Stereoselective (2π + 2π) Photocycloaddition of Arylalkenes to Chrysene

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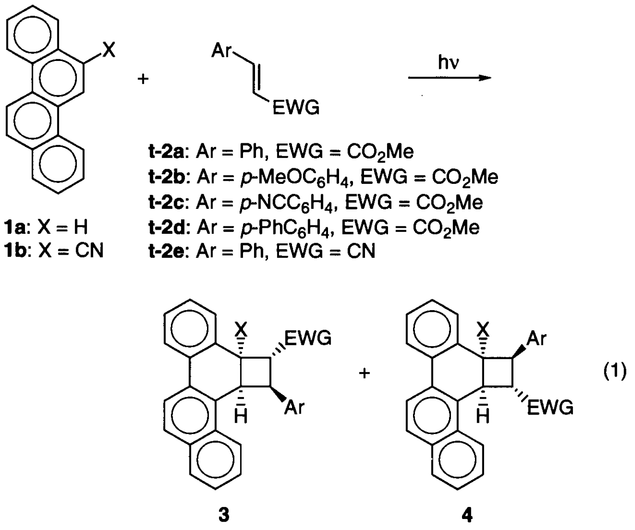
(Received August 7, 2000; CL-000757)

Photocycloaddition of electron-deficient arylalkenes to chrysene stereoselectively occurred at 5,6-position of chrysene ring to give two (2π + 2π) photocycloadducts through sandwich-type singlet exciplexes. Photocycloreversion took place via the excited singlet states of the photocycloadducts.

Photocycloaddition of unsaturated molecules to aromatic rings is not only an interesting subject on organic photochemistry, but a useful synthetic method for the synthesis of conformationally rigid cyclobutanes.[1] Most of studies were developed through the inter- or intramolecular photocycloaddition of unsaturated compounds to benzene, naphthalene, anthracene, phenanthrene, and pyrene rings.[2] On the contrary, photocycloaddition to more condensed polynuclear aromatic hydrocarbons is scarcely known.[3] Chrysene is one of the most usable aromatic hydrocarbons as photosensitizer,[4] but the study about the photocycloaddition to chrysene ring is hitherto only known about the (4π + 2π) photocycloaddition with maleic anhydride to give a benzopyrene derivative.[5] Here we describe a novel (2π + 2π) photocycloaddition of arylalkenes to chrysene ring.



1a: X = H
1b: X = CN

t-2a: Ar = Ph, EWG = CO_2Me
t-2b: Ar = *p*-$MeOC_6H_4$, EWG = CO_2Me
t-2c: Ar = *p*-NCC_6H_4, EWG = CO_2Me
t-2d: Ar = *p*-PhC_6H_4, EWG = CO_2Me
t-2e: Ar = Ph, EWG = CN

Irradiation of a benzene solution containing chrysene (**1a**) and methyl *trans*-cinnamate (**t-2a**) by a high-pressure Hg lamp through Pyrex filter under argon atmosphere gave two regioisomeric (2π + 2π) photocycloadducts (**3aa** and **4aa**) in a stereoselective manner (eq 1, Table 1). In this photoreaction, the cycloadduct derived from *cis*-alkene was not detected at all, although *cis*-isomer (**c-2a**) was produced in detectable amounts. The yields of products increased with increasing the irradiation time less than 2 h (runs 1–3). When CH_3CN, THF, and CH_2Cl_2 were used as a solvent, the efficiency was lower than that in benzene (runs 4–6). Methoxy group on *para* position of methyl *trans*-cinnamate accelerated the reaction, however, introduction of *p*-cyano group caused the almost recovery of **1a** (runs 7, 8). Reaction with *p*-phenyl derivative (**t-2d**) gave poor selectivity of **3** / **4** in moderate yields of products (runs 9, 10). Reaction of **1a** with cinnamonitrile (**t-2e**) also proceeded (run 11). Photocycloaddition of **t-2a** to 6-cyanochrysene (**1b**) occurred at 5,6-position of **1b** in low efficiency compared with **1a** (runs 12, 13), but the photoreaction of **1b** with **t-2b** proceeded in >10 : 1 selectivity (run 14). The other alkenes such as anethole, *trans*-stilbene, *trans*-crotononitrile, α-cyanostilbene, and benzylidenemalononitrile did not add to **1a** under the same irradiation conditions.[6]

Table 1. (2π+2π) Photocycloaddition of chrysene (**1**) with electron-deficient arylalkenes (**2**)[a]

Run	1	2	Solvent	Irradn Time / h	Yields[b] / % 3	4	Recovery of 1 / %
1	**1a**	**t-2a**	benzene	0.5	26	5	69
2	**1a**	**t-2a**	benzene	2	46	10	35
3	**1a**	**t-2a**	benzene	5	44	9	27
4	**1a**	**t-2a**	CH_3CN	2	25	7	45
5	**1a**	**t-2a**	THF	2	13	3	66
6	**1a**	**t-2a**	CH_2Cl_2	2	<1	<1	83
7	**1a**	**t-2b**	benzene	2	60	13	16
8	**1a**	**t-2c**[c]	benzene	2	<1	<1	>99
9	**1a**	**t-2d**[c]	benzene	2	24	10	66
10	**1a**	**t-2d**[c]	benzene	5	24	14	61
11	**1a**	**t-2e**	benzene	2	23	6	69
12	**1b**	**t-2a**	benzene	2	4	<1	71
13	**1b**	**t-2a**	benzene	5	7	<1	59
14	**1b**	**t-2b**	benzene	2	53	5	24

[a] [**1**] = 0.01 M, [**2**] = 0.1 M. [b] Yields were determined by ^{1}H NMR using *o*-xylene as an internal standard. [c] [**t-2c-d**] = 0.02 M.

The structures of the products were determined by their spectral and analytical data, especially by ^{1}H NMR. The structure of **3aa** was confirmed by X-ray analysis shown in Figure 1.

The fluorescence of **1a** in benzene was efficiently quenched by **t-2a** ($k_q = 1.21 \times 10^9$ M^{-1}s^{-1}). The formation of photocycloadducts was not sensitized by the addition of benzophenone, and was not quenched by molecular dioxygen. From these facts, the regio- and stereoselectivity to give **3** and **4** was explained by two possible structures of sandwich-type singlet exciplexes formed via excited singlet state of **1a** shown in Scheme 1. Aromatic groups of the electron-deficient arylalkenes might favor to overlap on the naphthalene ring than on the benzene ring. Higher efficiency in benzene than other solvents and low selectivity in the reaction with **t-2d** were also rationalized by this mechanism. Arylalkene having electron-donating substituent gave photocycloadducts efficiently. Higher regioselectivity of the reaction of **1b** with **t-2b** may be explained by their dipole moments in the excited states.[1c]

UV–vis absorption maximum of **3aa** showed at 334 nm.[7]

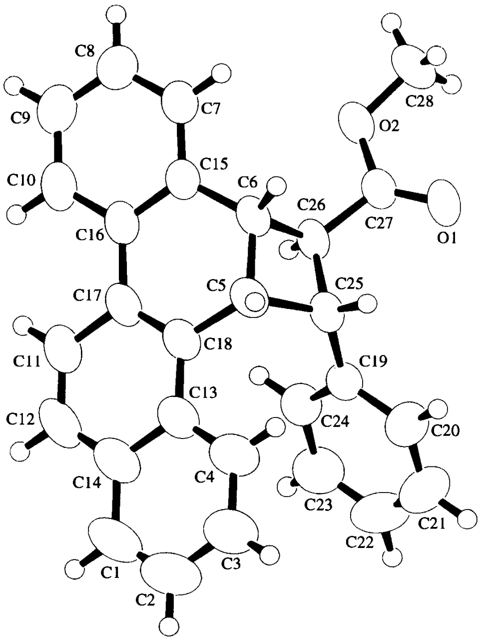
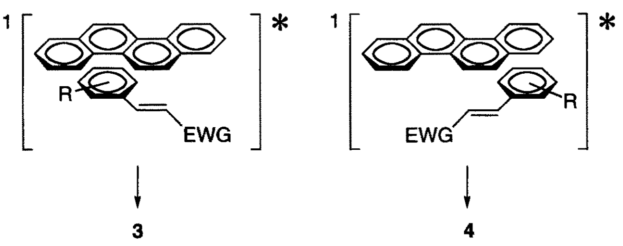
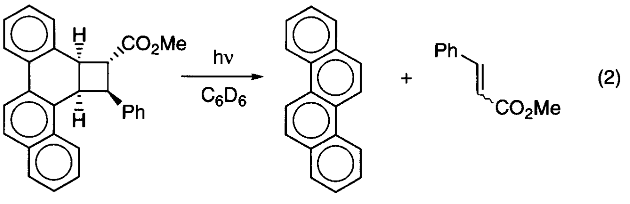


Figure 1. ORTEP drawing of **3aa**. $C_{28}H_{22}O_2$, FW = 390.48, monoclinic, *C2/c* (#15), *Z* = 8, *R*1 = 0.053, *a* = 17.833(4), *b* = 10.012(4), *c* = 23.375(5) Å, *β* = 103.03(2)°, *V* = 4066(1) Å^3, D_{calcd} = 1.276 g cm^{-3}. Selected bond lengths (Å); C(5)-C(6): 1.541(3), C(6)-C(26): 1.554(3), C(26)-C(25): 1.540(3), C(25)-C(5): 1.582(3).



Scheme 1. Structures of two possible exciplexes to give photocycloadducts.

Therefore, photocycloreversion from **3** and **4** to **1** and **2** competitively occurred in this reaction.[8] Photoirradiation of isolated **3aa** in benzene-d_6 was monitored by ^1H NMR spectroscopy (eq 2). At the initial stage of this cycloreversion, **2a** was obtained only its *trans*-isomer. The prolonged irradiation caused the isomerization of **t-2a** to **c-2a**. These results support the fact that the photocycloreversion occurs via excited singlet state of **3aa**.



3aa, 0.003 M	**1**	**t-, c-2a**
1 min	18%	17% (*trans* / *cis* = >95 / <5)
5 min	60%	62% (*trans* / *cis* = 68 / 32)
10 min	80%	74% (*trans* / *cis* = 60 / 40)

In conclusion, we have found the first example of (2π + 2π) photocycloaddition of chrysene with alkenes. The highly regioselective photocycloaddition of **t-2b** to **1b** has been achieved by the combination of π–π overlapping and favorable dipole moment in the exciplex state. The scope and mechanism in detail are now under investigation.

This study was performed through Special Coodination Funds for Promoting Science and Technology (Leading Research Utilizing Potential of Regional Science and Technology) of the Science and Technology Agency of the Japanese Government. We thank Dr. A. Sugimoto for X-ray crystallographic analysis. We also indebted to Professor R. A. Caldwell at University of Texas at Dallas for helpful discussions.

References and Notes

1 a) A. Gilbert, in "Synthetic Organic Photochemistry," ed. by W. M. Horspool, Plenum Press, London (1984), p. 1. b) J. J. McCullough, *Chem. Rev.*, **87**, 811 (1987). c) R. A. Caldwell and D. Creed, *Acc. Chem. Res.*, **13**, 45 (1980).

2 a) K. Mizuno, R. A. Caldwell, A. Tachibana, and Y. Otsuji, *Tetrahedron Lett.*, **33**, 5779 (1992). b) K. Mizuno, S. Konishi, T. Takata, and H. Inoue, *Tetrahedron Lett.*, **37**, 7775 (1996). c) K. Mizuno, H. Maeda, Y. Inoue, A. Sugimoto, L. P. Vo, and R. A. Caldwell, *Tetrahedron Lett.*, **41**, 4913 (2000).

3 a) H. Karpf, O. E. Polansky, and M. Zander, *Tetrahedron Lett.*, **1978**, 339. b) N. C. Yang, J. Masnovi, and W. Chiang, *J. Am. Chem. Soc.*, **101**, 6465 (1979). c) N. C. Yang, J. Masnovi, W. -L. Chiang, T. Wang, H. Shou, and D. -D. H. Yang, *Tetrahedron*, **37**, 3285 (1981). d) R. Bunte, K. -D. Gundermann, J. Leitich, O. E. Polansky, and M. Zander, *Chem. Ber.*, **119**, 3521 (1986). e) N. C. Yang, H. Gan, S. S. Kim, J. M. Masnovi, P. W. Rafalko, E. F. Ezell, and G. R. Lenz, *Tetrahedron Lett.*, **31**, 3825 (1990).

4 Chrysene-sensitized photoreactions: a) D. I. Schuster and D. J. Blythin, *J. Org. Chem.*, **35**, 3190 (1970). b) T. Arai, H. Sakuragi, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **55**, 2204 (1982). c) P. S. Engel, D. W. Horsey, D. E. Keys, C. J. Nalepa, and L. R. Soltero, *J. Am. Chem. Soc.*, **105**, 7108 (1983). d) T. Karatsu, T. Hiresaki, T. Arai, H. Sakuragi, K. Tokumaru, and J. Wirz, *Bull. Chem. Soc. Jpn.*, **64**, 3355 (1991). e) F. Elisei, G. G. Aloisi, L. Latterini, G. Galiazzo, and H. Görner, *J. Chem. Soc., Faraday Trans.*, **91**, 3117 (1995). f) F. J. Steemers, H. G. Meuris, W. Verboom, D. N. Reinhoudt, E. B. van der Tol, and J. W. Verhoeven, *J. Org. Chem.*, **62**, 4229 (1997).

5 a) H. Karpf, O. E. Polansky, and M. Zander, *Tetrahedron Lett.*, **1978**, 2069. b) H. Karpf, O. E. Polansky, and M. Zander, *Monatsh. Chem.*, **112**, 659 (1981). c) L. D. Melikadze and E. G. Lekveishvili, *Gazokondensaty Nefti, Mater. Sredneaziat. Nauch. Soveshch. Neftekhim. Khim. Pererab. Uglevodorodov, 2nd*, **1967**, 304; *Chem. Abstr.*, **72**, 3271m (1970).

6 Prolonged irradiation of **1a** with α-cyanostilbene in benzene afforded (2π + 2π) photocycloadduct: R. A. Caldwell, personal communication.

7 **1a**: λ_{max} = 320 nm (ε = 1.8 × 10^4), **3aa**: λ_{max} = 334 nm (ε = 8.1 × 10^3), both in cyclohexane.

8 a) K. Mizuno and C. Pac, in "CRC Handbook of Organic Photochemistry and Photobiology," ed. by W. M. Horspool, P. -S. Song, CRC, London (1994), p. 358. b) C. Pac, *Pure Appl. Chem.*, **58**, 1249 (1986).