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First examples of hypervalent enhancement of photoallylation by allylsilicon compounds via photoinduced electron transfer

Yutaka Nishigaichi,* Akira Suzuki, Takahiro Saito and Akio Takuwa

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

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Abstract—Hypervalency (pentacoordination) of silicon atom enhanced photoallylation of 1,2-diketones with allylsilicon reagents, while normal tetracoordinated ones could not. This reaction seems to proceed via photoinduced electron transfer from the silicon reagent to the photoexcited ketone judged from its reactivity and selectivity. © 2005 Elsevier Ltd. All rights reserved.

Allylation of carbonyl compounds is one of the fundamental synthetic reactions. Thermal reactions using anionic and thus strongly basic reagents such as lithium and Grignard reagents have been mostly employed. More recently, less basic allylmetals including those in Lewis acid mediated reactions have also been utilized to achieve various selectivities.¹ In contrast to such thermal allylations, photochemically promoted allylation has potential advantages that include neutral reaction conditions and clean acceleration by light. One successful example is the reaction between unsaturated carbonyl compounds and allyltin reagents via photoinduced electron transfer (PET).² As shown in Scheme 1, a quantitative yield of the allyl adduct (5) was realized in the reaction of allyltrimethyltin (2) with benzil (1). However, toxicity of organotin reagents is a serious drawback, thus analogous silicon reagents can be a promising candidate for their substitute. Actually, allyltrimethylsilicon (3) is known to behave as an electron donor in the photoallylation of iminium ions,³ aromatic cyanides,⁴ and aromatic imides,⁵ but it is far less reactive toward carbonyl compounds⁶ and acts as an ordinary alkene to give oxetane (6) as a major product² (Scheme 1). Therefore, we have investigated into the activation of such silicon reagents toward photoallylation of carbonyl compounds and found that it could be realized by hypercoordination of the silicon atom, which is described herein.

Though hypercoordinated allylsilicon reagents such as fluorosilicates, biscatecholatosiliconates, and silatranes have been applied to the thermal carbonyl allylation,⁷ their photochemical application has not yet been reported as far as we know. Such silicon reagents are considered to be more electron-rich than tetracoordinated ones



Scheme 1. Photochemical allylation with tin and silicon reagents.

Keywords: Photoallylation; Allylsilicon; Hypervalency; Electron transfer.

^{*} Corresponding author. Tel.: +81 852326415; fax: +81 852326429; e-mail: nishigai@riko.shimane-u.ac.jp

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	$Ph \stackrel{O}{\longrightarrow} Ph + R^{2} \stackrel{R^{1}}{\xrightarrow{\gamma}} \mathbf{s}_{i} \xrightarrow{hv (>400 \text{ nm})} H^{+}$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
	1 7 or 8	5 (α -adduct) 5 (γ -adduct)
Entry	Reagent	Adduct (yield/%) $[\alpha/\gamma]$
1	7a	5a (6)
2	8a	5a (22)
3	7b	5b (18)
4	8b	5b (73)
5	7c	5c (26) [72/28]
6	7d	5d (46) [83/17]
7	8d	5d (72) [85/15]
8	7e	5e (15)
9	8e	5e (29)

Table 1. Photoreaction of benzil with 7 or 8

due to the extra ligand's electron donation. Thus, reduced oxidation potential (i.e., hypervalent activation) of silicon reagents was expected and we attempted their application toward photoreaction of 1,2-diketones.

First, addition of Bu₄NF (TBAF) to the reaction between **1** and **3** was employed and was found to give the allyl adduct **5** in a moderate yield. But this was proved to be due to the thermal reaction because the same yield was obtained in the dark.⁸ Thus, we next tried less thermally reactive and more Lewis acidic allyltriethoxysilicon (**4**) with fluoride ion. Then, the photoallylation was actually realized for the first time by the hypercoordinated allylsilicon reagent though the yield was less than 20% (Scheme 1).

Encouraged by this result, we next attempted stable and readily preparable pentacoordinated silicon reagents such as silatrane 7 and catecholatosiliconate 8. Unsubstituted allyl reagents 7a and 8a were allowed to react with 1 in acetonitrile under photochemical conditions (Table 1, entries 1 and 2). Though 7a afforded only 6% of allylated product, 8a gave 22% after 7 h of irradiation.⁹ More reducible substrates, phenanthrenequinone and acenaphthenequinone, with 8a afforded the corresponding allyl adducts in much higher yields, 84% and 63%, respectively, under similar reaction conditions (Scheme 2).

Substituted allylic reagents, 7b-d and 8b,d were also prepared and applied to the photoreaction with benzil. The results are also summarized in Table 1. Again, catecholates 8 gave the higher yields. Especially, 8b and 8dafforded rather high yields up to 70%. Interestingly, α -regioselectivity was observed in the cases of 7c,d and 8d, which is very similar to the photoreaction with allylic tin reagents and is characteristic to the reaction via PET.

Table 2. Oxidation potentials of silicon and tin reagents

Entry	Silicon reagent	$E_{\rm ox}/{\rm V}^{\rm a}$	$\Delta G_{\rm ET}$ /kcal mol ^{-1 b}
1	Allyltrimethylsilicon (3)	1.64	8.4
2	7a	1.26	-0.4
3	8a	1.12	-3.6
4	Allyltrimethyltin (2)	1.06	-5.0
5	Benzyltrimethylsilicon	1.46	4.2
6	7e	1.20	-1.8
7	8e	1.10	-4.1

^a Values were measured in acetonitrile versus SCE.

^b $\Delta G_{\text{ET}} = 23.06(E_{\text{ox}} - E_{\text{red}} - \Delta E_{0-0}) + E_{\text{coul}}$, where E_{red} is the reduction potential of benzil (-1.13 V), ΔE_{0-0} is the excitation energy of benzil (2.35 eV), and E_{coul} is the electrostatic term for acetonitrile (-1.3 kcal mol⁻¹).



Scheme 2. Photoallylation of o-quinones with 8a.



Scheme 3. Plausible reaction mechanism for photoallylation with a hypervalent silicon reagent.

It is also noteworthy that benzylsilicon reagents 7e and 8e, which hardly react thermally, also underwent photobenzylation.

Activation of silicon reagents by the hypervalency for PET was supported by the measurement of oxidation potentials of 7 and 8. Selected data are listed in Table 2 with those of the corresponding trimethylsilyl reagents. In addition, the tin reagent 2 for which photoallylation is well known, is compared. All these hypervalent reagents show significantly lower values than the corresponding tetravalent silicon reagents. By means of the Rehm-Weller equation,10 the tetravalent ones give positive $\Delta G_{\rm ET}$ values (entries 1 and 5), which mean unfavorable PET. In contrast, the hypervalent ones show negative values, which mean PET can occur exothermally and approximately parallel to their reactivity. This trend is consistent with the reactivity of the tin reagent (entry 4).^{2b} These results point to the electron transfer mechanism of the present photoreaction.

From the above results, the following reaction scheme can be depicted as shown in Scheme 3. This is very similar to that with the corresponding tin reagents. Electron transfer from silicon reagents to the excited ketone is facilitated by the hypervalency, that is, extra donation of electrons from the ligand toward the silicon atom. In the allylation with allylsilicon reagents via the single electron transfer, C-Si bond fission of the cation radical is a very important step as well, because the back electron transfer (BET) would be preferred if the fission is slow. Therefore, it is probable that the extra ligand also facilitates the C-Si fission as an intramolecular nucleophile.¹¹ Then, the ketyl radical and the allyl radical are coupled to result in the adduct formation, where the sterically less hindered α -position of the allyl radical is preferred.

In conclusion, the photoallylation of aromatic diones with silicon reagents could be enhanced by the hypervalency of the silicon atom for the first time. These results suggest the hypervalency is an efficient method to promote photoinduced electron transfer. As the ligands employed here can be modified, development of the more effective photoreaction systems is in progress in our laboratory and will appear in due course.

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