

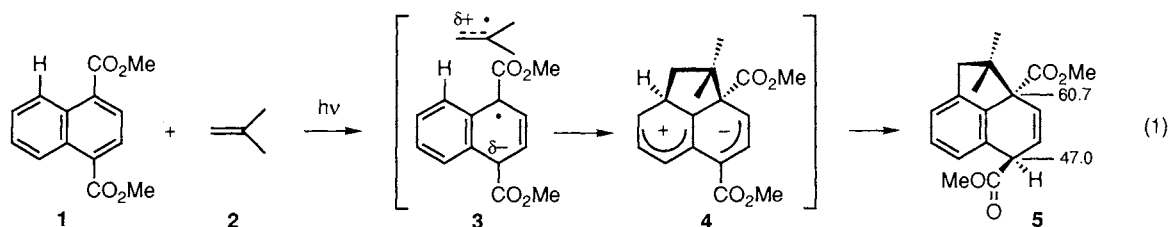
A Novel 1,8-Photoaddition of Methyl 4-Cyanonaphthalenecarboxylate
and 1,4-Naphthalenedicarbonitrile to Alkenes

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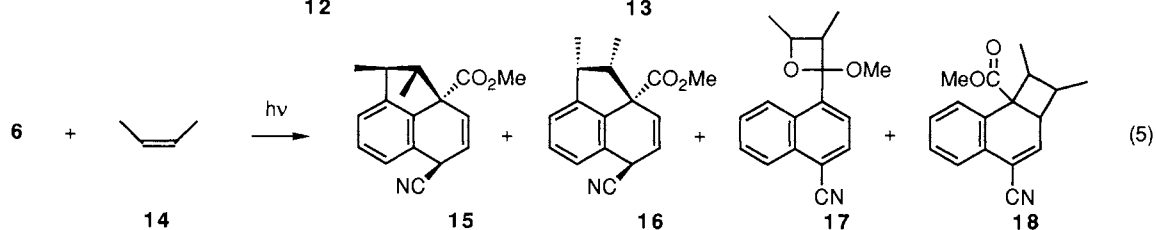
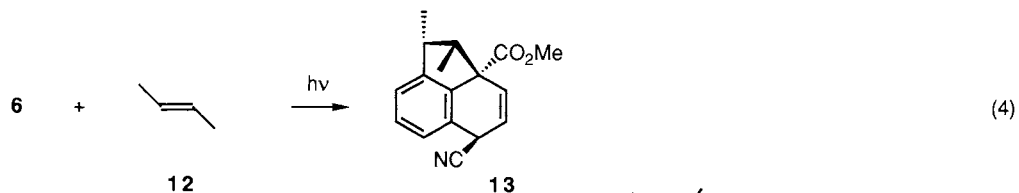
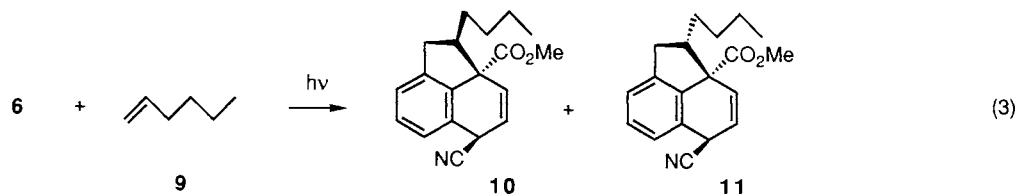
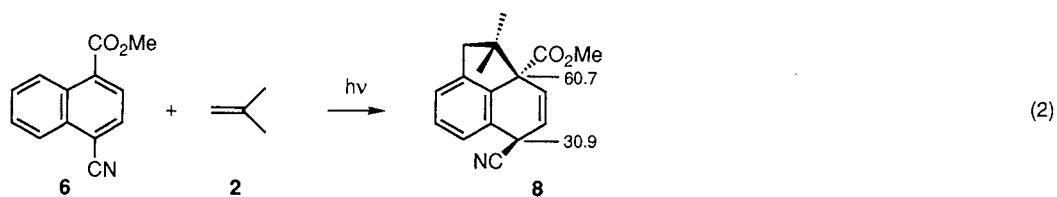
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A novel 1,8-photoaddition of methyl 4-cyano-1-naphthalenecarboxylate and 1,4-naphthalenedicarbonitrile to alkenes with high ionization potentials, a formal [3 + 2] photoaddition, was found to proceed stereospecifically possibly via a unique zwitter-ionic intermediate.

Photoadditions of aromatic compounds to alkenes have been extensively investigated for the elucidation of the role of exciplexes and for the exploitation of the synthetic potentials, but considerable interest is still evident.¹⁾ For naphthalene derivatives, a number of instances of 1,2- and 1,4-photoaddition have been reported, but other types of photoaddition have seldom been observed. We have found a novel 1,8-photoaddition of dimethyl 1,4-naphthalenedicarboxylate (**1**) to alkenes with high ionization potentials,²⁾ a formal [3 + 2] photoaddition,³⁾ which proceeds



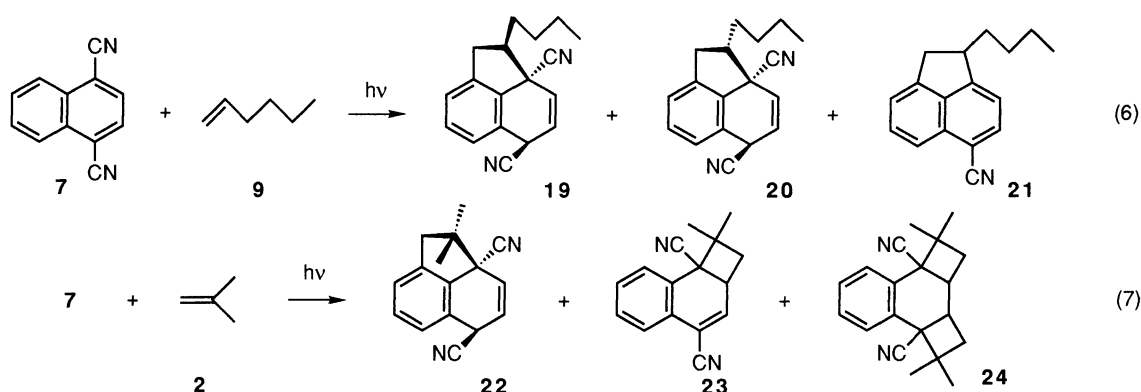
stereospecifically possibly via an exciplex **3** and a unique zwitter-ionic intermediate **4** (Eq. 1). Here, we report on the 1,8-photoaddition of methyl 4-cyano-1-naphthalenecarboxylate (**6**) and 1,4-naphthalenedicarbonitrile (**7**) to alkenes. Although **7** has been used in a large number of photochemical studies as one of the most typical acceptors,⁴⁾ no reports concerning the 1,8-photoaddition to alkenes have appeared so far. The results clearly indicate that the 1,8-photoaddition is fairly general in photoreactions of arenecarbonitriles and alkenes with high ionization potentials as well as in the photoreactions of **1** and alkenes.



Irradiation (>340 nm)⁵⁾ of **6** (4.7 mM, 1 mM = 1×10^{-3} mol dm⁻³) in the presence of isobutene (**2**) (1 M) in N₂-purged benzene led to efficient (71%) production of a 1,8-adduct **8** (Eq. 2). The structure and stereochemistry of **8** were assigned on the basis of the NMR⁶⁾ spectral resemblance to the 1,8-adduct **5** obtained from the reaction of **1** with **2**.²⁾ A smaller chemical shift value ($\delta = 30.9$) of the α -carbon to the cyano group in **8** compared with that ($\delta = 47.0$) of the corresponding carbon in **5** clearly indicates the position of the cyano group in **8**.

Irradiation of **6** (4.7 mM) in the presence of 1-hexene (**9**) (0.8 M) in benzene gave a 1,8-adduct **10** (60%) (Eq. 3). Reactions also proceeded in ether and in acetonitrile to give **10** (40% and 52%, respectively) and **11** (9% and 9%, respectively).

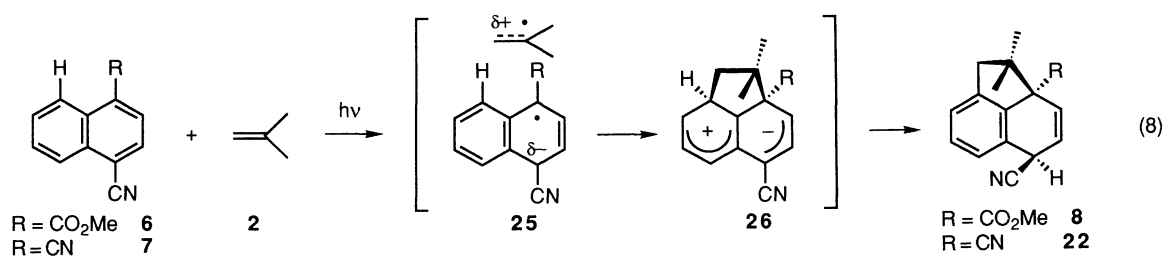
The 1,8-photoaddition of **6** was found to proceed with retention of the stereochemistry of alkenes in a manner similar to that of **1**.²⁾ Thus, irradiation of **6** (4.7 mM) in the presence of trans-2-butene (**12**) (1 M) in ether gave **13** (45%) and that in the presence of cis-2-butene (**14**) (1 M) afforded **15** (24%) and **16** (12%) (Eqs. 4, 5). A pair of stereoisomers of oxetanes **17** (15 + 9%) and a cyclobutane **18** (7%) were also obtained together with **15** and **16** in the reaction in the presence of **14**. None of the corresponding oxetanes and cyclobutanes were obtained in the photoreaction



of **6** in the presence of **2**, **9**, or **12**. The structures and stereochemistry of **13**, **15**, and **16** were also assigned on the basis of the NMR spectral resemblance to the corresponding 1,8-adducts obtained from the reaction of **1** with **12** and **14**.²⁾

The 1,8-photoaddition was found to proceed also in reactions of **7**. Thus, irradiation of **7** (5.6 mM) in the presence of **9** (0.8 M) in ether gave 1,8-adducts **19** (38%) and **20** (6%) (Eq. 6). The reaction also proceeded in acetonitrile to give an aromatized product **21** (42%) with loss of HCN. Irradiation of **7** (5.6 mM) in the presence of **2** (1 M) in ether gave a 1,8-adduct **22** (14%) together with cyclobutanes **23** (11%) and **24** (13%) (Eq. 7). Arnold and his coworkers reported that 1,4-dicyano-2,3-benzotricyclo[3.3.1.0^{4,7}]nonane derivatives were obtained in the photoreaction of **7** and 2,3-dimethyl-2-butene in acetonitrile via initial photochemical electron transfer from 2,3-dimethyl-2-butene to **7**.^{4a)} No such products were obtained in the photoreaction of **7** in the presence of **2** or **9**.

There is no evidence on the UV spectra for a preformed ground-state complex between **6** and alkenes, and also between **7** and alkenes. Thus, the 1,8-addition proceeds from the singlet excited state of **6** and **7**, as suggested by the stereospecificity observed in the reactions of **6** in the presence of **12** and **14**. Fluorescence of **6** and **7** is inefficiently but significantly quenched by alkenes to support the singlet mechanism.⁷⁾ Application of the Rehm-Weller equation⁸⁾ suggests that the electron



transfer from alkenes to the singlet excited states of **6** and **7** is mostly endothermic.⁹⁾ Thus, the 1,8-photoaddition may proceed via an exciplex **25**, in which the alkene moiety has some radical cationic nature and the nitrile moiety some radical anionic nature (Eq. 8). Almost synchronous two-bond formation, namely coupling between the radical center in the alkene moiety and that (1-position of the naphthalene ring) in the nitrile moiety, and electrophilic attack of the cationic center of the alkene moiety at 8-position of the naphthalene ring of the nitrile moiety, may thus proceed within **25** to give a zwitter-ionic intermediate **26** which gives the final products **8** and **22** upon proton transfer.

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References

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- 2) Y. Kubo, T. Inoue, and H. Sakai, J. Am. Chem. Soc., 114, in press (1992).
- 3) Formal [3 + 2] photoaddition has seldom been reported. See, for example, H. -J. Rathjen, P. Margaretha, S. Wolff, and W. C. Agosta, J. Am. Chem. Soc., 113, 3904 (1991) and references therein.
- 4) a) D. R. Arnold, P. C. Wong, A. J. Maroulis, and T. S. Cameron, Pure Appl. Chem., 52, 2609 (1980); b) W. Xu, X. Zhang, P. S. Mariano, J. Am. Chem. Soc., 113, 8863 (1991).
- 5) Irradiation was carried out with a Hg-lamp through a uranium-filter.
- 6) **8**: ¹H NMR (CDCl₃) δ= 0.76 (s, 3H), 1.25 (s, 3H), 2.50 and 3.33 (ABq, J= 15.1 Hz, 2H), 3.57 (s, 3H), 4.41 (dd, J= 2.0, 3.3 Hz, 1H), 6.06 (dd, J= 2.0, 9.5 Hz, 1H), 6.32 (dd, J= 3.3, 9.5 Hz, 1H), 7.1-7.4 (m, 3H); ¹³C NMR (CDCl₃) δ= 23.66 (q), 25.09 (q), 30.87 (d), 46.79 (t), 49.21 (s), 51.99 (q), 60.70 (s), 119.07 (s), 123.15 (d), 123.60 (d), 124.55 (d), 128.31 (d), 128.43 (d), 130.40 (s), 139.25 (s), 142.40 (s), 172.12 (s).
- 7) Fluorescence quenching rate constants by **9** in air-saturated ether were 2.1X10⁷ and 3.2X10⁷ dm³ mol⁻¹ s⁻¹ for **6** and **7**, respectively.
- 8) D. Rehm and A. Weller, Isr. J. Chem., 8, 259 (1970).
- 9) The ΔG_{et} values from **2** and **9** to the singlet excited state of **6** in acetonitrile are 0.9 and 6.7 kcal mol⁻¹, and those from **2** and **9** to the singlet excited state of **7** are -1.5 and 4.2 kcal mol⁻¹, respectively.

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