

# Remarkable enhancement of photo-allylation of aromatic carbonyl compounds with a hypervalent allylsilicon reagent by donor molecules

Yutaka Nishigaichi,\* Akira Suzuki and Akio Takuwa

*Department of Material Science, Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu-cho, Matsue, Shimane 690-8504, Japan*

Received 25 September 2006; revised 8 November 2006; accepted 10 November 2006

**Abstract**—Photo-allylation of various aromatic carbonyl compounds with a penta-coordinated allylsiliconate reagent was remarkably accelerated by the addition of a donor molecule. As the oxidation potential of the allylsiliconate was significantly decreased in the presence of a donor molecule, the more efficient photo-induced electron transfer from the allylsiliconate to the excited substrate was enabled by the hexa-coordination of the silicon atom.

© 2006 Elsevier Ltd. All rights reserved.

Nucleophilic allylation of carbonyl compounds is an important process in organic synthesis. Many organometallic methods have been developed on the basis of thermal reactions; classically, anionic and thus strongly basic reagents have been widely used and, recently, less basic ones have been employed with the aid of Lewis acid activation to afford various selectivities.<sup>1</sup> In contrast to such thermal allylations, photochemical carbonyl-allylation has been much less popular though its reactivity and selectivity are very characteristic.<sup>2</sup> In most cases, allylic tin reagents have been utilized due to their high reactivity in the photo-induced electron transfer (PET) process. However, the toxic drawback of organotin reagents makes the corresponding silicon reagents preferable instead, while their reported use is very limited for their lower reactivity. One successful example is photo-allylation of naphthaldehydes activated by the metal ion coordination.<sup>3</sup>

As another promising example, our previous report<sup>4</sup> has revealed that allylsilicon reagents can be activated toward photo-induced allylation of carbonyl compounds by the hypercoordination of the silicon atom. Though the reaction mode was very similar to that of the corre-

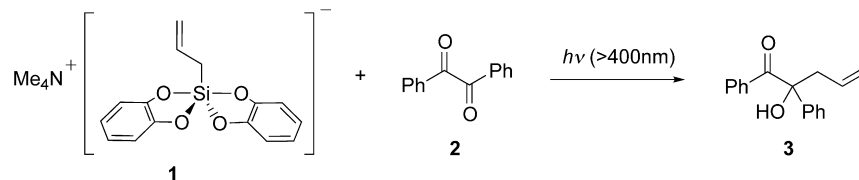
sponding allyltin reagents,<sup>5</sup> its reactivity was far from satisfaction: in the photoreaction<sup>6</sup> of benzil **2**, allylbisacetylcholosiliconate **1** gave only 22% of the allyl adduct **3** (Scheme 1 and Table 1, entry 2) while allyltrimethyltin afforded a nearly quantitative yield.<sup>5</sup> Thus, we have been making an effort to improve the reactivity.

As mentioned earlier,<sup>4</sup> the present photo-allylation is considered to proceed via photo-induced single electron transfer, which is known to be preferred in a polar solvent due to the stabilization of the resulting ion radicals by the solvation.<sup>7</sup> Therefore, methanol was attempted as a more polar solvent ( $E_T^N$  in Table 1)<sup>7</sup> than acetonitrile for the photoreaction between allylsiliconate **1** and benzil **2** and, indeed, found to give a much higher yield of the allyl adduct (Table 1, entry 3)<sup>8</sup> than acetonitrile (entry 2). In contrast, less polar solvent such as benzene<sup>9</sup> did not improve the yield of the adduct along with the formation of unidentified complex by-products (entry 1). As another polar solvent, DMF was also employed, which has a similar  $E_T^N$  value to acetonitrile. The result was unexpectedly successful; the adduct was obtained in a quantitative yield (entry 4). These results suggested that the solvent polarity might not be the dominant reason for the enhancement of the photo-allylation.

Accordingly, we next paid attention to the donicity (Lewis basicity) of the solvent. As shown in Table 1 in

*Keywords:* Allylation; Hypervalent elements; Photochemistry; Silicon and compounds; Solvents and solvent effects.

\* Corresponding author. E-mail: [nishigai@riko.shimane-u.ac.jp](mailto:nishigai@riko.shimane-u.ac.jp)



Scheme 1.

Table 1. Solvent effect on the allyl adduct (**3**) formation<sup>a</sup>

Entry	Solvent	$E_T^N$	$DN^N$	Yield of <b>3</b> (%)	Recovered <b>2</b> (%)
1	C <sub>6</sub> H <sub>6</sub> /CH <sub>3</sub> CN (8/2)	0.111 <sup>b</sup>	0.00 <sup>b</sup>	19	28
2	CH <sub>3</sub> CN	0.460	0.36	22 <sup>c</sup>	64
3	CH <sub>3</sub> OH	0.762	0.49	80	6
4	DMF	0.404	0.69	99	0

<sup>a</sup> Light was irradiated for 7 h.<sup>b</sup> Values are for benzene alone.<sup>c</sup> Taken from Ref. 4.

comparison to the  $E_T^N$  value, the solvent donicity,  $DN^N$ ,<sup>10</sup> appears more consistent with the corresponding yield. This fact indicated that the electron-donation of the solvent promoted the photo-allylation. Along this line, it was likely that a donor molecule would also be able to activate the photo-allylation even in a small amount but not as a solvent. As summarized in Table 2, to obtain a mechanistic insight, various donor molecules were added in an equivalent amount to the reaction mixture in acetonitrile. Interestingly, as the  $DN^N$  increased, the photoreaction exhibited a higher yield of the allyl adduct except for triethylamine. Methanol and DMF, which worked well as a solvent, were not effective as an additive of one equivalent (entries 1 and 2). But 6 equiv of DMF afforded much increased yield (entry 2). More donating DMSO was more effective as an additive (entry 3). When nitrogen donors, which are even more donating, were employed, more than 70% of the allyl adduct was obtained as shown in entries 4–7. Against these results, triethylamine, which has the highest  $DN$  among the attempted additives, showed a very poor yield (entry 8).

This additive effect was also supported by the measurement<sup>11</sup> of the oxidation potential  $E_{OX}$  of **1**, which is also shown in Table 2. Without any additive, **1** showed

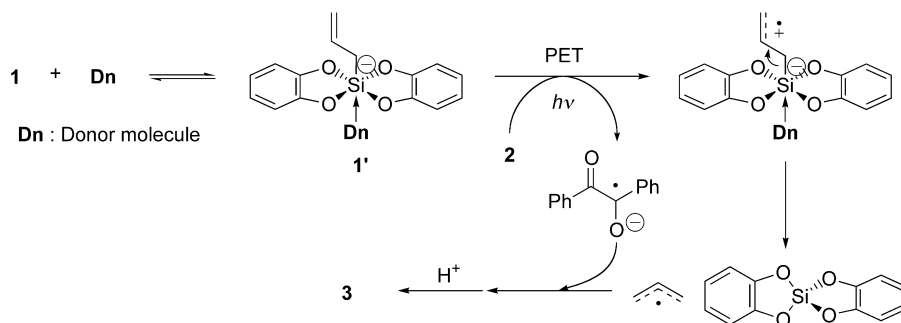
1.12 V (vs SCE) in acetonitrile.<sup>4</sup> When DMF or DMSO was added,  $E_{OX}$  was decreased to 1.08 or 1.06 V, respectively. More donating amines further decreased the value to 0.78–0.80 V, which is even lower than that of allyltrimethyltin (1.06 V). These results apparently indicate that the added donor molecule facilitates the electron transfer from **1** to the excited benzil **2**.

Therefore, a reaction path is proposed as shown in Scheme 2. The hexa-coordinated allylsiliconate species **1'** is supposed as a reacting intermediate, though such highly coordinated species could not be observed spectroscopically. In addition, it was reported that the thermal reaction of penta-coordinated allylsiliconates<sup>12</sup> such as **1** toward aldehydes proceeded via a cyclic transition state with a hexa-coordinated silicon center. Furthermore, that the thermal reaction of **1** was disturbed in a donor solvent<sup>12a</sup> strongly indicates the formation of a hexa-coordinated silicon species from **1** and the donor solvent. According to this scheme, the inconsistency of triethylamine can be explained by its oxidation potential. It showed the lower value (0.74 V) than **1**, while the other donor molecules showed the values higher than 0.98 V. Thus, uncoordinated triethylamine itself underwent the preferential electron transfer over **1**, which resulted in poor formation of the allyl adduct.

Table 2. Additive effect of donor molecules on the allyl adduct formation in CH<sub>3</sub>CN<sup>a</sup>

Entry	Donor molecule <sup>b</sup>	$DN^N$	$E_{OX}$ of <b>1</b> <sup>c</sup> (V)	Yield of <b>3</b> <sup>d</sup> (%)	Recovered <b>2</b> <sup>d</sup> (%)
1	CH <sub>3</sub> OH	0.49	—	11 (22)	80 (63)
2	DMF	0.69	1.08	38 (80)	61 (19)
3	DMSO	0.77	1.06	52	45
4	Pyridine	0.85	0.80	70	30
5	Imidazole	—	0.80	79	16
6 <sup>e</sup>	<i>n</i> -Butylamine	1.08	0.79	82	18
7 <sup>e</sup>	Piperidine	1.03	0.78	79	11
8	Triethylamine	1.57	—	9	62

<sup>a</sup> Irradiation time was 7 h unless otherwise noted.<sup>b</sup> An equimolar amount of the additive toward **1** was used.<sup>c</sup> See Ref. 11.<sup>d</sup> The values in the parentheses are for the reactions with 6 equiv of an additive.<sup>e</sup> Irradiation time was 4 h.



Scheme 2.

Since a donating solvent such as DMF or methanol remarkably enhanced the photo-allylation as mentioned above in Table 1, this method was applied to other aromatic carbonyl compounds. The results are collected in Table 3 compared with those in acetonitrile. It should be noted that donating solvents exhibited better results than acetonitrile in every case here but DMF was not necessarily the superior solvent for the substrates other than **2** because not only donicity but also polarity of the solvent should affect the reaction efficiency. As shown in entries 1 and 2, quinones, which are good electron acceptors, gave high yields of the corresponding adduct in methanol or DMF. Unsymmetrical 1,2-dione in entry 3 also underwent remarkable enhancement of the photo-allylation in methanol. It is interesting that

the benzoyl selectivity was observed as previously reported for the photo-allylation by the allyltin reagent.<sup>13</sup> This supports the radical mechanism of the present photo-allylation.

Mono-carbonyl compounds shown in entries 4–6 also experienced significant enhancement in a donating solvent, where they afforded moderate and comparable yields of allyl adducts to those of allyltin reagent.<sup>14</sup> The inefficient allylation was mainly due to the formation of pinacols, which were probably given by the photoreduction via rapid hydrogen abstraction.

In conclusion, efficient photo-allylation of aromatic carbonyl compounds by a hypercoordinated allylsilicate

Table 3. Photo-allylation of various carbonyl compounds with **1**

Entry	Substrate	Solvent, reaction time (h), wave length (nm)	Allyl adduct	Yield <sup>a</sup> (%)
1		MeOH, 3, >400		95 (84)
2		DMF, 1, >400		88 (47)
3		MeOH, 7, >400		47/26 (16/5) <sup>b</sup>
4		MeOH, 7, >330		58 (28)
5		MeOH, 7, >330		46 (11)
6		MeOH, 7, >330		32 (22)

<sup>a</sup> Values in parentheses are yields obtained by 7 h irradiation in acetonitrile as a solvent.

<sup>b</sup> Benzoyl adduct/acetyl adduct.

was realized in a donating solvent or by the addition of a donor molecule. The efficiency has been improved to as high as that of the corresponding tin reagent. These results possess considerable significance from both mechanistic and synthetic viewpoints. The hypercoordination-driven photo-allylation is more efficient with a hexa-coordinated reagent than with a penta-coordinated one. Furthermore, it opens up a way to the use of organosilicon reagents in the photo-allylation instead of the harmful tin counterpart. The present methodology will be applied to other substrates and other hyper-coordinated siliconate reagents including stereoselective reaction.<sup>14b,15</sup> Such projects are now in progress in our laboratory and the results will appear in due course.

### References and notes

1. Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207; Nishigaichi, Y.; Takuwa, A.; Naruta, Y.; Maruyama, K. *Tetrahedron* **1993**, *49*, 7395.
2. Nishigaichi, Y.; Takuwa, A. *Photochemistry* **2003**, *34*, 183.
3. Fukuzumi, S.; Okamoto, T.; Otera, J. *J. Am. Chem. Soc.* **1994**, *116*, 5503.
4. Nishigaichi, Y.; Suzuki, A.; Saito, T.; Takuwa, A. *Tetrahedron Lett.* **2005**, *46*, 5149.
5. Takuwa, A.; Nishigaichi, Y.; Yamashita, K.; Iwamoto, H. *Chem. Lett.* **1990**, 639.
6. A solution of a substrate (0.2 mmol) and **1** (0.3 mmol) in an indicated solvent (10 ml) was irradiated by a high pressure mercury lamp (300 W) through a suitable filter solution ( $\lambda > 400$  nm or 330 nm) at an ambient temperature under a nitrogen atmosphere. After an indicated period, the reaction mixture was condensed and chromatographed on silica gel to afford the products.
7. Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1988.
8. Photo-promotion of the allylation was confirmed by the control reaction in the dark, where no allyl adduct was obtained both in methanol and in DMF.
9. The allylsiliconate **1** was not soluble enough in benzene alone, thus 20% of acetonitrile was used as a co-solvent.
10. Marcus, Y. *J. Solution Chem.* **1984**, *13*, 599.
11. Redox potentials were measured using a DPV technique at 20 mV/s scan rate in acetonitrile. The values are reported versus SCE.
12. (a) Hosomi, A.; Kohra, S.; Ogata, K.; Yanagi, T.; Tominaga, Y. *J. Org. Chem.* **1990**, *55*, 2415; (b) Kira, M.; Sato, K.; Sakurai, H. *J. Am. Chem. Soc.* **1988**, *110*, 4599; (c) Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *J. Organomet. Chem.* **1987**, *328*, C17.
13. Takuwa, A.; Nishigaichi, Y.; Yamashita, K.; Iwamoto, H. *Chem. Lett.* **1990**, 1761.
14. (a) Takuwa, A.; Tagawa, H.; Iwamoto, H.; Soga, O.; Maruyama, K. *Chem. Lett.* **1987**, 1091; (b) Takuwa, A.; Shiigi, J.; Nishigaichi, Y. *Tetrahedron Lett.* **1993**, *34*, 3457.
15. Takuwa, A.; Nishigaichi, Y.; Yamaoka, T.; Iihama, K. *J. Chem. Soc., Chem. Commun.* **1991**, 1359.