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Site-Selective and Stereoselective Intramolecular ($2\pi + 2\pi$) Photocycloaddition of Arylalkenes to Pyrene and Its Photocycloreversion

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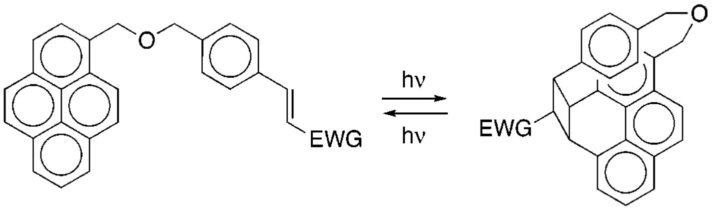
ABSTRACT



1a: EWG = CO_2Me
1b: EWG = CN

2a-b

Irradiation of a benzene solution containing methyl *p*-(1-pyrenylmethoxymethyl)cinnamate (1a) with a high-pressure Hg lamp through Pyrex filter stereoselectively gave an intramolecular ($2\pi + 2\pi$) photocycloadduct (2a) in an 83% yield in a site-selective manner at the 4,5-position of the pyrene ring. Similar irradiation of an *ortho*-substituted derivative (3) afforded the corresponding ($2\pi + 2\pi$) cycloadduct (4) as a sole product at the 9,10-position of pyrene. The site-selective photocycloaddition can be reasonably explained by the intramolecular sandwich-type singlet exciplexes between the pyrene and phenyl rings.

The photocycloaddition reaction of alkenes to aromatic rings is a stimulating subject in organic photochemistry, because it is one of the most useful methods for the synthesis of a variety of carbon skeleton compounds that are difficult or impossible to obtain by thermal reactions.[1−3] Singlet and triplet exciplexes, which play important roles in the control of the regio- and stereochemistry of products, have been postulated as reactive intermediates. However, the photocycloaddition of alkenes to a pyrene ring has been less frequently reported,[4] although the fluorescence behavior of pyrene and its derivatives has been well investigated. In addition, the cycloreversion of the ($2\pi + 2\pi$) photocycload-

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(1) (a) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45−50. (b) Gilbert, A. In *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum Press: London, 1984; pp 1−60. (c) McCullough, J. J. *Chem. Rev.* **1987**, *87*, 811−860. (d) Wender, P. A.; Dore, T. M. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC: London, 1994; pp 280−290.

(2) (a) Pac, C.; Mizuno, K.; Sugioka, T.; Sakurai, H. *Chem. Lett.* **1973**, 187−188. (b) Mizuno, K.; Pac, C.; Sakurai, H. *J. Chem. Soc., Chem. Commun.* **1974**, 648−649. (c) Caldwell, R. A.; Ghali, N. I.; Chien, C.-K.; DeMarco, D.; Smith, L. *J. Am. Chem. Soc.* **1978**, *100*, 2857−2863. (d) Caldwell, R. A.; Mizuno, K.; Hansen, P. E.; Vo, L. P.; Frentrup, M.; Ho, C. D. *J. Am. Chem. Soc.* **1981**, *103*, 7263−7269. (e) Mizuno, K.; Caldwell, R. A.; Tachibana, A.; Otsuji, Y. *Tetrahedron Lett.* **1992**, *33*, 5779−5782.

(3) Intramolecular ($2\pi + 2\pi$) photocycloaddition of alkenes to aromatic rings: (a) McCullough, J. J.; MacInnis, W. K.; Lock, C. J. L.; Faggiani, R. *J. Am. Chem. Soc.* **1982**, *104*, 4644−4658. (b) Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 4404−4405. (c) Wagner, P. J.; Nahm, K. *J. Am. Chem. Soc.* **1987**, *109*, 6528−6530. (d) Cosstick, K. B.; Drew, M. G. B.; Gilbert, A. *J. Chem. Soc., Chem. Commun.* **1987**, 1867−1868. (e) Blakemore, D. C.; Gilbert, A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2265−2270. (f) Tanaka, N.; Yamazaki, H.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1434−1440. (g) Nuss, J. M.; Chinn, J. P.; Murphy, M. M. *J. Am. Chem. Soc.* **1995**, *117*, 6801−6802. (h) Mizuno, K.; Konishi, S.; Takata, T.; Inoue, H. *Tetrahedron Lett.* **1996**, *37*, 7775−7778.

(4) Intermolecular ($2\pi + 2\pi$) photocycloaddition of alkenes to pyrene ring: (a) Mizuno, K.; Maeda, H.; Inoue, Y.; Sugimoto, A.; Vo, L. P.; Caldwell, R. A. *Tetrahedron Lett.* **2000**, *41*, 4913−4916. (b) Williams, J. L. R.; Farid, S. Y.; Doty, J. C.; Daly, R. C.; Specht, D. P.; Searle, R.; Borden, D. G.; Chang, H. J.; Martic, P. A. *Pure Appl. Chem.* **1977**, *49*, 523−538. (c) Kimura, M.; Nukada, K.; Satake, K.; Morosawa, S.; Tamagake, K. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1431−1433.

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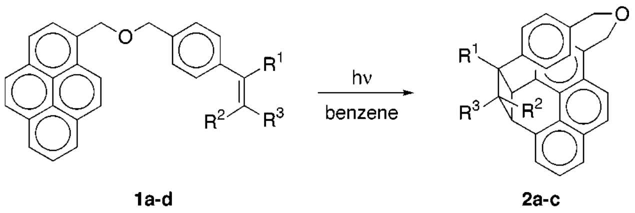
ducts between pyrene and alkenes has not been investigated.[5] We now report the site- and stereoselective intramolecular photocycloaddition of alkenes to pyrene and its cycloreversion based on our interests in the synthesis of phenanthrenophanes[6] and the photoswitching ability.

We have designed and synthesized compounds **1a**−**d**, **3**, and **5** which were connected by ether linkages between the pyrene and electron-deficient arylalkenes.[7] Irradiation of benzene solutions of **1a**,**b** by use of a 300 W high-pressure Hg lamp through a Pyrex filter under an argon atmosphere efficiently gave intramolecular ($2\pi + 2\pi$) photocycloadducts (**2a**,**b**)[8] as sole products in 83% and 81% yields, respectively, together with the recovery of **1a**,**b** with no photoisomerization of the alkenyl group (Table 1). A similar irradiation of **3** (*trans*/*cis* = 78/22), which connects pyrene and cinnamonitrile at the *ortho*-position of the benzene ring, afforded the corresponding intramolecular photocycloadducts (**4t** and **4c**) in 75% and 11% isolated yields, respectively (Scheme 1). It should be noted here that the reactive site of **3** (the 9,10-position of pyrene ring) was different from that of **1a**,**b** (their 4,5-position). However, the photoreaction of the *meta* derivative (**5t**) resulted in a brief photoisomerization to the *cis* isomer (**5c**) and did not give the cycloadduct (Scheme 2).

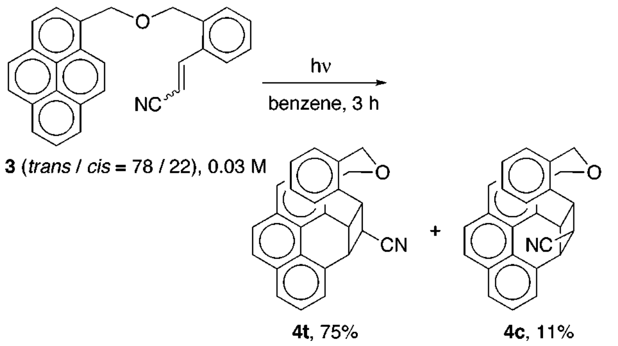
Table 1. Intramolecular ($2\pi + 2\pi$) Photocycloaddition of **1a**−**d**[a]



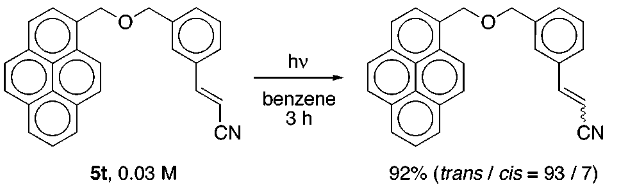
substrate				product	yield of **2** (%)	recovery of **1** (%)
	R¹	R²	R³			
1a	H	H	CO_2Me	**2a**	83	17 (E/Z = 100/0)
1b	H	H	CN	**2b**	81	19 (E/Z = 100/0)
1c	CN	H	Ph	**2c**	22	78 (E/Z = 59/41)
1d	H	CN	Ph		0	100 (E/Z = 69/31)

[a] Reactions were carried out using a high-pressure Hg lamp through a Pyrex filter under an argon atmosphere for 1 h. [**1**] = 0.03 M in benzene (5 mL).

Scheme 1

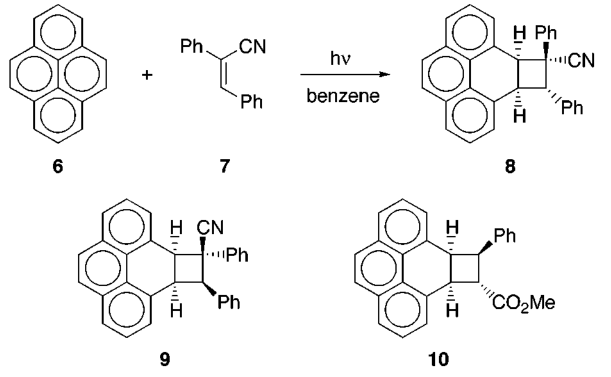


Scheme 2



Irradiation of **1c** afforded **2c** in a 22% yield, but in the case of **1d**, **2d** was not obtained at all. In both cases, E−Z photoisomerization of arylalkenyl groups was observed. The different reactivity between **1c** and **1d** can be reasonably explained by the steric hindrance of *endo*-phenyl ring with *endo*-*Z*-cyano group. In fact, the intermolecular photocycloaddition of α-cyanostilbene (**7**) to pyrene (**6**) exclusively afforded **8** in a high yield, and **9** was not obtained (Scheme 3).

Scheme 3



The structures of these photocycloadducts were determined by their spectral and analytical data. In the cases of **2a**−**c**,

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(5) (a) Mizuno, K.; Pac, C. In *CRC Handbook of Organic Photochemistry and Photobiology*; Horspool, W. M., Song, P.-S., Eds.; CRC: London, 1994; pp 358−374. (b) Pac, C. *Pure Appl. Chem.* **1986**, *58*, 1249−1256.

(6) (a) Takeuchi, M.; Nishimura, J. *Tetrahedron Lett.* **1992**, *33*, 5563−5566. (b) Nishimura, J.; Okada, Y.; Inokuma, S.; Nakamura, Y.; Gao, S. R. *Synlett* **1994**, 884−894. (c) Nakamura, Y.; Tsuihiji, T.; Mita, T.; Minowa, T.; Tobita, S.; Shizuka, H.; Nishimura, J. *J. Am. Chem. Soc.* **1996**, *118*, 1006−1012.

(7) We have also prepared several pyrene derivatives bearing cinnamyl and cinnamoyl groups. However, they were less reactive than **1a**−**c**.

(8) Data for **2a**: mp 175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 (t, J = 4.9 Hz, 1 H), 3.89 (s, 3 H), 4.20 (d, J = 13.2 Hz, 1 H), 4.43 (d, J = 13.2 Hz, 1 H), 4.45 (dd, J = 9.8, 5.9 Hz, 1 H), 4.63 (dd, J = 9.8, 4.4 Hz, 1 H), 4.78 (t, J = 10.0 Hz, 1 H), 4.86 (d, J = 13.2 Hz, 1 H), 5.63 (dd, J = 8.1, 1.7 Hz, 1 H), 5.69 (d, J = 13.2 Hz, 1 H), 6.07 (dd, J = 8.1, 1.7 Hz, 1 H), 6.38 (dd, J = 7.8, 2.0 Hz, 1 H), 6.42 (d, J = 7.3 Hz, 1 H), 6.60 (dd, J = 7.8, 2.0 Hz, 1 H), 6.80 (d, J = 7.3 Hz, 1 H), 7.42 (d, J = 6.8 Hz, 1 H), 7.55 (t, J = 7.6 Hz, 1 H), 7.71 (d, J = 8.8 Hz, 1 H), 7.72 (d, J = 7.3 Hz, 1 H), 7.85 (d, J = 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.04, 42.84, 50.20, 51.22, 52.32, 73.04, 74.42, 123.53, 125.23, 125.64, 126.20, 126.63, 127.05, 127.35, 128.04, 129.88, 130.28, 130.44, 130.54, 130.71, 131.97, 134.85, 136.04, 137.11, 138.39, 175.07; MS (EI), m/z (%) = 216 (100), 406 (M^+, 33).

^{1}H NMR chemical shifts of some aromatic protons on the benzene rings and 2,3-positions of dihydropyrene rings appeared farther upfield than normal owing to the ring current effect (for example, 5.63−6.80 ppm in **2a**, 5.92−6.99 ppm in **2c**, both in $CDCl_3$). The chemical shifts of aromatic protons of **4t** and **4c** also shifted upfield moderately. These results clearly show that **2a**−**c** have complete sandwich structures as phenanthrenophanes. Finally, the structures of **2a** and **4t** were confirmed by the X-ray analyses shown in Figures 1 and 2.

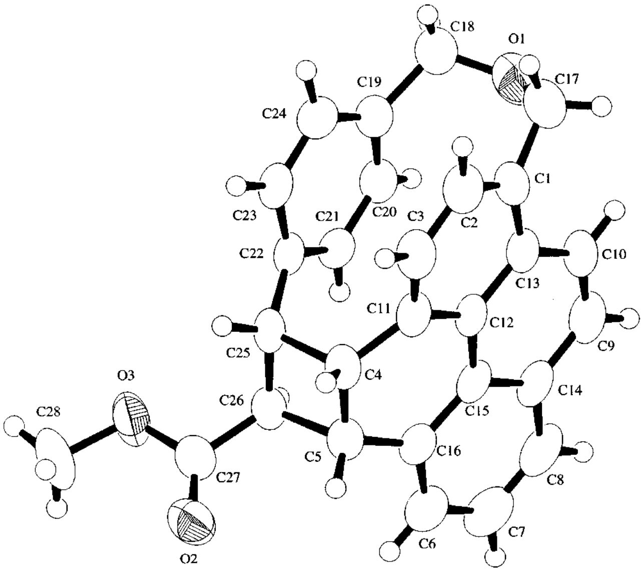


Figure 1. ORTEP drawing of **2a**: monoclinic, $P21/a$ (No. 14), $z = 8$, $R = 0.052$, $a = 9.608(4)$, $b = 19.801(5)$, $c = 21.540(5)$, $\beta = 98.64(3)$, $V = 4051(2)$. Selected bond lengths: C(5)−C(26) 1.560(4) Å, C(4)−C(5) 1.544(5) Å, C(4)−C(25) 1.614(4) Å, C(25)−C(26) 1.553(4) Å.

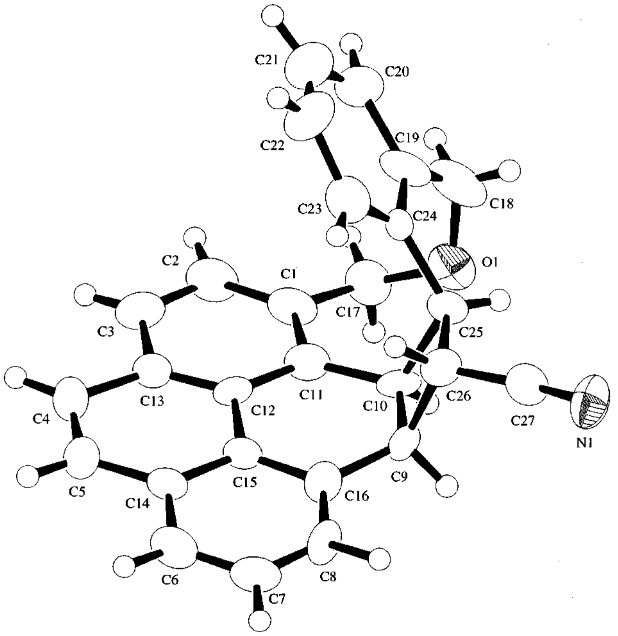
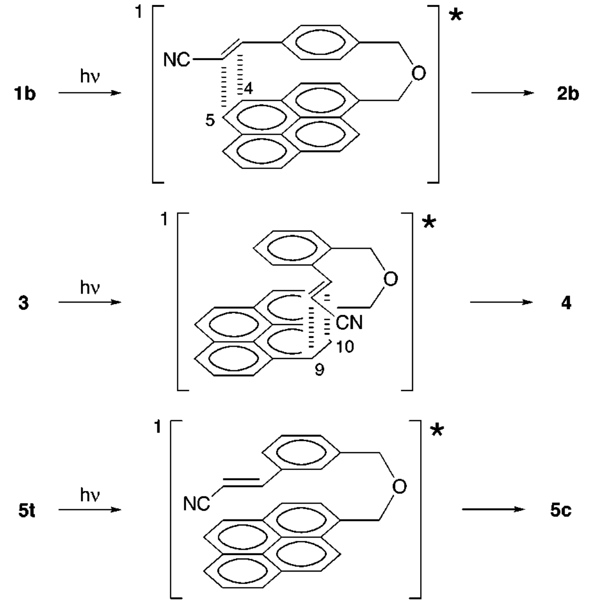


Figure 2. ORTEP drawing of **4t**: monoclinic, Pa (No. 7), $z = 4$, R1 = 0.056, $a = 9.086(4)$, $b = 23.816(2)$, $c = 9.923(4)$, $\beta = 107.04(3)$, $V = 2052(1)$. Selected bond lengths: C(9)−C(10) 1.55(1) Å, C(10)−C(25) 1.63(2) Å, C(25)−C(26) 1.61(1) Å, C(26)−C(9) 1.57(2) Å.

The photocycloreversion of **2a**−**c** and **4t** was examined. Irradiation of the isolated **2a**,**b** in benzene through a Pyrex filter gave a mixture of **1a**,**b** and **2a**,**b** in an ca. 80:20 ratio. These ratios were almost the same as those in the photoreactions of **1a**,**b**, and the prolonged irradiation did not affect these ratios. The *cis* isomers of **1a**,**b** (*c*-**1a**,**b**) were not observed at all. In the case of **2c**, the cycloreversion also occurred smoothly, but the $E-Z$ photoisomerization took place in high efficiency. On the other hand, **4t** was not cyclorevered. In addition, cycloreversion of the intermolecular photocycloadduct (**10**) was barely observed under the same irradiation conditions.[4a,9] The marked difference of efficiency of cycloreversion was rationalized by the higher strain energy of **2a**−**c**. The $E-Z$ photoisomerization of alkenyl groups took place via their excited triplet states generated by energy transfer from the triplet state of the pyrenyl group in most cases. The alkenyl groups of **1a**,**b**, with higher triplet energies, did not isomerize, but those of **1c**,**d** efficiently isomerized because of their lower triplet energies.[10]

UV−vis absorption spectra of *para*, *ortho*, and *meta* derivatives (**1b**, **3**, and **5**) were quite similar to that of 1-(methoxymethyl)pyrene and did not show the formation

Scheme 4



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(9) Zertani, R.; Meier, H. *Chem. Ber.* **1986**, *119*, 1704−1715.

(10) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry, Second Edition, Revised and Expanded*; Marcel Dekker: New York, 1993.

of the intramolecular charge transfer complexes in the ground states. Fluorescence spectra of these compounds in cyclohexane showed that the monomer fluorescence of the pyrene chromophore was efficiently quenched intramolecularly by the arylalkenyl group accompanying the intramolecular exciplex emission.[11] The photoreaction did not proceed by way of triplet sensitizers as the benzophenone and Michler's ketone photoreactions do.

These results can be reasonably explained by the intramolecular sandwich-type exciplex mechanism.[1−3] The $\pi-\pi$ overlap interaction between the pyrene and benzene rings in the excited singlet state controls the site selectivity of the photocycloaddition.[4a,b,12,13] The proposed structures of the exciplexes derived from *para*, *ortho*, and *meta* derivatives are shown in Scheme 4. *Para*-substituted derivatives (**1a**−**c**) react at the 4,5-position of pyrene to give cyclophanes (**2a**−**c**) reversibly. On the other hand, *ortho* derivative **3** reacts at the 9,10-position of pyrene to give the intramolecular photocycloadducts (**4t** and **4c**). An unfavorable exciplex for photocycloaddition from *meta* derivative **5** does not give any photocycloadduct.

The photoswitching ability of **1a**−**c** and **2a**−**c** systems is now under investigation.

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(11) The fluorescence spectra of **1a**,**b**, **3**, and **5t** in cyclohexane showed the weak intramolecular exciplex emission at a longer wavelength than the monomer fluorescence of pyrene. In the cases of **1c**,**d**, the exciplex maxima were clearly observed at 450 and 470 nm, respectively.

(12) (a) Förster, Th. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 333−343. (b) Zachariasse, K.; Kühnle, W. *Z. Phys. Chem.* **1976**, *101*, S. 267−276. (c) DeSchryver, F. C.; Collart, P.; Vandendriessche, J.; Goedeweeck, R.; Swinnen, A. M.; Van der Auweraer, M. *Acc. Chem. Res.* **1987**, *20*, 159−166. (d) Declercq, D.; Delbeke, P.; DeSchryver, F. C.; Van Meervelt, L.; Miller, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 5702−5708.

(13) For studies of fluorescence behavior of pyrene derivatives bearing electron-withdrawing or -releasing groups: (a) Swinnen, A. M.; Van der Auweraer, M.; DeSchryver, F. C.; Nakatani, K.; Okada, T.; Mataga, N. *J. Am. Chem. Soc.* **1987**, *109*, 321−330. (b) Kawakami, J.; Iwamura, M. *J. Phys. Org. Chem.* **1994**, *7*, 31−42. (c) Kawakami, J.; Furuta, T.; Nakamura, J.; Uchida, A.; Iwamura, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 47−54.