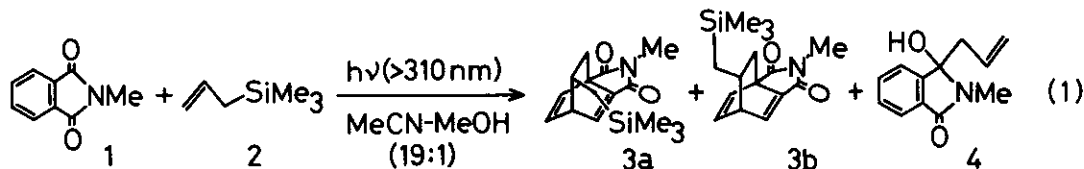


PHOTOCHEMICAL [2+2]- AND [4+2]CYCLOADDITIONS OF
N-METHYLPHthalIMIDE TO ALLYLTRIMETHYLSILANE

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Abstract — Irradiation of N-methylphthalimide (1) with allyltrimethylsilane (2) gave a [2+2]cycloadduct (9) possibly from the singlet excited state of 1 together with [4+2]-cycloadducts (3a,b) from the triplet excited state of 1. The adduct 9 was found to be extremely photoreactive.

The photochemistry of phthalimide, the simplest aromatic imide, with alkene has been the central subject in the photochemistry of imide¹ and extensively investigated for more than a decade.²⁻⁶ Numerous examples of photoreaction of phthalimides with alkene have been published mainly on alcohol-incorporated addition,² insertion of the alkene into C-N bond of the imide moiety,³ oxetane formation,⁴ and reduction.⁵ To our knowledge, however, little information concerning with photoaddition of the benzene moiety of phthalimides to alkene has been reported.⁶ In this paper we report novel [2+2]- and [4+2]photochemical cycloadditions of N-methylphthalimide (1) to allyltrimethylsilane (2). Irradiation (>310 nm)⁷ of 1 (12 mM) with 2 in N₂-purged MeCN-MeOH (v/v 19:1) gave two stereo-isomers of [4+2]cycloadducts of the benzene moiety of 1 to 2 (3a,b) and an allylation product of the carbonyl group of 1 (4) (Eq. 1). The structures



of 3a,b were deduced from the ir and ¹H nmr spectra. The ir spectra of 3a,b showed imide carbonyl bands (1764 and 1718 cm⁻¹). The ¹H nmr spectra of 3a,b⁸ showed three olefinic protons (H^B-Hⁱ) and one bridge head proton (H^d) coupled with H^B-Hⁱ, supporting the [2.2.2]octadiene structures. The stereochemistry

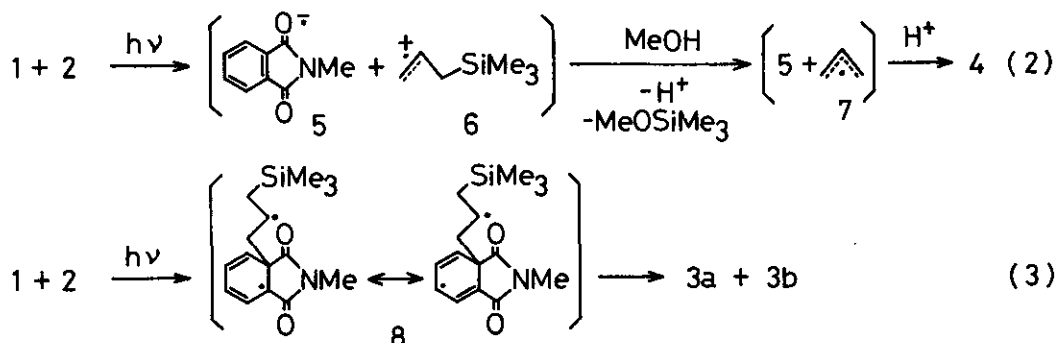
of **3a,b** is deduced as follows. Trans configuration between H^d and H^c in **3a,b** was assigned by the smaller coupling constants (4.6 Hz) compared with those (8.9 Hz) between H^d and H^e. The H^c signals of **3a** ($\delta = 0.83$) and H^e signals of **3b** ($\delta = 1.69$) showed high field shift relative to H^c of **3b** ($\delta = 1.17$) and H^e of **3a** ($\delta = 2.03$), respectively. The fact suggests that the H^c of **3a** and H^e of **3b** are located above one of the imide carbonyl groups as shown in the structural formula.⁸

The examination of the concentration effect of **2** on the yields of **3a,b** and **4** shows that the yields of **3a,b** decrease and that of **4** increases as increase of the concentration of **2** (Table 1). On the other hand, isomer ratios of **3a** to **3b** remain almost constant throughout the examined concentration of **2**. The result indicates that **4** arises mainly from the relatively short-lived singlet excited state of **1** and **3a,b** mainly from the triplet excited state, since marked decrease of yields of photoproducts derived from the triplet excited state of **1** with increase of the concentration of alkene is reported when the distinct products are generated from the singlet and triplet excited states of **1**.^{4b,5b} Mechanisms which can interpret the formation of **4** and **3a,b** are shown in Eqs. 2 and 3, respectively. The electron transfer mechanism

Table 1. Concentration Effect of **2** on Yields of **3a**, **3b**, and **4** in the Photoreaction of **1** with **2** in Acetonitrile-Methanol (v/v 19:1)^{a)}

[2] mM	Yield/%			3a 3b
	3a	3b	4	
2	37	17	13	2.2
8	30	14	32	2.1
20	25	11	42	2.3
40	19	8	61	2.4

a) Reaction conditions: [**1**] = 12 mM, $h\nu$ ($\lambda > 310$ nm), under N₂.



(Eq. 2) for the formation of **4** is similar to that of the photoallylation of other arenedicarboximides.⁹ The products **3a,b** are derived from the reaction of the triplet excited state of **1** with **2** via a triplet biradical **8** (Eq. 3). This

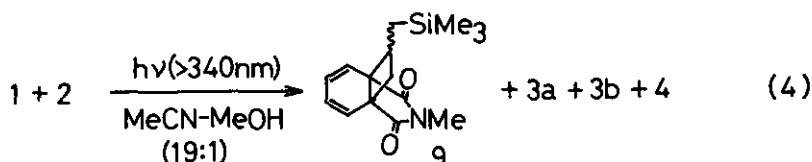
Table 2. Relative Yields of **9** to **3a+3b** in the Photoreaction of **1** with **2** in Acetonitrile-Methanol (v/v 19:1)^{a)}

Time h	Relative Yield	
	9	3a+3b
4	4.5	1
6	3.4	1
8	2.7	1

a) Reaction conditions: [1] = 12 mM, [2] = 25 mM, $h\nu$ ($\lambda > 340$ nm), under N_2 .

mechanism may be supported by the constant isomer-ratio of **3a** to **3b** at the different concentration of **2**, since the ratio should be changed if the reaction proceeded from the singlet and triplet excited states of **1** at the same time.

On the other hand, irradiation of light with longer wavelength (>340 nm)¹⁰ to a solution of **1** (12 mM) and **2** (25 mM) gave a [2+2]-cycloadduct of the benzene moiety of **1** to **2** (**9**) in addition to **3a,b** and **4** (Eq. 4). The structure of **9** was deduced from the ir, 1H and ^{13}C nmr spectra. The ir spectrum also showed imide carbonyl bands (1764 and 1700



cm^{-1}). The 1H nmr spectrum showed four olefinic protons.¹¹ The ^{13}C nmr signals of four carbons [δ 43.3 (CH_2 , $J_{C,H} = 135$ Hz), 46.5 (CH , $J_{C,H} = 135$ Hz), 51.5, 51.5] strongly suggested the cyclobutane structure.¹¹ The adduct **9** was found to be extremely photoreactive. Irradiation (>340 nm) of **9** (2 mM) in the same solvent system quantitatively afforded **1**. Relative yields of **9** to **3a+3b** are shown in Table 2, which indicate the relative yield of **9** decreases with the passage of irradiation time due to the photodecomposition of **9**. The Table however reveals that **9** is the main product at least at the initial stage of the reaction. The [2+2]cycloaddition thus seems to be essentially the most important type of the reaction in this system.

Sensitization (1-indanone)^{4b} studies in this system established that **3a,b** arose from the triplet excited state of **1**, and **9** from the singlet state.

[2+2]Cycloaddition was also found to be the main reaction pathway in the reaction with other electron rich alkenes such as crotyltrimethylsilane, cyclohexene, and ethyl vinyl ether. The result clearly indicates the importance of the hitherto unknown [2+2]photocycloaddition in the photochemistry of **1**. Photolability of the [2+2]adducts appears to be the reason of passing over the [2+2]cycloaddition for

a long time.

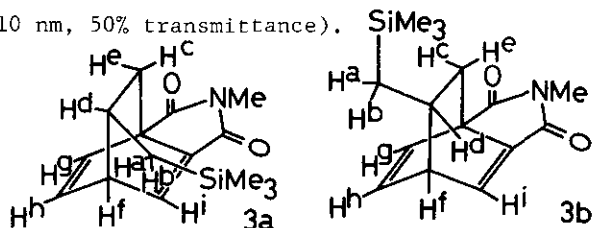
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7. Using a Pyrex glass filter (310 nm, 50% transmittance).

8. 3a: ^1H Nmr (270 MHz, CDCl_3)

$\delta = -0.06$ (SiMe_3), 0.40 (dd, $J = 11.0, 14.3$ Hz, H^a), 0.64 (dd, $J = 4.0, 14.3$ Hz, H^b),



0.83 (dd, $J_{\text{H}^c, \text{H}^d} = 4.6$ Hz, $J_{\text{H}^c, \text{H}^e} = 11.0$ Hz, H^c), 1.86 (m, H^d), 2.03 (dd, $J_{\text{H}^d, \text{H}^e} = 8.9$ Hz, $J_{\text{H}^c, \text{H}^e} = 11.0$ Hz, H^e), 3.06 (NMe), 3.69 (m, H^f), 6.31 (d, $J = 7.3$ Hz, H^g), 6.44 (dd, $J = 6.1, 7.3$ Hz, H^h), 7.10 (d, $J = 5.8$ Hz, H^i). 3b: $\delta = -0.06$ (SiMe_3), 0.45 (dd, $J = 11.0, 14.7$ Hz, H^a), 0.62 (dd, $J = 4.0, 14.7$ Hz, H^b), 1.17 (dd, $J_{\text{H}^c, \text{H}^d} = 4.6$ Hz, $J_{\text{H}^c, \text{H}^e} = 11.0$ Hz, H^c), 1.69 (dd, $J_{\text{H}^d, \text{H}^e} = 8.9$ Hz, $J_{\text{H}^c, \text{H}^e} = 11.0$ Hz, H^e), 1.85 (m, H^d), 3.04 (NMe), 3.69 (m, H^f), 6.31 (d, $J = 7.3$ Hz, H^g), 6.46 (dd, $J = 6.1, 7.3$ Hz, H^h), 7.20 (d, $J = 6.1$ Hz, H^i).

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10. Using 1 cm path length saturated CuSO_4 filter (340 nm, 50% transmittance).
11. 9: ^1H Nmr (CDCl_3) $\delta = -0.04$ (SiMe_3), 0.93 (dd, 1H), 1.03 (dd, 1H), 2.16 (dd, 1H), 2.59 (dd, 1H), 2.89 (m, 1H), 3.07 (NMe), 5.71 (d, 1H), 5.76 (d, 1H), 5.81 (dd, 1H), 6.00 (dd, 1H); ^{13}C nmr $\delta = -1.0$ (q), 19.4 (t), 25.3 (q), 43.3 (t, $J_{\text{C}, \text{H}} = 135$ Hz), 46.5 (d, $J_{\text{C}, \text{H}} = 135$ Hz), 51.5 (s), 51.5 (s), 120.9 (d), 122.7 (d), 123.4 (d), 125.8 (d), 180.4 (s, C=O), 180.4 (s, C=O).

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