

Photocycloaddition of Cyclohexa-1,3-diene to Methyl Naphthoates

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The photocycloaddition reactions of cyclohexa-1,3-diene to methyl naphthoates were studied at low temperature in order to prevent facile thermal reactions during irradiation. By product analyses and low-temperature ^1H NMR studies of the irradiated mixtures, the primary products were found to be the corresponding *exo*-[4+4] adducts fused at the 1,4-position of the naphthalene skeleton and the *syn*-[2+2] adducts fused at the 1,2-position. In the irradiation of methyl 1-naphthoate and cyclohexa-1,3-diene, the *endo*-[4+2] adduct was also isolated. The low-temperature ^1H NMR studies indicated that the *syn*-[2+2] adduct was the major primary product in the case of methyl 1-naphthoate, and the *syn*-[2+2] and *exo*-[4+4] adducts in the case of methyl 2-naphthoate. The results were compared with those in the photocycloaddition reactions to naphthalenecarbonitriles. The regiochemistry and stereochemistry of the primary products were explained by the LUMO-LUMO interaction between the substrates.

Introduction

Due to their unique strained structures, arene-arene cyclodimers have interesting physical and chemical properties such as adiabatic photodissociation,¹⁻⁵ chemiluminescence,⁶ multi-photon IR absorption,^{4c} and through-bond interaction.⁷ The substituents of the cyclodimers have been found to influence these properties significantly. For example, electron withdrawing groups substituted at the 9,10-positions of the anthracene portion of anthracene-benzene cyclodimer facilitate thermal dissociation,⁴ increase the efficiency of chemiluminescence, and decrease the efficiency of adiabatic photodissociation.⁶ Electron withdrawing groups substituted at the 1,4-positions of the benzene portion also facilitate thermal dissociation, but decrease the efficiency of chemiluminescence. Although naphthalene-benzene cyclodimers were realized more than ten years ago,⁸ we recently reported that the *syn*-[2+2] and cage cyclodimers underwent an adiabatic photodissociation to yield the excited naphthalene.³ In order to study the substituent effect, we needed to synthesize the derivatives of naphthalene-benzene cyclodimer.

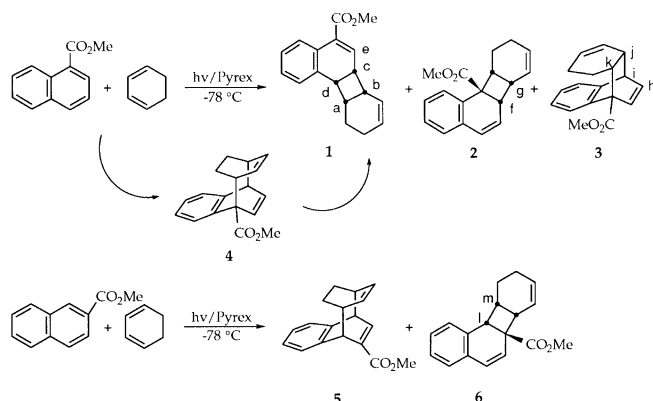
The synthesis of arene-benzene cyclodimers has been generally achieved indirectly by the photocycloaddition of substituted diene to arene followed by the transformation of the substituent functionality to an olefinic bond.^{1-6,8} Therefore, we are interested in the photocycloaddition of cyclic 1,3-dienes to naphthalene derivatives. While naphthalene itself is known to react with cyclohexa-1,3-diene (CHD) upon irradiation to give the corresponding [4+4] cycloadducts and [4+2] cycloadducts,^{9,10} there have been few examples of the photocycloaddition of 1,3-dienes to naphthalene derivatives. Moreover, the products in the reactions were reported to be quite different from those with naphthalene. It was known that the photoreaction of 1-naphthalenecarbonitrile and furan exclusively yielded the *endo*-[4+4] cycloadduct, which is opposed to the prediction based on the secondary orbital interaction between the LUMO's of the substrates.¹¹ The

irradiation of 1-naphthalenecarbonitrile and CHD at ambient temperature yielded three cycloadducts, which are also opposed to the prediction.¹² The results were previously explained by the dominant interaction between the HOMO of CHD and the LUMO of 1-naphthalenecarbonitrile due to the lowering of the 1-naphthalenecarbonitrile orbitals by the cyano group.

However, we recently reinvestigated the photocycloaddition reaction of CHD or furan to 1-naphthalenecarbonitrile, and found that the primary [4+4] cycloadduct undergoes a facile rearrangement to the *syn*-[2+2] cycloadduct at ambient temperature which is then dissociated to regenerate the starting materials under the irradiation conditions.^{13,14} The structures of the primary *exo*-[4+4] cycloadducts studied by low-temperature NMR analyses are also consistent with the prediction based on secondary orbital interactions affecting the stereochemistry. As a preliminary stage in the synthesis of some derivatives of naphthalene-benzene cyclodimer, we investigated the photocycloaddition of CHD to methyl 1-naphthoate (1-MN) and methyl 2-naphthoate (2-MN). The photocycloaddition of dienes to naphthalene derivatives other than naphthalenecarbonitriles appears to be rather limitedly studied. In the photoreaction of 1-MN and furan at low temperature, the major primary product was the *exo*-[4+4] cycloadduct.¹⁵ The irradiation of 1-MN and an enol of β -ketone was reported to induce 1,2-photocycloaddition.¹⁶

Results and Discussion

In order to prevent secondary thermal processes during irradiation, a low-temperature irradiation experiment was conducted. A dichloromethane solution of 1-MN and CHD at $-78\text{ }^\circ\text{C}$ under a nitrogen atmosphere was irradiated through a Pyrex filter for 4 hours to furnish a mixture of two [2+2] adducts (**1** and **2**) and the [4+2] adduct (**3**) (Scheme 1). The reaction mixture was not separated completely by column chromatography and recrystallization. The isolated yield of **3** was 9%, and small amounts of **1** and **2** were



Scheme 1. Irradiation of 1-MN and 2-MN in the presence of CHD.

obtained pure for analytical purpose. As expected on the basis of the weak bridgehead linkage carrying the methoxycarbonyl group,^{15,17} the ¹H NMR spectrum of the irradiated mixture did not show any evidence for the existence of the [4+4] adducts. No cage adduct was found, which was observed in the photoreaction of 1-MN and furan.¹⁵ The relative ratio of **1**, **2**, and **3** in the irradiated mixture was estimated to be 30 : 58 : 12. It is interesting to note that the *endo*-[4+2] adduct (**3**) was isolated. Although the compound with the same skeleton was produced in the photoreaction of naphthalene and CHD,¹⁰ it is the first example in the photocycloaddition of cyclic 1,3-diene to substituted naphthalenes. The photoexcitation of xanthone in the presence of 1-MN and CHD with a Uranium filter did not produce any cycloadduct, which indicated that **3** was formed in the singlet state. Heating a benzene solution of 1-MN and CHD in the presence of boron trifluoride diethyl etherate or diethylaluminum chloride at 55–60 °C for 5 hours failed to provide **3**.

The mass (CI) spectra of the adducts exhibit the parent peaks (MH⁺) and peaks fragmented to their unit components indicating 1 : 1 adducts of 1-MN and CHD. Three proton peaks at the olefinic region in the ¹H NMR spectrum of **1** and four intense peaks at 37–41 ppm in its ¹³C NMR spectrum indicated that the CHD ring is fused to the 3,4-position of 1-MN. The characteristics of the 1,2-dihydronaphthalene chromophore in the UV spectrum and strong couplings of H-c with H-b, H-d, and H-e in the COSY spectrum also supported the interpretation (Scheme 1). The large coupling constant (9.3 Hz) between H-a (2.81 ppm) and H-d (3.91 ppm) suggested the *syn*-[2+2] structure of **1**. The spectroscopic data of **2** are similar to those of the *syn*-[2+2] cycloadduct of 1-naphthalenecarbonitrile and CHD fused at the 1,2-position.¹⁴ The large coupling constant (9.7 Hz) between H-f (3.79 ppm) and H-g (3.20 ppm) is consistent with the *syn*-orientation. Four proton peaks at the aromatic region in the ¹H NMR spectrum of **3** indicated that CHD is added to the substituted ring of 1-MN. Four olefinic proton peaks in the ¹H NMR spectrum, and three intense peaks (38–47 ppm) and one weak peak (57.19 ppm) at the bridged carbon region of the ¹³C NMR suggested the [4+2] structure. Strong coupling of H-i with H-h and H-j, and no coupling between H-h and H-k in the COSY spectrum (Figure 1) con-

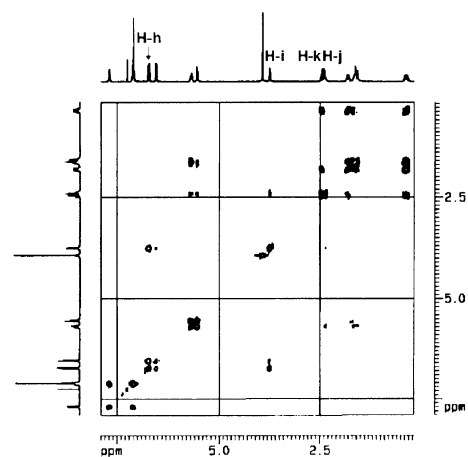


Figure 1. COSY spectrum of **3** in CDCl₃.

firmed the analysis. The stereochemistry was determined by considering the chemical shifts of the methylene protons. Due to the anisotropic effect of the benzene ring, one methylene proton (0.38 ppm) of **3** is shifted to higher field than the others, which suggests the *endo*-orientation. The upfield shift of the methylene proton and the UV spectrum of **3** are similar to those of the *endo*-[4+2] cycloadduct of naphthalene and CHD.¹⁰

A dichloromethane solution of 2-MN and CHD at -78 °C was irradiated through a Pyrex filter for 5 hours to afford the *exo*-[4+4] adduct (**5**) and the *syn*-[2+2] adduct (**6**) (Scheme 1). The cage compound, which was reported in the photoreaction of 2-naphthalenecarbonitrile and furan,^{11c} was not found. The reaction mixture was separated by column chromatographies. Although the ratio of **5** and **6** in the irradiated mixture was estimated to be 83 : 17 by the ¹H NMR analysis, most compound isolated was **6** and only a few mg of **5** was isolated. No other product was formed during the chromatographies. These indicated that **5** may quantitatively undergo a facile Cope rearrangement to **6** under the relatively mild purification conditions. Upon heating a CDCl₃ solution of **5** at 53 °C for 4 hours, **5** was rearranged to **6** in 71% conversion. In contrast to the thermal rearrangement of the *exo*-[4+4] cycloadduct¹⁴ of naphthalenecarbonitrile and CHD, the conversion to the *syn*-[2+2] adduct fused at the 3,4-position was not observed. The facile Cope rearrangement of **5** compared with the *exo*-[4+4] cycloadduct⁹ of naphthalene and CHD may result from the stabilization of a transition state by the methoxycarbonyl group.^{14,18}

Four proton peaks at the aromatic region in the ¹H NMR spectrum of **5** indicated that the cycloaddition of CHD occurs to the substituted ring of 2-MN. Four intense peaks at 40–50 ppm in the ¹³C NMR spectrum, three olefinic proton peaks in the ¹H NMR spectrum, and strong coupling between the peaks at 3.08 ppm and 4.23 ppm, and at 3.08 ppm and 3.79 ppm in the COSY spectrum (Figure 2) suggested the [4+4] structure. The observed facile Cope rearrangement to **6** indicated the *exo*-structure of **5**. The spectroscopic data of **6** are similar to those of the *syn*-[2+2] cycloadduct¹⁴ of 2-naphthalenecarbonitrile and CHD. Four

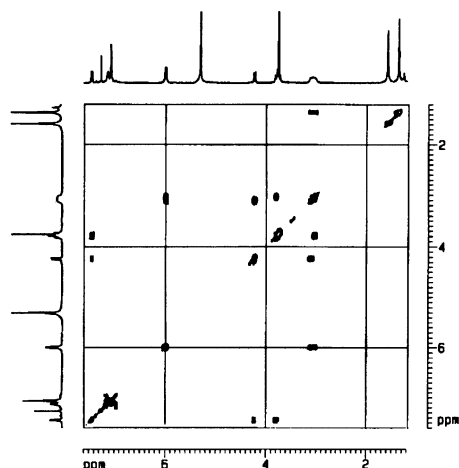


Figure 2. COSY spectrum of **5** in CDCl_3 .

olefinic proton peaks and the large coupling constant (9.4 Hz) between H-l (4.31 ppm) and H-m (2.71 ppm) led to assign **6** as the *syn*-[2+2] adduct fused at the 1,2-position.

In order to study the relative yields of the primary products in a low conversion, low-temperature NMR studies were conducted. After the irradiation of the mixture of 1-MN and CHD in CDCl_3 at $-60\sim-50\text{ }^\circ\text{C}$, a ^1H NMR spectrum was taken at $-50\text{ }^\circ\text{C}$ immediately (Figure 3a). Another ^1H NMR spectrum was taken after leaving the reaction mixture at higher temperature (Figure 3b). In Figure 3a, significant amount of **3** was not observed in 12% conversion of 1-MN. Since **3** does not absorb the light at the wavelengths transmitted by the filter used, the results indicated that **3** had been accumulated under the irradiation conditions of the synthetic scale reaction. Some ^1H NMR peaks (6.85 and 3.02 ppm) of **4** were identified by examining the disappearance of the peaks. The comparison of both spectra also indicated the

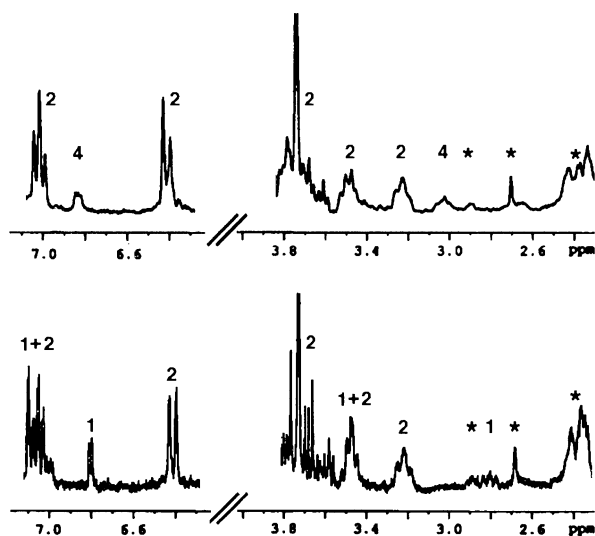


Figure 3. Low-temperature NMR study for the photoreaction of 1-MN and CHD. (a) ^1H NMR spectrum at $-50\text{ }^\circ\text{C}$ for the irradiated solution of 1-MN and CHD at $-60\sim-50\text{ }^\circ\text{C}$ (* peaks of CHD dimers), (b) ^1H NMR spectrum at $18\text{ }^\circ\text{C}$ for the resulting solution after standing at room temperature.

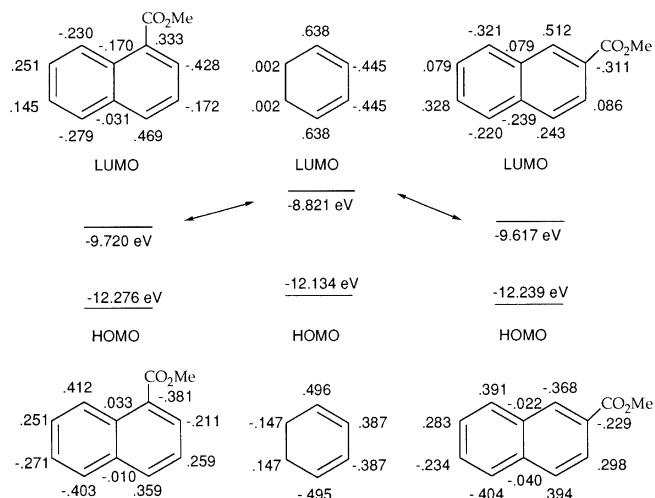


Figure 4. Orbital interactions between methyl naphthoates and CHD.

exclusive conversion of **4** into **1**. The ratio of **4** and **2** in Figure 3a was estimated to be about 17 : 83, which indicated that **2** was the major primary product. In a similar experiment with 2-MN and CHD in 20 minute irradiation, the ratio of **5** and **6** was estimated to be about 54 : 46 in 7% conversion. The lower yields of both *syn*-[2+2] adducts (**2** and **6**) in the synthetic scale reactions are related to the dissociative pathway. Since both UV spectra of **2** and **6** reach beyond 315 nm, the adducts formed can be easily dissociated to the starting materials.

In the irradiation of methyl naphthoates and CHD, both [2+2] and [4+4] photocycloadditions occurred. The [4+4] adducts are expected to be in the *exo*-form on the basis of the secondary orbital interactions between the LUMO's of methyl naphthoates and CHD (Figure 4).^{19,20} This is in good agreement with our experimental results. For both primary *syn*-[2+2] adducts (**2** and **6**), the CHD ring was fused to the 1,2-position. This can be explained by the larger coefficients at C-1 and C-2 of the LUMO's of methyl naphthoates than those at C-3 and C-4. The major product was the *syn*-[2+2] adduct in the case of 1-MN, while the major products were the *syn*-[2+2] and *exo*-[4+4] adducts in the case of 2-MN. The less formation of the *exo*-[4+4] adduct in the photocycloaddition to 1-MN than 2-MN may be explained by the steric repulsion of the methoxycarbonyl group in the *exo*-[4+4] approach of CHD to 1-MN.¹⁴

Experimental

Materials and instruments. All the reagents were purified by the procedures in the literature.²¹ Solvent for photoreaction was purified by refluxing over phosphorus pentoxide followed by distillation. Melting points were determined on a MEL-TEMP II melting point apparatus and reported uncorrected. ^1H and ^{13}C NMR spectra were routinely recorded at 300 MHz and/or 500 MHz on AMX Bruker spectrometers. IR spectra were recorded on a Perkin Elmer Spectrum 2000 Explorer FT-IR spectrometer. UV spectra

were recorded on a Cary 300 Bio UV/VIS spectrophotometer. Mass spectra (MS) were obtained on a Hewlett-Packard 5890-JMS AX505WA double focusing magnetic sector mass spectrometer.

Low-temperature irradiation of 1-MN and CHD. 1-MN (2.013 g, 10.81 mmol) and CHD (7.35 mL, 77.14 mmol) were dissolved in 100 mL dichloromethane and purged with nitrogen for 20 minutes. The solution in a dry ice/methanol bath was irradiated through a Pyrex glass filter with a 450 watt Hanovia medium-pressure mercury lamp for 4 hours. During the irradiation, a gentle stream of nitrogen was maintained. No precipitates were observed during the irradiation. The ^1H NMR analysis of the reaction mixture indicated that the relative ratio of **1**, **2**, and **3** was 30 : 58 : 12 with about 6% of the unreacted 1-MN. Silica gel chromatographies in several solvent conditions did not resolve the mixture completely. **1** was slowly changed to a complex mixture during the chromatographies. **3** (236.1 mg, 9%) was isolated by repeated recrystallizations from the fractions containing **3** in dichloromethane and *n*-hexane. Small amounts of **1** and **2** were purified by the silica gel chromatographies eluting with *n*-hexane/benzene and/or *n*-hexane/diethyl ether of increasing polarity for the purpose of characterization. **1**: ^1H NMR (300 MHz, CDCl_3 , TMS) δ 7.77 (1H, m, aromatic), 7.13 (2H, m, aromatic), 6.92 (1H, m, aromatic), 6.72 (1H, d, $J=4.0$ Hz, H-e), 5.93 (1H, m, CH=C-C-C₂), 5.66 (1H, m, $J=9.9$ Hz, C=CH-C-C₂), 3.91 (1H, dd, $J=9.9$, 9.3 Hz, H-d), 3.83 (3H, s, CO_2CH_3), 3.62 (1H, m, $J=9.9$ Hz, H-c), 3.45 (1H, m, H-b), 2.81 (1H, m, H-a), 1.79 (1H, m, methylene), 1.62 (2H, m, methylene), 1.40 (1H, m, methylene); ^{13}C NMR (75 MHz, CDCl_3 , TMS) δ 167.64, 140.08, 133.40, 130.50, 130.00, 128.27, 128.04, 126.58, 125.99, 125.23, 51.78, 40.66, 40.14, 38.68, 37.05, 22.97, 22.22; IR (CHCl_3) 3020, 2952, 1716, 1519, 1436, 1278 cm^{-1} ; UV (MeOH) λ_{nm} (ϵ) 291.8 (2200), 343.9 (830); MS (CI, methane) m/e 267 (M+1), 187 (100), 155, 81. **2**: ^1H NMR (300 MHz, CDCl_3 , TMS) δ 7.11 (2H, m, aromatic), 6.97 (2H, m, aromatic), 6.33 (1H, d, $J=9.9$ Hz, Ar-CH=C), 5.80 (1H, dddd, $J=10.0$, 4.0, 4.0, 1.8 Hz, CH=C-C-C₂), 5.68 (1H, dd, $J=9.9$, 4.9 Hz, Ar-C=CH), 5.58 (1H, dddd, $J=10.0$, 3.8, 2.0, 2.0 Hz, C=CH-C-C₂), 3.79 (1H, dddd, $J=9.7$, 4.9, 1.5, 1.5 Hz, H-f), 3.72 (3H, s, CO_2CH_3), 3.45 (1H, dd, $J=14.8$, 7.0 Hz, C=C-C-C-H), 3.20 (1H, m, $J=9.7$, 3.8 Hz, H-g), 1.65 (2H, m, methylene), 1.40 (2H, m, methylene); ^{13}C NMR (75 MHz, CDCl_3 , TMS) δ 176.68, 132.69, 130.70, 129.59, 127.70, 127.49, 127.37, 127.13, 127.05, 126.13, 125.74, 52.49, 49.94, 42.54, 42.38, 37.35, 21.88, 21.34; IR (CHCl_3) 3020, 2953, 1721, 1666, 1520, 1490, 1266 cm^{-1} ; UV (MeOH) λ_{nm} (ϵ) 273.4 (3600); MS (CI, methane) m/e 267 (M+1), 207, 187 (100), 81. **3**: mp 135-136 °C (dichloromethane/*n*-hexane); ^1H NMR (500 MHz, CDCl_3 , TMS) δ 7.69 (1H, m, aromatic), 7.10 (3H, m, aromatic), 6.72 (1H, dd, $J=7.8$, 6.2 Hz, H-h), 6.54 (1H, dd, $J=7.8$, 1.4 Hz, O₂C-C-CH=C), 5.68 (1H, m, CH=C-C-C₂), 5.54 (1H, ddd, $J=9.8$, 2.4, 2.4 Hz, C=CH-C-C₂), 3.92 (3H, s, CO_2CH_3), 3.74 (1H, ddd, $J=6.2$, 1.6, 1.6 Hz, H-i), 2.45 (1H, ddd, $J=10.5$, 10.5, 6.0 Hz, H-k), 2.38 (1H, ddd, $J=10.2$, 2.4, 2.4 Hz, H-j), 1.81 (1H, m, methylene), 1.63 (2H, m, methyl-

ene), 0.38 (1H, m, methylene); ^{13}C NMR (75 MHz, CDCl_3 , TMS) δ 173.63, 140.87, 139.86, 136.92, 134.53, 130.30, 129.99, 125.28, 124.98, 124.65, 124.46, 57.19, 52.00, 47.01, 40.87, 38.19, 25.02, 23.56; IR (CHCl_3) 3020, 2953, 1733, 1521, 1436, 1258 cm^{-1} ; UV (MeOH) λ_{nm} (ϵ) 199.8 (37000), 261.8 (220); MS (CI, methane) m/e 267 (M+1), 215, 187 (100), 155, 81.

Low-temperature irradiation of 2-MN and CHD. 2-MN (2.063 g, 11.08 mmol) and CHD (7.00 mL, 73.47 mmol) in 100 mL dichloromethane were irradiated at -78 °C through a Pyrex glass filter for 5 hours. The relative ratio of **5** and **6** in the irradiated mixture was estimated by the ^1H NMR analysis to be 83 : 17. Because of the gradual rearrangement of **5** to **6**, several silica gel and/or alumina chromatographies eluting with *n*-hexane/benzene did not separate the mixture completely. Eventually 2.416 g of **5** (82%) and 8.6 mg of **6** (0.3%) were isolated after repeated column chromatographies. **5**: mp 71-73 °C (dichloromethane/*n*-hexane); ^1H NMR (300 MHz, CDCl_3 , TMS) δ 7.44 (1H, dd, $J=7.5$, 1.4 Hz, CH=C-CO₂), 7.13 (1H, m, aromatic), 7.06 (3H, m, aromatic), 5.99 (2H, m, olefinic), 4.23 (1H, d, $J=11.0$ Hz, Ar-CH-C-CO₂), 3.79 (1H, m, Ar-CH), 3.75 (3H, s, CO_2CH_3), 3.08 (2H, m, Ar-C-CH), 1.36 (4H, m, methylene); ^{13}C NMR (75 MHz, CDCl_3 , TMS) δ 167.34, 146.87, 144.37, 143.41, 139.52, 135.14, 134.01, 128.18, 127.65, 125.27, 125.20, 51.69, 47.08, 46.96, 41.53, 41.49, 25.26, 24.79; IR (CHCl_3) 3019, 2952, 1704, 1633, 1520, 1480, 1282 cm^{-1} ; UV (MeOH) λ_{nm} (ϵ) 269.4 (1000), 277.0 (940); MS (CI, methane) m/e 267 (M+1), 187 (100), 81. **6**: mp 74-76 °C (dichloromethane/*n*-hexane); ^1H NMR (300 MHz, CDCl_3 , TMS) δ 7.13 (2H, m, aromatic), 6.97 (2H, m, aromatic), 6.44 (1H, d, $J=9.9$ Hz, Ar-CH=C), 6.00 (1H, m, $J=10.0$, 6.1 Hz, CH=C-C-C₂), 5.81 (1H, dd, $J=9.9$, 0.6 Hz, Ar-C=CH), 5.69 (1H, m, $J=10.0$, 3.6 Hz, C=CH-C-C₂), 4.31 (1H, d, $J=9.4$ Hz, H-l), 3.72 (3H, s, CO_2CH_3), 3.45 (1H, m, C=C-CH-C₂), 2.71 (1H, m, $J=11.8$ Hz, H-m), 1.83 (2H, m, methylene), 1.55 (1H, m, methylene), 1.30 (1H, m, methylene); ^{13}C NMR (75 MHz, CDCl_3 , TMS) δ 174.93, 132.56, 131.79, 131.08, 129.41, 128.10, 127.79, 127.11, 126.85, 126.34, 124.31, 52.22, 51.33, 45.04, 39.70, 36.83, 22.39, 22.15; IR (CHCl_3) 3020, 2953, 1722, 1521, 1435, 1274 cm^{-1} ; UV (MeOH) λ_{nm} (ϵ) 276.1 (5800); MS (CI, methane) m/e 267 (M+1), 187 (100), 81.

Low-temperature NMR studies of the irradiated mixtures. A CDCl_3 solution (0.5 mL) of 1-MN (23.3 mg, 0.125 mmol) and CHD (0.035 mL, 0.38 mmol) in an NMR tube was deaerated with nitrogen purging for 10 minutes. The mixture in a dry ice/chloroform bath was irradiated through a Pyrex glass filter for 20 minutes. During the irradiation, the temperature of the bath was maintained at -60~-50 °C. A ^1H NMR spectrum was then taken at -50 °C immediately. After leaving the solution at room temperature for 1 hour, another spectrum was taken. In the case of 2-MN (23.6 mg, 0.127 mmol) and CHD (0.035 mL, 0.38 mmol), the solution was irradiated for 20 minutes.

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