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LETTERS

Intramolecular [3+2]-Photocycloadditions of Alkenyl Methyl 1,4-Naphthalenedicarboxylates

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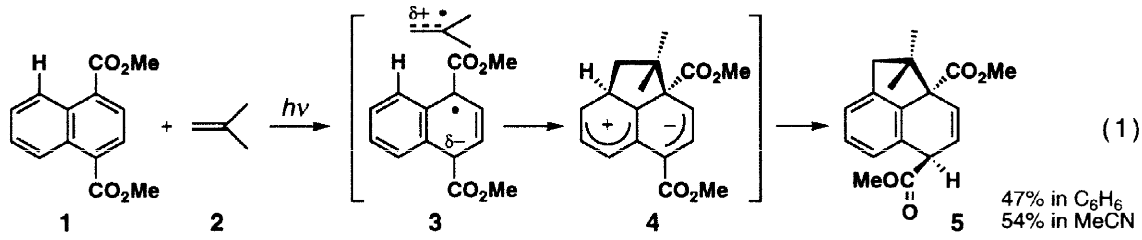
Abstract: Intramolecular [3+2]-photocycloadditions of alkenyl methyl 1,4-naphthalenedicarboxylates, which contain rather remote alkene moieties corresponding to isobutene or α-methylstyrene, proceeded largely depending on the chain lengths to give [3+2]-adducts having nine- to eleven-membered ring systems as well as the characteristic five-membered ring structures. Intramolecular quenching of the fluorescence of the diester moiety by the alkene moiety was observed in response to the occurrence of the [3+2]-photocycloadditions.

Keywords: Photochemistry; Cycloadditions; Esters; Alkenes

Intramolecular photochemical strategy has been recognized to be a highly valuable for the design and generation of complex medium- to macrocyclic naturally occurring compounds [1,2], and [2+2]-cycloadditions are among the most utilized synthetic photoreactions [3,4]. Other photocyclizations that have found its way into the synthetic approaches of medium- to macrocycles are oxetane formations [5], ring contractions [6], Norrish type I reactions [7], hydrogen abstractions [8,9], aromatic substitutions [2], and photoinitiated electron transfer cyclizations [10,11].

We have studied a novel 1,8-photoaddition of alkenes, such as isobutene (**2**), to dimethyl 1,4-naphthalenedicarboxylate (**1**), a formal [3+2]-photocycloaddition, which proceeds stereospecifically possibly from the singlet excited state of **1** via a formation of an exciplex **3** and an almost synchronous two bond formation in **1** to give a zwitterionic intermediate **4** followed by proton transfer (eq 1) [12].



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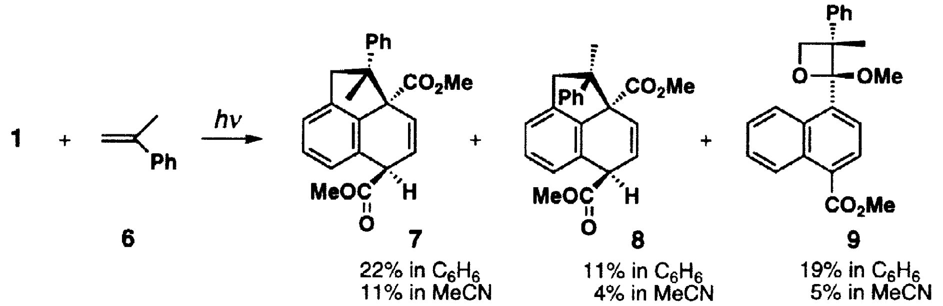
In this letter, we report on intramolecular photoreactions of series of alkenyl methyl 1,4-naphthalenedicarboxylates, in which alkene moieties corresponding to **2** or α-methylstyrene (**6**) are linked to the diester moiety with chains of various lengths. The corresponding intermolecular photoreactions of **1** and **2** gave a [3+2]-adduct **5** (eq 1) and those of **1** and **6** simultaneously afforded two stereoisomeric [3+2]-adducts **7**,**8** as the main products and an oxetane **9** as a minor product (eq 2).



(2)

Results of the intramolecular photoreactions of two series of alkenyl esters **10** (n=1-3) and **11** (n=2-6), which contain an alkene moiety corresponding to **2**, are summarized in Scheme 1. On irradiation of benzene or acetonitrile solutions of **10** (n=1-3) (1×10^{-3} mol/dm^3) with a high-pressure Hg lamp through an uranium filter (> 320 nm) under a nitrogen atmosphere no reactions were observed despite its chain length. On the other hand, in the photoreactions of **11** (n=2-6) having longer chains compared with **10** (n=1-3) intramolecular [3+2]-cycloadditions were found to proceed only in the cases of n = 3, 4, and 5 to give adducts **12** (n=3-5) in moderate yields, while in the cases of n = 2 and 6 no photoreactions were observed. The adducts were isolated by column chromatography on silica gel. Their structures were assigned on the basis of their spectral properties, especially of the similarity of the ^{1}H NMR spectra of **12** (n=3-5)[2] to that of **5**. Furthermore, the NOE investigations showed that one of the vinyl hydrogens was in close proximity to the methyl group attached to the five-membered ring.

Results of the photoreactions of a series of alkenyl esters **13** (n=2-5), which contain an alkene moiety corresponding to **6**, are summarized in Scheme 2. The results clearly showed that the photoreactions were almost completely controlled by the chain lengths. Thus, in the case of n = 2 an exclusive intramolecular oxetane formation was observed to give **14** in almost quantitative yields. On the contrary, in the cases of n = 3, 4, and 5 only intramolecular [3+2]-cycloadditions proceeded to afford adducts **15** (n=3-5) in good yields. The structures of the products were also assigned on the basis of their spectral properties, especially of the similarity of the ^{1}H NMR spectra of **14**[2] to that of **9**, and of those of **15** (n=3-5)[2] to that of **8**.

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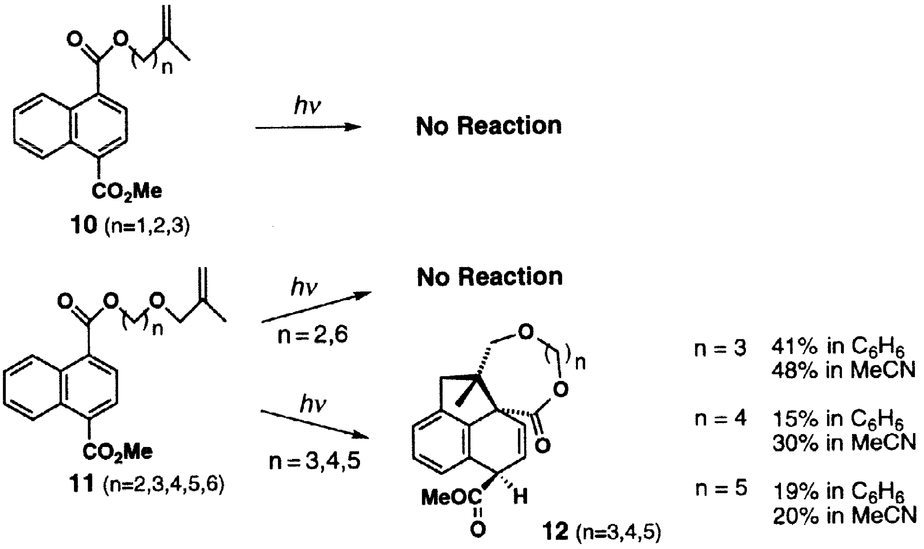
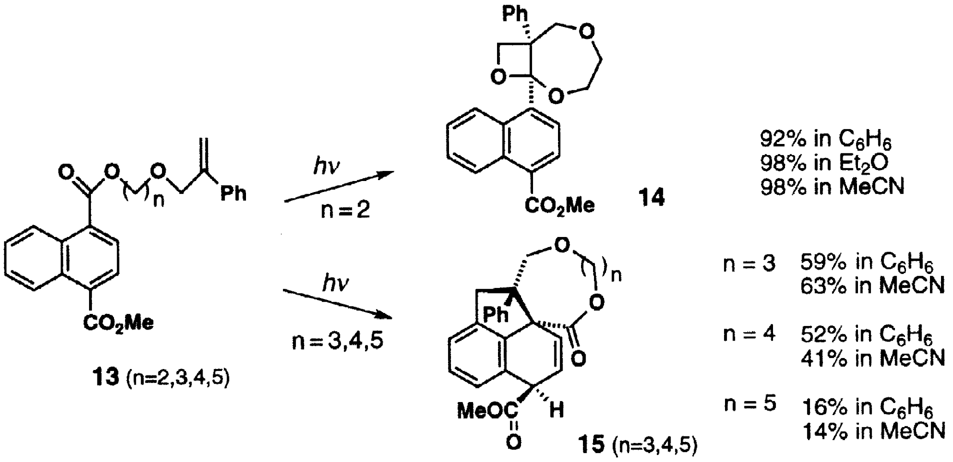
[2] ^{1}H NMR (CDCl$_3$, 270 MHz): **12** (n=3); δ 0.76 (s, 3H), 3.82 (s, 3H), 1.85 (m, 1H), 3.85 (ddd, *J* = 4.4, 8.3, 11.3 Hz, 1H), 1.98 (m, 1H), 4.05 (ddd, *J* = 3.4, 7.3, 11.8 Hz, 1H), 2.29 (d, *J* = 15.1 Hz, 1H), 4.29 (dd, *J* = 1.7, 2.9 Hz, 1H), 3.51 (ddd, *J* = 2.9, 6.9, 11.8 Hz, 1H), 4.83 (ddd, *J* = 5.0, 5.0, 11.3 Hz, 1H), 3.69 (d, *J* = 10.4 Hz, 1H), 6.09 (dd, *J* = 1.7, 9.8 Hz, 1H), 3.74 (d, *J* = 15.1 Hz, 1H), 6.30 (dd, *J* = 2.9, 9.8 Hz, 1H), 3.79 (d, *J* = 10.4 Hz, 1H), 7.06-7.23 (m, 3H): **14**; δ 3.86 (s, 3H), 3.86 (ddd, *J* = 1.5, 1.9, 13.3 Hz, 1H), 3.97 (ddd, *J* = 1.9, 11.2, 13.3 Hz, 1H), 4.16 (ddd, *J* = 1.5, 1.9, 13.3 Hz, 1H), 4.85 (ddd, *J* = 1.9, 11.2, 13.3 Hz, 1H), 4.17 and 4.66 (ABq, *J* = 13.4 Hz, 2H), 4.81 and 5.23 (ABq, *J* = 6.4 Hz, 2H), 6.62-6.92 (m, 5H), 7.26-7.38 (m, 2H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 8.16-8.24 (m, 1H), 8.54-8.62 (m, 1H): **15** (n=3); δ 1.93-2.10 (m, 2H), 2.98 (d, *J* = 16.1 Hz, 1H), 3.68 (m, 1H), 3.71 (s, 3H), 3.94 (m, 1H), 3.95 (d, *J* = 9.9 Hz, 1H), 4.12 (d, *J* = 16.1 Hz, 1H), 4.15 (m, 1H), 4.18 (dd, *J* = 1.7, 2.9 Hz, 1H), 4.60 (d, *J* = 9.9 Hz, 1H), 4.90 (ddd, *J* = 5.4, 5.4, 10.8 Hz, 1H), 5.74 (dd, *J* = 1.7, 9.8 Hz, 1H), 6.00 (dd, *J* = 2.9, 9.8 Hz, 1H), 6.90-7.14 (m, 5H), 7.25-7.31 (m, 3H) ppm.



Scheme 1



Scheme 2

Observed preference for n = 3, 4, and 5 in the intramolecular [3+2]-photocycloaddition of **13** (n=2-5) corresponds well to that in the reactions of **11** (n=2-6).

While the UV spectra of **13** (n=3-5), which gave the [3+2]-adducts in the photoreactions, were the almost identical with that of **1** in benzene, the spectrum of **13** (n=2), which afforded the oxetane, showed a broad weak absorption band in a longer wavelengths region (340-370 nm) compared with that of **1** possibly due to the intramolecular CT complex formation between the alkene and the diester moieties.

On the other hand, the fluorescence spectra of **1** and **13** (n=2-5) in benzene are shown in Figure 1. Interestingly the fluorescence spectrum of **13** (n=2) was shifted to longer wavelength compared with those of **1** and the other alkenyl esters **13** (n=3-5) in consistent with the CT complex formation of **13** (n=2) speculated by the UV examinations. In the cases of **13** (n=3-5) only intramolecular fluorescence quenching was observed and the quenching became less efficient with increase of the chain lengths. From the fluorescence spectra of **1** and **13**

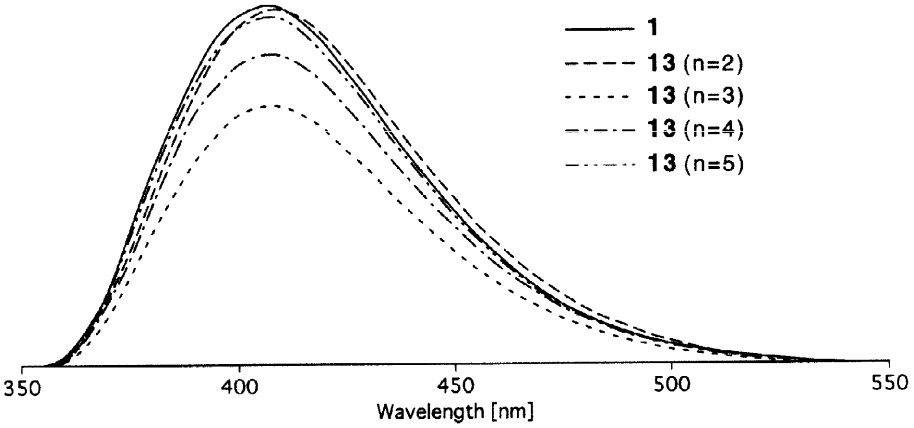


Figure 1. Fluorescence spectra of **1** and **13** (n=2-5) in benzene ([**1**] = [**13** (n=2-5)] = 1×10^{-4} mol/dm^3).

(n=3-5), the intramolecular fluorescence quenching rate constants k_q, assuming that the process is irreversible, can be calculated to be 4.8×10^7, 2.0×10^7, and 3.6×10^6 s^{-1} for **13** n = 3, 4, and 5, respectively, by using $\Phi_0/\Phi = 1 + k_q\tau$, where Φ_0 is the quantum yield of the fluorescence of **1**, Φ is that of **13** (n=3-5), and τ is the lifetime of the singlet excited state of **1** (8.2 ns in benzene) [12].

In summary, the formation of medium-sized, nine- to eleven-membered, ring systems as well as the characteristic five-membered ring structures can be attained by the intramolecular [3+2]-photocycloadditions of alkenyl methyl 1,4-naphthalenedicarboxylates. Thus, synthetic potentials of the intramolecular [3+2]-photocycloadditions would be emphasized. Furthermore, the reactions, the [3+2]-cycloaddition and the oxetane formation, were found to be almost completely controlled by the chain lengths in the photoreactions of the alkenyl esters **13** (n=2-5), while the reactions simultaneously occurred in the intermolecular counterparts (eq 2). The intramolecular fluorescence quenching was observed in **13** (n=3-5) in response to the occurrence of the [3+2]-photocycloadditions. The results may indicate that the [3+2]-cycloadditions directly occur from the singlet excited state of the diester moiety, and that the oxetane formation from the excitation of the intramolecular CT complex.

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