## Photosubstitution of Dicyanoarenes by Hypervalent Allylsilicon Reagents via Photoinduced Electron Transfer

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Photosubstitution of dicyanoarenes with hypervalent allylsilicon reagents in the presence of anthracene efficiently proceeded to afford the allyl-substituted product in moderate to good yields. The efficiency for the present photoreaction was much higher than that for the tetracoordinate allylsilanes, because hypervalent allylsilicon reagents possess lower oxidation potential than the tetracoordinate ones, which resulted in more efficient photoinduced electron-transfer process.

Photoreaction is one of the important reactions employing environmentally friendly energy source for organic synthesis. In particular, photoinduced electron-transfer reactions involving group 14 organometallic compounds have received considerable attention.<sup>1–7</sup> Allylsilicon reagents such as allyltrimethylsilane (**2a**) possess relatively low oxidation potential and are known to behave as electron donors in the photoallylation of iminium salts,<sup>3</sup> aromatic imides,<sup>4</sup> unsaturated nitriles,<sup>5</sup> and aromatic nitriles.<sup>6</sup> Mizuno and co-workers have reported the photoallylation of dicyanobenzenes with allylsilanes such as **2a**, which afforded allylbenzonitriles **3**, products substituted by an allyl group for a cyano group, in good yield. However, it required long reaction time and large excess of the reagent (Scheme 1).<sup>6a–6e</sup>

Recently, we reported that the photoallylation reaction of carbonyl compounds was effectively achieved by employing a hypervalent allylsilicon reagent,<sup>7</sup> which was hardly achieved using allylsilane. We anticipated that the hypervalent allylsilicon reagents could be employed for more efficient photoallylation owing to their lower oxidation potentials than allyltrimethylsilane. In this paper, we will report the photoallylation reagent **2b** (Scheme 1).

Initially, we investigated the photoreaction of *p*-dicyanobenzene (1a) with 2b in various solvents in the presence of phenanthrene as a photosensitizer.<sup>8</sup> The results are shown in Table 1 along with the donor numbers and  $E_{\rm T}$  values of the solvents.<sup>10</sup> A nonpolar solvent such as benzene<sup>11</sup> afforded 4-





allylbenzonitrile (**3a**) in a low yield (Entry 1). When polar solvents with moderate donisity such as acetonitrile and methanol were employed, the product yield was still low (Entries 2 and 3). Then, polar and highly donating solvents such as DMF and DMSO were investigated (Entries 4 and 5). In these cases, moderate to good yields were obtained. Among the solvents examined, DMF was found to provide the best result, affording **3a** in 69% yield (Entry 4).

Next, the effect of a photosensitizer was examined in DMF (Table 2). When naphthalene was employed, the product **3a** was obtained in only 14% yield (Entry 1). A higher yield was observed when pyrene or anthracene was employed, which afforded the product in 80% or 82% yield, respectively (Entries 3 and 4). These results indicated that a photosensitizer possessing comparable oxidation potential to that of **2b** (+1.12 V) was more effective in the present reaction. In contrast, photoreaction without a photosensitizer afforded the product in very low yields (Entry 5). Therefore, a photosensitizer plays an important role in the present reaction. Thus, we selected anthracene as an optimized photosensitizer.

To demonstrate the efficiency of this photoreaction using hypervalent allylsilicon reagent **2b**, the photoreaction of **1a** with

**Table 1.** Screening of reaction solvent<sup>a</sup>

Entry	Solvent	$DN^{b}$ /kcal mol <sup>-1</sup>	$E_{\rm T}{}^{\rm b}$ /kcal mol <sup>-1</sup>	Yield /% <sup>c</sup>
1	C <sub>6</sub> H <sub>6</sub> -MeCN (4:1)	0.1 <sup>d</sup>	34.3 <sup>d</sup>	16
2	MeCN	14.1	45.6	20
3	MeOH	19.0	55.4	24
4	DMF	26.6	43.8	69
5	DMSO	29.8	45.1	30

<sup>a</sup>Reaction conditions: a mixture of **1a** (0.2 mmol), **2b** (0.3 mmol), and phenanthrene (0.1 mmol) in a solvent (10 mL) was irradiated ( $\lambda > 280$  nm) for 7 h under N<sub>2</sub>. <sup>b</sup>See ref 10. <sup>c</sup>Isolated yield. <sup>d</sup>Values are for benzene alone.

Table 2. Screening of photosensitizer (sens.)<sup>a</sup>

Entry	Photosensitizer	$E_{\rm ox}$ of sens./V <sup>b</sup>	$E^*_{ox}$ of sens./V <sup>b</sup>	Yield/% <sup>c</sup>
1	naphthalene	+1.54	-2.45	14
2	phenanthrene	+1.50	-2.10	69
3	pyrene	+1.16	-2.18	80
4	anthracene	+1.09	-2.22	82
5	none			8

<sup>a</sup>Reaction conditions: a mixture of **1a** (0.2 mmol), **2b** (0.3 mmol), and a photosensitizer (0.1 mmol) in DMF (10 mL) was irradiated ( $\lambda > 280$  nm) for 7 h under N<sub>2</sub>. <sup>b</sup>vs. SCE in MeCN. See ref 12. <sup>c</sup>Isolated yield.



Scheme 2. Plausible reaction mechanism.



Table 3. Photosubstitution reaction of dicyanoarenes 1 with 2b<sup>a</sup>

<sup>a</sup>Reaction conditions: a mixture of **1** (0.2 mmol), **2b** (0.3 mmol), and anthracene (0.1 mmol) in DMF (10 mL) was irradiated for 7 h under  $N_2$ . <sup>b</sup>Isolated yield. <sup>c</sup>Yield was determined by <sup>1</sup>H NMR. <sup>d</sup>Reaction conditions: a mixture of **1e** (0.1 mmol) and **2b** (0.15 mmol) in DMF (10 mL) was irradiated without anthracene.

allyltrimethylsilane (2a) was examined under the same reaction conditions as shown in Table 2. In the presence of anthracene, *p*dicyanobenzene (1a) was not reacted with 2a, and most of 1a was recovered. When phenanthrene was employed as a photosensitizer in place of anthracene, allylated product 3a was obtained in 14% yield, which was much lower than that with 2b.<sup>13</sup> In addition, only a small amount of 1a was recovered after the photoreaction, which indicated the decomposition of 1a in DMF under the present conditions.<sup>14</sup> These results showed that the reaction efficiency of photoreaction between 1a and allylsilane 2a in DMF was lower than that of hypervalent allylsilicon reagent 2b.

The plausible mechanism for the photosubstitution reaction with hypervalent allylsilicon reagents in the presence of anthracene is shown in Scheme 2. This photoreaction should be initiated by the photoinduced electron transfer (PET) from excited anthracene to **1** to afford radical ions **A** and **B**. This process is rationalized by the oxidation potential of excited anthracene  $(-2.22 \text{ V})^{12}$  and the reduction potential of **1** (-1.53 V).<sup>15</sup> Then, secondary single electron transfer (SET) occurs from **2** to radical cation **A** to regenerate neutral anthracene and radical cation **C**. This process is also operative because of the comparative oxidation potentials of anthracene (i.e., reduction potential of **A**) and **2b**. When allylsilane **2a** is employed, this step hardly proceeds because oxidation potential of anthracene (ground state) is much lower than that of **2a**. The radical cation **C** is attacked on the silicon atom by a nucleophile<sup>7b,16,17</sup> such as DMF to promote the C–Si bond cleavage and affords allyl radical **D**. Then, allyl radical **D** and radical anion **B** form the C–C bond by radical coupling to afford anionic intermediate **E**. Finally, elimination of cyanide ion proceeds to afford the allyl-substituted product 3.

With the optimized reaction conditions in hand, we examined the photochemical allyl-substitution reaction between other dicyanoarenes and allylsilicon reagent 2b (Table 3). o-Dicvanobenzene (1b) reacted with 2b to afford 2-allylbenzonitrile (3b) in 36% yield along with 4-allyl-1,2-dicyanobenzene (4b) in 21% yield as a by-product (Entry 1). This result can be explained by the steric hindrance of the neighboring cyano group at the ipso attack. m-Dicyanobenzene (1c) also reacted with 2b (Entry 2); however, the substitution product, 3-allylbenzonitrile (3c), was hardly obtained. Instead, 4-allyl-1,3dicyanobenzene (4c) that was substituted by the allyl group for the 4-position hydrogen was obtained in 40% yield as the main product. Polycyclic dicyanoarenes such as 1,4-dicyanonaphthalene (1d) and 9,10-dicyanoanthracene (1e) also reacted with 2b to afford 1-allyl-4-cyanonaphthalene (3d) and 9-allyl-10-cyanoanthracene (3e) in 71% and 38% yield, respectively (Entries 3 and 4).

In summary, the photoallylation reaction (i.e., photocoupling reaction) of dicyanoarenes with hypervalent allylsilicon reagent 2b was found to proceed efficiently to afford allylsubstituted product in good yield in DMF. We consider that single electron transfer from 2b is apt to take place because of its lower oxidation potential than that of 2a. In addition, polycyclic dicyanoarenes was also applicable to obtain the corresponding allylated product in moderate to good yield. Further photochemical applications of hypervalent organosilicon reagents are now under way.

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