4.6—5.1(m, 2H)
Ic	196	61.45	6.17	1768(C=O) 1158(C-O-C)	1.32(d, J=6.3 Hz, 6H) 2.82(m, 2H)[e] 3.32(m, 2H)[e] 4.69(quartet, J=6.3 and 0 Hz, 2H)

a) Obtained from m/e value for the parent peak of the mass spectra. b) Calculated values for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17%. c) KBr pellet. d) In $CDCl_3$. e) Obtained by the simulation of the cyclobutane ring proton signals (AA′BB′ system).

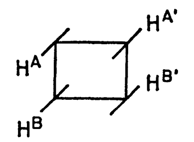
Table 2. NMR parameters estimated by simulation (Hz)

	Ia	Ic
$\Delta\delta\nu$	23.5	29.6
$J_{AA'}$	−0.9	1.9
$J_{BB'}$	−0.9	5.0
J_{AB}	7.4	6.8
$J_{AB'}$	3.4	−1.0



Ia

$J_{AB} > J_{AB'}$



Ic

$J_{AB} > J_{AA'}, J_{BB'}$

The solvent effects on the relative formation yields in acetone-photosensitized reactions are also in favor of the above assigned structures. On going from acetonitrile to benzene, Ic/Ia decreases rapidly (from 3.0 to 1.0) while Ib/Ia remains almost constant (0.93 and 1.1). Since Ib/Ia is little affected by the change in solvent polarity, it may be reasonable to assign an *anti, head-to-tail* structure to Ib and Ia. The shorter retention time in VPC for Ib (15.0 min) than Ic (18.1 min) is also in agreement with a less polar structure of the former. The assignment is further supported by the fact that the mass-spectrum of Ib is much closer to that of Ia than to that of Ic.

The configurations of the methyl groups were determined by means of NMR spectroscopy. The two methyl groups in either Ia or Ic are in equivalent positions. The vicinal coupling constants between the proton on the lactone ring and that on the cyclobutane ring are close to zero in both isomers (Table 1); 1.8 Hz for Ia and 0 Hz for Ic. It seems that the vicinal protons are roughly at right angle to each other. We see from the molecular model that such dihedral angles can be obtained when the methyl groups are at the *exo* positions. If the methyl groups were at the *endo* positions, the dihedral angles should be nearly zero, and the vicinal coupling constants should be much larger. The methyl groups of Ib, on the other hand, are not equivalent as shown by the NMR spectra. Accordingly, Ib is concluded to be an *endo, exo*-isomer.

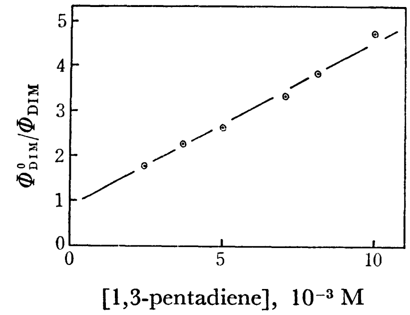


Fig. 2. Quenching of the photodimerization by 1,3-pentadiene.

Reaction Scheme and Kinetic Parameters. The photodimerization of I can be sensitized by ketones (Table 3) with triplet energies higher than that of xanthone, and the reaction is quenched by 1,3-pentadiene. The relative yields of the photodimers in both the sensitizing and quenching experiments are the same as those in the case of the direct irradiation with 254 nm light. Moreover, the Stern-Volmer plot is linear, and the intercept is close to unity (Fig. 2). These results suggest that all of the three photodimers are formed through an identical excited triplet state.

On the basis of a series of sensitization experiments, the energy level of the excited triplet state is estimated to be about 70 kcal/mol in acetonitrile, since neither benzophenone nor fluorenone could sensitize the photodimerization any more as shown in Table 3. The energy level is close to that of the $T_1(\pi,\pi^*)$ state of 2-ethylidene-4-butanolide.[2)]

The variations of the quantum yields for the formations of the dimers with the concentrations of I on

TABLE 3. PHOTOSENSITIZED DIMERIZATION IN ACETONITRILE

Sensitizer	E_T kcal/mol	Dimer ratio	
		Ib/Ia	Ic/Ia
Acetone	80	0.93	3.0
Acetophenone	74	0.93	2.9
p-Methylacetophenone	73	0.96	3.0
p-Methoxyacetophenone	72	0.90	2.9
Xanthone	71	0.83	—[a]
Benzophenone	69	—	—
Fluorenone	53	—	—
(Direct irradiation)		0.94	3.0

a) Not determined because of the overlapping of the VPC peaks for Ic and xanthone.

TABLE 4. DIMER QUANTUM YIELDS AT VARIOUS CONCENTRATIONS OF I IN ACETONITRILE

Concn M (10^{-1})	Quantum yield		
	Ia(10^{-2})	Ib(10^{-2})	Ic(10^{-2})
0.79	5.7	5.1	1.7
1.00	5.8	5.1	1.7
1.12	6.0	5.5	1.8
1.25	5.9	5.6	1.9
1.44	6.2	5.5	1.9
1.62	6.2	6.1	1.9
2.23	6.4	6.3	2.1
4.08	6.6	6.4	2.1
10.00	6.6	6.5	2.2

irradiation with 254 nm light in acetonitrile are shown in Table 4. The relative yields of the photodimers are independent of the concentrations of I in the concentration ranges investigated. It has been proposed by Wagner[6)] and also by de-Mayo and his coworkers[7)] that photodimers and/or photocycloadducts to olefins of α,β-unsaturated cyclic ketones are formed through metastable intermediates from the excited triplet states. The same mechanism may be used to explain the concentration dependence of the quantum yield for I:

$$I_0 \xrightarrow{h\nu} {}^1I^* \xrightarrow{\Phi_{ISC}} {}^3I^*$$

$$^3I^* \xrightarrow{k_1} I_0$$

$$^3I^* + I_0 \xrightarrow{k_r} {}^*I\text{-}I^*$$

$$^*I\text{-}I^* \xrightarrow{k_c} \text{dimer}$$

$$^*I\text{-}I^* \xrightarrow{k_{-r}} 2I_0$$

In this case, the relation between the quantum yield for the photodimerization, Φ_{DIM}, and the concentration of I, [I], may be given by the following equation:

$$\Phi_{DIM}^{-1} = \Phi_{ISC}^{-1}\Phi_p^{-1}(1+k_1/k_r[I])$$

where Φ_{ISC} and Φ_P denote the intersystem crossing yield for I and branching ratio for the decay to the final product from the metastable dimeric species, *I-I*. The rate constant for the unimolecular radiationless decay of the triplet I, $^3I^*$, and that for the addition of $^3I^*$ to I at the ground state are denoted by k_1 and k_r, respectively.

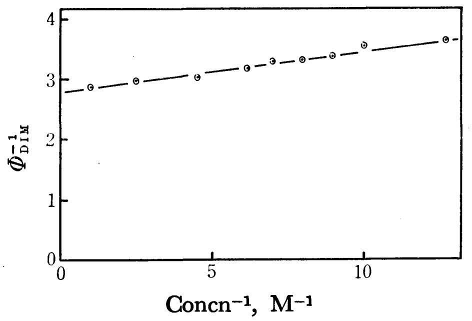


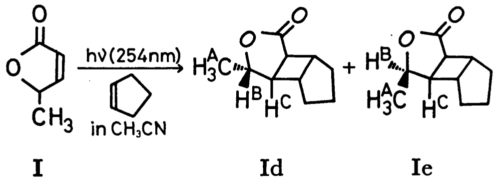
Fig. 3. Variations of the dimer quantum yield in acetonitrile as a function of the concentration of I.

TABLE 5. KINETIC PARAMETERS FOR THE PHOTODIMERIZATION OF I IN ACETONITRILE

Compound	k_r, $M^{-1}s^{-1}$	k_1, s^{-1}	$\Phi_{ISC}\cdot\Phi_p$
I	2.2×10^3	5.5×10^3	0.36
Cyclopentenone	6.6×10^8	0.4×10^8	0.36

The experimental data were accordingly plotted (Fig. 3), and the kinetic parameters were evaluated (Table 5) on the assumption that a rate constant for quenching by 1,3-pentadiene is $1.0\times10^{10}\,M\,s^{-1}$ in acetonitrile.[6)] While the values for k_r and $\Phi_{ISC}\cdot\Phi_p$ are almost the same between I and 2-cyclopentenone, the k_1-value for the former is only one-sevenths of that for the latter. It is surprising that replacement of methylene alpha to the carbonyl group with etherial oxygen atom caused a remarkable decrease in k_1. It is also interesting that the value for $\Phi_{ISC}\cdot\Phi_p$ is more than ten times as that for either thymine or uracil.[8)] As a net result of these variations in the kinetic parameters, the photodimerization yield of I turned out to be one of the highest among the related compounds.

Photocycloaddition to Cyclopentene. On the irradiation of I in acetonitrile in the presence of excess cyclopentene with a 30 W low-pressure mercury lamp for 19 h, two isomeric 1 : 1 cycloadducts were obtained: Id(36%) and Ie(24%). In analogy to the case of 2-buten-4-olide,[9)] the steric structures of the adducts were concluded to be *cis-anti-cis* form. Analysis of the NMR spectra indicates that the difference between the two isomers are due to the stereochemistry of the methyl group. On the basis of the vicinal coupling constants, Id(J_{BC}=1.8 Hz) and Ie(J_{BC}=6.3 Hz) were assigned to an *exo*- and *endo*-isomers, respectively.



I Id Ie

Acetonitrile solution of I(0.1 M) was irradiated at 254 nm in the presence of various amounts of cyclopentene. The relative yields between the photodimers, as well as the ratio of cycloadducts (Id/Ie), were independent of cyclopentene concentration. The photodimerization reaction itself was partly quenched by

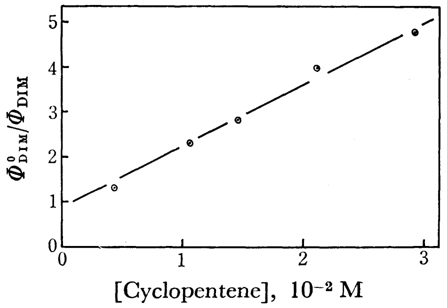


Fig. 4. Quenching of the photodimerization by cyclopentene in acetonitrile ([I]) = 0.1 M).

the addition of cyclopentene (Fig. 4). It is clear that both photodimerization and photocycloaddition proceed *via* the same excited species of I.

The rate constant (k_{ra}) for the reaction between ^{3}I* and cyclopentene is evaluated from the slope of the Stern-Volmer plot ($k_{\mathrm{ra}}\tau = 136\ \mathrm{M}^{-1}$) and the lifetime of ^{3}I* obtained in the analysis of the photodimerization (3.7×10^{-8} s at 0.1 M solution of I). The k_{ra}-value ($3.7 \times 10^9\ \mathrm{s}^{-1}\ \mathrm{M}^{-1}$), thus obtained, is more than ten times as large as k_{r}. The difference in the rate constants may be due to electrophilic property of ^{3}I*, which should favor more nucleophilic cyclopentene rather than I. In agreement with this suggestion, the photodimerization of I was quenched much more effectively by the use of 1,4-dioxene.

Interaction with Benzene Homologues. The above suggested electrophilic character of ^{3}I* was also varified by the investigation of interactions between ^{3}I* and benzene homologues. The photodimerization yields were measured in the presence of benzene, toluene, and anisole (Table 6). The amount of 254 nm light absorbed by the added benzene homologue was subtraced from the total intensity of light in evaluating the quantum yield. In other words, $\Phi_{\mathrm{DIM}}/\Phi^0_{\mathrm{DIM}}$ should remain unity as far as the benzene homologues do not affect the reaction. In the case of benzene, however, the quantum yield increased, the photodimerization being apparently sensitized. A similar photosensitization would be expected to take place in the case of toluene and anisole. The experimental results indicate that the quantum yield was significantly reduced by anisole while it was hardly affected by toluene. It is clear that quenching and sensitization compete with each other in the presence of the benzene homologue. The highest quenching effect observed with anisole may be associated with the fact that the ionization potential of anisole is the lowest among the benzene homologues investigated. Quenching is quite likely to take place due to charge-transfer interactions between ^{3}I* and benzene homologues, which lead to the formation of exciplexes as an intermediate responsible for radiationless decay.

TABLE 6. VARIATIONS OF THE RELATIVE VALUES, $\Phi_{\mathrm{DIM}}/\Phi^0_{\mathrm{DIM}}$, BY THE ADDITION OF BENZENE HOMOLOGUES

Compound	Concn 10^{-2} M	Light absorbed by I,[a] %	$\Phi_{\mathrm{DIM}}/\Phi^0_{\mathrm{DIM}}$ Ia	Ib	Ic
Benzene	1.50	52.4	1.5	1.2	1.4
Toluene	1.47	52.2	0.98	0.93	0.95
Anisole	0.541	55.4	0.67	0.80	0.74

a) The fractions of 254 nm light absorbed by I.

Experimental

The NMR spectra were obtained on a Varian Model A-60 analytical spectrometer with tetramethylsilane as an internal standard. The IR and mass spectra were recorded on a JASCO Model DS-301 spectrometer and JEOL Model JMS-01SG mass spectrometer respectively. VPC analysis was carried out on a Shimadzu Model GC-3BF gas chromatograph equipped with a flame ionization detector, with the use of a column (2 m × 3 mm) packed with 2% polyphenyl ether (six rings) on Diasolid L 60/80. The column temperature was 220 °C for the analysis of the dimers, 190 °C for that of the cyclopentene cycloadducts. The melting points were measured on a Yanagimoto micro melting-point measurement apparatus and are uncorrected.

Materials. The starting material, I, was prepared as described previously[10] and distilled under reduced pressure; bp 62.0 °C (3 mmHg). The distillate showed a single peak by VPC (10% polyphenyl ether (five rings) on Chamelite CS 60/80). *p*-Methylacetophenone (reagent grade) was purified by fractional distillation under reduced pressure just before use. Extra pure xanthone and fluorenone obtained from Tokyo Kasei Co. were used without further purification. Another ketone-sensitizers were purified as described previously.[2] 1,3-Pentadiene (76 : 24 *trans/cis* isomer ratio) was distilled at atmospheric pressure just before use, its purity being found to be 99.5% by VPC (20% benzyl cyanide and 12% silver nitrate on Chamelite CK 60/80). Cyclopentene was purified with ferric sulfate, followed by fractional distillation just before use. The distillate showed a single peak on inspection by VPC under the same conditions as those for 1,3-pentadiene.

Isolation of the Photodimers. The acetonitrile solution of I was irradiated with a 30 W low-pressure mercury lamp under the same conditions as those for the photodimerization of 2-buten-4-olide.[3] The three photodimers, Ia, Ib, and Ic were isolated from the reaction mixture by means of chromatography on silica gel with benzene-ethyl acetate (10 : 1) as an eluent, and successive preparative VPC with the use of a column packed with 1.5% polyphenyl ether (six rings) on Diasolid L. The photodimers were then recrystallized; mp : Ia, 194.0—195.0 °C (from benzene); Ib, 145.0—146.0 °C (from benzene-hexane); Ic, 222.5—224.0 °C (from ethyl acetate). MS(75 eV) : Ia, 196 (M^+, 19%), 181($\mathrm{M}^+ - \mathrm{CH}_3$, 38%), 108($\mathrm{M}^+ - 2\mathrm{CO}_2$, 33%), 97(33%), 93($\mathrm{M}^+ - 2\mathrm{CO}_2 - \mathrm{CH}_3$, 88%), 80(74%), 79($\mathrm{M}^+ - 2\mathrm{CO}_2 - 2\mathrm{CH}_3 + \mathrm{H}$, 100%); Ib, 196(12%), 181(15%), 108(44%), 97(24%), 93(94%), 80(63%), 79(100%); Ic, 196(3%), 181(5%), 108(9%), 97(12%), 93(100%), 80 (37%), 79(59%).

Quantum Yields for Photodimerization. Appropriate amounts of I were dissolved in acetonitrile of spectrograde purity (0.79×10^{-1} – 10.00×10^{-1} M). Eight ml of each acetonitrile solution was pipetted into the same sample tube[2] which was degassed by three freeze-pump-thaw cycles at less than 10^{-4} mmHg. The samples and the potassium ferrioxalate actinometer solution (6×10^{-3} M) were irradiated with light filtered through an aqueous solution containing $\mathrm{NiSO_4 \cdot 6H_2O}$ (450 g/l), $\mathrm{CoSO_4 \cdot 7H_2O}$ (150 g/l), and 5,7-dimetyl-1H-2,3-dihydro-1,4-diazepinium perchlorate (175 mg/l).[11] The irradiation apparatus used was described previously.[2] After irradiation at 20.0±0.1 °C for

1.5 h, the amount of each dimer was determined by VPC analysis with 4,4′-dimethoxydiphenylmethane as an internal standard. The yield of all dimers did not exceed 5%.

Photosensitized Dimerization of I. A solution of I and a sensitizer in acetonitrile was sealed after flushing with nitrogen and irradiated externally with a high-pressure mercury lamp (Riko-Sha UVL-700P) through Pyrex filter at near 21 °C for 3 h. The reaction was carried out in an ordinary glass sample tube except for the case of acetone sensitization where a Pyrex tube was used. Under such conditions, incident light is absorbed almost by the sensitizer alone. Dimer ratio was analyzed by means of VPC.

Quenching of the Photodimerization by 1,3-Pentadiene. The degassed samples containing I (1.00×10^{-1} M) and varying concentrations of 1,3-pentadiene in acetonitrile were irradiated with a merry-go-round apparatus. The relative quantum yields were determined with the same procedure as in the case of the determination of dimerization quantum yield except that an aqueous solution containing only 5,7-dimethyl-1*H*-2,3-dihydro-1,4-diazepinium perchlorate (177 mg/l) was used as a filter solution. By the use of the extinction coefficients measured at 254 nm on a Shimadzu Model UV-200 spectrophotometer, the amount of light absorbed by I was estimated after correcting the absorption due to 1,3-pentadiene.

Photocycloaddition of I to Cyclopentene. A 0.063 M solution of I in acetonitrile (160 ml) containing 0.56 M cyclopentene was irradiated with a 30 W low-pressure mercury lamp through quartz for 19 h under nitrogen gas. The VPC analysis of the irradiated sample, with oxanthrene as an internal standard, indicated that the cycloadduct, Id and Ie were formed in 36 and 24% yields, respectively. Preparative VPC was applied to isolate each cycloadduct. The cycloadduct Id was the sole adduct, but Ie was still contaminated by 3% Id after preparative VPC had been carried out twice. Id, Found: C, 71.99; H, 8.54%. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%. IR(neat): 1776 (C=O), 1170 (C–O–C), 1450, 1471 cm^{-1} (cyclopentane ring). NMR(CDCl$_3$): 1.27 (d, $J_{AB}=6.3$ Hz, 3H), 1.2—2.3 (m, 7H), 2.5—3.0(m, 3H), 4.66 (quartet-d, $J_{AB}=6.3$, $J_{BC}=1.8$ Hz, 1H). MS(75 eV): 166(M$^+$, 18%), 121 (M$^+-$CO$_2-$H, 27%), 99($C_5H_6O_2^+$+H, 75%), 68($C_5H_8^+$, 100%). Ie, Found: C, 71.95; H, 8.61%. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%. IR(neat): 1770(C=O), 1175(C–O–C), 1450, 1469 cm^{-1} (cyclopentane ring). NMR(CDCl$_3$): 1.43 (d, $J_{AB}=6.3$ Hz, 3H), 1.3—2.0(m, 6H), 2.1—3.0(m, 4H), 4.69(quintet, $J_{AB}=J_{BC}=6.3$ Hz, 1H). MS(75 eV): 166 (M$^+$, 14%), 121(M$^+-$CO$_2-$H, 26%), 99($C_5H_6O_2^+$+H, 66%), 68($C_5H_8^+$, 100%).

Quenching of the Photodimerization by Cyclopentene. The degassed samples containing I (1.00×10^{-1} M) and varying concentrations of cyclopentene (from 0.438×10^{-2} to 2.92×10^{-2} M) in acetonitrile were irradiated for 2 h under the same conditions as in the case of quenching by 1,3-pentadiene.

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