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PHOTOCYCLOADDITION OF 6-CYANOPHENANTHRIDINE TO ELECTRON-RICH OLEFINS

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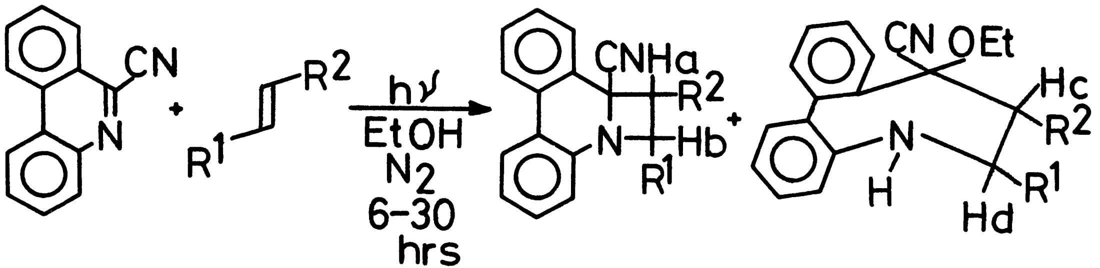
Irradiations of 6-cyanophenanthridine in the presence of electron-rich olefins afforded the corresponding azocine and azetidine derivatives regiospecifically via their exciplex intermediates.

Intermolecular photocycloaddition reactions of the carbon-nitrogen double bond are known only for the systems which are conjugated with the imino[1)] or the carbonyl group.[2,3)] Phenanthridine, which is isoelectronic to phenanthrene, can be also expected to undergo photocycloaddition reactions with olefins similar to phenanthrene derivatives.[4-7)] In order to explore the synthetic potential of these reactions, we have investigated the photocycloaddition of 6-cyanophenanthridine to electron-rich olefins such as *trans*-anethole and phenyl vinyl ether. This communication describes the novel photocycloaddition reaction of 6-cyanophenanthridine which gives eight-membered nitrogen heterocycles as final products.

On irradiation of 6-cyanophenanthridine (1) (10^{-2}M) and an electron-rich olefin (2) (10^{-1}M) with a 400 W high pressure mercury arc in ethanol under nitrogen, an azetidine derivative (3) and an azocine derivative (4) were afforded in the yields listed below.

The IR and NMR data of 3 and 4 are summarized in Table 1 and Table 2, respectively.

LC analysis and NMR spectroscopy revealed that this photocycloaddition reaction proceeds regiospecifically. 4 was given as a mixture of the two stereoisomers. The molar ratio of A to B is 4:3 in 4a, and 8:5 in 4b. A predominated over B, and the above ratio reflects the ratio of 3 which is the precursor of 4. The irradiation of 1 and 2a in benzene afforded 3a in 52% yield as a mixture of the



Yield Yield

1 2a: R^1=Me 3a: 16% 4a: 84%

R^2=4-Methoxyphenyl 4b: 42%

2b: R^1=H

R^2=PhO

Table 1 IR Data of 3 and 4[1)]

Compd	$\nu_{C\equiv N}$	ν_{MeO}	ν_{N-H}
3a	2250	2860	
4a	2250	2860	3330
4b	2250		3320

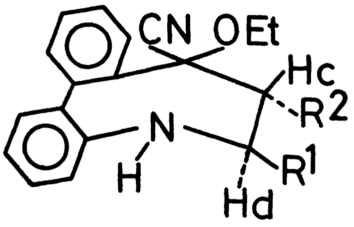
Table 2 NMR Data of 3 and 4[2)]

Compd	Ha	Hb	Hc	Hd	R^1	R^2	NH	OEt	Aromatic H
3aA	2.65	3.46			1.24	3.75			6.75-8.74
	Ja,b=7.2 Hz				(Me)	(MeO)			
3aB	2.83	3.53			1.51	3.79			6.75-8.74
	Ja,b=6.8 Hz				(Me)	(MeO)			
4aA			3.37	3.78	1.21	3.62	3.70	3.70	7.10-8.59
			Jc,d=6.0 Hz		(Me)	(MeO)		1.05	
4aB			3.41	3.81	1.23	3.62	3.70	3.70	7.10-8.59
			Jc,d=6.0 Hz		(Me)	(MeO)		1.05	
4bA			5.12	4.47	4.62		3.39	3.36	6.50-8.47
		Jc,d=6.4 Hz, Jc,e(R^1=H)=7.4 Hz						0.95	
4bB			5.24	4.04	4.17		3.39	3.36	6.50-8.47
		Jc,d=6.4 Hz, Jc,e(R^1=H)=7.4 Hz						0.95	

1) Wavenumber in cm^{-1}

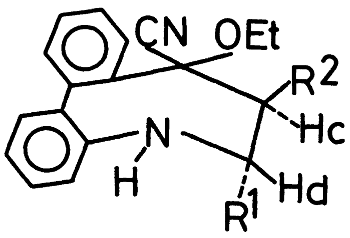
2) δ in ppm, relative to internal TMS

stereoisomers in a 5:2 (3aA:3aB) ratio. As Table 2 shows, the Hb proton of 3aA appeared at the higher field than that of 3aB. This fact can be explained in terms of the diamagnetic anisotropy of the cyano group which is trans to the Hb proton. Although about 50% of recovered anethole (60%) isomerized to its cis form, no



A

4



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incorporation of *cis*-anethole into the cycloadduct was observed. The stereochemical assignment was based on the fact that the methyl protons of the cycloadduct absorb at the magnetic field lower than 1 ppm.[8] This fact suggests that the photoisomerization from 2a to *cis*-anethole competes with the photocycloaddition reaction of 1 to 2a and that the collapse of the exciplex to a biradical which gives a stereoisomeric mixture of the adducts is unfavorable.

The quantum yield for the formation of 3a in benzene was obtained as $\Phi=0.04$.[9] This value is around a tenth as large as that for the formation of the cycloadduct between 9-cyanophenanthrene and 2a.[6]

1,3-Pentadiene did not quench formation of 3a in the photochemical reaction of 1 with 2a in benzene. This fact suggests that 3a is formed via the lowest excited singlet state of 1.

The fluorescence of 1 in ethanol (λ_{max}=410 nm) was quenched efficiently by 2a (K_{SV}=105 M^{-1}), accompanied by a weak exciplex emission at 503 nm. This exciplex emission was attenuated by acrylonitrile, while it did not quench the fluorescence of 1. LC analysis revealed that it also quenched formation of 3a. These facts afford spectroscopic evidence that the exciplex is the precursor of the cycloadduct.

Irradiation of 3a in ethanol under nitrogen for 1 h afforded 4a in 50% yield. This finding supports that 3a is the intermediate of 4a.

Scheme

$$1 \xrightarrow{h\nu} 1^{*} \underset{}{\overset{2}{\rightleftarrows}} (1\cdots2)^{*}_{\text{Exciplex}}$$

$$\longrightarrow 3 \xrightarrow{h\nu,\text{EtOH}} 4$$

Therefore, the mechanism of this photocycloaddition reaction would be written as the above scheme shows.

It is well known that exciplexes dissociate into radical ions in polar solvents.[10)] In this investigation, however, the anti-Markownikov adduct derived from the cation radical of 2a and ethanol was formed only in trace amounts, making contrast to the photochemical reactivity of the exciplex formed between 2a and 6-methylphenanthridine.[11)] When 2b was used, a cyclobutane derivative derived from the cation radical of 2b could be obtained, but its yield is low and its reaction mechanism remains to be seen.

References and Notes

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