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A Photoallylation of N-Methylarenedicarboximides by Allylsilanes

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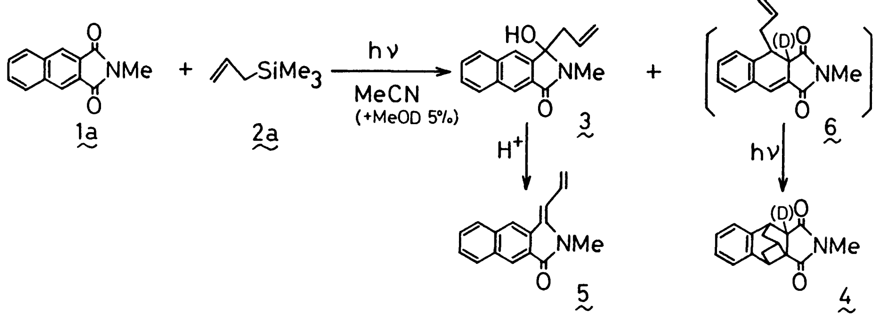
The photoallylation of N-methylarenedicarboximides by allylsilanes in acetonitrile or methanol efficiently occurred at a carbonyl carbon atom and at an aromatic carbon atom possibly via single electron transfer.

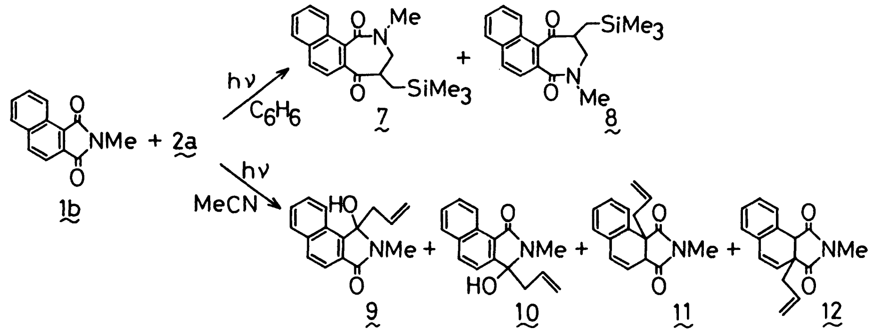
Recently, photoreactions involving single electron transfer from allylsilanes to excited electron acceptors have received much attention from synthetic and mechanistic aspects in organic photochemistry.1,2) However, the electron acceptors employed in the previous investigations have been confined to iminium cations1) and cyanoaromatics,2) and little information has been reported on the reaction of other electron acceptors such as carbonyl compounds. In the course of our systematic investigation on photochemistry of arenedicarboximides, we have revealed that alcohol (solvent)-incorporated addition occurs in the photolysis of the arenedicarboximides with alkenes via single electron transfer.3) We have newly found that allylsilanes are reactive in the photoreaction with N-methylarenedicarboximides, and cause allylation at a carbonyl carbon atom and at an aromatic carbon atom of the N-methylarenedicarboximides. Importantly, the photoallylation proceeds under nearly neutral conditions, in contrast to that thermal allylation of carbonyl compounds by allylsilanes generally occurs under acidic conditions.4)

Irradiation (>320 nm) of N-methyl-2,3-naphthalenedicarboximide (1a, 12 mM, 1 mM= 1X10^{-3} mol dm^{-3}) and allyltrimethylsilane (2a, 120 mM) in N$_2$-purged acetonitrile gave an allylation product (3, 73%) at the carbonyl carbon atom of 1a and a cyclobutane (4, 18%). These products were isolated by chromatography. The structure of 3 was supported by spectroscopic properties and by acid dehydration to 5. The structure of 4 was deduced from the ^{1}H NMR data,5) including the decoupling experiments, as well as from the other spectroscopic properties. The possibility that the products might be derived from thermal reaction was excluded by a control (dark) experiment. The formation of 4 can be rationalized by photo-

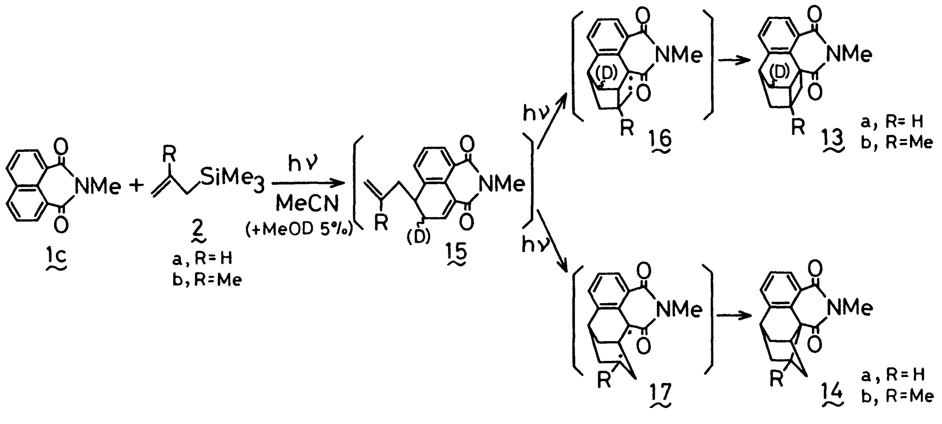


allylation at an aromatic carbon atom of 1a to give 6 followed by intramolecular $2\pi+2\pi$ photocyclization, though 6 could not be isolated probably due to the facile secondary photoreaction. The yields of the products remained almost constant over the 2a concentration range of 24 to 240 mM. The result suggests that the products arise from a singlet excited state of 1a, since the product composition would have been highly affected by concentration of reactant, if the products were generated from different excited states, as observed for the photoreaction of phthalimides with alkene.6) When the reaction was carried out in the presence of MeOD (5%), one hydrogen atom (H^d)5) of 4 was replaced by deuterium atom. However, no deuterium incorporation was observed in the reaction in CD_3CN. Hence, a small amount of H_2O contained in the solvent may be a proton source of the reaction. Irradiation of 1a and 2a in methanol gave 3 (81%) and 4 (5%).

Irradiation (>320 nm) of N-methyl-1,2-naphthalenedicarboximide (1b, 12 mM) and 2a (120 mM) in benzene gave 7 (42%) and 8 (31%) by insertion of double bond of 2a into C(=O)-N bonds of 1b.7) In constant, irradiation in acetonitrile afforded allylation products at the carbonyl carbon atoms of 1b (9, 27%; 10, 17%) and at the aromatic carbon atoms (11, 16%; 12, 9%) instead of the insertion products (7 and 8). Since the insertion leading to 7 and 8 occurs from the singlet excited state of 1b,7) the allylation seems to occur also from the singlet excited state of 1b. Irradiation in methanol gave 9 (35%), 10 (26%), 11 (6%), and 12 (trace).

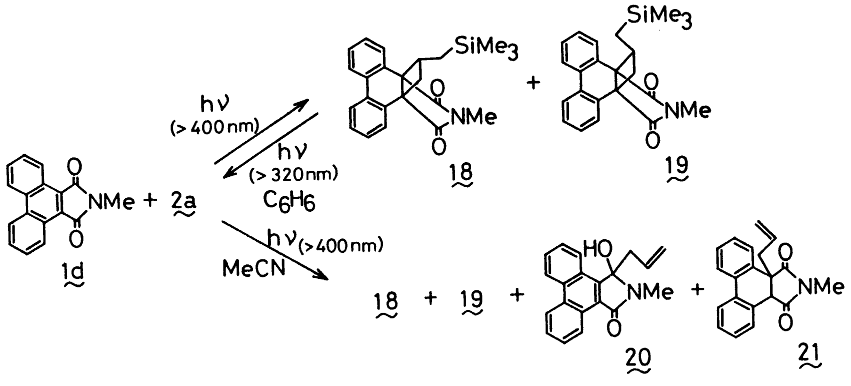


Irradiation (>320 nm) of N-methyl-1,8-naphthalenedicarboximide (1c, 12 mM) and 2a (120 mM) in acetonitrile gave mainly one type of cyclobutane (13a, 45%) with only a trace amount of 14a possibly by the secondary photoreaction of an allylation product (15). The structure of 13a and 14a was also deduced from the ^{1}H NMR data.8) When the reaction was carried out in the presence of MeOD (5%),



one molar equivalent of hydrogen atom (1/2 each of H^a and H^d)[8] of 13a was replaced by deuterium atom. Irradiation in methanol afforded the same products (13a, 40%; 14a, trace). Photolysis of 1c and methallyltrimethylsilane (2b), on the other hand, gave equimolar mixture of isomeric cyclobutanes (13b, 20%; 14b, 21%). This is possibly due to the stabilization of an intermediate 17 by the methyl substituent (R).

Irradiation (>400 nm) of N-methyl-9,10-phenanthrenedicarboximide (1d, 9 mM) and 2a (120 mM) in benzene gave two isomeric cyclobutanes (18, 78%; 19, 17%) which were derived from the triplet state of 1d.[9] Photolysis in acetonitrile afforded products allylated at the carbonyl carbon atom of 1d (20, 36%) and at the aromatic carbon atom (21, 12%) together with 18 (29%) and 19 (7%). Irradiation in methanol gave 18 (40%), 19 (10%), 20 (20%), and 21 (21%).



The fluorescence of 1a-d was effectively quenched by 2a, reflecting the estimated negative values of free energy changes (ΔG) associated with the electron transfer from 2a to the singlet excited states of 1a-d (Table 1).

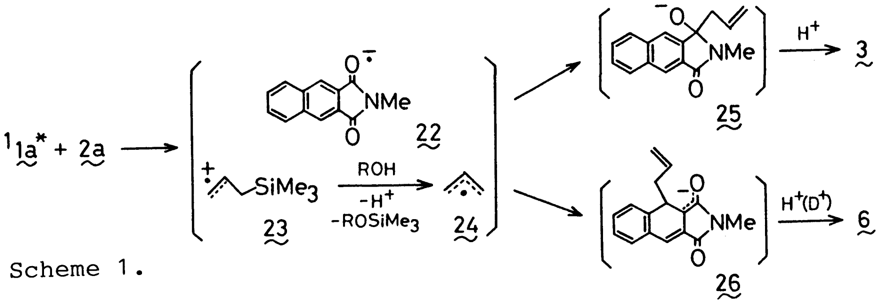
These results indicate that the allylation is characteristic of the photoreactions of a wide variety of N-methylarenedicarboximides with 2a. The position at which allylation occurs, however, largely depends on the structure of the imide. A possible mechanism which can interpret our results of the photo

Table 1. Fluorescence Quenching Rate Constants (kq) and Free Energy Changes (ΔG) Associated with Electron Transfer for N-Methylarenedicarboximides (1a-d) and Allyltrimethylsilane (2a) Systems

Imide	$k_q\tau$[a]	τ[b]	$k_q \times 10^{-8}$	E^{red}[c]	E_S[d]	ΔG[e]
	$mol^{-1}dm^3$	ns	$mol^{-1}dm^3s^{-1}$	V	$kcal\ mol^{-1}$	$kcal\ mol^{-1}$
1a	2.05	6.1	3.4	1.47	79.4	-0.8
1b	16.5	54.7	3.0	1.13	73.7	-2.9
	0.53[f]	42.0[f]	0.13[f]			
1c	2.26	1.3	17	1.22	79.4	-6.5
1d	3.48	14.6	2.41	1.02	68.9	-0.6

a) In air-saturated acetonitrile at 25 °C. b) Fluorescence lifetime of 1a-d in air-saturated acetonitrile. c) Reduction potentials of 1a-d in acetonitrile vs. Ag/Ag^+. d) Excited singlet energies of 1a-d. e) $\Delta G = 23.06(E^{ox}-E^{red})-E_S$:[10] E^{ox}; oxidation potential of 2a (1.94 V).[1a] f) In air-saturated benzene.

reactions of 1a and 2a is shown in Scheme 1. Initial step of the reaction is single electron transfer from 2a to the singlet excited state of 1a followed by desililation giving a pair of 22 and 24. Coupling of 24 at the carbonyl or at the aromatic carbon atom of 22 results in the formation of anion (25 or 26). Then, successive protonation gave 3 or 6, respectively.



Scheme 1.

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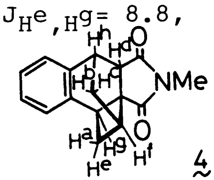
5) 4: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.27 (dd, H^a, J_{H^a,H^g}= 1.2, J_{H^a,H^e}= 11.0 Hz), 1.90 (d, H^b, J_{H^b,H^c}= 13.7 Hz), 2.25 (ddd, H^c, J_{H^c,H^h}= 5.4, J_{H^c,H^f}= 9.6, J_{H^b,H^c}= 13.7 Hz), 2.77 (s, H^d), 2.92 (ddd, H^e, J_{H^e,H^f}= 8.6, J_{H^e,H^g}= 8.8, J_{H^a,H^e}= 11.0 Hz), 2.94 (ddd, H^f, J_{H^f,H^g}= 3.8, J_{H^e,H^f}= 8.6, J_{H^c,H^f}= 9.6 Hz), 2.96 (s, 3H, NMe), 3.85 (ddd, H^g, J_{H^a,H^g}= 1.2, J_{H^f,H^g}= 3.8, J_{H^e,H^g}= 8.8 Hz), 3.88 (d, H^h, J_{H^c,H^h}= 5.4 Hz), 7.1-7.2 (4H).



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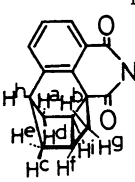
8) 13a: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.34 (d, H^a, J_{H^a,H^d}= 12.0 Hz), 1.53 (d, H^b, J_{H^b,H^g}= 10.3 Hz), 1.76 (d, H^c, J_{H^c,H^e}= 12.8 Hz), 1.86 (ddd, H^d, J_{H^d,H^h}= J_{H^d,H^i}= 4.3, J_{H^a,H^d}= 12.0 Hz), 2.10 (ddd, H^e, J_{H^e,H^h}= 5.7, J_{H^e,H^f}= 6.1, J_{H^c,H^e}= 12.8 Hz), 2.77 (ddd, H^f, J_{H^f,H^i}= 5.7, J_{H^e,H^f}= 6.1, J_{H^f,H^g}= 8.5 Hz), 2.86 (dd, H^g, J_{H^f,H^g}= 8.5, J_{H^b,H^g}= 10.3 Hz), 3.33 (s, 3H, NMe), 3.44 (dd, H^h, J_{H^d,H^h}= 4.3, J_{H^e,H^h}= 5.7 Hz), 4.02 (dd, H^i, J_{H^d,H^i}= 4.3, J_{H^f,H^i}= 5.7 Hz), 7.4-8.1 (3H). 14a: ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.18 (d, H^a, J_{H^a,H^f}= 9.4 Hz), 1.36 (dd, H^b, 2H, J_{H^b,H^d}= 6.2, J_{H^b,H^c}= 12.8 Hz), 2.16 (dd, H^c, 2H, J_{H^c,H^e}= 4.3, J_{H^b,H^c}= 12.8 Hz), 2.67 (dd, H^d, 2H, J_{H^b,H^d}= J_{H^d,H^f}= 6.2 Hz), 3.42 (s, 3H, NMe), 3.52 (t, H^e, J_{H^c,H^e}= 4.3 Hz), 3.71 (dt, H^f, J_{H^a,H^f}= 9.4, J_{H^d,H^f}= 6.2 Hz), 7.4-8.1 (3H).



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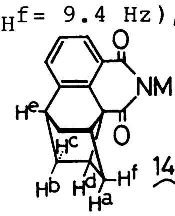

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