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Regio- and Stereo-Selective [2π+2π] Photocycloaddition of Electron-Deficient Alkenes to Naphthalene Ring Bearing Si- and Ge-Containing Substituents

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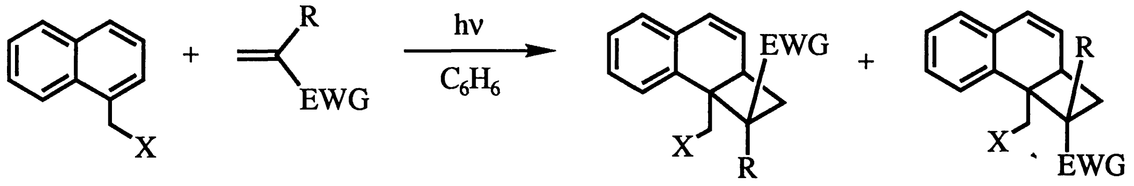
Irradiation of benzene solutions of 1- and 2-naphthylmethyltrimethylsilanes or their germane and disilane analogues in the presence of electron deficient alkenes afforded [2π+2π] photocycloadducts with high regio- and stereo-selectivities.

The photocycloaddition of unsaturated compounds to naphthalene ring has been extensively studied from a synthetic viewpoint as an entry to the construction of a variety of polycyclic compounds.[1-3] Mechanistically, this photoreaction is thought to proceed via exciplexes that are formed by interaction between naphthalenes and unsaturated compounds at their excited states. However, such a photocycloaddition using group 14 organometallic compounds as a substrate has little been developed, though this photoreaction is supposed to provide synthetically useful intermediates; the photochemistry so far studied for this class of compounds mostly concerns with the photofragmentation and rearrangement that involve the cleavage of C-M and M-M (M = Si, Ge, Sn) bonds.[4] We now report the regio- and stereo-selective [2π+2π] photocycloaddition of electron-deficient alkenes to 1- and 2-naphthylmethylsilanes or their germane and disilane analogues.

Irradiation of a benzene solution containing 1-naphthylmethyltrimethylsilane (**1a**, 0.6 mmol) and an excess of acrylonitrile (**2a**, 6 mmol) through Pyrex under nitrogen atmosphere afforded a mixture of two kinds of [2π+2π] photocycloadducts, **3a** and **4a**, in a 15 : 1 ratio. This photoreaction proceeded smoothly until 50-60% conversion, giving only **3a** and **4a** as detectable products. Further irradiation afforded 1 : 2 adducts along with several unidentified products. An isosbestic point was observed at 280 nm, accompanying a decrease in the absorbance at 291 nm due to **1a** and an increase in the absorbance at 270 nm due to **3a** when a dilute cyclohexane solution of **1a** and **2a** was irradiated with 313 nm light. Similar photoreaction occurred between **1a** and other electron-deficient alkenes, affording a pair of **3b** and **4b** from



1a-c **2a-c** **3a-c, 5a-b, 7** **4a-c, 6a-b**

1a : X=$SiMe_3$
1b : X=$GeMe_3$
1c : X=$SiMe_2SiMe_3$
1d : X=$SnBu_3$

2a : R=H, EWG=CN
2b : R=Me, EWG=CN
2c : R=H, EWG=CO_2Me

3a-c, 4a-c : X=$SiMe_3$
5a-b, 6a-b : X=$GeMe_3$
7 : X=$SiMe_2SiMe_3$

1a and 2-methylpropenecarbonitrile **2b** and a pair of **3c** and **4c** from **1a** and methyl acrylate **2c**. However, in these cases both the yields of the products and the endoselectivity decreased, compared with those in the photoreaction of **1a** with **2a**.

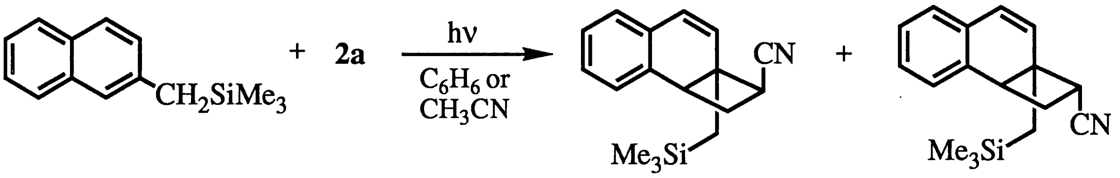
The photocycloadducts were isolated by column chromatography on silica gel. The structures of the products were determined by their spectral properties and elemental analyses.[5)] Treatment of **3a** with t-BuOK in DMF at room temperature

Table 1. Photocycloadditions of Electron-Deficient Alkenes to Naphthalene Derivatives

Compd ($E^{ox}_{p/2}$ /V)[a)]	Alkene	Time/h	Product(s)	Ratio	Yield/%[b)]	Recovery of 1 and 8/%	$k_q\tau/M^{-1}$[c)]	$k_q/M^{-1}s^{-1}\times10^{-7}$[d)]
1a (0.96)	**2a**	4	**3a+4a**	15:1	50	50	1.6	3.8
	2a[e)]	3	**3a+4a**	15:1	5	<5		
	2b	32	**3b+4b**	2:1	20	50	0.4	0.9
	2c	12	**3c+4c**	1:1	10	60	3.6	8.5
1b (0.80)	**2a**	5	**5a+6a**	15:1	40	46	2.9	
	2b	35	**5b+6b**	3:1	39	46	1.7	
	2c	13	-	-	0	100		
1c	**2a**	3	**7**	-	27	50	1.1	
1d (0.60)	**2a**	5	-	-	0	<5		
8	**2a**	6	**9+10**	2:1	49	50	0.9	2.6
	2a[e)]	4	**9+10**	4:1	50	20		

a) Oxidation potentials vs. Ag/Ag^+ in acetonitrile. b) Yields based on **1** and **8** used. c) M^{-1}=$mol^{-1}dm^3$.
d) τ; **1a** = 42.2 ns, **8** = 34.6 ns. e) In acetonitrile.

gave **4a**. This chemical conversion also supports the assigned structure. The photoreaction of **2a** with 1-naphthylmethyltrimethylgermane **1b** under similar conditions gave the cycloadducts **5a** and **6a**, and the photoreaction of **2a** with 1-naphthylmethyldisilane **1c** afforded **7** in good yields with high regio- and endo-selectivities. The photocycloaddition also occurred even between **2a** and 2-naphthylmethyltrimethylsilane **8**, giving a pair of the cycloadducts **9** and **10** in a 2 : 1 ratio. The endoselectivity in this photoreaction rose to give **9** and **10** in a 4 : 1 ratio when the photoreaction was carried out in acetonitrile instead of benzene.



8 **9** **10**

Irradiation of 1-naphthylmethyltributylstannane **1d** and 1-methylnaphthalene[6] **1e** in the presence of **2a** in benzene and acetonitrile gave complex mixtures. In the case of **1d**, 1,2-bis(1-naphthyl)ethane was obtained as a major product, probably via the homolysis of the C-Sn bond.

The fluorescence of **1a-c** and **8** in cyclohexane was effectively quenched by **2a-c**, but the quenching rates were rather slow; the rate constants for the quenching were in the range of 10^7 - 10^8 $M^{-1}s^{-1}$ (Table 1). The oxidation potentials of the naphthalene derivatives were lowered by group 14 metal-containing substituents, indicating that the naphthalene ring is activated by these electron-donating substituents; it is known that the photocycloaddition of electron-deficient alkenes to naphthalene ring is facilitated by strong electron-donating substituents on the naphthalene ring.[3] The C-Sn bond of **1d** at the excited state is very weak, so that this bond is cleaved upon photoirradiation. From these results, we tentatively propose the mechanism shown in Scheme 1, which involves exciplexes as key intermediates, for these photocycloadditions, although the exciplex emmision was not

$$\mathrm{A} + \mathrm{D} \xrightarrow{h\nu} \mathrm{A} + {}^{1}\mathrm{D}^{*} \longrightarrow \underset{\text{Exciplex}}{{}^{1}[\mathrm{A}\cdots\mathrm{D}]^{*}} \longrightarrow \text{Cycloadducts}$$

A : Alkenes **D** : Naphthalene derivatives

Scheme 1.

observed. It is noteworthy that in the photocycloaddition presented here, (1) the regioselectivity is extremely high, and (2) the endoselectivity is also high except for the **1a-2c** system.

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5) Spectral data of cycloadducts: **3a**; oil; ^1H NMR (270 MHz, $CDCl_3$) δ -0.01(s, $SiMe_3$), 1.58(ABq, $\Delta\nu$=29.7 Hz, J=16.2 Hz, CH_2Si), 2.37-2.49(m, CH_2), 2.66-2.80(m, CH_2), 3.06-3.19(m, C=C-CH), 3.45-3.55(m, CHCN), 5.83(dd, J=1.2 and 2.4 Hz, PhC=CH), 6.37(d, J=2.4 Hz, PhCH=C), 6.90-7.40(m, ArH), **4a**; oil; ^1H NMR (270 MHz, $CDCl_3$) δ -0.11 (s, $SiMe_3$), 1.13(ABq, $\Delta\nu$=27.0 Hz, J=16.2 Hz, CH_2Si), 2.22-2.35(m, CH_2), 2.51-2.64(m, CH_2), 2.90-3.05(m, C=C-CH), 3.35-3.45(m, CHCN), 5.83(dd, J=1.2 and 2.4 Hz, PhC=CH), 6.36(d, J=2.4 Hz, PhCH=C), 6.96-7.40(m,ArH), **9**; mp 82-83 °C, ^1H NMR (270 MHz, $CDCl_3$) δ -0.15(s, $SiMe_3$), 1.08(ABq, $\Delta\nu$=28.3 Hz, J=12.1 Hz, CH_2Si), 2.30-2.52(m, CH_2), 3.12(t, J=2.4 Hz, PhCH), 3.29(t, J=2.4 Hz, CHCN), 5.83(dd, J=0.4 and 2.4 Hz, PhC=CH), 6.59(d, J=2.4 Hz, PhCH=C), 6.90-7.25(m, ArH),**10**; mp 94-95 °C, ^1H NMR (270 MHz, $CDCl_3$) δ -0.13(s, $SiMe_3$), 1.22(ABq, $\Delta\nu$=89.1 Hz, J=13.5 Hz, CH_2Si), 2.40-2.50(m, CH_2), 3.12(t, J=2.4 Hz, PhCH), 3.55(t, J=2.4 Hz, CHCN), 5.62(dd, J=0.4 and 2.4 Hz, PhC=CH), 6.46(d, J=2.4 Hz, PhCH=C), 6.90-7.25(m, ArH).
6) Very recently, the photocycloaddition of **2a** to 1- and 2-methylnaphthalenes was reported, although the regioselectivity was not high: J. J. McCullough, T. B. McMurry, and D. N. Work, *J. Chem. Soc., Perkin Trans. 1*, **1991**, 461.

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