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Stereospecific (2π+2π) photocycloaddition of arylalkenes to pyrene via exciplex: formation of 1:1- and 2:1-cycloadducts

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Abstract

Irradiation of benzene solutions containing pyrene and electron-deficient arylalkenes such as *E*- and *Z*-methyl cinnamates afforded (2π+2π) photocycloadducts including 1:2-cycloadduct in high yields in a stereospecific and *endo*-selective manner. Sandwich-type singlet exciplexes between pyrene and arylalkenes were proposed as reactive intermediates.

Keywords: stereospecific photocycloaddition; arylalkene; exciplex; pyrene.

Photocycloaddition of unsaturated compounds to aromatic rings has received considerable attention from synthetic and mechanistic viewpoints in the last three decades.[1,2] Pyrene is a typical aromatic hydrocarbon which has wide-spread π-electrons and emits quite an intense blue monomer fluorescence and strong excimer fluorescence.[3] Therefore, the photochemical and photophysical properties of pyrene monomer and/or excimer have been well investigated in the fields of the electron donor–acceptor interactions, the fluorescent probes, the chemosensors and so on.[4] However, the photochemical reactivity of pyrene including the conversion of pyrene itself has been scarcely known.[5] We now report the stereospecific and *endo*-selective (2π+2π) photocycloaddition of pyrene and pyrene derivatives with arylalkenes, giving 1:1- and 1:2-cycloadducts.

Irradiation of a benzene solution containing pyrene (**1**, 0.02 mol/dm^3) and an excess amount of *E*-methyl cinnamate (***t*-2a**, 0.1 mol/dm^3) with a high-pressure Hg lamp through a Pyrex filter under an argon atmosphere for 1 h afforded two kinds of (2π+2π) photocycloadducts ***t*-3a** and ***t*-4a** in a 25:1 ratio in high yields (80–90%) (Scheme 1). For prolonged irradiation, a 1:2-cycloadduct **5a** was precipitated accompanying the formation of *Z*-methyl cinnamate (***c*-2a**) and trace

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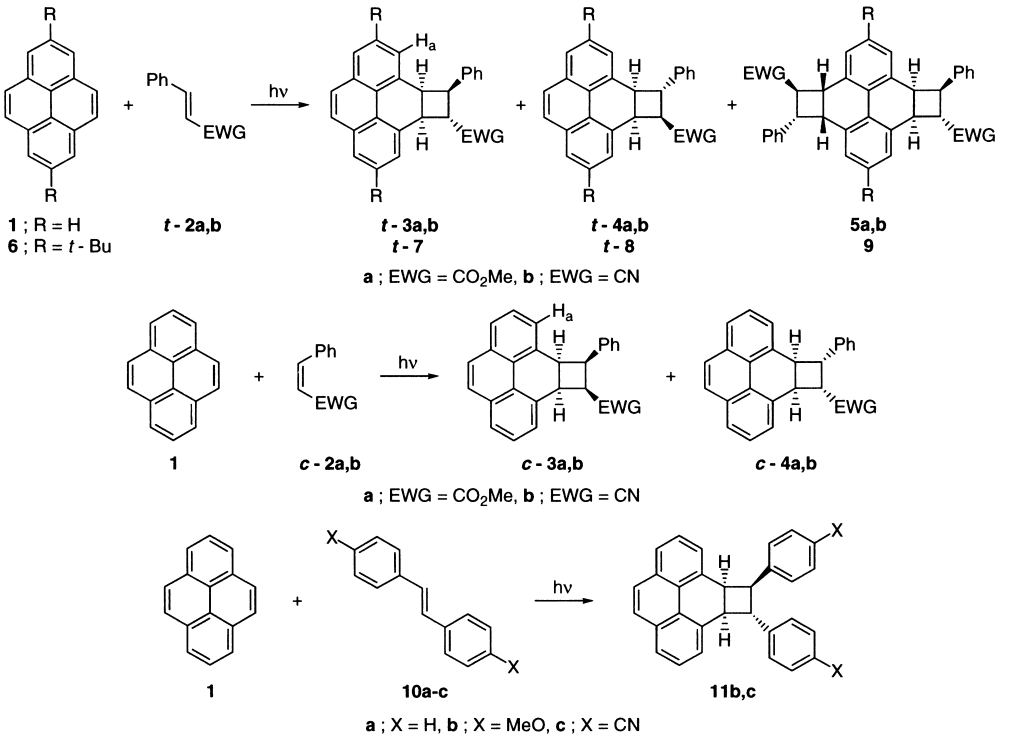
amounts of other isomeric photocycloadducts ***c*-3a** and ***c*-4a**. Similar irradiation of **1** and ***c*-2a** stereospecifically afforded ***c*-3a** and ***c*-4a** in a 7:1 ratio in good yields.



Scheme 1.

These photocycloadducts were isolated by column chromatography on silica gel. Their structures were determined by their spectral properties. The ^{1}H NMR spectra of ***t*-3a** and ***c*-3a** showed the up-field shifted H_a protons at δ 6.38 and 6.65, which was due to an anisotropic effect of the phenyl ring. The methyl protons of ***t*-4a** and ***c*-3a** (δ 3.50 and 2.95) appeared at much higher fields than those of ***t*-3a** and ***c*-4a** (δ 3.65 and 3.64). Finally, the structure of ***t*-3a** was confirmed by X-ray crystallographic analysis.[6] The structure of **5a**, which was insoluble in chloroform and benzene, was also determined by the ^{1}H NMR spectrum in DMSO-d_6 at 130°C. The spectrum showed the symmetrical proton signals. The photoreaction of ***t*-3a** with ***t*-2a** afforded **5a** exclusively. These results support the assigned structures for ***t*-3a**, ***t*-4a**, **5a**, ***c*-3a**, and ***c*-4a**. It is noteworthy that the phenyl group lies at the *endo*-position in the major 1:1 adducts (***t*-3a** and ***c*-3a**) and 1:2 adduct (**5a**) in spite of the predictable steric repulsion. Thus, it becomes clear that the photoreaction proceeds stereospecifically with stereoretention of the alkene used. Photochemical cycloreversion of ***t*-3a** hardly proceeded under the present reaction conditions, although it is well known that the cyclobutanes obtained by the photocycloaddition of alkenes to aromatic rings photocleaved to the starting substrates.[1a,2a,7]

The photocycloaddition of **1** with *trans*- and *cis*-cinnamonitriles (***t*-2b** and ***c*-2b**) similarly gave the 1:1 and 1:2 cycloadducts (***t*-3b**, ***t*-4b**, ***c*-3b**, ***c*-4b**, and **5b**) in a stereospecific and *endo*-selective manner. The photoreaction of sterically hindered 2,7-di-*tert*-butylpyrene (**6**) with ***t*-2a** also gave the 1:1- and 1:2-cycloadducts ***t*-7**, ***t*-8**, and **9** in 61, 6, and 7% yields, respectively. Although

trans-stilbene (**10a**) and styrene did not react with **1** under the same reaction conditions, more electron-donating or electron-deficient stilbene derivatives such as 1,2-bis(4-methoxyphenyl)-ethene (**10b**) and 1,2-bis(4-cyanophenyl)ethene (**10c**) stereospecifically afforded the corresponding ($2\pi+2\pi$) photocycloadducts in 14 and 13% yields, respectively. Electron-deficient alkenes having no aryl substituent such as acrylonitrile and methyl acrylate, and electron-donating alkenes such as 2,3-dimethyl-2-butene and ethyl vinyl ether did not add to **1** under the same conditions.

From the mechanistic viewpoints, the triplet sensitized photoreaction and the fluorescence quenching experiments were carried out as follows: The photocycloaddition of ***t*-2a** or ***t*-2b** to **1** was not sensitized by triplet sensitizers such as benzophenone (69 kcal/mol) and Michler's ketone (61 kcal/mol). The monomer fluorescence of **1** (1×10^{-5} mol/dm^3) in benzene was efficiently quenched by ***t*-2a**,**b**, accompanying the appearance of a weak exciplex emission at longer wavelength (λ_{max} ~450 nm) than the former emission of **1**. The excimer fluorescence of **1** (1×10^{-3} mol/dm^3, λ_{max} ~500 nm) was also efficiently quenched by ***t*-2a**, accompanying the appearance of a weak exciplex emission at a shorter wavelength than the excimer emission. These results were reasonably elucidated by the singlet exciplex mechanism for the stereospecific and *endo*-selective photocycloaddition of arylalkenes to **1**. Under the present reaction conditions ([**1**] >0.01 mol/dm^3), the primary process may be the formation of pyrene excimer $^1\mathbf{1}_2$* followed by the formation of exciplex ^{1}[**1**···**2**]* via exciplex (excimer) substitution.[8,9] This exciplex produces the photocycloadduct efficiently. The *endo*-selectivity can be explained by the π–π overlap interaction between **1** and the styryl chromophores of the arylalkenes via sandwich-type exciplexes as previously reported.[1a,10] It is notable that the photoisomerization of arylalkenes was effectively suppressed by the presence of **1** under the reaction conditions, because the triplet energy of **1** is quite a bit lower than those of arylalkenes. Scope and detailed mechanism are now under investigation.

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6. Compound ***t*-3a**: mp 150°C; crystal data for ***t*-3a**: $C_{26}H_{20}O_2$, space group: $P2_1/a$(#14), $z=4$, $a=19.328(3)$, $b=5.571(3)$, $c=19.527(4)$ Å, $\beta=114.83(1)^\circ$, $V=1908(1)$ Å^3, $R=0.047$.
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9. The direct formation of the exciplex ^{1}[**1**···**2**]* from ^{1}**1*** and **2** is also a plausible pathway even in the high concentration of **1**, because the formation of ^{1}**1**$_2$* from ^{1}**1*** and **1** is reversible.
10. The excitation of bis(1-pyrenylmethyl) ether at 350 nm in benzene shows the excimer fluorescence at 507 nm almost exclusively even at low concentrations. This excimer fluorescence in benzene was efficiently quenched by ***t*-2a** accompanying the exciplex emission at shorter wavelength than the excimer emission. In addition, irradiation of bis(1-pyrenylmethyl) ether with ***t*-2a** afforded a mixture of 1:1-cycloadducts although the structures were not decided. These results also support the exciplex mechanism, not the triplex mechanism.