A novel intramolecular photocyclization of methyl 2-(2,3-dimethylbut-2-enyloxymethyl)naphthalene-1-carboxylate *via* 1,9-hydrogen abstraction

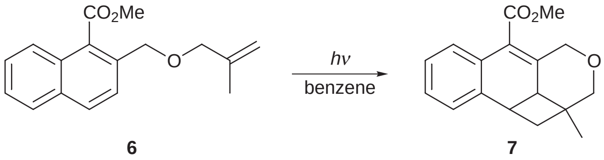
Kazuhiko Mizuno,*† Shin-ichi Konishi, Yasuharu Yoshimi and Akira Sugimoto

Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

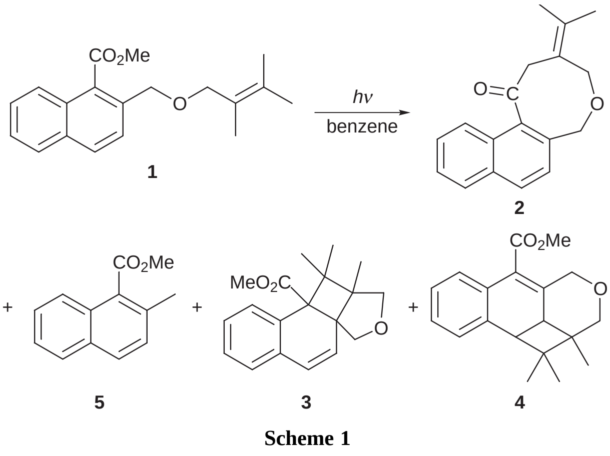
Irradiation of a benzene solution containing methyl 2-(2,3-dimethylbut-2-enyloxymethyl)naphthalene-1-carboxylate 1 gave an eight-membered keto ether 2 as the main product *via* a novel 1,9-hydrogen abstraction of the ester carbonyl group.

Photochemical hydrogen abstraction reactions have been extensively investigated from synthetic and mechanistic viewpoints.[1] Intramolecular long-range hydrogen abstraction such as 'remote oxidation' is one of the most attractive subjects in the photochemistry of carbonyl groups.[2] However, little is known about the hydrogen abstraction of an excited state of an ester carbonyl group except for an intramolecular 1,5-hydrogen abstraction *via* a 6-membered transition state.[3] Intermolecular hydrogen abstraction has also been reported as a rare case although the efficiency was quite low.[4] We now report a novel intramolecular 1,9-hydrogen abstraction of an ester carbonyl group to give an eight-membered keto ether *via* an exciplex.

Irradiation of a benzene solution containing methyl 2-(2,3-dimethylbut-2-enyloxymethyl)naphthalene-1-carboxylate **1** through a Pyrex filter (> 280 nm light) under an argon atmosphere gave **2** as the main product accompanied by $(2\pi + 2\pi)$ photocycloadducts **3** and **4** and C–O bond cleavage product **5** (Scheme 1). Similar irradiation of **1** in MeCN also gave **2**, but **5** was mainly obtained (Table 1). Irradiation of **6** in benzene did not afford the corresponding eight-membered ring compound, but instead gave $(2\pi + 2\pi)$ photocycloadduct **7** in low yield (Scheme 2).



Scheme 2



Scheme 1

Table 1 Yields for photoreaction of **1** in benzene and MeCN

	Yield (%)[a]			
Solvent	**2**	**3**	**4**	**5**
Benzene	48	6	33	13
MeCN	10	< 5	< 5	80

[a] Yields based on unrecovered **1** were determined by GLC analysis after irradiation with a 500 W high-pressure mercury lamp for 100 h.

The products were isolated by column chromatography on silica gel. The structure of **2** was determined from its spectral data.‡ The FT-IR spectrum of **2** showed the disappearance of the ester carbonyl group of **1** at 1743 cm^{-1} and the appearance of an aromatic carbonyl group at 1682 cm^{-1}. The ^{1}H NMR spectrum showed the existence of three kinds of methylene group, two nonequivalent methyl groups and six aromatic protons. These data indicate the elimination of MeOH from the starting material **1**. Finally, the structure of **2** was confirmed by X-ray crystallography (Fig. 1). The structures of $(2\pi + 2\pi)$ photocycloadducts **3** and **4** were determined from their spectral properties and comparison with the intramolecular photocycloadducts obtained from 2-(2,3-dimethylbut-2-enyloxymethyl)naphthalene-1-nitrile, previously reported by McCullough *et al.*[5] and by us.[6]

The formation of the eight-membered keto ether **2** and the photocycloadducts **3** and **4** was not sensitized by the addition of 0.1 mol dm^{-3} of Michler's ketone (E_T = 275 kJ mol^{-1}),[7] and was not quenched by 0.5 mol dm^{-3} of 2-methylbuta-1,3-diene (E_T = 251 kJ mol^{-1})[7] and molecular dioxygen. The relative intensity of the fluorescence of **1** in cyclohexane was smaller than that of methyl naphthalene-1-carboxylate. This is due to the intramolecular quenching of the fluorescence of the methyl naphthalene-1-carboxylate chromophore by the alkene moiety, although an intramolecular exciplex emission between the methyl naphthalene-1-carboxylate chromophore and the 2,3-dimethylbut-2-ene chromophore was not observed. When the

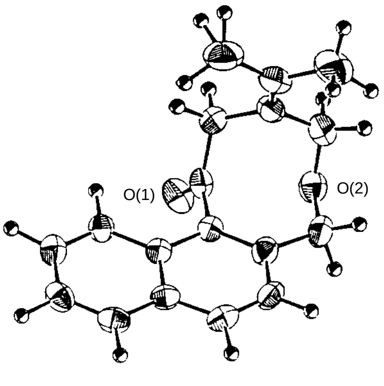
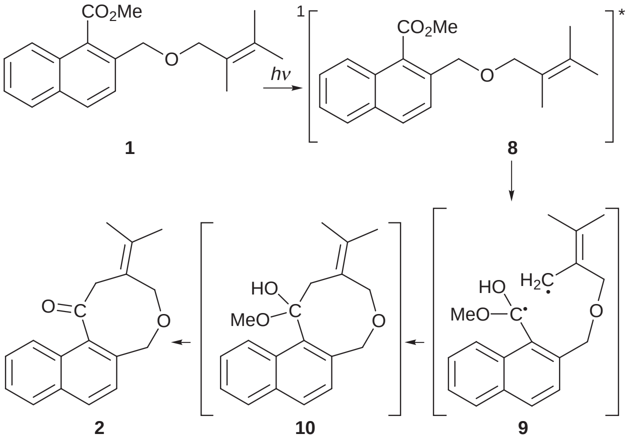


Fig. 1 X-Ray crystal structure of **2**



Scheme 3

fluorescence lifetime of **1** was measured by single photon counting in cyclohexane, the major component (short-lived, < 0.3 ns) was assigned to the methyl naphthalene-1-carboxylate moiety and the minor component (long-lived, 5.8 ns) to the singlet exciplex, because the fluorescence lifetime of methyl naphthalene-1-carboxylate has a value of 1.3 ns.

From these results, we propose the mechanism for the formation of the eight-membered keto ether shown in Scheme 3. The first step is the formation of an intramolecular exciplex **8** *via* the excited singlet state of the methyl naphthalene-1-carboxylate chromophore. The second step is the abstraction of an allylic hydrogen by the ester carbonyl group followed by radical coupling of **9** to give the hemiacetal **10**, which then eliminates MeOH to afford the eight-membered keto ether **2**. Although intramolecular 1,5-hydrogen abstraction by an ester carbonyl group *via* a six-memebered transition state is known, long-range intramolecular hydrogen abstraction has never been reported. The exciplex **8** also gives (2π + 2π) photocycloadducts **3** and **4**. The cleavage product **5** is probably produced *via* **9**. In the photoreaction of **1**, the charge transfer nature of the intramolecular exciplex plays an important role in the novel intramolecular 1,9-hydrogen abstraction. It is because the ester carbonyl group of **6** has a less electron donating alkene that it did not abstract the allylic hydrogen. In MeCN, the formation of the eight-membered keto ether **2** is observed in trace amounts, but the C–O bond cleavage product **5** was mainly obtained. This is reasonably explained by a photoinduced electron transfer process.[8]

We are indebted to Professor T. Takata and Emeritus Professor H. Inoue (Osaka Prefecture University) for helpful discussions. This work is partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan, and the Nagase Science and Technology Foundation.

Notes and References

† E-mail: mizuno@chem.osakafu-u.ac.jp

‡ *Selected data* for **2**: mp 172–173 °C; δ_H(270 MHz, $CDCl_3$) 7.82–7.69 (m, 3 H), 7.50–7.45 (m, 2 H), 7.07 (d, J 8.54, 1 H), 4.89 (br s, 2 H), 4.41 (s, 2 H), 3.51 (s, 2 H); δ_C(68 MHz, $CDCl_3$) 135.5, 133.8, 132.5, 132.2, 129.2, 128.8, 128.2, 127.2, 125.9, 125.8, 123.7, 121.9, 73.5, 73.4, 48.4, 20.8, 20.2; ν_{max}(KBr)/cm^{-1} 1682; *m*/*z* 266 (M$^+$).

Crystal data for **2**: $C_{18}H_{18}O_2$, M = 266.34, monoclinic, space group $P2_1/n$ (#14), a = 8.6862(6), b = 12.468(2), c = 13.468(1) Å, β = 105.418(7)°, V = 1406.0(3) Å^3, Z = 4, D_c = 1.258 g cm^{-3}, T = 296 K, μ = 0.80 cm^{-1}, $F(000)$ = 568, crystal size = 0.650 × 0.600 × 0.330 mm, Rigaku AFC5R diffractometer. Final R value was 0.038 for 2105 reflections (R_w = 0.043). CCDC 182/914.

1 For a review, see: P. J. Wagner, *Acc. Chem. Res.*, 1971, **4**, 168; 1983, **16**, 461; 1989, **22**, 83.

2 For a review, see: R. Breslow, *Acc. Chem. Res.*, 1980, **13**, 170.

3 R. M. Duhaime, D. A. Lombardo, I. A. Skinner and A. C. Weedon, *J. Org. Chem.*, 1985, **50**, 873; T. Gomibuchi, K. Fujiwara, T. Nehira and M. Hirama, *Tetrahedron Lett.*, 1993, **34**, 5753.

4 K. Fukui and Y. Odaira, *Tetrahedron Lett.*, 1969, **10**, 2887.

5 J. J. McCullough, W. K. MacInnis, C. J. L. Lock and R. Faggiani, *J. Am. Chem. Soc.*, 1982, **104**, 4644.

6 K. Mizuno, S. Konishi, T. Takata and H. Inoue, *Tetrahedron Lett.*, 1996, **37**, 7775.

7 Methyl naphthalene-1-carboxylate (E_T = 256 kJ mol^{-1}); S. L. Murov, I. Carmichael and G. L. Hug, *Handbook of Photochemistry*, Marcel Dekker, New York, 1993, p. 17, 76 and 77.

8 Photocleavage reaction *via* photoinduced electron transfer: F. D. Saeva, in *Photoinduced Electron Transfer I*, ed. J. Mattay, Springer-Verlag, Berlin, 1990, pp. 59–92.

Received in Cambridge, UK, 18th May 1998; 8/03711F