Allyl-transfer Reaction from Photoexcited Hypervalent Allylsilicon Reagent toward Dicyanobenzenes

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Photoreaction between dicyanobenzenes and a hypervalent allylsilicon reagent using 2,3-dihydroxynaphthalene as a ligand on silicon efficiently proceeded to afford allyl-substituted benzonitriles in moderate to good yields. The present photoreaction was found to occur based on the excitation of the hypervalent allylsilicon reagent.

Photoinduced electron-transfer (PET) reaction, which gives a radical ion pair $(D + A \rightarrow D^{+} + A^{-})$, is an important reaction employed as a key step in organic photochemistry. However, the competitive back electron transfer (BET; from A⁻⁻ to D⁺⁺) decreases the efficiency of PET, thus various methods to suppress BET have been developed.¹ Among them, the use of group 14 organometallic compounds has received considerable attention due to their easy handling and C-M bond cleavage of D^{++, 2-8} Since allylsilicon reagents such as allyltrimethylsilane (2a) possess a relatively low oxidation potential, it is already known to behave as an electron donor in the photoallylation of iminium salts,⁴ aromatic imides,⁵ unsaturated nitriles,⁶ and aromatic nitriles.⁷ We have reported that hypervalent allylsilicon reagent 2b was found to facilitate the photoallylation reaction of carbonyl compounds more effectively than allylsilane 2a.⁸ The reason for the efficiency is much lower oxidation potential of 2b than 2a.

Recently, we have also reported efficient photoreaction of dicyanoarenes with 2b.9 In contrast to the photoreaction of pdicyanobenzene (1a) with 2a (Table 1, Entry 1),¹⁰ photoreaction with 2b proceeded effectively to afford *p*-allylbenzonitrile (3a) in 82% yield after 7h (Table 1, Entry 2). The presence of a photosensitizer was critical; without anthracene, only 8% of 3a was obtained (Entry 3). When a novel hypervalent allylsilicon reagent 2c, which was prepared from allyltrimethoxysilane, 2,3dihydroxynaphthalene, and tetramethylammonium hydroxide, was employed under similar reaction conditions, 1a was completely consumed after 4h to afford the product 3a in 85% yield (Entry 4). Interestingly, photoreaction of 1a with 2c in the absence of anthracene also proceeded to give 3a in 78% vield (Entry 5), in contrast to the result in Entry 3. However, it was difficult to explain the large difference of the reactivity for this photoreaction by the small difference of oxidation potentials between 2b and 2c.

To explore the reason of the large enhancement of the photoreaction with 2c, UV-vis spectra of hypervalent allylsilicon reagents 2b and 2c along with *p*-dicyanobenzene (1a) were measured (Figure 1). The UV-vis spectrum of 2c showed characteristic absorption between 310 and 360 nm in contrast to those of 2b and 1a. This observation prompted us to assume that the photoreaction between 1a and 2c proceeded by the preferential excitation of 2c. To demonstrate our hypothesis, we



^aReaction conditions: a mixture of **1a** (0.2 mmol), **2** (0.3 mmol), and photosensitizer (0.1 mmol) in DMF (10 mL) in a Pyrex test tube was irradiated by a high-pressure mercury lamp under N_2 . ^bIsolated yield. ^cReaction time was 4 h.



Figure 1. UV-vis spectra of 2b, 2c, and 1a $(1.0 \times 10^{-4} \text{ M in DMF})$.

 Table 2. Photosubstitution reaction of 1a under the irradiation of various light^a

Entry	Silicon reagent	Light, λ /nm	Yield of $3a/\%^b$
1	2c	>310	68
2	2c	>330	45
3	2b	>310	trace
4	2b	>330	trace

^aReaction conditions: as shown in Table 1 with an appropriate filter solution. Also see Supporting Information. ^bIsolated yield of **3a**.



Figure 2. Stern–Volmer plot of 2c with 1a as a quencher.

next investigated the photoreaction using light of $\lambda > 310 \text{ nm}^{11}$ and $> 330 \text{ nm}^{12}$ which were not absorbed by **1a**. The results are summarized in Table 2. As expected, the irradiation of light of $\lambda > 310 \text{ nm}$ afforded the product **3a** in a good yield (Entry 1). Furthermore, the irradiation at even longer wavelength also afforded **3a** in a moderate yield (Entry 2). In contrast, no reaction proceeded with **2b** under the irradiation of $\lambda > 310 \text{ nm}$ or > 330 nm light and **1a** was recovered almost quantitatively (Entries 3 and 4). These results clearly suggested that photoreaction as shown in Table 2 proceeded based on the excitation of allylsilicon reagent **2c**.

This characteristic feature was further confirmed by the fluorescence quenching experiment of **2c**. No charge-transfer interaction between silicon reagent **2c** and **1a** was detected in the UV–vis spectra. The fluorescence maximum of **2c** was observed at 348 nm and efficiently quenched by **1a** in acetonitrile. A Stern–Volmer plot showed good linearity with $k_q\tau = 105.9 \text{ M}^{-1}$ (Figure 2). In addition, the free energy change ΔG for the single electron transfer from excited **2c** (S₁ state) to **1a** was calculated to be negative ($-25.4 \text{ kcal mol}^{-1}$) in acetonitrile.¹³ These results indicated the S₁ state of **2c** was quenched by PET to give **1**⁻ and **2c**⁺⁺, then allyl transfer occurred according to radical mechanism accompanied by the elimination of silicate (C–Si bond cleavage) (Scheme 1).^{9,14}

Next, we investigated the photoreaction of analogous hypervalent organosilicon reagents 2d and 2e with 1a under irradiation with $\lambda > 280$ nm, > 310 nm, and > 330 nm. The results are shown in Table 3. β -Methallylsilicon reagent 2d afforded the corresponding product 3b in the indicated yields (Entries 1–3). Selective irradiation of 2d also promoted the reaction (Entries 2 and 3). Benzylsilicon reagent 2e was also attempted under the same conditions and was found to be



Scheme 1. Plausible reaction mechanism.

Table 3. Photosubstitution reaction of 1a with hypervalent organosilicon reagents $2^{\rm a}$



2		0 /		
1		>280	3b	58
2	2d	>310		48
3		>330		38
4^{c}	PhCH ₂	>280	3c	53
5°	2e	>310		21
6 ^c		>330		10

^aReaction conditions: as shown in Table 1 with an appropriate filter solution. Also see Supporting Information. ^bIsolated yield. ^cDMF (5 mL) was used.

reactive toward **1a** affording **3c** (Entries 4–6). But the efficiency was lower than those of **2c** and **2d**, especially when irradiated at the longer wavelength. The reason is so far unclear, but stability of the radical cation 2^{+} may be involved (C–Si bond cleavage step),¹⁵ because oxidation potentials of **2d** (+0.80 V) and **2e** (+0.80 V) are lower than that of **2c** and thus the efficiency of PET step should be also high.

To confirm the generality of the photoreaction via excited 2, we then examined the application to other isomers of dicyanobenzene. Both *o*-dicyanobenzene (**1b**) and *m*-dicyanobenzene (**1c**) underwent photoallylation with allylsilicon reagent **2c**. Here again, irradiations with three different wavelengths were attempted (Table 4). In every case, the corresponding allylated products were obtained. In the case of **1b**, the cyano-substituted

Table 4. Photosubstitution reaction of o- and *m*-dicyanobenzenes (1b and 1c) with hypervalent organosilicon reagents $2c^{a}$

Entry	1	Light, λ /nm	Products	Yield/% ^b	
	1		Flouters	4, 6	5, 7
1	1b	>280	CN	56	13
2		>310		33	11
3		>330	4 5	15	7
4	1c	>280		7	28
5		>310		trace	18
6		>330	6 7	trace	18

^aReaction conditions: as shown in Table 1 with an appropriate filter solution. Also see Supporting Information. ^bIsolated yield.

4 was mainly provided, accompanied by the hydrogen-substituted **5** (Entries 1–3). In contrast, the reaction with **1c** hardly afforded the cyano-substituted **6**, while the hydrogen-substituted **7** was mainly obtained in low yield (Entries 4–6).

In summary, it was found that photoreaction of dicynobenzenes 1 with hypervalent organosilicon reagents 2c using the 2,3-dihydroxynaphthalene as a ligand proceeded via photoexcited 2c. To the best of our knowledge, the photopromoted allylation reactions with organometallic reagents were generally initiated by the excitation of the electron acceptor or the sensitizer. This is the first example of photoallylation based on the excitation of organosilicon reagent.¹⁶ The present approach would enable photoreaction to proceed independent from the absorption wavelength of the electron accepting substrate. Further investigation for the application to a variety of substrates using the present approach is ongoing in our laboratory.

The authors thank Dr. Takehiro Ohta and Prof. Yoshinori Naruta, Institute for Materials Chemistry and Engineering, Kyushu University, for their measurement of the ESI-MS spectrum.

Supporting Information is available electronically on J-STAGE.

References and Notes

- a) A. G. Griesbeck, N. Hoffmann, K. Warzecha, Acc. Chem. Res. 2007, 40, 128. b) N. Hoffmann, J. Photochem. Photobiol., C 2008, 9, 43.
- 2 a) A. Takuwa, H. Tagawa, H. Iwamoto, O. Soga, K. Maruyama, *Chem. Lett.* 1987, 1091. b) A. Takuwa, Y. Nishigaichi, K. Yamashita, H. Iwamoto, *Chem. Lett.* 1990, 639. c) A. Takuwa, Y. Nishigaichi, K. Yamashita, H. Iwamoto, *Chem. Lett.* 1990, 1761. d) A. Takuwa, Y. Nishigaichi, H. Iwamoto, *Chem. Lett.* 1991, 1013. e) Y. Nishigaichi, N. Yoshida, M. Matsuura, A. Takuwa, *Chem. Lett.* 1999, 803. f) S. Kyushin, S. Otani, T. Takahashi, Y. Nakadaira, M. Ohashi, *Chem. Lett.* 1991, 775.
- 3 a) E. Hasegawa, W. Xu, P. S. Mariano, U. C. Yoon, J. U. Kim, *J. Am. Chem. Soc.* 1988, *110*, 8099. b) U. C. Yoon, Y. C. Kim, J. J. Choi, D. U. Kim, P. S. Mariano, I.-S. Cho, Y. T. Jeon, *J. Org. Chem.* 1992, *57*, 1422. c) E. Hasegawa, M. A. Brumfield, P. S. Mariano, U.-C. Yoon, *J. Org. Chem.* 1988, *53*, 5435. d) D. W. Cho, U. C. Yoon, P. S. Mariano,

Acc. Chem. Res. 2011, 44, 204.

- 4 a) K. Ohga, P. S. Mariano, J. Am. Chem. Soc. 1982, 104, 617. b) A. J. Y. Lan, R. O. Heuckeroth, P. S. Mariano, J. Am. Chem. Soc. 1987, 109, 2738. c) I.-S. Cho, C.-L. Tu, P. S. Mariano, J. Am. Chem. Soc. 1990, 112, 3594. d) S. Fukuzumi, M. Fujita, S. Noura, K. Ohkubo, T. Suenobu, Y. Araki, O. Ito, J. Phys. Chem. A 2001, 105, 1857.
- 5 Y. Kubo, T. Imaoka, T. Shiragami, T. Araki, *Chem. Lett.* 1986, 1749.
- 6 K. Mizuno, M. Ikeda, Y. Otsuji, Chem. Lett. 1988, 1507.
- 7 a) K. Mizuno, K. Nakanishi, Y. Otsuji, *Chem. Lett.* 1988, 1833. b) M. Mella, E. Fasani, A. Albini, *J. Org. Chem.* 1992, 57, 6210. c) K. Nakanishi, K. Mizuno, Y. Otsuji, *Bull. Chem. Soc. Jpn.* 1993, 66, 2371. d) T. Tamai, K. Mizuno, I. Hashida, Y. Otsuji, *Bull. Chem. Soc. Jpn.* 1993, 66, 3747.
- 8 a) Y. Nishigaichi, A. Suzuki, T. Saito, A. Takuwa, *Tetrahedron Lett.* 2005, 46, 5149. b) Y. Nishigaichi, A. Suzuki, A. Takuwa, *Tetrahedron Lett.* 2007, 48, 211.
- 9 D. Matsuoka, Y. Nishigaichi, Chem. Lett. 2014, 43, 559.
- 10 In ref 7c, Mizuno et al. reported a good yield of **3a** in the reaction between **1a** and **2a**, though large excess of **2a**, long reaction time, and phenanthrene as a sensitizer were employed.
- 11 T. Sakurai, H. Sukegawa, H. Inoue, *Bull. Chem. Soc. Jpn.* 1985, 58, 2875.
- 12 Acetone filter was used.
- 13 Oxidation potential of **2c** was measured to be 0.99 V. Reduction potential of **1a** was -1.53 V.⁹ E_{0-0} value for **2c** is taken as 82.2 kcal mol⁻¹. ΔG is determined according to the following literature. D. Rehm, A. Weller, *Isr. J. Chem.* **1970**, *8*, 259.
- 14 In the reaction mixture, hexacoordinate tris(2,3-naphthalenediolato)silicate was observed by means of ¹H NMR. It was probably derived by the ligand redistribution from the eliminated silicon moiety. A. Suvitha, B. Varghese, M. N. S. Rao, G. Sundararajan, B. Viswanathan, *Indian J. Chem.* 2006, 45A, 2193.
- 15 K. P. Dockery, J. P. Dinnocenzo, S. Farid, J. L. Goodman, I. R. Gould, W. P. Todd, J. Am. Chem. Soc. 1997, 119, 1876.
- 16 Photopromoted intramolecular alkyl-transfer of 6-coordinate organosilicon reagents: a) J. Wagler, T. Doert, G. Roewer, *Angew. Chem., Int. Ed.* 2004, 43, 2441. b) J. Wagler, G. Roewer, D. Gerlach, Z. Anorg. Allg. Chem. 2009, 635, 1279.