Allylsilylation and stannylation of 1,2-diketones using bifunctional allylsilane–allylstannane reagents *via* photoinduced electron transfer reaction

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Received (in Cambridge, UK) 16th August 1999, Accepted 31st August 1999

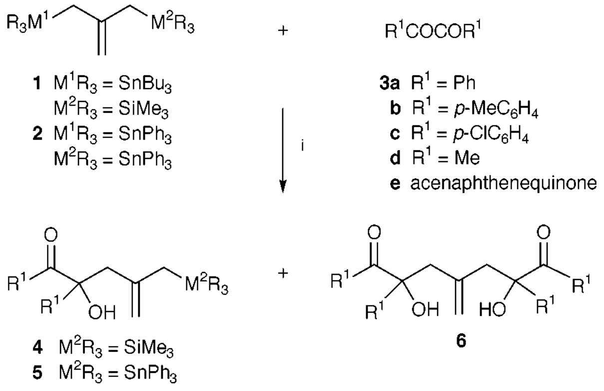
Bifunctional allylsilane–allylstannane and allylstannane–allylstannane reagents react photochemically with 1,2-diketones to give α-ketohomoallyl alcohols having an allylsilane moiety and α-ketohomoally alcohols having an allylstannane moiety respectively in excellent yields, and the remaining allylstannane moiety further reacts effectively with another diketone in the presence of $Mg(ClO_4)_2$ to afford a bis-α-ketohomoallyl alcohol.

The addition of allylsilane[1] and allylstannane[2] with various carbonyl compounds has been widely used as one of the most useful procedures for C–C bond formation. The process generally requires promoters such as Lewis acids which activate the electrophilic function of carbonyl compounds towards nucleophilic attack by the allylmetal reagents.[1–3] On the other hand, light-promoted addition *via* photoinduced electron transfer (PET) from allylstannane[4] and allylsilane[5] to the photoexcited carbonyl compounds has recently attracted considerable interest from both synthetic and mechanistic viewpoints. In these photoadditions, allylstannanes are good electron donors compared with the corresponding allylsilanes. For example, we found that the reaction of allylstannanes with benzophenones gave homoallylic alcohols *via* PET,[4] whereas allylsilanes behaved as an ordinary alkene to produce oxetanes and hydrogen abstraction products[6] without PET reaction. This observation prompted us to examine the photoadditon reactions of bifuntional allylsilane–allylstannane reagent **1** and allylstannane–allylstannane reagent **2** with 1,2-diketones. We expected that the differences in the reactivity of allylstannane and allylsilane would permit their differentiation in the bifunctional reagents under photochemical conditions.

Irradiation (>400 nm) of the absorption band of benzil **3a** (0.02 mol dm^{-3}) in a N_2-purged MeCN–benzene (5:1 v/v) solution containing 3-tributylstannyl-2-[(trimethylsilyl)methyl-]propene[7] **1** (0.03 mmol dm^{-3}) for 3 h at ambient temperature (Scheme 1) afforded an α-ketohomoallyl alcohol having an allylsilane moiety (**4a**). The 1:1 adduct **4a** was isolated in 90% yield by preparative TLC (silica gel, hexane–Et_2O, 4:1 v/v) and the structure was determined from its spectral properties and elemental analysis.† The allylsilane unit in the product **4a** does not react further with benzil even under prolonged irradiation or even under irradiation in the presence of $Mg(ClO_4)_2$ (*vide infra*).

The bifunctional allylsilane–allylstannane reagent **1** also reacted photochemically with other diketones **3** to produce the corresponding α-ketohomoallyl alcohols containing allylsilane moieties in moderate to good yields (Table 1, entries 1–4).

On the other hand, the light promoted reaction of **3** with 3-triphenylstannyl-2-[(triphenylstannyl)methyl]propene[8] **2** afforded two types of addition products, an α-ketohomoallyl alcohol with an allylstannane moiety **5** (1:1 adduct) and a bis-α-ketohomoallyl alcohol **6** (1:2 adduct), depending on the ratio of

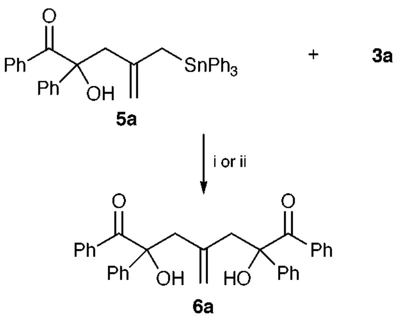


Scheme 1 *Reagents and conditions*: i, $h\nu$ (>400 nm), MeCN–benzene (4:1, v/v).

Table 1 Photoaddition reaction of the bifunctional allylmetal reagents with diketones

Entry	Allylmetal	Diketone	Ratio **1** (or **2**):**3**	*t*/h	Products	(% yield)[a]
1	**1**	**3a**	1.5:1	3	**4a** (90)[b]	**6a** (0)
2	**1**	**3b**	1.5:1	3	**4b** (92)[b]	**6b** (0)
3	**1**	**3c**	1.5:1	3	**4c** (78)[b]	**6c** (0)
4	**1**	**3d**	1.5:1	3	**4d** (57)	**6d** (0)
5	**2**	**3a**	1.5:1	3	**5a** (96)	**6a** (0)
6	**2**	**3a**	1.5:1	3[c]	**5a** (86)	**6a** (8)
7	**2**	**3a**	0.5:1	12	**5a** (25)	**6a** (56)[d]
8	**2**	**3a**	0.5:1	3[c]	**5a** (4)	**6a** (90)[d]
9	**2**	**3b**	1.5:1	3	**5b** (98)	**6b** (0)
10	**2**	**3b**	0.5:1	12	**5b** (14)	**6b** (67)[d]
11	**2**	**3c**	1.5:1	3	**5c** (98)	**6c** (0)
12	**2**	**3c**	0.5:1	12	**5c** (17)	**6c** (71)[d]
13	**2**	**3c**	0.5:1	3[c]	**5c** (<1)	**6c** (91)[d]
14	**2**	**3e**	1.5:1	3	**5e** (61)	**6e** (0)

[a] Isolated yields. [b] A small amount of butylated product, 1,2-diaryl-2-hydroxyhexan-1-one, was also produced. [c] Irradiation was carried out in the presence of 5 equiv. of $Mg(ClO_4)_2$. [d] Diastereomer ratio was 1:1.



Scheme 2 *Reagents and conditions*: i, *hν* (> 400 nm), MeCN-benzene (4 : 1, v/v); ii, *hν* (> 400 nm), $Mg(ClO_4)_2$, MeCN-benzene (4 : 1, v/v).

the bifunctional reagent **2** to the 1,2-diketones (Table 1). Thus irradiation of benzil in the presence of a 1.5-fold molar excess of the reagent **2** for 3 h produced the 1 : 1 adduct **5a** in very high yield (96%),‡ while irradiation in the presence of 0.5 equiv. of **2** gave both **5a** and 1 : 2 adduct **6a**, where the ratio of **5a** : **6a** gradually decreased with increasing irradiation time; these two adducts were isolated respectively in 25 and 56% yield after irradiation for 12 h (entry 7). These results show that the addition reactions proceed stepwise. Other diketones **3** also gave the 1 : 1 adduct **5** and/or the 1 : 2 adduct **6** in good yields, depending on the ratio of the substrates and the reagent as shown in Table 1.

The present allylsilylation and stannylation may be initiated by PET from the bifunctional reagents to the photoexcited diketones to generate the organometalic radical cation (**1**$^{\bullet+}$ or **2**$^{\bullet+}$)-ketyl radical anion (**3**$^{\bullet-}$) pair. The selective cleavage of the Sn–C(allyl) bond of the radical cation **1**$^{\bullet+}$ produces β-[(trimethylsilyl)methyl]allyl radical because of the Si–C bond being stronger than the Sn-C bond.[9] The resulting allyl radical couples with **3**$^{\bullet-}$ to give allylsilylated product **4**. In the case of the reaction using allylstannane–allylstannane reagent **2**, the β-[(triphenylstannyl)methyl]allyl radical formed by the fragmentation of **2**$^{\bullet+}$ couples with the ketyl radical **3**$^{\bullet-}$ to yield the allylstannylated product **5**.

Next we examined the subsequent addition step from 1 : 1 adduct **5** to 1 : 2 adduct **6**. Irradiation of an MeCN–benzene solution containing benzil (0.01 mmol dm^{-3}) and isolated **5a** (0.01 mmol dm^{-3}) for 3 h gave the 1 : 2 adduct **6a** in 55% yield (Scheme 2).

Interestingly, when the irradiation was carried out in the presence of 5 equiv. of $Mg(ClO4)_2$ under otherwise identical conditions, the yield of **6a** increased to 90%. These results suggest that the second addition reaction also proceeds *via* PET and Mg^{2+} accelerates the PET reaction, probably due to the higher reducing ability of the Mg^{2+}–benzil complex compared to that of uncomplexed benzil.[10] Therefore, the photochemical reaction of the bifunctional reagent **2** with 1,2-diketones in the presence of $Mg(ClO_4)_2$ was examined. The 1 : 2 adduct **6** was obtained in very high yield (> 90%) from the reaction with 0.5 equiv. of **2** in the presence of $Mg(ClO_4)_2$ (entries 8 and 13). Even in the reaction of benzil with an excess amount of **2** a small amount (8%) of **6** was also produced in the presence of the metal salt (entry 6). These results show that the first step of the PET reaction is faster than the second one and that Mg^{2+} should catalyze the present PET reaction.

In conclusion, the light-promoted addition reaction of bifunctional allylmetal reagents to 1,2-diketones yielded α-ketohomoallyl alcohols bearing allylsilane or allylstannane groups in high yields *via* single electron transfer reaction. These products are unlikely to be obtained from well known Lewis acid-promoted reactions, as they have both nucleophilic (allylmetal group) and electrophilic (carbonyl) functions in the same molecule which are sensitive to Lewis acids.[11] In addition, bis-α-ketohomoallyl alcohols were effectively produced by stepwise photoinduced electron transfer reaction between allylstannane–allylstannane reagent and 1,2-diketones. More detailed studies on the bifunctional reagents under photochemical conditions and the intramolecular cyclization reaction of the resulting α-ketohomoallyl alcohols are in progress in our laboratory.

This work was supported by a Grand-in-aid for Scientific Research (No 11640535) from the Ministry of Education, Science, Sports and Culture, Japan.

Notes and references

† *Selected data for* **4a** : needles, mp 77–79 °C; δ_H($CDCl_3$, 270 MHz) −0.02 [s, $Si(CH_3)_3$, 9H], 1.16 (d, *J* 13.2, C*H*HSiMe$_3$, 1H), 1.39 (d, *J* 13.2, CH*H*SiMe$_3$, 1H), 2.86 (d, *J* 13.4 , C*H*H, 1H), 3.18 (d, *J* 13.4, CH*H*, 1H), 4.08 (s, OH, 1H), 4.56 (s, C*H*H=, 1H), 4.72 (s, CH*H*=, 1H) and 7.26-7.86 (m, Ar*H*, 10H); ν_{max}(KBr)/cm^{-1} 3487, 1679, 1249, 1234 and 842; *m*/*z* 233 [(M − PhCO)$^+$], 105 (PhCO$^+$) and 73 (Me_3Si^+).

‡ *Selected data for* **5a**: prisms, mp 110–111 °C; δ_H($CDCl_3$, 270 MHz) 2.19 (d, *J* 11.0, C*H*HSnPh$_3$, 1H), 2.30 (d, *J* 11.0, CH*H*SnPh$_3$, 1H), 2.77 (d, *J* 13.7, C*H*H, 1H), 3.02 (d, *J* 13.7, CH*H*, 1H), 4.10 (s, OH, 1H), 4.47 (s, C*H*H=, 1H), 4.87 (s, CH*H*=, 1H) and 7.21–7.74 (m, Ar*H*, 25H); ν_{max}(KBr)/cm^{-1} 3515, 3059, 1671, 1428, 1239, 1073, 729 and 701.

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Communication 9/06620I