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Alcohol-Incorporated Photoaddition of Alkenes to 1,2-Naphthalenedicarboxylic Anhydride

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Irradiation of 1,2-naphthalenedicarboxylic anhydride (**1**) with alkenes in methanol-benzene or in methanol-acetonitrile gave methanol-incorporated adducts at a carbonyl carbon atom in **1** and those at a naphthalene ring carbon atom in **1**.

The area of electron transfer photochemistry has received much attention with regard to both synthetic and mechanistic aspects in organic photochemistry.[1)] During the course of investigations of the photochemistry of imides, a wide variety of alcohol (solvent)-incorporated intramolecular cyclization[2)] and intermolecular addition reactions[3)] in the photoreactions of arenedicarboximide-alkene systems, via an electron transfer process, has been found. However, compounds employed in the previous investigations have been confined to arenedicarboximides, and little information has been reported on the reaction of other acid derivatives.

Here, we report on the first example of methanol-incorporated photoaddition of an arenedicarboxylic anhydride-alkene system and the results may indicate that in the photoreactions with electron donors arenedicarboxylic anhydrides can act as potent electron acceptors comparable to arenedicarboximides. To our knowledge, few systematic investigations on the photochemistry of arenedicarboxylic anhydrides have been carried out in spite of the fundamental simplicity and importance of anhydrides. Only photodecomposition in gas phase,[4)] oxetane formation from photoexcited charge-transfer complexes,[5)] and photoinsertion of alkenes into C(=O)-O bond of anhydrides have been reported.[6)]

Irradiation (>340 nm)[7)] of 1,2-naphthalenedicarboxylic anhydride (**1**)

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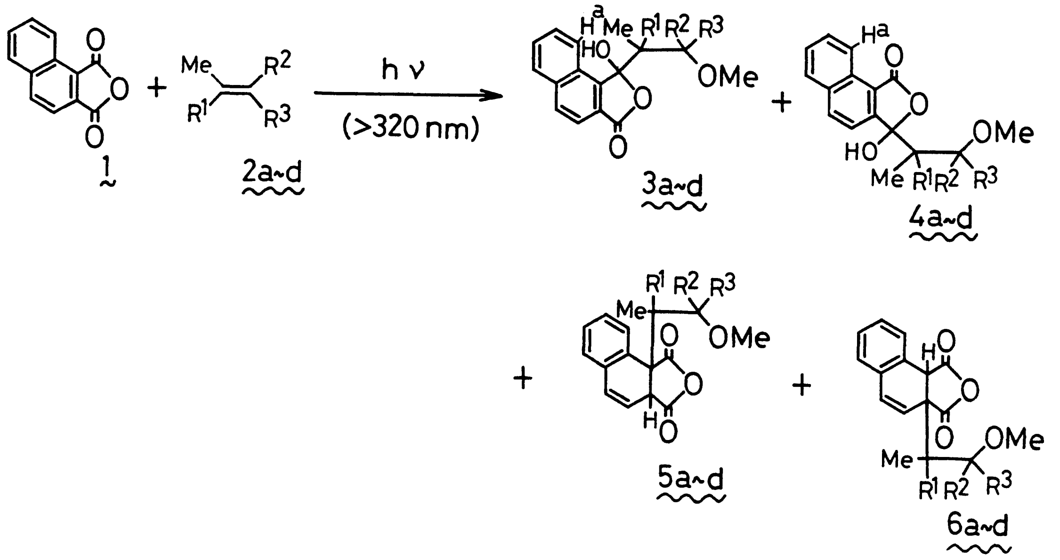


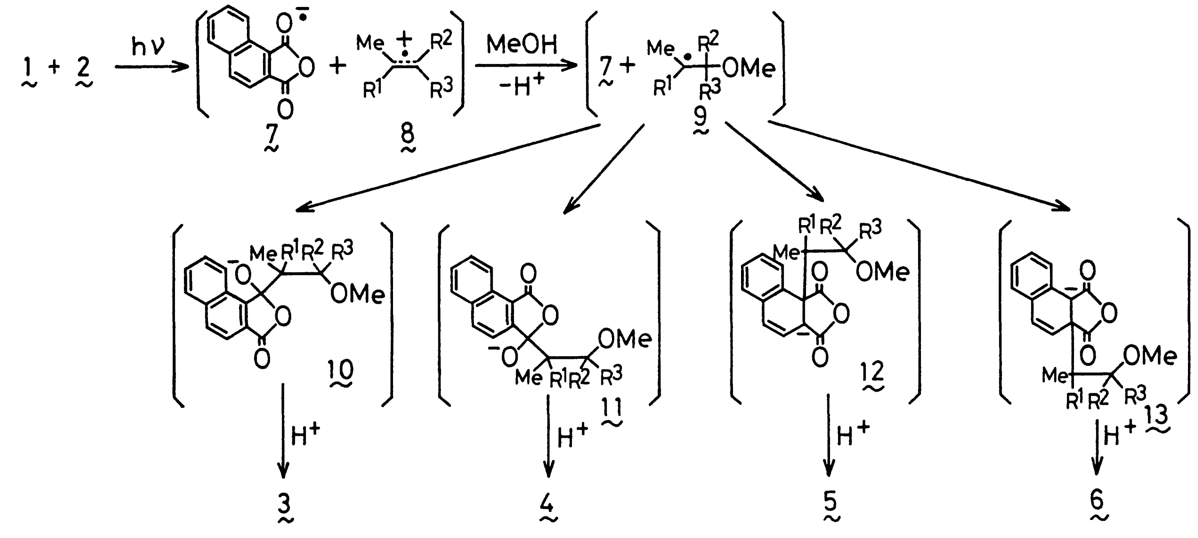
(1)

Table 1. Yields of Methanol-incorporated Adducts **3a-d**, **4a-d**, **5a-d**, and **6a-d** from Photoreactions of 1,2-Naphthalenedicarboxylic Anhydride (**1**) with Alkenes **2a-d**[a)]

R^1	R^2	R^3	**2a-d**	[**2a-d**] / mM	Yield/% in MeOH(5%)-C_6H_6				Yield/% in MeOH(5%)-CH_3CN			
					3a-d	**4a-d**	**5a-d**	**6a-d**	**3a-d**	**4a-d**	**5a-d**	**6a-d**
Me	H	H	**2a**	360	**3a** 39	**4a** 16	**5a** 7	**6a** 7	**3a** 18	**4a** 15	**5a** 4	**6a** 4
H	Me	H	**2b**	360	**3b** 34	**4b** 21	**5b** 9	**6b** 7	**3b** 29	**4b** 25	**5b** 12	**6b** 9
H	H	Me	**2c**	360	**3c** 36	**4c** 22	**5c** 10	**6c** 9	**3c** 26	**4c** 23	**5c** 12	**6c** 10
Me	Me	H	**2d**	380	**3d** 34	**4d** 20	**5d** 2	**6d** 1	**3d** 18	**4d** 18	**5d** 9	**6d** 5

a) Reaction conditions: [**1**]= 13 mM, hν (λ> 340 nm), under N_2. Yields of **3b-d**, **4b-d**, **5b-d**, **6b-d** are combined yields of the stereoisomers.

(6.5 mM, 1 mM= 1×10^{-3} mol dm^{-3}) with isobutene (**2a**, R^1= Me, R^2= R^3= H, 360 mM) in N_2-purged methanol (5%)-benzene gave a pair of regioisomers of a methanol-incorporated adduct at a carbonyl carbon atom in **1** [**3a** (39%) and **4a** (16%)] and a pair of regioisomers of a methanol-incorporated adduct at a naphthalene ring carbon atom in **1** [**5a** (7%) and **6a** (7%)] (Eq. 1 and Table 1). The structures of **3a** and **4a** were assigned on the basis of the NMR[8)] spectral resemblance to methanol-incorporated adducts obtained from the reactions of arenedicarboximides with alkenes.[3)] The regiochemistry of **3a** and **4a** is deduced from low field shift of H^a in **4a** (δ= 9.02) compared with that in **3a** (δ= 8.45). This shift suggests that the H^a in **4a** is close to the lactone-carbonyl group.[3d,e)] The structures and regiochemistry of **5a** and **6a** are also deduced from the ^1H NMR spectra.[9)]



Scheme 1.

Other examples of photoreactions of **1** with alkenes **2b-d** in methanol (5%)-benzene are shown in Table 1 together with those in methanol (5%)-acetonitrile. The table shows that addition at the more sterically hindered carbonyl carbon atom in **1** predominates in methanol (5%)-benzene to give **3a-d** in preference to **4a-d**. The selectivity may be rationalized by relative spin density at carbonyl carbons of radical anion of **1**.[3d] In the reactions with cis-2-butene (**2b**) and trans-2-butene (**2c**) similar mixtures of the same stereoisomers of products were obtained. The result indicates intervention of an intermediate in which the methyl groups can rotate around the single bond (MeC-CMe).

No clear evidence for the charge-transfer complex formation between **1** and the alkene molecules in the ground state was obtained by the UV spectrum measurements. The fluorescence of **1** in air-saturated benzene (τ= 17.3 ns) or in acetonitrile (τ= 25.1 ns) was effectively quenched by the alkenes without varying the shape and the maximum wavelength of the emission. The fluorescence quenching rate constants (k_q) calculated from the Stern-Volmer slopes by use of **2a** and **2d** were 2.0×10^7 and 5.6×10^9 $M^{-1}s^{-1}$ in benzene, and 8.6×10^8 and 1.3×10^{10} $M^{-1}s^{-1}$ in acetonitrile, respectively. The large k_q values may indicate an electron-transfer mechanism for the methanol-incorporated addition.

A possible mechanism which can interpret the general feature of methanol-incorporated addition of alkenes both at the carbonyl carbon atom and at the naphthalene ring carbon atom in **1** is shown in Scheme 1. The initial step of the reaction is an electron-transfer process from the alkenes to the singlet excited state of **1** to give **7** and **8**.

The results indicate that the alcohol-incorporated addition of alkenes is an important type of the photoreactions of anhydrides as well as imides. Other electron transfer reactions observed in the photoreactions of arenedicarboximides may be expected to occur in photoreactions of arenedicarboxylic anhydrides. Furthermore, reactivity of anhydrides toward the alcohol-incorporated addition seems to be higher than that of the corresponding imides, because no methanol-incorporated adducts were observed in the reaction of N-methyl-1,2-naphthalenedicarboximide with **2a**.[3d)]

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7) Irradiation was carried out through about 1 cm path length saturated $CuSO_4$ aqueous filter (340 nm, 50% transmittance).
8) **3a**: ^1H NMR ($CDCl_3$) δ= 0.48 (s, 3H), 1.47 (s, 3H), 3.33 and 4.16 (ABq, J= 8.8 Hz, 2H), 3.54 (s, 3H, OMe), 7.20 (s, 1H, OH), 7.5-7.7 (m, 2H), 7.79 and 7.98 (ABq, J= 8.2 Hz, 2H), 7.96 (br d, 1H), 8.45 (br d, 1H, H^a). **4a**: ^1H NMR ($CDCl_3$) δ= 0.57 (s, 3H), 1.51 (s, 3H), 3.32 and 4.14 (ABq, J= 8.8 Hz, 2H), 3.52 (s, 3H, OMe), 6.88 (s, 1H, OH), 7.5-7.8 (m, 2H), 7.66 and 8.14 (ABq, J= 8.3 Hz, 2H), 7.97 (br d, 1H), 9.02 (br d, 1H, H^a).
9) **5a**: ^1H NMR ($CDCl_3$) δ= 0.92 (s, 3H), 1.14 (s, 3H), 3.23 and 3.34 (ABq, J= 9.8 Hz, 2H), 3.27 (s, 3H, OMe), 4.59 (d, J= 6.6 Hz, 1H), 6.11 (dd, J= 6.6, 9.8 Hz, 1H), 6.63 (d, J= 9.8 Hz, 1H), 7.15 (d, 1H), 7.2-7.5 (m, 2H), 7.64 (d, 1H). **6a**: ^1H NMR ($CDCl_3$) δ= 0.90 (s, 3H), 1.22 (s, 3H), 3.16 (s, 3H, OMe), 3.22 and 3.35 (ABq, J= 9.8 Hz, 2H), 4.83 (s, 1H), 5.81 and 6.75 (ABq, J= 10.0 Hz, 2H), 7.15 (d, 1H), 7.2-7.5 (m, 3H).

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