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Photochemistry of Arenedicarboxylic Thioanhydride. Insertion of Alkene into C(=O)-S Bond of 1,2- and 2,3-Naphthalenedicarboxylic Thioanhydride[†]

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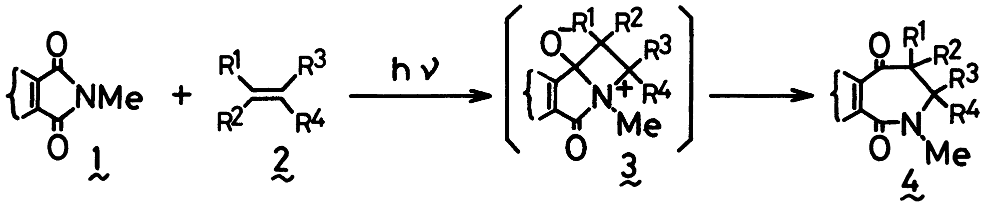
Irradiation of 1,2-naphthalenedicarboxylic thioanhydride (5a) or its 2,3-isomer with alkenes in acetonitrile gave naphthothiepindiones by insertion of alkenes into C(=O)-S bond of the thioanhydride. Reactions of 5a with cis- and trans-2-butene were stereospecific, demonstrating that the insertion was caused from the singlet excited state of 5a.

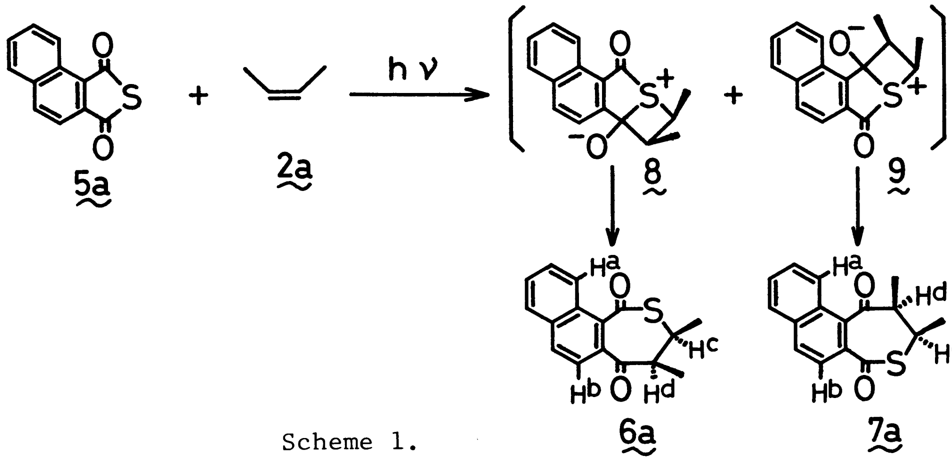
Arenedicarboximides undergo a novel photochemical insertion reaction with a variety of alkenes1) and dienes2) to give arene-fused azepinediones (Eq. 1). The reaction proceeds stereospecifically from the singlet excited state of the imide possibly through a zwitter ionic state (3). However, compounds that undergo such a type of reaction have been confined to arenedicarboximides and little information concerning with possibility of such a type of reaction has been reported on the photoreaction of other types of compounds. Since the sulfur atom substituted at the place of the nitrogen atom may also stabilize a state corresponding to 3, our attention has been focused on the photoreaction of arenedicarboxylic thioanhydrides with alkenes. We newly found that 1,2- and 2,3-naphthalenedicarboxylic thioanhydride (5a,b) readily undergo the same insertion reaction with alkenes as the case of the corresponding imides. This reaction seems to be the first example of the photoreaction of thioanhydrides, although numerous photoreactions of thioesters [R-C(=O)S-R' and R-C(=S)O-R']3) and thioimides [R-C(=S)N(R')C(=O)-R'']4) have been reported.



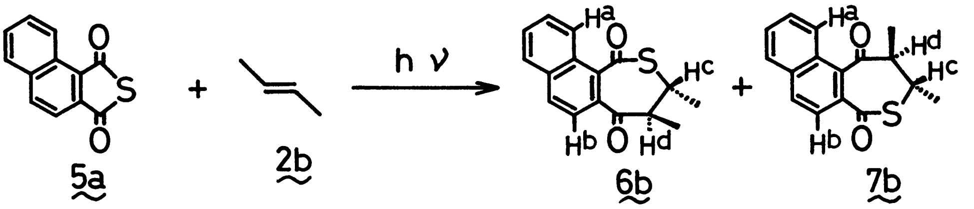
(1)

Irradiation (>320 nm) of 5a (2 mM, 1 mM= 1X10^{-3} mol dm^{-3}) and cis-2-butene (2a, 1.5 M) in N_2-purged acetonitrile gave mainly two regio-isomers of naphthothiepindiones [6a (11%) and 7a (11%)], together with minor unidentified products (Scheme 1). These products were isolated by chromatography. Irradiation of 5a (2

[†] This paper is dedicated to the late Professor Ryozo Goto, Kyoto University.



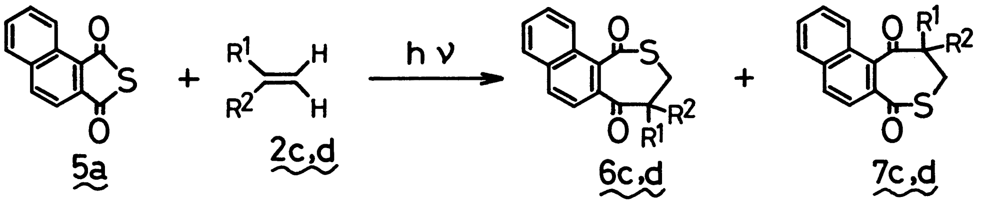
Scheme 1.



(2)

mM) with trans-2-butene (2b, 1.5 M) also gave 6b (14%) and 7b (14%) (Eq. 2). The IR spectra of 6a,b and 7a,b show keto-carbonyl [-C(=O)-] band (≈ 1705 cm^{-1}) and thiolactone [-C(=O)S-] band (≈ 1655 cm^{-1}),[5] respectively. The structures of the 6a,b and 7a,b, including the position of the alkyl substituent of the thiepin ring, were supported by the ^{1}H NMR spectral resemblance[6] to the naphthazepinedione analogues obtained by the photoreactions of N-methyl-1,2-naphthalenedicarboximide with the alkenes.[1h,k] The regiochemistry of 6a,b and 7a,b shown in the structural formula are deduced as follows. The H^a signals (double doublets) of 7a,b showed low field shifts (δ= 8.26, 8.29) relative to those of 6a,b (δ≈ 8). This fact suggests that the H^a is close to the keto-carbonyl groups, in accord with the observations that the keto-carbonyl group exerts a stronger deshielding effect on the peri-hydrogens than the lactam-carbonyl group.[1k] Furthermore, the H^b signals (doublet) of 7a,b (δ= 8.00, 8.01) were observed at slightly higher fields compared with those of 6a,b (δ= 8.06, 8.05).

An important characteristic of the naphthothiepinedione formation is stereochemical course of the reactions. The stereochemistry of the 6a,b and 7a,b could be assigned by comparison of the coupling constants of H^c-H^d with those of corresponding arene fused azepinediones, which were reported to be J= 2.3,[1d] 2,[1i] and 3.2 Hz[1k] for the cis-isomer and J= 10.1,[1d] 12,[1i] 11.0, and 11.6 Hz[1k] for the trans-isomer. The products (6a,b and 7a,b) had the coupling constants of J= 3.9, 11.2, 3.7, and 11.2 Hz, respectively. These coupling constants suggested the cis-stereochemistry for 6a and 7a, and trans-stereochemistry for 6b and 7b as shown in Scheme 1 and Eq. 2. The stereochemistry of the products corresponds to that of the alkenes (2a,b) used. The facts that no detectable amounts of cis-trans isomerization products are observed in the irradiation of 5a with 2a and 2b obviously indicate the stereospecific formation of the naphthothiepindiones. At the early stages of the inter-[1d] and intramolecular[1i] photoreactions of phthalimides and alkenes, the stereospecific benzazepinedione formation was already

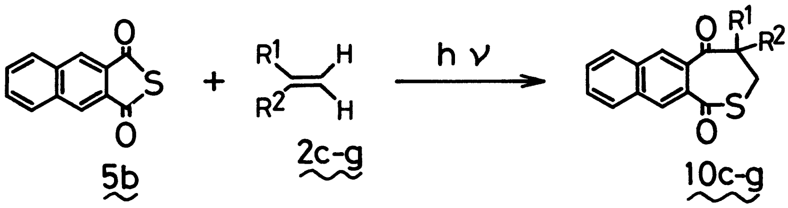


(3)

Table 1. Yields of Naphthothiepindiones (6c,d and 7c,d) from Photoreactions of 1,2-Naphthalenedicarboxylic Thioanhydride (5a) with Alkenes (2c,d) in Acetonitrile[a)]

R^1	R^2	2	[2]/M	6	Yield/%	7	Yield/%
Me	Me	2c	1.5	6c	20	7c	20
Ph	Me	2d	0.16	6d	20	7d	10

a) Reaction conditions: [5a]= 2 mM, under N_2.



(4)

Table 2. Yields of Naphthothiepindiones (10c-g) from Photoreactions of 2,3-Naphthalenedicarboxylic Thioanhydride (5b) with Alkenes (2c-g) in Acetonitrile[a)]

R^1	R^2	2	[2]/M	10	Yield/%
Me	Me	2c	1.5	10c	15
Ph	Me	2d	0.16	10d	54
Ph	Ph	2e	0.12	10e	53
Ph	H	2f	0.17	10f	25
n-C_4H_9	H	2g	0.16	10g	0[b)]

a) Reaction conditions: [5b]= 2 mM, under N_2. b) No reaction.

reported, but concomitant cis-trans isomerization of alkenes always occurred to give non-stereospecific mixtures of the products after a prolonged irradiation. No such secondary cis-trans isomerization was observed in the photoreactions of 5a with 2a and 2b as in the case of 1,2-naphthalenedicarboximide.[1k)]

The naphthothiepindione formation may be rationalized by a mechanism (Scheme 1) similar to that of the naphthazepinedione formation[1k)] on the basis of the stereospecificity of the reaction. Thus, reaction of the singlet excited state of 5a and 2a gave two regioisomers of a zwitter ionic state (8 and 9) with retention of the stereochemistry of the alkene, and then the $C(O^-)-S^+$ bond cleavage results in formation of 6a and 7a, respectively.

Other examples of photoreactions of 5a and alkenes (2c,d) are shown in Table 1. The yields of the regio-isomers (6a-d) are generally comparable to those of the other isomers (7a-d). Examples of those of 5b with alkenes (2c-g) are summarized in Table 2. The structures of 10c-f, including the position of the alkyl substituent of the thiepin ring, were supported by the ^{1}H NMR spectral resemblance to 6a-d and 7a-d. These results indicate that the insertion of alkene into the C(=O)-S bond of thioanhydride, thiepindione formation, is characteristic of the reactions with a wide variety of alkenes. Furthermore, the results of Table 2 suggest that 5b possesses a singlet excited state more favorable to the insertion reaction compared with that of the corresponding imide, since no insertion reaction was observed in the photoreaction of N-methyl-2,3-naphthalenedicarboximide with 2-methylpropene (2c) and oxetane formation was the major reaction in the reaction with ethylenes substituted by a phenyl group (2d-f).[1h,1l]

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6) 6a: ^{1}H NMR (270 MHz, in $CDCl_3$) δ= 1.38 (d, J= 7.3 Hz, 3H, Me), 1.46 (d, J= 6.6 Hz, 3H, Me), 3.28 (dq, J_{H^c,H^d}= 3.9 Hz, $J_{H^d,Me}$= 6.6 Hz, 1H, H^d), 4.16 (dq, J_{H^c,H^d}= 3.9 Hz, $J_{H^c,Me}$= 7.3 Hz, 1H, H^c), 7.5-8.0 (m, 5H, Arom H), 8.06 (d, J= 8.1 Hz, 1H, H^b). 6b: ^{1}H NMR δ= 1.25 (d, J= 7.1 Hz, 3H, Me), 1.34 (d, J= 7.1 Hz, 3H, Me), 3.15 (dq, J_{H^c,H^d}= 11.2 Hz, $J_{H^d,Me}$= 7.1 Hz, 1H, H^d), 3.29 (dq, J_{H^c,H^d}= 11.2 Hz, $J_{H^c,Me}$= 7.1 Hz, 1H, H^c), 7.5-8.0 (m, 5H, Arom H), 8.05 (d, J= 8.3 Hz, 1H, H^b). 7a: ^{1}H NMR δ= 1.38 (d, J= 7.3 Hz, 3H, Me), 1.42 (d, J= 6.6 Hz, 3H, Me), 3.09 (dq, J_{H^c,H^d}= 3.7 Hz, $J_{H^d,Me}$= 6.6 Hz, 1H, H^d), 4.12 (dq, J_{H^c,H^d}= 3.7 Hz, $J_{H^c,Me}$= 7.3 Hz, 1H, H^c), 7.5-8.0 (m, 4H, Arom H), 8.00 (d, J= 8.5 Hz, 1H, H^b), 8.26 (dd, 1H, H^a). 7b: ^{1}H NMR δ= 1.21 (d, J= 7.1 Hz, 3H, Me), 1.30 (d, J= 7.1 Hz, 3H, Me), 3.00 (dq, J_{H^c,H^d}= 11.2 Hz, $J_{H^d,Me}$= 7.1 Hz, 1H, H^d), 4.22 (dq, J_{H^c,H^d}= 11.2 Hz, $J_{H^c,Me}$= 7.1 Hz, 1H, H^c), 7.5-8.0 (m, 4H, Arom H), 8.01 (d, J= 8.7 Hz, 1H, H^b), 8.29 (dd, 1H, H^a).

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