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Photochemistry of Arenedicarboxylic Anhydrides. Insertion of Alkenes into C(=O)-O Bond and Oxetane Formation of 1,2- and 2,3-Naphthalenedicarboxylic Anhydrides

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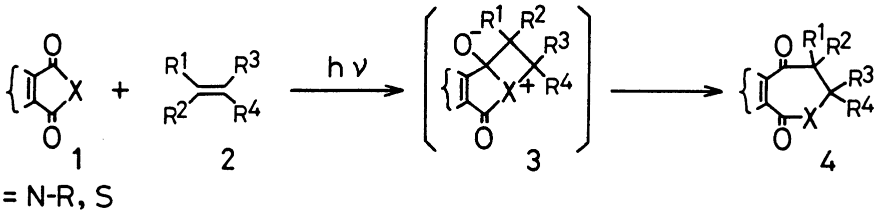
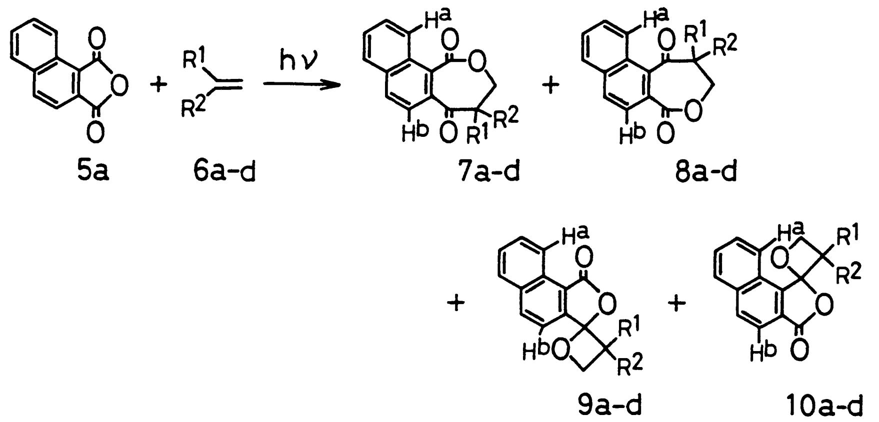
Irradiation of 1,2- and 2,3-naphthalenedicarboxylic anhydrides (**5a,b**) with alkenes in benzene gave naphthoxepindiones, by insertion of the alkenes into C(=O)-O bond, and oxetanes. The insertion predominated in the reactions of **5a** with the alkenes, while the oxetanes were mainly produced in those of **5b**.

Arenedicarboximides$^{1)}$ and arenedicarboxylic thioanhydrides$^{2)}$ undergo novel photochemical insertion of a variety of alkenes to give arene-fused azepinediones and thiepindiones, respectively (Eq. 1). The reaction proceeds stereospecifically from the singlet excited state of the imide or the thioanhydride possibly through a dipolar intermediate or transition state (**3**). Since the oxygen atom substituted at the place of the nitrogen or the sulfur atom can also stabilize an intermediate or transition state corresponding to **3** to some extent, our attention has been focused on the photoreaction of arenedicarboxylic anhydrides. To our knowledge, few systematic investigations on the photochemistry of the arenedicarboxylic anhydride have been carried out in spite of the fundamental simplicity and importance of the anhydride. Only photodecomposition of arenedicarboxylic anhydrides in gas phase$^{3)}$ and oxetane formation of phthalic and 1,8-naphthalenedicarboxylic anhydrides with dimethylindene via photoexcited charge-transfer complexes$^{4)}$ have been reported. In this paper we report the novel photochemical insertion of alkenes into C(=O)-O bond of 1,2- and 2,3-naphthalenedicarboxylic anhydrides (**5a** and **5b**) competing with oxetane formation.



(1)

Irradiation (>340 nm)$^{5)}$ of **5a** (13 mM, 1 mM= 1X10^{-3} mol dm^{-3}) with 1,1-diphenylethylene (**6a**, 150 mM) in N_2-purged benzene gave mainly a pair of regioisomers of naphthoxepindiones (**7a** and **8a**) and a pair of regioisomers of oxetanes (**9a** and **10a**) (Eq. 1 and Table 1). The structures of **7a** and **8a**, including the position of the substituents of the oxepin ring, were assigned on the basis of the IR and the NMR$^{6)}$ spectral resemblance to insertion products obtained from the



(2)

Table 1. Yields of Naphthoxepindiones (**7a-d** and **8a-d**) and Oxetanes (**9a-d** and **10a-d**) from Photoreactions of 1,2-Naphthalenedicarboxylic Anhydride (**5a**) with Alkenes (**6a-d**) in Benzene[a)]

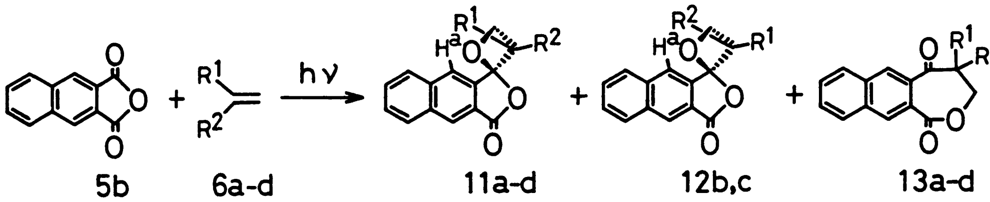
R^1	R^2	**6a-d**	[**6a-d**]	Yield/%							
			mM	**7a-d**		**8a-d**		**9a-d**		**10a-d**	
Ph	Ph	**6a**	150	**7a**	50	**8a**	14	**9a**	15	**10a**	7
Ph	Me	**6b**	12	**7b**	28	**8b**	10	**9b**	2	**10b**	1
Ph	H	**6c**	10	**7c**	12	**8c**	4	**9c**	5	**10c**	3
Me	Me	**6d**	100	**7d**	20	**8d**	6	**9d**	25	**10d**	10

a) Reaction conditions: [**5a**]= 13 mM, hν (λ> 340 nm), under N_2.

photoreactions of the corresponding imide[7)] and thioanhydride with alkenes.[2)] The IR spectra of **7a** and **8a** show the ketone-carbonyl bands (1698 and 1684 cm^{-1}) and the lactone carbonyl bands (1736 and 1722 cm^{-1}), respectively. The regiochemistry of **7a** and **8a** is deduced from low field shift of H^a of **8a** (δ= 8.50, multiplet) compared with that of **7a** (δ= 7.85), indicating that the H^a of **8a** is close to the ketone-carbonyl groups, in accord with the observations that the ketone-carbonyl group exerts a stronger deshielding effect on the peri-hydrogens than the lactam-carbonyl group.[7b)] The structures and the regiochemistry of **9a** and **10a** are also deduced from the IR and the ^1H NMR spectra.[8)]

The yields of the products were little affected by saturation of O_2 to the solvent. Little concentration dependence of the yields of the four products in the concentration range of 17 to 700 mM on **6a** may indicate that these products result from only one excited state of **5a**, since remarkable concentration dependence of yields of products has been reported when different products are generated from the singlet and the triplet excited states in the photoreactions of arenedicarboximides with alkenes.[9)] Other examples of photoreactions of **5a** with alkenes (**6b-d**) are shown in Table 1.

Irradiation (>340 nm) of **5b** with **6a** gave mainly an oxetane (**11a**) and a naphthoxepindione (**13a**) although only oxetanes (**11b-d** and **12b,c**) were obtained in the photoreactions with **6b-d** (Eq. 2 and Table 2). In the reaction with styrene (**6b**) or α-methylstyrene (**6c**) a pair of stereoisomers of oxetanes (**11b+12b** or



(3)

Table 2. Yields of Oxetanes (**11a-d** and **12b,c**) and Naphthoxepindiones (**13a-d**) from Photoreactions of 2,3-Naphthalenedicarboxylic Anhydride (**5b**) with Alkenes (**6a-d**) in Benzene[a)]

R^1	R^2	**6a-d**	[**6a-d**]	Yield/%					
			mM	**11a-d**		**12b,c**		**13a-d**	
Ph	Ph	**6a**	86	**11a**	58	——		**13a**	6
Ph	Me	**6b**	116	**11b**	57	**12b**	trace	**13b**	0
Ph	H	**6c**	130	**11c**	32	**12c**	10	**13c**	0
Me	Me	**6d**	100	**11d**	10	——		**13d**	0

a) Reaction conditions: [**5b**]= 13 mM, hν (λ> 340 nm), under N_2.

11c+**12c**) was obtained. The stereochemistry is assigned on high field shift of H^a in **11b** and **11c** (δ= 7.54, 7.54) compared with H^a in **12b** and **12c** (δ= 8.36, 8.38), respectively, caused by the anisotropic shielding effect of the phenyl ring (R^1). Similar high field shift of H^a was observed for **11a** (δ= 7.57). The predominant formation of the more sterically hindered isomers (**11b,c**) indicates that π-overlapping between the aromatic rings of the anhydride and the alkene molecules is favored in intermediates or transition states leading to these products.

No clear evidence for the charge-transfer complex formation between the anhydride and the alkene molecules in the ground state was obtained by the UV spectral measurements. The fluorescence of **5a** in air-saturated benzene (lifetime= 17.3 ns at room temperature) was effectively quenched by the alkenes without varying the shape and the maximum wavelength of the emission. The fluorescence quenching rate constants calculated from the Stern-Volmer slopes for **6b**, **6c**, and **6d** were 7.4×10^9, 6.4×10^9, and 2.0×10^7 $M^{-1}s^{-1}$, respectively.

In the photoreactions of **5a,b** the novel insertion of the alkenes into the C(=O)-O bond and the oxetane formation were observed. The insertion reaction seems to be an important type of the photoreactions of anhydrides as well as imides and thioanhydrides, though the oxygen atom appeared to less stabilize the intermediate or transition state corresponding to **3** than the nitrogen or the sulfur atom. The predominant types of reactions are found to depend largely upon the arene structures of the arenedicarboxylic anhydrides. Thus, **5a** is advantageous for the insertion, while the insertion reaction is minor for **5b** compared with the oxetane formation. The dependence on the arene structures seems to be closely related to that observed in the photoreactions of arenedicarboximides, in which the predominant reactions of N-methyl-1,2-, -2,3-, and -1,8-naphthalenedicarboximides with alkenes in benzene are the insertion of the alkenes into C(=O)-N bond of the imide moiety,[7)] the oxetane formation,[7a,10)] and cyclobutane formation,$^{7a,11)}$ respectively.

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5) Irradiation (7 h) was carried out with Eikosha EHB-W-300 (300 W) high-pressure Hg-lamp through about 1 cm path length saturated CuSO$_4$ aqueous filter (340 nm, 50% transmittance).

6) **7a**: ^{1}H NMR (270 MHz, CDCl$_3$) δ= 5.13 (br s, 2H, CH$_2$), 7.4-7.6 (m, 12H), 7.53 (ddd, J= 1.4, 6.3, 8.0 Hz, 1H), 7.85 (m, H^a), 7.90 (d, J= 8.3 Hz, C$\underline{\mathrm{H}}$CH^b), 8.07 (d, J= 8.3 Hz, H^b); ^{13}C NMR (CDCl$_3$) δ= 68.8 (s), 73.5 (t, CH$_2$), 124.9 (s), 125.4 (d), 126.4 (d), 128.1 (d), 128.5 (d), 128.7 (d), 128.9 (d), 129.1 (s), 129.3 (d), 129.3 (d), 132.3 (d), 135.6 (s), 136.1 (s), 138.6 (s), 169.2 (s, lactone), 201.1 (s, ketone). **8a**: ^{1}H NMR (270 MHz, CDCl$_3$) δ= 5.16 (br s, CH$_2$), 7.2-7.5 (m, 13H), 7.7-7.9 (m, 1H), 8.03 (d, J= 8.5 Hz, H^b), 8.50 (m, H^a).

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8) **9a**: ^{1}H NMR (270 MHz, CDCl$_3$) δ= 5.41 (d, J= 5.6 Hz, 1H), 5.57 (d, J= 5.6 Hz, 1H), 6.79 (d, J= 8.5 Hz, 1H), 7.1-7.4 (m, 10H), 7.64 (ddd, J= 1.2, 6.8, 8.2 Hz, 1H), 7.74 (ddd, J= 1.5, 7.1, 12.6 Hz, 1H), 7.82 (d, J= 8.8 Hz, H^b), 7.89 (br d, J= 8.2 Hz, 1H), 8.97 (br d, J= 7.1 Hz, H^a); IR (KBr) 1765 (lactone) cm^{-1}. **10a**: ^{1}H NMR (270 MHz, CDCl$_3$) δ= 5.71 (d, J= 6.4 Hz, 1H), 5.86 (d, J= 6.4 Hz, 1H), 6.8-7.0 (m, 3H), 7.1-7.4 (m, 8H), 7.46 (ddd, J= 1.0, 6.8, 8.1 Hz, 1H), 7.58 (br d, J= 8.4 Hz, 1H), 7.87 (br d, J= 8.4 Hz, H^a), 7.89 (d, J= 8.3 Hz, 1H), 8.05 (d, J= 8.3 Hz, H^b); IR (KBr) 1780 (lactone) cm^{-1}.

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