Photocycloaddition of Cyclo-1,3-dienes to 9-Cyanophenanthrene

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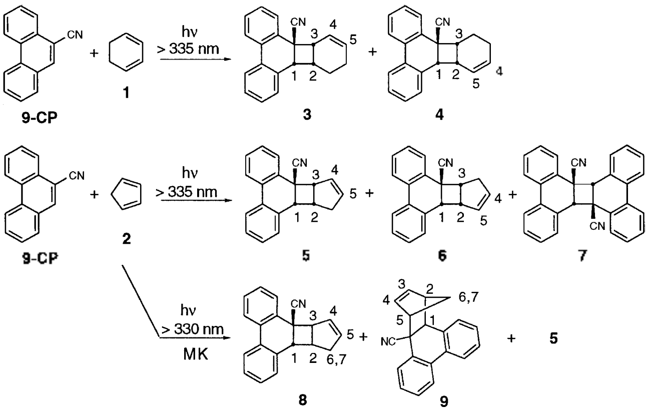
There has been considerable interest in the photoadditions of olefins to arenes.[1] With cyclo-1,3-dienes, this reaction provides a synthetic route to energy-rich arenes cyclodimers, which could be potential systems for adiabatic photodissociation and chemiluminescence.[2] Therefore, synthetic and mechanistic studies on the photocycloadditions of 1,3-dienes to naphthalenes and anthracenes have been extensively carried out,[1a,3] and applied to the syntheses of arenes cyclodimers.[2] On the other hand, limited studies have been reported on the photocycloaddition of 1,3-dienes to phenanthrenes, although there have been many reports on the photoadditions of olefins to 9-cyanophenanthrene (9-CP).[4] Irradiation of 9-CP and 2,5-dimethyl-2,4-hexadiene quantitatively gave a single [2+2] adduct through the singlet state of 9-CP,[5] but the stereochemistry of the adduct was not studied. Irradiation of 9-CP and furan was reported to induce the photodimerization of 9-CP exclusively. However, recent reinvestigation in our laboratory found that the cycloaddition of furan to 9-CP occurred through the triplet state of 9-CP to form the *anti*-[2+2] adduct of 9-CP and furan.[6] In this paper, we report the results of photochemical cycloadditions of cyclohexa-1,3-diene (**1**) and cyclopentadiene (**2**) to 9-CP, and discuss the mechanism and the regiochemistry and stereochemistry of the products.

Results and Discussion

Since the reaction mixtures from irradiation of 9-CP and **1** (or **2**) were not separated completely by column chromatography and recrystallization, the products were isolated by preparative HPLC for the purpose of characterization. In the irradiation of a dichloromethane solution of 9-CP (2.5×10^{-2} M) and **1** (0.75 M) through an aqueous filter solution (> 335 nm) of sodium bromide and lead acetate[7] for 5 min, the yields of the *syn*-[2+2] adducts (**3** and **4**) based on consumed 9-CP were estimated by HPLC to be 23 and 68% in 15% conversion (Scheme 1). In contrast to the irradiation of 9-CP in the presence of furan,[6] no significant formation of the head-to-tail *syn*-[2+2] cyclodimer (**7**)[8] of 9-CP (less than 1% by HPLC) was observed even in prolonged irradiation. In the irradiation of 9-CP (2.5×10^{-2} M) and **2** (0.75 M) through the same filter solution for 5 h in an ice-water bath to minimize thermal dimerization of **2**, the yields of **5**, **6**, and **7** on the basis of consumed 9-CP were estimated to be 24, 7, and 54% in 14% conversion.

The regiochemistry of the adducts was assigned with their COSY spectra. For example, the connectivity of **5** was assigned by strong interactions of the peak at 3.68 ppm (H_2) with the peaks at both 4.47 and 4.17 ppm (H_1 and H_3) in its COSY spectrum. The large values of J_{12} (9.3 Hz for **3**, 9.7 Hz for **4**, 10.1 Hz for **5**, and 8.7 Hz for **6**) and downfield shifted peaks of cyclobutyl protons, compared with those of *anti*-[2+2] cyclodimer of 9-CP and benzene,[6] in their ^{1}H NMR spectra might suggest the syn orientation. This was confirmed by strong proximity effects between olefinic/aliphatic protons and aromatic protons in their NOESY spectra.



Scheme 1. Photocycloaddition of cyclo-1,3-dienes to 9-CP.

In order to study the multiplicity of excited 9-CP, relative rate studies for the photocycloadditions of **1** to 9-CP were conducted (Table 1). The photocycloaddition of **1** to 9-CP was not quenched by isoprene. The irradiation of a solution of 1.0×10^{-4} M Michler's ketone (MK, E_s = 70 kcal/mol, E_t = 65 kcal/mol)[9], 9-CP (E_s = 79 kcal/mol, E_t = 59 kcal/mol)[1b], and **1** (E_t = 52 kcal/mol)[9] reduced the formation of **3** and **4** to about 40%. The ^{1}H NMR spectrum of the mixture indicated no existence of other adducts. Considering that MK absorbs some 60% of the light in this condition,[10] the relative rates imply that both **3** and **4** are formed from the singlet state. Complete quenching in pyridine suggests that the reaction proceeds *via* a singlet exciplex.[11]

Table 1. Effect of sensitizer and quencher on the photocycloaddition of **1** to 9-CP[a,b]

entry	additive (M)	**3**[c]	**4**[c]	conversion
1		1.0	3.0	15
2	MK (1×10^{-4})	0.4	1.2	6
3	isoprene (6.0)	1.0	3.0	17
4	pyridine (solvent)	0.0	0.0	0

[a] Numbers reported are the average of at least two measurements (error limit, ±5%). [b] Irradiated (> 335 nm) in dichloromethane for 5 min, conc of 9-CP = 2.5×10^{-2} M, conc of **1** = 0.75 M. [c] Relative yields compared to **3** of entry 1.

On the other hand, the sensitized irradiation of 9-CP (2.5×10^{-2} M) and **2** (0.75 M, E_t – 58 kcal/mol)[9] in the presence of MK (1.0×10^{-4} M) through the filter solution afforded two more adducts (**8** and **9**). However, these were not separated completely from **5** and **6** by HPLC (Scheme 1). The adducts were partly separated by preparative HPLC, and the structures were determined by spectroscopic data analyses. The stereochemistry of **8** was assigned to be anti by considering the upfield shift of cyclobutyl protons (3.67, 3.59, and 2.95 ppm) and the downfield shift of olefinic protons (6.25 and 6.14 ppm) in comparison with those of **5**. The stereochemistry of **9** was also assigned by considering the downfield shift of olefinic protons (6.67 and 6.56 ppm) in comparison with those of *endo*-form (around 5.3 ppm).[12]

Since all the adducts in the irradiation of 9-CP and **2** in the presence of MK under the conditions were not separated completely, relative rate studies were not feasible. Therefore, two experiments (longer wavelength and excess sensitizer) to make the sensitized reaction exclusively were conducted. The photoexcitation of MK (2.5×10^{-2} M) in the presence of 9-CP (3.1×10^{-2} M) and **2** (0.94 M) through an aqueous filter solution (395 nm < λ < 490 nm) of sodium nitrite and copper(II) sulfate in aqueous ammonia[13] produced **8** and **9** with less than 5% of **5** (estimated by ^{1}H NMR). The irradiation of a dichloromethane solution of 9-CP (4.1×10^{-2} M), **2** (2.6 M), and excess MK (9.6×10^{-3} M) through a Uranium filter for 9 h gave a mixture that did not have **7**, which indicated that MK had completely absorbed the light during irradiation. The ratio of **8**, **9**, and **5** in the mixture was estimated by ^{1}H NMR to be 8.8 : 10.6 : 1 in 7.6% conversion. These indicated that **5** and **6** produced in the direct irradiation were formed through the singlet state of 9-CP.

The mechanism of the photocycloaddition was found to be related to the ionization potential (IP) of dienes (Table 2). With **1** of low IP (8.30 eV), the photocycloaddition proceeds exclusively via a singlet exciplex. In the case of **2** (IP – 8.55 eV), singlet state is also involved in the formation of **5** and **6**. On the other hand, the reaction with furan of high IP occurs from triplet state due to unfavorable exciplex formation (ΔG – 0.32 eV).[6]

The stereospecificity and regioselectivity observed in the cycloaddition of 9-CP and **1** are consistent with singlet exciplex mechanism. The photocycloaddition of **1** is stereospecific as observed in the olefins of low IP.[4] The regioselectivity is also consistent with that in the photocycloaddition of 2,5-dimethyl-2,4-hexadiene.[5] However, the singlet photocycloadditions of **1** and **2** to 9-CP appear to be less regioselective than those of olefins and 2,5-dimethyl-2,4-hexadiene. It is also noteworthy that the regioselectivity observed in the singlet photocycloaddition of **1** and **2** is different. This may be related to the different magnitude of secondary orbital interaction. More favorable formation of **4** over **3** may be explained by the favorable orbital interaction between the butadiene units of the LUMO's of 9-CP (9,10,11,12 positions) and **1** (1,2,3,4 positions) approaching to form **4** (Figure 1). Since the secondary orbital overlap between 5-membered ring (**2**) and 6-membered ring (9-CP) is not expected to be strong due to their rigid structures, the favorable formation of **5** over **6** may be related to the primary orbital interaction between the ethylene units of the LUMO's of 9-CP (9,10 positions) and **2** (2,1 positions). This interpretation is consistent with the result that the singlet state photodimerization of 9-CP is the major pathway in the irradiation of 9-CP and **2**.

Table 2. Free energy changes for exciplex formation

Dienes	IP (eV)	E_{ox}(diene) (eV)[a]	DG (eV)[b,c]
1	8.30[9]	1.12	-0.42
2	8.55[9]	1.53	-0.09
furan	8.88[14]	1.86	−0.32

[a] E_{ox}(diene) was calculated with IP by E_{ox}(diene) = 0.89(IP) – 6.04.[15] [b] Free energy changes were estimated while disregarding ion separation energy term: ΔG – E_{ox}(diene) – E_{red}(9-CP) – $E_{0,0}$(9-CP).[16] [c] E_{red}(9-CP) – -1.88 eV, $E_{0,0}$(9-CP) = 3.42 eV.[17]

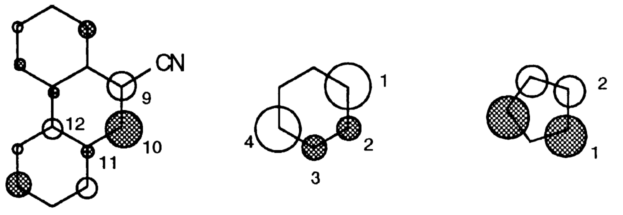


Figure 1. LUMO's of 9-CP, **1**, and **2**. Coefficients were calculated by the extended HMO after geometry optimization.

Experimental Section

Irradiation of 9-CP and 1. A dichloromethane solution (120 mL) of 9-CP (1.05 g, 5.2 mmol) and **1** (15 mL, 160 mmol) was irradiated with a 450-watt Hanovia medium-pressure mercury lamp through a Uranium filter for 5 h under a nitrogen atmosphere. Evaporation of the solvent followed by silica gel chromatography with *n*-hexane and dichloromethane provided the fractions containing **3** and **4**. Adduct **3** was isolated by HPLC with an Econosil C_{18} column using water and methanol as eluting solvents, and **4** with a Nova-Pak silica column using *n*-hexane and dichloromethane. **3**: mp 147-149 °C (from dichloromethane and *n*-hexane); ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ 7.92-7.88 (2H, m, ArH), 7.36-7.25 (4H, m, ArH), 7.21 (1H, m, ArH), 7.09 (1H, dd, J – 7.4, 0.7 Hz, ArH), 5.77 (1H, m, H_5), 5.63 (1H, m, H_4), 4.40 (1H, d, J – 9.3 Hz, H_1), 3.84 (1H, m, H_3), 2.99 (1H, m, H_2), 1.70-1.53 (2H, m, C–C-CH_2), 1.31-1.12 (2H, m, C–C-C-CH_2); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si) δ 133.16, 132.71, 132.17, 131.31, 131.12, 129.79, 129.16, 128.72, 128.40, 128.23, 124.47, 123.82, 123.59, 123.55, 45.75, 43.24, 39.59, 38.34, 22.07, 21.69; IR ($CHCl_3$) 3019, 2929, 2229 (CN), 1522, 1450, 724 cm^{-1}; UV (acetonitrile) λ_{nm} (ε) 308.2 (1460), 274.3 (14000), 242.1 (11100), 234.0 (15400); MS (CI^+) m/e 284 (MH^+, 11%), 257 (11), 232 (15), 205 (16), 204 (100), 203 (10), 81 (33), 80 (23); HRMS calcd for $C_{21}H_{18}N$ (MH^+) *m/z* 284.1440, found 284.1436. **4**: mp 138.5-140.5 °C (from dichloromethane and *n*-hexane); ^{1}H NMR (500 MHz; $CDCl_3$; Me_4Si) δ 7.89-7.84 (2H, m, ArH), 7.44 (1H, dd, J = 7.6, 1.4 Hz, ArH), 7.37-7.34 (1H, m, ArH), 7.30-7.23 (3H, m, ArH), 7.04 (1H, m, ArH), 5.47 (1H, m, J = 10.4 Hz, H_4), 5.18 (1H, m, J = 10.4, 2.0 Hz, H_5), 4.47 (1H, d, J = 9.7 Hz, H_1), 3.61 (1H, m, H_3), 3.44 (1H, m, H_2), 1.72 (1H, m, C=C-C-CH$_2$), 1.61 (1H, m, C=C-CH$_2$), 1.53 (1H, m, C=C-C-CH$_2$), 0.87 (1H, m, C=C-CH$_2$); ^{13}C NMR (75 MHz; CDCl$_3$; Me$_4$Si) δ 133.13, 131.83, 131.57, 130.14, 130.05, 129.33, 129.19, 128.90, 128.55, 128.27, 128.01, 125.08, 124.84, 123.60, 45.74, 44.13, 37.77, 37.42, 20.96, 20.80; IR (CHCl$_3$) 3019, 2931, 2231 (CN), 1520, 1450, 1431, 746 cm^{-1}; UV (acetonitrile) λ_{nm} (ε) 309.0 (1500), 277.1 (11800), 242.4 (10600), 234.6 (14100); MS (CI$^+$) m/e 284 (MH$^+$, 25%), 258 (22), 257 (100), 204 (31), 203 (11), 81 (17), 80 (15); HRMS calcd for $C_{21}H_{18}N$ (MH$^+$) m/z 284.1440, found 284.1436.

Irradiation of 9-CP and 2. A dichloromethane solution (120 mL) of 9-CP (1.03 g, 5.1 mmol) and **2** (26 mL, 320 mmol) in an ice-water bath was irradiated through a Uranium filter for 5 h. After some residues were evaporated off under 0.1 mmHg, the mixture was separated by silica gel chromatography eluting with *n*-hexane and dichloromethane to afford unreacted 9-CP, **7**, and a mixture of **5** and **6**. The adducts, **5** and **6**, were partially separated by HPLC with a Nova-Pak silica column using *n*-hexane and ethyl acetate. **5**: ^{1}H NMR (500 MHz; CDCl$_3$; Me$_4$Si) δ 7.88-7.84 (2H, m, ArH), 7.31-7.20 (5H, m, ArH), 6.88 (1H, m, ArH), 5.47 (1H, ddd, J = 5.7, 3.7, 2.1 Hz, H_5), 5.07 (1H, m, H_4), 4.47 (1H, d, J = 10.1 Hz, H_1), 4.17 (1H, m, H_3), 3.68 (1H, m, H_2), 2.28 (1H, dddd, J = 17.7, 8.9, 4.0, 2.1 Hz, C=C-CH$_2$), 2.06 (1H, dddd, J = 17.7, 5.5, 2.3, 2.2 Hz, C=C-CH$_2$); ^{13}C NMR (75 MHz; CDCl$_3$; Me$_4$Si) δ 135.76, 131.71, 131.15, 130.81, 129.22, 128.99, 128.54, 128.41, 128.39, 127.79, 127.38, 124.79, 123.01, 122.94, 59.42, 42.32, 40.50, 39.42, 33.94; IR (CHCl$_3$) 3010, 2960, 2925, 2220 (CN), 1485, 1450, 1440, 1230 cm^{-1}; UV (acetonitrile) λ_{nm} (ε) 310.2 (2020), 277.0 (12900), 243.4 (11900), 235.2 (16100); MS (CI$^+$) m/e 270 (MH$^+$, 10%), 232 (35), 205 (24), 204 (100), 203 (60), 67 (13); HRMS calcd for $C_{20}H_{16}N$ (MH$^+$) m/z 270.1284, found 270.1282. **6**: mp 152-154 °C (from dichloromethane and *n*-hexane); ^{1}H NMR (500 MHz; CDCl$_3$; Me$_4$Si) δ 7.88 (1H, dd, J = 7.8, 1.4 Hz, ArH), 7.84 (1H, dd, J = 7.2, 1.9 Hz, ArH), 7.34-7.20 (5H, m, ArH), 7.05 (1H, m, J = 6.9, 1.9 Hz, ArH), 5.28 (1H, m, H_4), 5.13 (1H, m, J = 7.9, 2.2 Hz, H_5), 4.54 (1H, d, J = 8.7 Hz, H_1), 3.90-3.83 (2H, m, H_2, H_3), 2.46 (1H, dddd, J = 17.9, 7.8, 4.5, 2.3 Hz, C=C-CH$_2$), 2.27 (1H, m, J = 17.9 Hz, C=C-CH$_2$); ^{13}C NMR (75 MHz; CDCl$_3$; Me$_4$Si) δ 132.92, 131.12, 130.76, 130.49, 130.08, 128.60, 128.55, 128.16, 128.00, 127.54, 127.50, 124.64, 123.12, 122.96, 51.83, 49.75, 44.69, 37.31, 34.39; IR (CHCl$_3$) 3005, 2925, 2210 (CN), 1485, 1445, 1435, 705 cm^{-1}; UV (acetonitrile) λ_{nm} (ε) 309.6 (2070), 276.8 (12500), 243.8 (13900), 236.2 (16800); MS (CI$^+$) m/e 270 (MH$^+$, 56%), 244 (25), 243 (100), 204 (38), 203 (85), 67 (13); HRMS calcd for $C_{20}H_{16}N$ (MH$^+$) m/z 270.1284, found 270.1289.

Product distribution and mechanistic study. Several reaction solutions (4 mL each) in Pyrex test tubes were purged with nitrogen for 20 min. The samples in a merry-go-round apparatus were irradiated through an aqueous solution of sodium bromide (0.54 g/mL) and lead acetate (7.0 × 10^{-3} g/mL).[7] In irradiation of 9-CP and **2**, an ice-water bath was used. Irradiation time was controlled to keep the conversion low and all the adducts detectable at a Waters 600 HPLC. After the irradiation of 9-CP and **1**, the solvent was removed under reduced pressure. The resulting mixtures were dissolved in acetonitrile, and subjected to HPLC analyses with a Nova-Pak C_{18} column (3.9 × 150 mm) using water and methanol. In the case of **2**, the reaction mixture was analyzed with a Nova-Pak silica column (3.9 × 150 mm) using *n*-hexane and ethyl acetate. The chromatogram was integrated relative to an internal standard of 9-acetyl phenanthrene.

Irradiation of MK in the presence of 9-CP and 2. A dichloromethane solution (120 mL) of 9-CP (0.986 g, 4.9 mmol), **2** (26 mL, 320 mmol), and MK (0.309 g, 1.2 mmol) in an ice-water bath was irradiated through a Uranium filter for 10 h. Similar work-up followed by silica gel chromatography eluting with *n*-hexane and dichloromethane afforded unreacted 9-CP, **9**, and some fractions containing mixtures of **5**, **8**, and **9**. The mixtures were further separated by preparative HPLC with a Nova-Pak silica column using *n*-hexane and ethyl acetate. **8**: mp 165-167 °C (from dichloromethane and *n*-hexane); ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si) δ 7.95 (1H, m, ArH), 7.88 (1H, dd, J = 7.9, 0.5 Hz, ArH), 7.53 (1H, m, ArH), 7.40 (2H, m, ArH), 7.35-7.22 (2H, m, ArH), 7.08 (1H, m, ArH), 6.25 (1H, ddd, J = 5.6, 4.3, 2.1 Hz, H_5), 6.14 (1H, dd, J = 5.6, 1.8 Hz, H_4), 3.67 (1H, d, J = 7.5 Hz, H_1), 3.59 (1H, m, H_3), 2.95 (1H, dd, J = 12.2, 5.7 Hz, H_2), 2.55 (2H, m, H_6, H_7); ^{13}C NMR (75 MHz; CDCl$_3$; Me$_4$Si) δ 134.83, 133.18, 133.06, 132.08, 130.67, 130.38, 129.65, 129.13, 128.81, 128.49, 128.19, 127.99, 123.75, 123.52, 121.09, 61.08, 47.28, 43.19, 39.12, 38.61; IR (CHCl$_3$) 3020, 2929, 2231 (CN), 1520, 1440, 1219, 928, 775 cm^{-1}; UV (CHCl$_3$) λ_{nm} (ε) 307 (1640), 293 (8080), 277 (14300); MS (CI$^+$) m/e 270 (MH$^+$, 20%), 243 (29), 232 (12), 204 (100), 203 (87), 66 (2). **9**: ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si) δ 7.98-7.95 (2H, m, ArH), 7.69 (1H, m, ArH), 7.37 (2H, m, ArH), 7.30 (3H, m, ArH), 6.67 (1H, dd, J = 5.8, 3.0 Hz, H_3), 6.56 (1H, dd, J = 5.8, 2.7 Hz, H_4), 3.39 (2H, broad s, H_1, H_5), 3.12 (1H, broad s, H_2), 1.41 (1H, d, J = 9.3 Hz, H_6), 1.32 (1H, ddd, J = 11.2, 3.5, 1.8 Hz, H_7); ^{13}C (75 MHz; CDCl$_3$; Me$_4$Si) δ 140.56, 135.31, 134.59, 132.72, 131.35, 130.00, 129.88, 129.56, 128.65, 128.51, 128.45, 127.27, 125.12, 122.93, 122.82, 60.33, 56.67, 49.86, 43.58, 43.10; IR (CHCl$_3$) 3070, 3017, 2989, 2233 (CN), 1488, 1331, 1227, 928, 729 cm^{-1}; UV (CHCl$_3$) λ_{nm} (ε) 308 (3440), 288 (11900), 275 (17500), 262 (19100); MS (CI$^+$) m/e 270 (MH$^+$, 0.16%), 232 (11), 204 (100), 203 (57), 67 (4).

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