A [3+2]-Photocycloaddition of 9,10-Dicyanophenanthrene to 1,3-Butadiene

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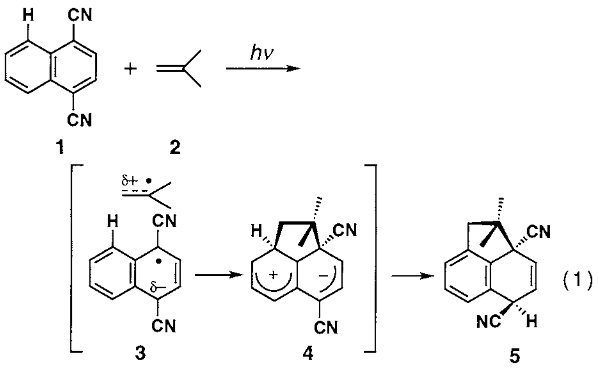
In the photoreactions of 9,10-dicyanophenanthrene (**6**) with 1,3-butadiene (**7**) a novel [3+2]-photocycloaddition at the 9,10-position of the phenanthrene ring of **6** to one of the double bond of **7** and a [2+2]-cycloaddition at the 9,10-position of **6** were found to proceed from the singlet and the triplet excited states of **6**, respectively.

There has been considerable interest in the photocycloadditions of arenes, such as benzene, naphthalene, anthracene, and phenanthrene derivatives, to alkenes and dienes from synthetic and mechanistic viewpoints.[1] Especially, [2+2]-photocycloadditions of phenanthrene derivatives, such as 9-cyanophenanthrene, to alkenes[2] and dienes,[3] which can occur both from the singlet and the triplet excited states, have been extensively investigated and have provided important clues to the mechanism of photocycloadditions. Thus, the emitting exciplexes have been shown to be the intermediates of the [2+2]-cycloadditions and to play an important role in controlling the regio- and stereochemistry of the reactions. In contrast with the numerous investigations on [2+2]-, [4+2]-, and [4+4]-photocycloadditions, a very limited number of [3+2]-cycloadditions, five-membered ring formation, has so far been known.[4-6] We have found a novel 1,8-photoaddition of naphthalene derivatives, such as 1,4-dicyanonaphthalene (**1**), to alkenes, a formal [3+2]-cycloaddition, which proceeds possibly from the singlet excited state via formation of an exciplex **3** and almost synchronous two bond formation in **3** to give a zwitterion **4** followed by proton transfer (eq 1).[7,8]



In this letter, we report on a novel [3+2]-photocycloaddition of 9,10-dicyanophenanthrene (**6**) to 1,3-butadiene (**7**), the first example of the [3+2]-cycloaddition of phenanthrene derivatives.

Irradiation of an acetonitrile solution of **6** (8.0×10^{-4} mol/dm^3) and **7** (1.0 mol/dm^3) with a high-pressure Hg lamp through about 1 cm path length saturated $CuSO_4$ aqueous filter (50% transmittance at 340 nm) under a nitrogen atmosphere gave a [3+2]-adduct **8** with loss of HCN in a yield of 34%, together with a pair of stereoisomers of [2+2]-adducts **9** and **10** in yields of 23% and 9%, respectively (eq 2).

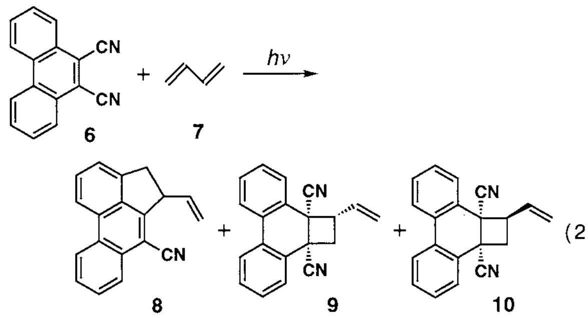


Table 1. Photoreactions of 9,10-dicyanophenanthrene (**6**) with 1,3-butadiene (**7**)[a]

Solvent	[7] / mol/dm^3	Additive	Yield[b]/% **8**	**9**	**10**
MeCN	1.0	—	34	23	9
	0.50	—	20	33	13
	0.25	—	17	34	13
	0.13	—	10	37	14
	1.0	9-fluorenone[c]	14	47	17
	1.0	9-fluorenone[d]	0	59	22
C_6H_6	1.0	—	0	61	18

[a] Irradiation conditions are as follows: hν through about 1 cm path length saturated $CuSO_4$ aqueous filter (50% transmittance at 340 nm), under N_2, at ambient temperature, [**6**] = 8.0×10^{-4} mol/dm^3. [b] Yields based on consumed **6** were determined by ^{1}H NMR analyses (irradiation time 15 min, conversion 65~80%). [c] [9-Fluorenone] = 2.2×10^{-3} mol/dm^3 (the absorbance at 366 nm = 0.44). [d] [9-Fluorenone] = 4.4×10^{-3} mol/dm^3.

These products were isolated by column chromatography on silica gel. Their structures were determined by their spectral properties, especially by their ^{1}H NMR spectra.[9] The ^{1}H NMR spectrum of **8** showed methylene protons of the five-membered ring at δ 3.32 and 3.80 weakly coupled with two phenanthrene ring protons at δ 7.53 and 8.53, indicating the position of the vinyl substituent on the five-membered ring. The stereochemistry of the cyclobutanes **9** and **10** were assigned mainly on the basis of the anisotropic shielding of the aromatic ring and the desielding of the cyano group in the ^{1}H NMR spectra. Thus, the $-C\underline{H}=CH_2$ signals of **10** (δ 5.34) showed remarkable high-field shift relative to the corresponding signals of **9** (δ 6.05).

To clarify the multiplicity of the excited state of **6**, from which the reactions occur, we have examined the concentration effect of **7** and the effect of the addition of a triplet sensitizer, 9-fluorenone, on the yields of **8**, **9**, and **10**, and the results are shown in Table 1. The Table shows that the yield of **8** increases and those of **9** and **10** decrease as increase of the concentration of **7**, and the isomer ratios of **9** to **10** remain almost constant throughout the examined concentrations. The results may indicate that **8** arises from the reaction of the relatively short-lived singlet excited state of **6** with **7**, and **9** and **10** from the reaction of the relatively long-lived triplet excited state of **6** with **7**, since marked increase of yields of photoproducts derived from the singlet excited state with increase of the concentration of alkenes due to the increase of the efficiency of the trap of the relatively short-lived singlet excited state by the alkenes has been reported when the distinct products are generated from the singlet and the triplet excited states.[5,10] On the other hand, Table 1 also shows that the addition of 9-fluorenone suppressed the formation of **8** and increase the yields of **9** and **10** with the isomer ratios of **9** to **10** keeping almost constant. Thus, the triplet sensitization supports the assumption that **8** arises from the singlet excited state of **6**, and **9** and **10** from the triplet excited state.

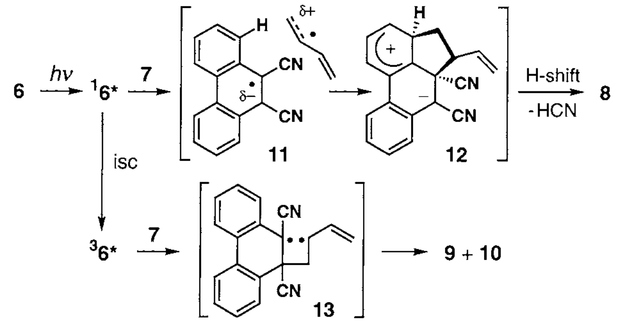
When the reaction was carried out in benzene, a less polar solvent, the [3+2]-cycloaddition was not observed (Table 1).

There was no evidence from the UV spectra for a preformed ground-state complex between **6** and **7**. On the other hand, fluorescence of **6** (τ = 15.0 ns) in MeCN was quenched by **7** and the quenching rate constant of 5.7×10^7 $\mathrm{dm^3 mol^{-1} s^{-1}}$ was obtained from the Stern-Volmer plot. The results imply that the 46% of the singlet excited state of **6** is quenched by **7** under the reaction conditions. No clear evidence for the exciplex emission was observed in the fluorescence quenching examinations.

For a given arene-alkene pair the ΔG associated with photoinduced electron transfer from the alkene to the excited state of the arene has been recognized to be a good measure for prediction of the mode of addition when the interaction between the arenes and alkenes involves extensive charge transfer.[11] As for the photoreactions of dicyanonaphthalenes with alkenes, [3+2]-cycloadditions were found to proceed in the region $+16 > \Delta G > -42$ kJ/mol. The calculated ΔG value of -3.7 kJ/mol[12] for the present system may be in a good situation for the occurrence of the [3+2]-photocycloaddition.

In summary, the [3+2]-cycloaddition at the 1,10-position of the phenanthrene ring of **6** was found to be a exclusive reaction occurred from the singlet excited state **6** in the photoreaction of **6** and **7**. This is the first example, to our knowledge, of the [3+2]-photocycloaddition of arene, other than naphthalene derivatives.

The reaction may proceed possibly via an exciplex **11** and a zwitterioninc intermediate **12** (Scheme 1). In the mechanism, the cyano group at the 9-position of **6** may play an important role in stabilizing the zwitterion **12**. On the other hand, [2+2]-photocycloaddition occurred from the triplet excited state of **6** possibly via a triplet 1,4-biradical **13**.



Scheme 1.

References and Notes

1 J. J. McCullough, *Chem. Rev.*, **87**, 811 (1987); J. Malkin, "Photophysical and Photochemical Properties of Aromatic Compounds," CRC Press, Boca Raton (1992).

2 R. A. Caldwell and L. Smith, *J. Am. Chem. Soc.*, **96**, 2994 (1974); R. A. Caldwell, N. I. Ghali, C.-K. Chien, D. DeMarco, and L. Smith, *J. Am. Chem. Soc.*, **100**, 2857 (1978); R. A. Caldwell and D. Creed, *J. Am. Chem. Soc.*, **100**, 2905 (1978); D. Creed, R. A. Caldwell, and M. M. Ulrich, *J. Am. Chem. Soc.*, **100**, 5831 (1978); R. A. Caldwell and D. Creed, *Acc. Chem. Res.*, **13**, 45 (1980); R. A. Caldwell, D. Creed, D. C. DeMarco, L. A. Melton, H. Ohta, and P. H. Wine, *J. Am. Chem. Soc.*, **102**, 2369 (1980); R. A. Caldwell, K. Mizuno, P. E. Hansen, L. P. Vo, M. Frentrup, and C. D. Ho, *J. Am. Chem. Soc.*, **103**, 7263 (1981); F. D. Lewis and R. J. DeVoe, *Tetrahedron*, **38**, 1069 (1982); K. Mizuno, R. A. Caldwell, A. Tachibana, and Y. Otsuji, *Tetrahedron Lett.*, **33**, 5779 (1992).

3 K. Mizuno, C. Pac, and H. Sakurai, *J. Am. Chem. Soc.*, **96**, 2993 (1974); K. Mizuno, C. Pac, and H. Sakurai, *Chem. Lett.*, **1973**, 309.

4 J. Cornelisse, *Chem. Rev.*, **93**, 615 (1993); P. A. Vender and T. M. Dore, "CRC Handbook of Organic Photochemistry and Photobiology," CRC Press, Boca Raton (1995), p. 280.

5 W. C. Agosta and P. Margaretha, *Acc. Chem. Res.*, **29**, 179 (1996) and references cited therein.

6 K. Nakatani, K. Tanabe, and I. Saito, *Tetrahedron Lett.*, **38**, 1207 (1997) and references cited therein.

7 Y. Kubo, T. Inoue, and H. Sakai, *J. Am. Chem. Soc.*, **114**, 7660 (1992).

8 Y. Kubo, T. Noguchi, and T. Inoue, *Chem. Lett.*, **1992**, 2027.

9 ^{1}H NMR for **8** ($\mathrm{CDCl_3}$, 270MHz) δ 3.32 (dddd, J = 0.7, 1.3, 2.9, 17.6 Hz, 1H) 3.80 (dddd, J = 1.2, 1.5, 8.1, 17.6 Hz, 1H), 4.54 (ddd, J = 2.9, 8.1, 8.3 Hz, 1H), 5.29 (d, J = 10.0 Hz, 1H), 5.43 (d, J = 17.0, 1H), 5.95 (ddd, J = 8.3, 10.0, 17.0 Hz, 1H), 7.53 (ddd, J = 1.3, 1.5, 7.2 Hz, 1H), 7.6-7.8 (m, 2H), 7.78 (dd, J = 7.2, 8.1 Hz, 1H), 8.30 (m, 1H), 8.33 (ddd, J = 0.7, 1.2, 8.1 Hz, 1H), 8.61 (m, 1H) ppm. ^{1}H NMR for **9** ($\mathrm{CDCl_3}$, 270MHz) δ 2.77 (dd, J = 5.2, 8.6 Hz, 1H), 3.2-3.3 (m, 2H), 5.08 (d, J = 17.1 Hz, 1H), 5.30 (d, J = 10.3 Hz, 1H), 6.05 (ddd, J = 7.1, 10.3, 17.1 Hz, 1H), 7.3-7.7 (m, 6H), 7.9-8.1 (m, 2H) ppm. ^{1}H NMR for **10** ($\mathrm{CDCl_3}$, 270MHz) δ 2.40 (dd, J = 10.6, 11.7 Hz, 1H), 2.93 (dd, J = 8.3, 11.7 Hz, 1H), 4.13 (ddd, J = 8.1, 8.3, 10.6 Hz, 1H), 5.15 (d, J = 9.8 Hz, 1H), 5.17 (d, J = 17.1 Hz, 1H), 5.34 (ddd, J = 8.1, 9.8, 17.1 Hz, 1H), 7.3-7.7 (m, 6H), 7.9-8.1 (m, 2H) ppm.

10 Y. Kubo, S. Togawa, K. Yamane, A. Takuwa, and T. Araki, *J. Org. Chem.*, **54**, 4929 (1989).

11 J. Mattay, *Tetrahedron*, **41**, 2393 (1985); J. Mattay, *Tetrahedron*, **41**, 2405 (1985); J. Mattay, *J. Photochem.*, **37**, 167 (1987).

12 The ΔG value was calculated by using $\Delta G = 96.4[E^{ox}(\mathbf{7}) - E^{red}(\mathbf{6})] - E_S(\mathbf{6}) - C$,[13] where the one-electron oxidation potential for **7** $E^{ox}(\mathbf{7}) = 2.12$ (as a peak potential at the scanning rate of 100 mV/s, $[\mathbf{7}] = 1 \times 10^{-3}$ $\mathrm{mol/dm^3}$ in 0.1 $\mathrm{mol/dm^3}$ $\mathrm{Bu_4NClO_4}$/MeCN, at an ambient temperature with a carbon electrode, normalized as E^{ox}(ferrocene) = 0.428 V), the one-electron reduction potential for **6** $E^{red}(\mathbf{6}) = -1.06$ V, the energy of the singlet excited state of **6** estimated from the 0-0 band of the fluorescence spectrum in MeCN $E_S(\mathbf{6}) = 304.9$ kJ/mol, and the "Coulombic attraction term" $C = 5.4$ kJ/mol.

13 D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).