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Regioselective Intramolecular Photocycloaddition of 1-Cyano-2-(2-oxa-4-alkenyl)naphthalenes in the Presence of Eu(III) Salt

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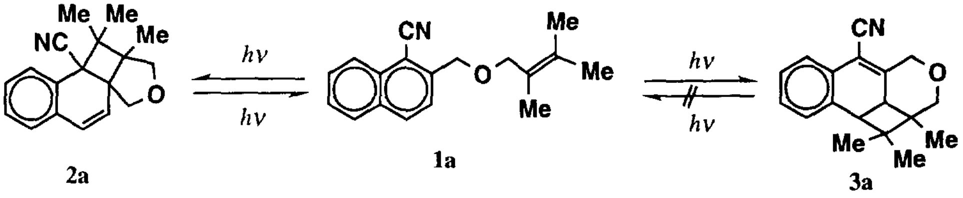
Abstract : Irradiation of 1-cyano-2-(2-oxa-4-alkenyl)naphthalenes in the presence of Eu(hfc)$_3$ regioselectively afforded (2π+2π) intramolecular photocycloadducts at 1,2-position on the naphthalene ring in good yields. The salt and solvent effects in this photoreaction are described.

Inter- and intramolecular photocycloadditions of alkenes to aromatic rings have been extensively investigated from synthetic and mechanistic viewpoints in recent three decades.[1] These are versatile tools for the construction of polycyclic compounds including natural products,[2] which are hardly prepared by other methods. Such photocycloadditions also provide an interesting subject about the structure-reactivity relationship of reactive intermediates such as exciplexes. Therefore, it is very important to develop a highly selective and efficient photocycloaddition of alkenes to aromatic rings. Recently, much attention has been paid to the salt effects on the photoreactions of electron-donor-acceptor systems.[3] However, the role of the salts added is still ambiguous. Previously, McCullough et al. have reported the intramolecular photocycloaddition of 1-cyano-2-(4,5-dimethyl-2-oxa-4-hexenyl)naphthalene **1a** to give two kinds of intramolecular (2π+2π) photocycloadducts **2a** and **3a** in good yields.[4] We have independently found that the product ratio of **2a** to **3a** remarkably depended on the reaction time and salts. We now report the effects of Eu(III) salt and solvents on the intramolecular photocycloaddition of 1-cyano-2-(2-oxa-4-alkenyl)naphthalenes.

In the photoreaction of **1a** in benzene, the cycloadduct **2a** at 1,2-position on the naphthalene ring was predominantly obtained in the initial stage. However, prolonged irradiation afforded the cycloadduct **3a** at the 3,4-position as a major product (Table 1).[4] Under the same irradiation conditions, the isolated **2a** efficiently



$$\mathbf{2a} \overset{h\nu\ /\ \mathrm{Eu(hfc)_3}}{\underset{h\nu\ /\mathrm{Eu(hfc)_3}\ /\ \mathrm{slow}}{\leftrightharpoons}} \mathbf{1a} \xrightarrow[\mathrm{slow}]{h\nu\ /\ \mathrm{Eu(hfc)_3}} \mathbf{3a}$$

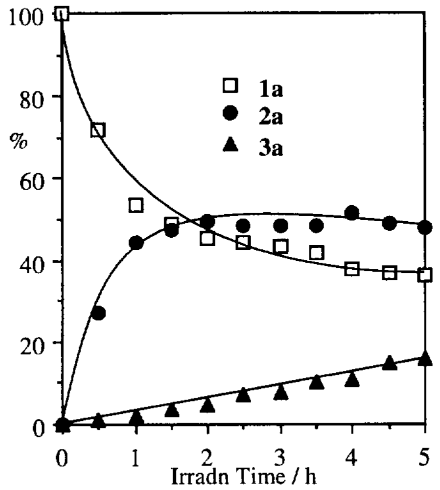


Figure 1. Intramolecular photocycloaddition of **1a** in the absence of Eu(hfc)$_3$ in benzene.

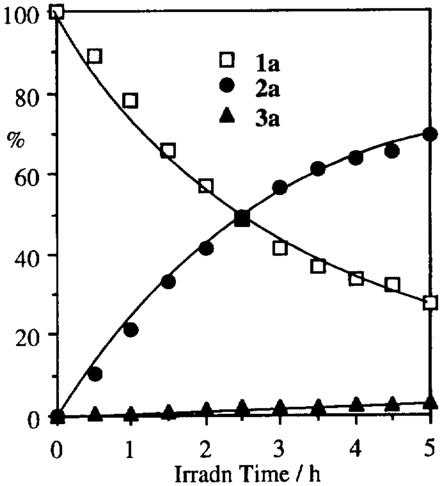
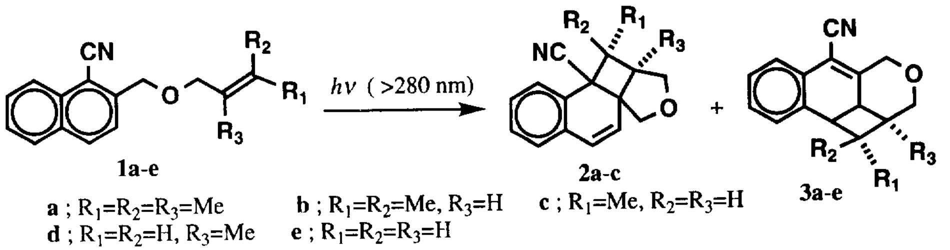


Figure 2. Intramolecular photocycloaddition of **1a** in the presence of 5.0 x 10^{-3} M Eu(hfc)$_3$ in benzene.

cyclorevesed to **1a**,^{5} but **3a** did not. In acetnitrile, this photoreaction proceeded in a similar manner. The addition of Eu(hfc)$_3$ (hfc; tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]) into the reaction system effectively suppressed not only the formation of **3a**, but also the cycloreversion of **2a** (Figs. 1 and 2). The relative quantum yield for the latter reaction was one fifth compared with that in the absence of Eu(hfc)$_3$. The regioselectivity for the formation of photoadduct increased with an increase of the amount of Eu(hfc)$_3$ added. However, Eu(hfc)$_3$ having chirality did not affect the enantioselectivity for the formation of **2a**.^{6}

Irradiations of 1-cyano-2-(5-methyl-2-oxa-4-hexenyl)naphthalene **1b** and trans-1-cyano-2-(2-oxa-4-hexenyl)naphthalene **1c** gave the corresponding (2π+2π) photocycloadducts **2b-c** and **3b-c** both in benzene and acetonitrile (70-80% yields). In these photoreactions, the 1,2-adducts **2b-c** were regioselectively obtained by the addition of Eu(hfc)$_3$. In the case of **1c**, the photocycloaddition has occurred in a stereospecific manner. The photoreactions of 1-cyano-2-(4-methyl-2-oxa-4-pentenyl)naphthalene **1d** and 1-cyano-2-(2-oxa-4-pentenyl)naphthalene **1e** in benzene did not give the corresponding (2π+2π) photocycloadducts **2d-e** and **3d-e** at all, and the starting compounds **1d-e** were almost recovered. In acetonitrile, **3d-e** were slowly produced in good yields (> 70%) and these reactions were accelerated about two times by the addition of Mg(ClO$_4$)$_2$ (5 x 10^{-3} M).^{3} The formation of **3d-e** was suppressed by the addition of Eu(hfc)$_3$ (Table 1).

The relative quantum yields for the formation of **2a+3a**, **2b+3b**, **2c+3c**, **3d**, and **3e** decreased in that



1a-e

2a-c

3a-e

a ; R_1=R_2=R_3=Me **b** ; R_1=R_2=Me, R_3=H **c** ; R_1=Me, R_2=R_3=H

d ; R_1=R_2=H, R_3=Me **e** ; R_1=R_2=R_3=H

Table 1. Salt and Solvent Effects on the Photocycloaddition of **1a** and **1e** [a]

entry	**1**	solvent [b]	irradn time / h	additive ($\times 10^{-3}$ M)	yield / % [c] **2**	yield / % [c] **3**
1	**1a**	benzene	3.0	none	48	16
2	**1a**	benzene	20.0	none	41	44
3	**1a**	benzene	3.0	$\mathrm{Eu(hfc)_3}$ (1.0)	58	7
4	**1a**	benzene	3.0	$\mathrm{Eu(hfc)_3}$ (5.0)	64	3
5	**1e**	benzene	5.0	none	0	0
6	**1e**	acetonitrile	5.0	none	0	45
7	**1e**	acetonitrile	20.0	none	trace	>95
8	**1e**	acetonitrile	5.0	$\mathrm{Eu(hfc)_3}$ (1.0)	0	38
9	**1e**	acetonitrile	5.0	$\mathrm{Eu(hfc)_3}$ (5.0)	0	0
10	**1e**	acetonitrile	5.0	$\mathrm{Mg(ClO_4)_2}$ (5.0)	0	75

[a] [**1a**] = [**1e**] = 3.0×10^{-2} M. [b] 5 mL. [c] GLC yields based on **1** used.

order with a decrease of electron-donating ability of the alkenes. The intermolecular photocycloaddition of less electron-rich alkenes such as 1-butene, 2-butenes, and 2-methyl-2-butene to 1-cyanonaphthalene (1-CN) and 1-cyano-2-methylnaphthalene (MCN) did not occur or inefficiently occurred, although the photocycloaddition of 2,3-dimethyl-2-butene and alkyl or aryl vinyl ethers to 1-CN giving the stereoselective ($2\pi+2\pi$) photocycloadducts was reported.[8]

The photoreaction of **1a-e** was not sensitized by triplet sensitizers such as benzophenone and Michler's ketone (> 350 nm light), and was not quenched by triplet quenchers such as molecular dioxygen and 2-methyl-1,3-butadiene (1 M).

The fluorescence spectra of **1a-e** and MCN in cyclohexane were shown in Fig. 3. The relative intensity of the emissions of **1b-e** decreased with an increase of electron-donating ability of attached alkenes, which must be due to the intramolecular quenching of the fluorescence of cyanonaphthalene chromophore by alkene moeity. In the case of **1a**, a weak exciplex emission[4] appeared at the longer wavelength than the emission of MCN, although the fluorescence of **1b-e** did not show any appreciable exciplex.

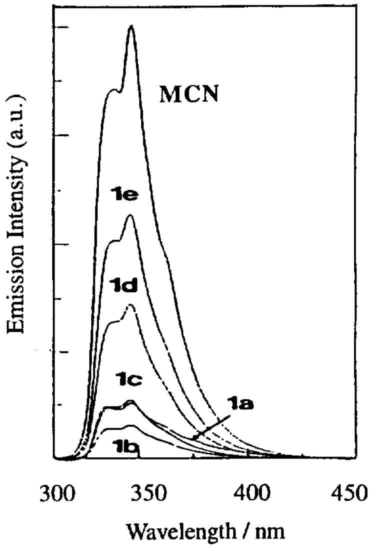
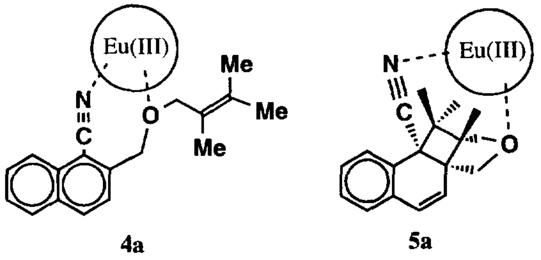


Figure 3. Fluorescence spectra of **1a-e** and MCN in cyclohexane ([**1**] = [MCN] = 1×10^{-4} M).

From these results, the photocycloaddition of **1a-e** can be reasonably explained by the intramolecular exciplex mechanism. The regioselective photocycloaddition of **1a** to **2a** and the photocycloreversion of **2a** to **1a** were remarkably affected by the addition of Eu(hfc) , which must be attributed to the coordination of Eu(hfc)$_3$ to the cyano and ether groups of **1a** and **2a** to generate **4a** and **5a** as postulated in Scheme 1. This explanation was supported by the observation that several protons interacted with Eu(hfc)$_3$ as a ^{1}H NMR shift reagent appeared in the lower field compared with those in the absence of Eu(hfc)$_3$.

The reactivity of **1d-e** can be explained by the charge transfer (CT) nature of the exciplex between the cyanonaphthalene chromophore and alkenes in polar solvents. The addition of Mg(ClO$_4$)$_2$ also accelerated the rate for the formation of **3e** probably via this CT interaction of intramolecular exciplex.



Scheme 1

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6. Two enantiomers of **2a** were separated by HPLC (CHIRALCEL OD), but those of **3a** were not separated.
7. **2a**: mp 140-141 °C (lit.[4] 141.5-142.5 °C); **3a**: mp 119-120 °C (lit.[4] 119-120 °C); **2b**: oil; **3b**: mp 125-126 °C; **2c**: oil; **3c**: mp 93-95 °C; **3d**: mp 123-125 °C; **3e**: mp 121-122 °C.
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