Photocycloaddition of Cyanonaphthalenes to 1,3Cyclohexadiene

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Photocycloaddition of Cyanonaphthalenes to 1,3-Cyclohexadiene

Taehee Noh,* Daekyun Kim, and Yong-Jae Kim

*Department of Chemistry Education, Seoul National University, Seoul, 151-742, Korea*

To prevent secondary processes due to facile thermal reaction, low-temperature irradiations of cyanonaphthalenes and 1,3-cyclohexadiene through a Pyrex filter were conducted. Along with the identification of the products, the results of the triplet-sensitized photoreaction of the irradiated mixture, low-temperature ¹H NMR study of the irradiated mixture, and the Cope rearrangement reaction of some products suggested that the primary major products are the corresponding exo-[4 + 4] adducts fused at 1,4 position of the naphthalene skeleton and the syn-[2 + 2] adducts fused at 1,2 position. The formations of the primary products in these singlet-state photocycloaddition reactions were interpreted by primary and secondary orbital interactions. A rationalization for the previous results on the photoreactions at room temperature was also provided.

Introduction

The stereoselectivity in many Diels−Alder reactions has been explained reasonably by the secondary orbital interaction between the HOMO and the LUMO of substrates.[1] Although the consideration of the frontier molecular orbitals does not establish the magnitude of stabilizing interaction, it has been shown to be quite useful and predictable in many circumstances. On the other hand, there have been relatively few examples of the photoreactions that exhibit stereoselectivity due to the secondary orbital interaction between the LUMO's.[2] Moreover, several photocycloaddition reactions exhibit the stereoselectivity which contradicts the prediction based on the LUMO−LUMO interaction between the substrates. These include the ambient-temperature photoreactions of 1-cyanonaphthalene (1-CN) with furan[3] and of 1-CN and 2-cyanonaphthalene (2-CN) with 1,3-cyclohexadiene (CHD).[4] In the latter cases, the explanation provided for this consequence was that the cyano group lowers the energy of the naphthalene orbitals and the interaction between the HOMO of CHD and the LUMO of cyanonaphthalenes becomes significant. On the other hand, the photocycloaddition of 1-CN to furan has been reinvestigated at low temperature in order to prevent secondary processes,[5] in which the stereoselectivity is consistent with the prediction based on the secondary orbital interaction. We have therefore reinvestigated the photocycloaddition reactions of 1-CN and 2-CN with CHD at low temperature.

Scheme 1. Direct Irradiations of Cyanonaphthalenes and CHD
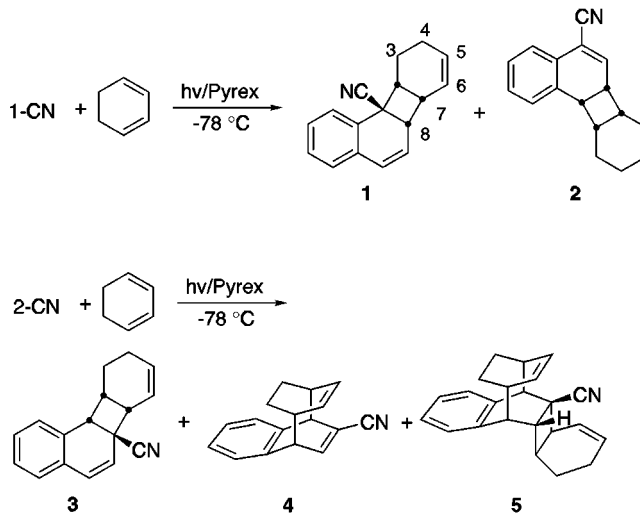
Results and Discussion

A dichloromethane solution of 1-CN and CHD at −78 °C was irradiated through a Pyrex filter for 4 h, and two [2 + 2] adducts (**1** and **2**) were isolated from the reaction mixture in 13% and 58% yields, respectively (Scheme 1). The mass spectrum (CI) of **1** exhibits the molecular ion peak at 234 (M + 1), indicating a 1:1 adduct of 1-CN and CHD. The structural assignment for **1** was made particularly by the analysis of its NMR spectra. Four aromatic protons, four olefinic protons (δ 5.6−6.3), and three cyclobutyl protons (δ 3.2−3.9) in its ¹H NMR spectrum indicated that the cyclohexadiene ring was fused to the 1,2 position of 1-CN. Strong coupling between the peaks at δ 3.62 (H-7) and 5.60 (H-6) in its COSY spectrum (Figure 1) indicated that the double bond in cyclohexene ring was not at the 3,4 position but at the 5,6 position. The strong 1,2 coupling (*J* = 9.4 Hz) between H-7 and H-8 in decoupling experiment, the NOE's with the cyclobutyl protons in its NOESY spectrum, and the singlet mechanism of the photocycloaddition[4] suggested the product to be a syn-[2 + 2] adduct. Similar spectroscopic data analyses of **2** showed that CHD was fused to the 3,4 position of 1-CN.

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(2) (a) Yang, N. C.; Masnovi, J.; Chiang, W.; Wang, T.; Shou, H.; Yang, D.-D. H. *Tetrahedron* **1981,** *37,* 3285. (b) Yang, N. C.; Gan, H.; Kim, S. S.; Masnovi, J. M.; Rafalko, P. W.; Ezell, E. F.; Lenz, G. R. *Tetrahedron Lett.* **1990,** *31,* 3825.
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(4) Albini, A.; Fasani, E.; Giavarini, F. *J. Org. Chem.* **1988,** *53,* 5601.
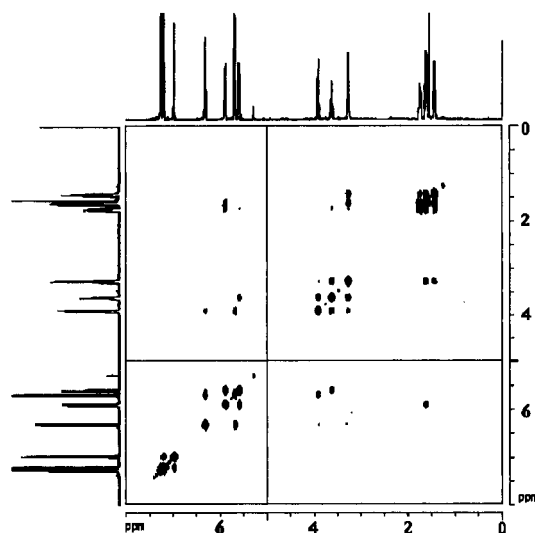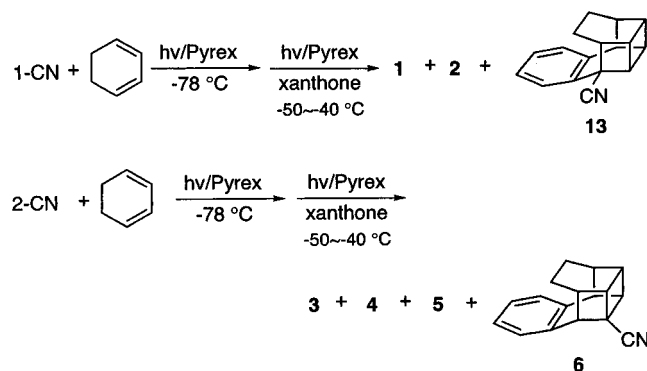(5) Noh, T.; Kim, D. *Tetrahedron Lett.* **1996,** *37,* 9329.

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

Scheme 2. Triplet-Sensitized Reactions of the Irradiated Mixtures of Cyanonaphthalenes and CHD

A dichloromethane solution of 2-CN and CHD at −78 °C was irradiated through a Pyrex filter for 5 h to give a complex mixture, from which three products were partially separated (Scheme 1). Two of these were 1:1 adducts of 2-CN and CHD as revealed by their MS spectra. The other product was a 1:2 adduct of 2-CN and CHD. Its ¹H NMR, COSY, and NOESY spectra allowed the assignment for **5**. Analysis of the spectroscopic data of the 1:1 adducts indicated that the major product was the exo-[4 + 4] adduct (**4**) and the minor product was the syn-[2 + 2] adduct (**3**) fused to the 1,2 position of the naphthalene skeleton. Strong coupling between the peaks at δ 3.69 and 5.68 in the COSY spectrum of **3** allowed the assignment for the position of the double bonds. From the ¹H NMR spectrum of the direct irradiated mixture of 2-CN and CHD, the ratio of **3**, **4**, and **5** was estimated to be 21:68:11. The isolated yield of **3** was 16% on the basis of the consumed 2-CN. The structure of the major product (**4**) was further confirmed by the triplet sensitization of the irradiated mixture of 2-CN and CHD (Scheme 2).[6] These consecutive photoreactions gave the corresponding cage adduct (**6**) in 39% yield as well as **3** (16%), **4** (22%), and **5** (23%). Interestingly, the yield of **5** was increased probably by the triplet-sensitized photocycloaddition. In the triplet sensitization of the purified **4**, the isolated yield of **6** was 79%.

(6) Kimura, M.; Kura, H.; Nukada, K.; Okamoto, H.; Satake, K.; Morosawa, S. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3307.
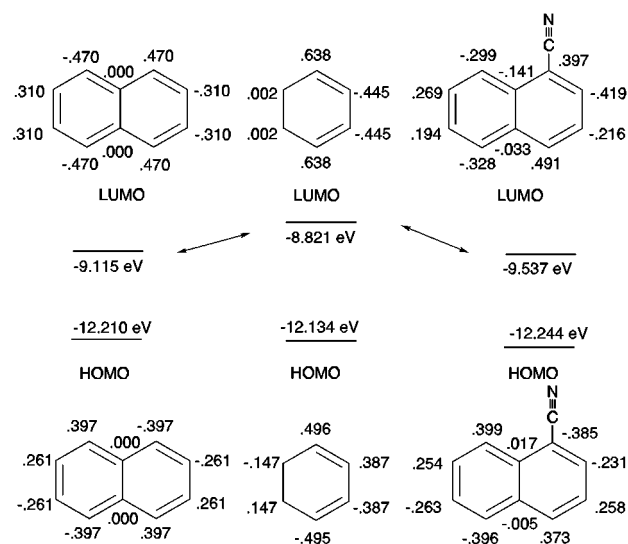

Figure 2. Orbital interactions between naphthalenes and CHD.

The products in the irradiation at −78 °C seem to be different from those at 17 °C. It was reported by Albini and co-workers that the products identified in the room-temperature irradiation of 1-CN and CHD were **7**, **8**, and **9** in 53%, 6%, and 7% yields, respectively.[4] The product distribution was also reported to be the same in the irradiation at 0 °C. However, their structural assignment for the major product (**7**), which was based on the absence of a cage adduct in the irradiation of the adduct in the presence of xanthone, turned out to be wrong, and its correct structure was assigned to be **1** (Figure 1). The products in the case of 2-CN and CHD in cyclohexane at 17 °C were reported to be **10** and **11** in 53% and 12% yields.[4] However, the products of the photoreaction at −78 °C in dichloromethane were found to be similar to those at room temperature in cyclohexane. The correct assignment for their major product was again turned out to be **3**.
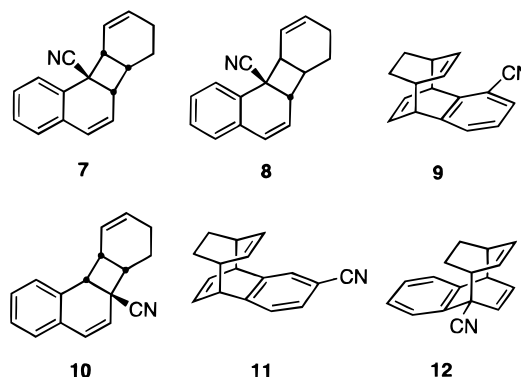
The product distribution in the singlet-state reaction was previously explained by the dominant interaction between the HOMO of CHD and the LUMO of 1-CN due to the lowering of the 1-CN orbitals by the cyano group.[4] However, a simple calculation showed that the lowering of the LUMO of 1-CN was not significant to change the components of the primary interaction (Figure 2).[7] Con-

(7) The energies and the coefficients were calculated by the Extended HMO after geometry optimization.

sidering the primary and secondary orbital interactions between the LUMO's of 1-CN and CHD, the major product is still expected to be the exo-[4 + 4] intermediate (**12**). By considering the primary orbital interaction, the formation of [2 + 2] adduct (e.g., **1**) is expected to be more favorable than the formation of **9**. Since the products in the irradiations of 1-CN and CHD at −78 °C and room temperature are different and the analysis of orbital interaction predicts the more favorable formation of **12** and **1** than **9** and **8**, we suspected that secondary processes occurred in the room-temperature irradiation.

Compounds **1** and **2** can be also formed from the Cope rearrangement of **12**. To explore the existence of **12**, a further irradiation to the photoreaction mixture in the presence of xanthone at −50 to −40 °C was conducted for an additional 4 h (Scheme 2).[6] Similar separatory methods resolved a new product (**13**) in 35% yield, as well as **1** and **2** in 18% and 39% yields. Seven proton peaks at the region of δ 2.9−4.1 in the ^{1}H NMR spectrum and 10 peaks at the region of δ 16−46 in the ^{13}C NMR spectrum are consistent with the structure of the cage adduct (**13**).

Although the formation of **13** supports the existence of **12** at the irradiation conditions and **12** is thought to undergo the facile Cope rearrangement to the [2 + 2] adducts at room temperature, the distribution of the products seems to indicate another route for their formation. In other words, if the adducts **1** and **2** were exclusively formed from the Cope rearrangement of **12**, the distribution of **1** and **2** (18% and 39%) after the sensitized reaction should be similar to those (13% and 58%) in the direct irradiation. Compounds **1** and **2** may also be photodissociated at different rates under the irradiation conditions, and this can be established from the accounts of the electronic absorption spectra of **1** and **2**. Adduct **1** has an absorption maximum at 271 nm and a tail up to 310 nm. Adduct **2** has an absorption maximum at 292 nm and a long tail that reaches beyond 370 nm. Considering the irradiation conditions with the electronic absorptions of **1** and **2**, the rate of photodissociation for **2** would be faster than that for **1**, making the yield of **1** higher.

This was resolved by a low-temperature NMR study for the photoreaction mixture of 1-CN and CHD. The ^{1}H NMR spectrum in CDCl$_3$, taken at −50 °C immediately after irradiation at −70 to −60 °C for 30 min, revealed that a novel product (**12**) was distinguishable with a certain amount of **1** (Figure 3a). Another ^{1}H NMR spectrum was taken at −50 °C after the reaction mixture was left at room temperature for 7 min (Figure 3b). Comparison of the two spectra indicates the total conversion of **12** into **2**. In this NMR study, the ratio of **1** and **12** was estimated to be about 56:44 at 60% conversion, which indicated that **1** was the major product. In another run of 23% conversion, the ratio was 61:39. Upon irradiation, **1** was formed, but was decomposed to the starting compounds under the irradiation conditions (direct and/or sensitized), whereas **2** was formed when it was left at room temperature through the facile Cope rearrangement of **12**. Among the two possible modes of the rearrangement, only the conversion of **12** to **2** was observed. The same mode of the rearrangement was previously observed with the exo-[4 + 4] cyclodimer of 1-CN and furan,[5] which may be explained by the stabilizing effect of the cyano group on the C-1 bond breaking for the rearrangement.
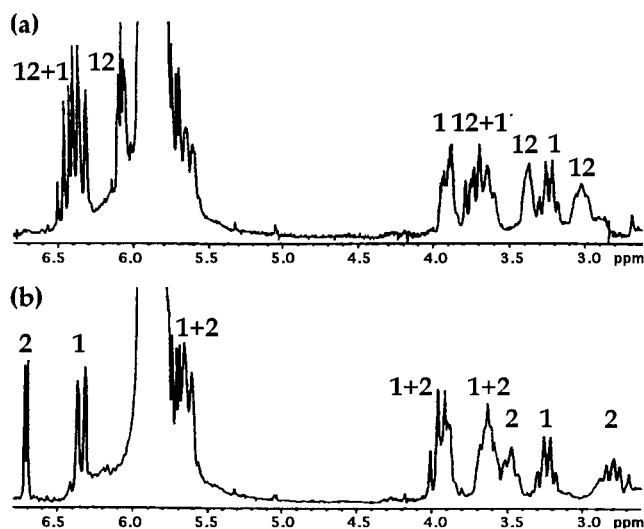

Figure 3. Low-temperature NMR study for the photoreaction of 1-CN and CHD. (a) ^{1}H NMR spectrum at −50 °C for the irradiated solution of 1-CN and CHD at −70 to −60 °C. (b) ^{1}H NMR spectrum at 25 °C for the resulting solution after standing at room temperature.
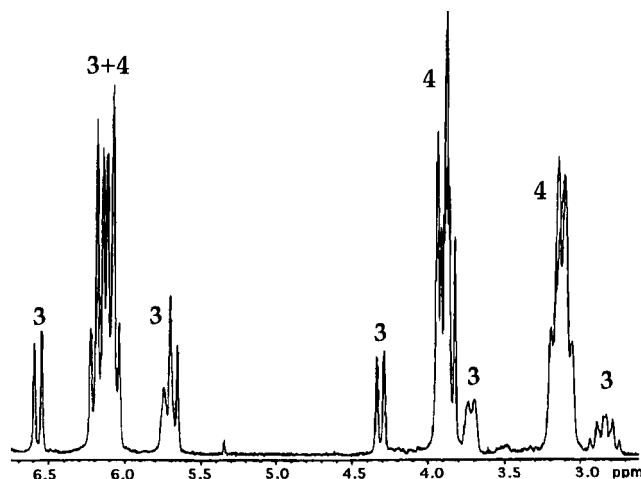
Figure 4. ^{1}H NMR spectrum at −50 °C for the irradiated solution of 2-CN and CHD at −70 to −60 °C.

Scheme 3. Cope Rearrangement of Exo-[4 + 4] Adduct of 2-CN and CHD
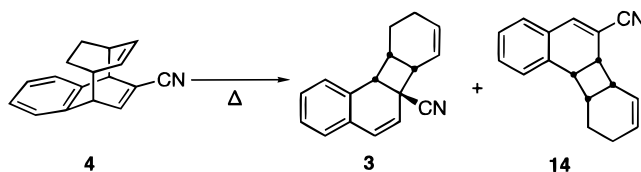
A low-temperature NMR study of the irradiated solution of 2-CN and CHD in CDCl$_3$ also showed the existence of **3** as well as **4** (Figure 4). The ratio of **3** and **4** was estimated to be 1:4 at 30% conversion. The results indicated that **3** was a primary product. The results of heating a solution of **4** also suggested **3** to be a primary product. Upon heating **4** at 100 °C for 30 min, both syn-[2 + 2] adducts (**3** and **14**) were produced in 37% and 50% isolated yields (Scheme 3). If the Cope rearrangement is a secondary process in the photoreaction of 2-CN and CHD, the formation of **14** should have been observed along with **3**. The greater difficulty of the Cope rearrangement of **4** than that of **12** may be explained by the

effect of the cyano group, which had also been observed in the thermolysis of cyclodimers of anthracenes and benzene,[8] and the isomerization of quadricyclane to norbornadiene.[9]

In both photocycloaddition reactions, the primary [4 + 4] adducts (**12** and **4**) are in the exo form. This can be explained by the secondary orbital interaction of the LUMO's of cyanonaphthalenes and the LUMO of CHD (Figure 2). The exo approach of CHD to cyanonaphthalenes makes the secondary orbital interaction more favorable, while the endo approach makes the interaction less favorable. Previous observation of **8**, **9**, and **11** is probably due to the decomposition of the primary products and the accumulation of photostable minor products.

It is interesting to note that [2 + 2] and [4 + 4] photocycloadditions occurred in the irradiations of cyanonaphthalenes and CHD, while [4 + 4] and [4 + 2] photocycloadditions were observed in the case of naphthalene and CHD.[10] For both [2 + 2] adducts, the cyclohexadiene ring was fused to the 1,2 position of cyanonaphthalenes, which is consistent with the larger coefficients at C-1 and C-2 of the LUMO's than those at C-3 and C-4 (Figure 2). Since the coefficients at C-1 and C-4 for the LUMO's of 1-CN and 2-CN are relatively smaller compared to those of naphthalene, less favorable orbital interaction in the [4 + 4] photocycloaddition of cyanonaphthalenes to CHD is expected. However, the [4 + 4] adduct was the major product in the case of 2-CN, while the [2 + 2] adduct was the major product in the case of 1-CN. Radical ion formation does not seem to occur because the ΔG's for electron transfer in the excited states, disregarding the ion separation energy term, are estimated to be -0.42 (1-CN, CHD), -0.20 (2-CN, CHD), and -0.33 (naphthalene, CHD) eV.[11-14] Failure to result in radical ion formation was also reported in the photodimerization of 1-CN and norbornadiene in acetonitrile.[15] Therefore, the different distribution of the [2 + 2] and [4 + 4] adducts may be due to increasing polar character of exciplex intermediacy[4,15] and/or steric repulsion of the cyano group in the exo-[4 + 4] approach of CHD to cyanonaphthalenes.

LUMO
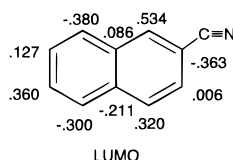
Experimental Section

Materials and General Procedures. Most reagents and solvents were purified by the procedures in the literature.[16] Melting points are uncorrected. ^{1}H (300 MHz) NMR and [13]C

(75 MHz) NMR spectra were recorded in CDCl$_3$ with TMS as internal standard unless otherwise noted. IR spectra were recorded in CHCl$_3$. All the preparative irradiations were performed with a 450-W Hanovia medium-pressure mercury lamp irradiating through a Pyrex filter. Triple-walled quartz immersion well with the outer two walls permanently sealed together and dry ice/solvent baths were used in low-temperature irradiations. The reaction solutions were purged with nitrogen for more than 20 min before irradiation and during irradiation. The reactions were followed with either TLC or ^{1}H NMR spectrum analysis.

Low-Temperature Irradiation of 1-CN with CHD. A solution of 1-CN (1.54 g, 1.00×10^{-2} mol) and CHD (3.75 g, 4.68×10^{-2} mol) in dichloromethane (150 mL) was irradiated at -78 °C for 4 h to produce a complex mixture, which was separated by consecutive silica gel chromatographies eluting with *n*-hexane/dichoromethane. In addition to the unreacted 1-CN (19.1 mg, 13% based on the consumed 1-CN) of **1** and 1.35 g of **2** (58% based on the consumed 1-CN) were isolated. **1**: mp 103–105 °C (dichloromethane/*n*-hexane); ^{1}H NMR (200 MHz) δ 7.24 (3H, m, aromatic), 7.01 (1H, m, aromatic), 6.32 (1H, dd, $J = 10.0$, 1.7 Hz, Ar–CH=C), 5.90 (1H, m, C–CH=C), 5.69 (1H, dd, $J = 10.0$, 4.4 Hz, Ar–C=CH), 5.60 (1H, m, C=CH–C–C$_2$), 3.91 (1H, m, C=C–CH–C–CN), 3.62 (1H, m, CH–C–C–CN), 3.27 (1H, m, CH–C–CN), 1.84–1.26 (4H, m, methylene); ^{13}C NMR δ 132.32, 130.18, 128.68, 128.32, 127.74, 127.70, 127.41, 127.19, 125.97, 125.19, 124.44, 46.88, 43.79, 38.22, 37.69, 22.03, 21.31; IR 3050, 2920, 2205, 1440 cm^{-1}; UV (cyclohexane) λ_{nm} (ϵ) 271.4 (10300); MS (CI$^+$) *m/z* 234 (M + 1), 207, 165, 154 (100), 141, 80; HRMS calcd for C$_{17}$H$_{16}$N (MH$^+$) *m/z* 234.1283, found 234.1283. **2**: ^{1}H NMR δ 7.18 (4H, m), 6.64 (1H, d, $J = 4.3$ Hz), 5.95 (1H, m), 5.63 (1H, m), 3.96 (1H, t, $J = 9.8$ Hz), 3.66 (1H, m), 3.48 (1H, m), 2.86 (1H, m), 1.78–1.32 (4H, m); ^{13}C NMR δ 145.65, 132.06, 130.88, 129.47, 128.22, 127.93, 127.15, 125.28, 124.64, 117.42, 113.78, 40.60, 40.56, 39.15, 36.28, 22.69, 21.97; IR 3060, 3025, 2220, 1495 cm^{-1}; UV (acetonitrile) λ_{nm} (ϵ) 291.6 (2930); MS (CI$^+$) *m/z* 234 (M + 1), 182, 168, 154 (100), 80; HRMS calcd for C$_{17}$H$_{16}$N (MH$^+$) *m/z* 234.1283, found 234.1284.

Low-Temperature Irradiation of 2-CN with CHD. A solution of 2-CN (1.77 g, 1.16×10^{-2} mol) and CHD (4.56 g, 5.69×10^{-2} mol) in dichloromethane (150 mL) was irradiated at -78 °C for 5 h. During the irradiation, all of 2-CN had been consumed and the reaction mixture consisted of **3**, **4**, and **5** in the ratio of 21:68:11 by the ^{1}H NMR analysis. Chromatographies in several solvent conditions did not resolve the mixture completely, and some of the products were purified by chromatographies and recrystallization for the purpose of full characterization. The isolated yield of **3** was 16% (440.3 mg) on the basis of consumed 2-CN. **3**: mp 122–123 °C (dichloromethane/*n*-hexane); ^{1}H NMR δ 7.19 (2H, m, aromatic), 7.03 (1H, m, aromatic), 6.95 (1H, m, aromatic), 6.50 (1H, d, $J = 9.8$ Hz, Ar–CH=C), 6.04 (1H, m, C–CH=C), 5.68 (1H, m, C=CH–C$_2$), 5.62 (1H, d, $J = 9.8$ Hz, Ar–C=CH), 4.26 (1H, d, $J = 9.4$ Hz, Ar–CH–C$_2$), 3.69 (1H, m, CH–C–CN), 2.85 (1H, m, Ar–C–CH), 1.84 (2H, m, methylene), 1.50 (1H, m, methylene), 1.32 (1H, m, methylene); ^{13}C NMR δ 132.49, 131.42, 130.90, 129.84, 128.91, 127.69, 127.59, 127.57, 122.24, 122.12, 45.41, 41.97, 38.04, 37.23, 21.93, 21.74; IR 3015, 2840, 2215, 1640, 1490 cm^{-1}; UV (cyclohexane) λ_{nm} (ϵ) 270.2 (7160); MS (CI$^+$) *m/z* 234 (M + 1), 207, 182, 154 (100), 81. Anal. Calcd for C$_{17}$H$_{15}$N: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.31; H, 6.50; N, 5.66. **4**: mp 95.5–96 °C (dichloromethane/*n*-hexane); ^{1}H NMR δ 7.23 (1H, m, CH=C–CN), 7.10 (4H, m, aromatic), 6.17 (1H, m, olefinic), 6.06 (1H, m, olefinic), 3.83 (2H, m, Ar–

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(11) The free energy changes for electron transfer in the excited state were estimated while disregarding the ion separation energy term: $\Delta G_{ET} = E_{ox}$(diene) $- E_{red}$(aromatic) $- E_{exc}$(aromatic).

(12) E_{ox}(CHD) = 1.35 V in CH$_3$CN (vs SCE). Lewis, F. D. In *Photoinduced electron transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part C.

(13) E_{red}(1-CN) = -1.98 V, E_{red}(2-CN) = -2.13 V, and E_{red}(naphthalene) = -2.29 V in CH$_3$CN (vs SCE). Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker: Inc.: New York, 1983; Vol. 6, Chapter 4. Gilbert, A., Baggot, J. *Essentials of Molecular Photochemistry*; CRC Press: Boca Raton, 1991.

(14) E_{exc}(1-CN) = 3.75 eV, E_{exc}(2-CN) = 3.68 eV, and E_{exc}(naphthalene) = 3.97 eV in CH$_3$CN.[13]

(15) Weng, H.; Roth, H. D. *Tetrahedron Lett.* **1996**, *37*, 4895.

(16) Perrin, D. D., Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.

CH), 3.09 (2H, m, Ar–C–CH), 1.35 (4H, m, methylene); ^{13}C NMR δ 152.47, 142.26, 141.87, 134.83, 134.48, 127.96, 127.87, 125.88, 125.64, 120.18, 119.41, 50.22, 47.43, 41.73, 41.39, 24.79, 24.56; IR 3020, 2875, 2205, 1485 cm^{-1}; UV (cyclohexane) λ_{nm} (ϵ) 276.8 (430), 254.8 (860); MS (CI$^+$) m/z 234 (M + 1), 207, 182, 154 (100), 81. Anal. Calcd for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.58; H, 6.52; N, 5.64. **5**: mp 177–178 °C (dichloromethane/*n*-hexane); ^{1}H NMR δ 7.22 (2H, m, aromatic), 7.10 (2H, m, aromatic), 6.63 (1H, t, J = 8.4 Hz, olefinic), 6.36 (1H, t, J = 8.5 Hz, olefinic), 6.10 (1H, m, olefinic), 5.64 (1H, m, olefinic), 3.46 (1H, d, J = 10.9 Hz, Ar–CH–C–CN), 3.19 (1H, dd, J = 11.2, 2.5 Hz, Ar–CH–C$_2$), 3.05 (1H, td, J = 9.2, 3.0 Hz, bridgehead), 2.96 (1H, m, cyclobutyl), 2.91 (1H, td, J = 9.2, 3.0 Hz, bridgehead), 2.04 (2H, m, cyclobutyl and methylene), 1.77 (1H, m, cyclobutyl), 1.58 (3H, m, cyclobutyl and methylene), 1.28 (4H, m, methylene); ^{13}C NMR δ 141.45, 140.80, 137.91, 135.49, 131.84, 130.28, 126.93, 126.54, 125.76, 124.57, 53.14, 49.12, 46.94, 43.56, 37.88, 36.12, 35.98, 34.73, 26.64, 24.83, 24.64, 21.85; IR 3025, 2940, 2875, 2850, 2225 cm^{-1}; UV (cyclohexane) λ_{nm} (ϵ) 275.4 (290), 267.2 (310); MS (CI$^+$) m/z 314 (M + 1, 100), 234, 154, 80; HRMS calcd for $C_{23}H_{24}N$ (MH$^+$) m/z 314.1909, found 314.1915.

Irradiation of the Irradiated Mixture of 2-CN and CHD in the Presence of Xanthone. After a dichloromethane (150 mL) solution of 2-CN (1.53 g, 9.98 × 10^{-3} mol) and CHD (3.52 g, 4.39 × 10^{-2} mol) was irradiated at −78 °C for 4 h, xanthone (313 mg) was added. The resulting solution was irradiated at −50 to −40 °C for 4 h. As estimated by ^{1}H NMR, the relative yields of **3**, **4**, **5**, and **6** based on the consumed 2-CN were 16%, 22%, 23%, and 39%, respectively. The reaction mixture was separated by a silica gel chromatography eluting with cyclohexane/benzene for the purpose of analysis. **6**: mp 159.5–160.5 °C (dichloromethane/cyclohexane); ^{1}H NMR δ 7.25 (2H, m), 7.15 (2H, m), 4.18 (1H, d, J = 11.8 Hz), 4.08 (1H, dd, J = 11.8, 8.3 Hz), 3.47 (2H, m), 3.33 (2H, m), 3.11 (1H, dd, J = 14.9, 8.1 Hz), 1.29 (2H, m), 1.13 (2H, m); ^{13}C NMR δ 137.48, 135.39, 129.46, 129.44, 127.44, 126.95, 122.60, 44.33, 41.05, 37.80, 37.48, 37.33, 36.05, 30.64, 30.60, 16.35, 16.25; IR 3010, 2890, 2220, 1455 cm^{-1}; UV (cyclohexane) λ_{nm} (ϵ) 273.8 (190), 265.0 (260); MS (CI$^+$) m/z 234 (M + 1), 207, 154, 80 (100); HRMS calcd for $C_{17}H_{16}N$ (MH$^+$) m/z 234.1283, found 234.1283.

Preparation of Cage Adduct of 2-CN and CHD. A dichloromethane solution (5 mL) of **4** (100 mg) and xanthone (30 mg) was irradiated for 2 h and separated by silica gel Chromatotron, eluting with cyclohexane/benzene to afford 78.7 mg of **6** (79%) and 15 mg of 2-CN.

Irradiation of the Irradiated Mixture of 1-CN and CHD in the Presence of Xanthone. To the photoreaction mixture of 1-CN (1.53 g, 9.99 × 10^{-3} mol) and CHD (3.87 g, 4.83 × 10^{-2} mol) was added xanthone (313 mg), and the resulting solution was irradiated at −50 to −40 °C for 4 h. The reaction mixture was separated by a silica gel chromatography, eluting with *n*-hexane/dichloromethane. Compound **13** was isolated in 35% yield (565 mg) on the basis of consumed 1-CN. **13**: mp 71–72 °C; ^{1}H NMR δ 7.63 (4H, m), 4.03 (1H, dd, J = 11.9, 8.3 Hz), 3.76 (1H, t, J = 8.4 Hz), 3.41 (1H, dd, J = 14.5, 7.0 Hz), 3.34 (1H, m), 3.23–3.09 (2H, m), 2.99 (1H, dd, J = 14.6, 7.7 Hz), 1.46–1.06 (4H, m); ^{13}C NMR δ 137.21, 132.11, 129.78, 127.94, 127.38, 127.10, 125.08, 45.94, 41.34, 40.07, 39.25, 37.64, 32.75, 31.92, 30.36, 16.66, 16.37; IR 3010, 2890, 2225, 1455, 1224 cm^{-1}; UV (acetonitrile) λ_{nm} (ϵ) 338.0 (170), 292.6 (370), 274.0 (490); MS (CI$^+$) m/z 234 (M + 1), 182, 154 (100), 80; HRMS calcd for $C_{17}H_{16}N$ (MH$^+$) m/z 234.1283, found 234.1276.

Cope Rearrangement of Exo-[4 + 4] Adduct of 2-CN and CHD. A solution of 195 mg (8.4 × 10^{-4} mol) of **4** in 2 mL of toluene was stirred at 100 °C for 30 min. The reaction mixture was separated by silica gel Chromatotron, eluting with cyclohexane to give 5.7 mg of unreacted **4**, 17.1 mg of 2-CN, 95 mg (50%) of **3**, and 70.3 mg (37%) of **14**. **14**: mp 120–122 °C (dichloromethane/*n*-hexane); ^{1}H NMR δ 7.23 (1H, m), 7.15 (1H, m), 7.00 (3H, m), 6.00 (1H, m), 5.86 (1H, m), 4.05 (1H, t, J = 9.9 Hz), 3.67 (1H, tt, J = 9.9, 1.5 Hz), 3.47 (1H, m, J = 8.9, 1.9 Hz), 2.95 (1H, m), 1.79–1.29 (4H, m); ^{13}C NMR δ 141.59, 133.56, 131.02, 130.71, 130.62, 128.86, 128.20, 127.01, 124.70, 120.09, 111.34, 40.74, 39.88, 39.16, 36.64, 22.54, 21.92; IR 3020, 2925, 2200, 1212, 1205 cm^{-1}; UV (cyclohexane) λ_{nm} (ϵ) 299.8 (960), 289.8 (920); MS (CI$^+$) m/z 234 (M + 1), 182, 154 (100), 80; HRMS calcd for $C_{17}H_{16}N$ (MH$^+$) m/z 234.1283, found 234.1276.

Supporting Information Available: ^{1}H NMR spectra of **1**, **2**, **3**, **4**, and **5**, NOESY spectrum of **1**, COSY spectrum of **3**, and COSY and NOESY spectra of **5** (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.