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Conjugate Addition of Allylic Groups to α,β-Enones via Photoinduced Electron Transfer Reaction of Allylic Stannanes

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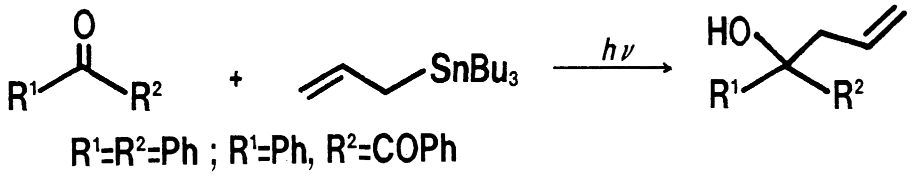
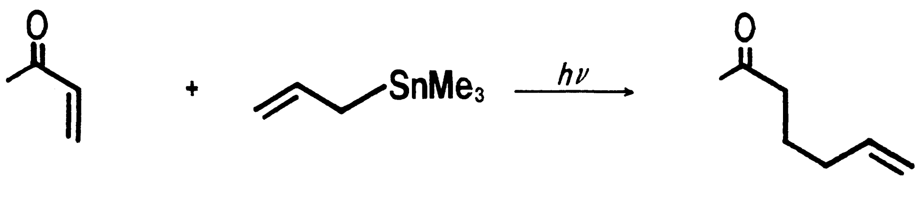
Conjugate addition of allylic groups, including allyl and cinnamyl systems, to a variety of α,β-unsaturated ketones could be achieved by photoirradiation with allylic stannanes.

Electron-transfer mediated photoallylation using allylic stannanes is the subject of a current interest from synthetic and mechanistic viewpoints. For example, photoallylation of iminium salts[1)] and cyanoaromatics[2)] using allylic stannanes has provided a novel method for carbon-carbon bond formation. Recently, we also reported that irradiation of benzophenones[3a)] or diphenylethanediones (benzils)[3b)] in the presence of allyltributylstannane resulted in the formation of homoallylic alcohols (1,2-addition products) via photoinduced electron-transfer (ET) pathway with fairly good to excellent yields (Eq. 1).[3)] Thoughts about the synthetic potential of the photoallylation led to an investigation of an additional manner (1,2- or 1,4-addition) of allylic groups to α,β-unsaturated ketones, and we describe here that the conjugate addition exclusively proceeds in this system (Eq. 2).



(1)



(2)

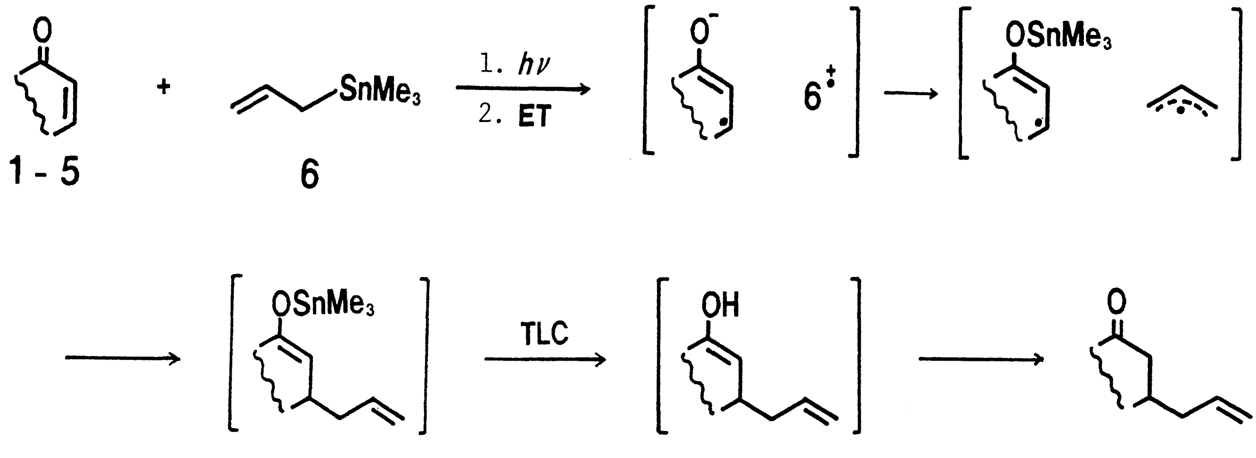
Irradiation[4)] of an acetonitrile solution of cyclohex-2-en-1-one (**1**) and allyltrimethylstannane (**6**) after purging with nitrogen gas followed by chromatographic separation (TLC) resulted in the formation of 3-allylcyclohexanone (**8**, 51%; Run 1 in Table

1).[5] No evidence was obtained for the formation of a 1,2-addition product by ^{1}H-NMR analysis of the irradiated solution prior to chromatography. Another cyclic enone, isophorone (**2**), afforded a similar conjugate addition product **9** (Run 2) as shown in Table 1. It is noteworthy that the allyl group can be introduced into the tertiary β-carbon under these conditions.

In order to explore this methodology for acyclic enones, we have examined the chalcone derivatives. Irradiation of 1,3-diphenyl-2-propen-1-one (**3**) with **1** afforded, however, [2+2]cycloadducts (cyclobutanes **10** and **11**)[6] without formation of any allylated products (Run 3). On the other hand, chalcones, **4** and **5**, having a cyano group on the phenyl ring yielded conjugate addition products, 5-hexen-1-one derivatives, **12**[5] and **13**, respectively (Runs 4 and 5). These results indicate that ET does not occur between photoexcited **3** and **1**, but it proceeds with **4** (E^{red} = -1.16 V) and **5** (E^{red} = -1.15 V) probably because of their lower reduction potentials than that of **3** (E^{red} = -1.45 V).[7]

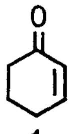
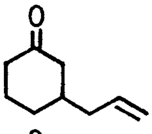
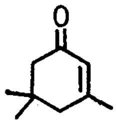
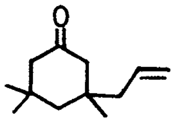
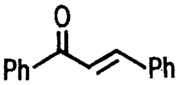
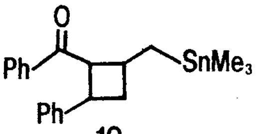
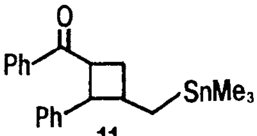
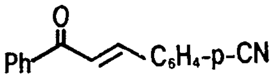
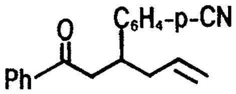
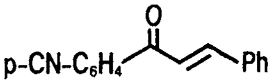
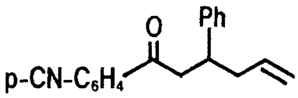
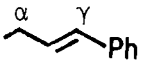
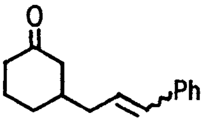
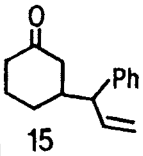
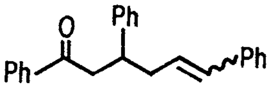
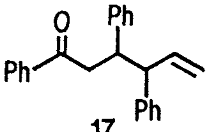
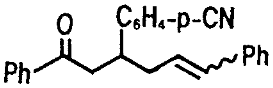
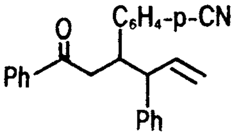
The photoallylation of enones with (E)-3-phenyl-2-propenyltrimethylstannane (cinnamylstannane, **7**) was also investigated to clarify the regiochemistry (α vs. γ-additions) of the introduced cinnamyl group, and the results are summarized in Table 1. In every case, the α-adduct was produced in preference to the γ-adduct, which can be explained by the steric bulk around the γ-terminus of cinnamyl group (Runs 6-8). The γ-adducts were always formed in an equimolar mixture of diastereoisomers. These results strongly indicate that the present addition reaction proceeds via a radical coupling process. In contrast to the reaction with **6** (Run 3), even chalcone **3** was smoothly cinnamylated with **7** (Run 6), which can be rationalized by the lower oxidation potentials of **7** (E^{ox} = 0.63 V) than that of **6** (E^{ox} = 1.24 V).[7]

From these findings, we propose the ET mechanism for the photoinduced conjugate-allylation of enones as shown in Scheme 1. ET from **6** to the excited enones gives a radical ion pair. The radical cation is dissociated to the trimethylstannyl cation and the allyl radical probably by nucleophilic attack of the enone radical anion,[8] and the resulting radical pair bonds to yield the products after ketonization.



Scheme 1.

Table 1. Photoallylation of Enones (**1**-**5**) with Allylic Stannanes (**6**-**7**)

Run	Allylic Stannane (Me_3Sn-R) R	Enone	Product(s) [Isomer ratio]	Yield/%[a]
1	 **6**	 **1**	 **8**	51
2	**6**	 **2**	 **9**	57
3	**6**	 **3**	 **10**  **11** [50 : 50]	40
4	**6**	 **4**	 **12**	50
5	**6**	 **5**	 **13**	55
6	 **7**	**1**	 **14**  **15** [64 : 36]	45
7	**7**	**3**	 **16**  **17** [60 : 40]	62
8	**7**	**4**	 **18**  **19** [60 : 40]	60

[a] Isolated yield based on enone used.

Thus, allylic groups of allylic stannanes were introduced to α,β-unsaturated ketones in a conjugate fashion under photochemical conditions.

References

1) R. M. Borg and P. S. Mariano, Tetrahedron Lett., **27**, 2821 (1986).

2) K. Mizuno, S. Toda, and Y. Otsuji, Chem. Lett., **1987**, 203; K. Mizuno, S. Toda, and Y. Otsuji, Nippon Kagaku Kaishi, **1987**, 1183; K. Mizuno, K. Nakanishi, and Y. Otsuji, Chem. Lett., **1988**, 1833.

3) a) A. Takuwa, H. Tagawa, H. Iwamoto, O. Soga, and K. Maruyama, Chem. Lett., **1987**, 1091; b) A. Takuwa, Y. Nishigaichi, K. Yamashita, and H. Iwamoto, ibid., **1990**, 639.

4) Typical experimental conditions are as follows: enone (0.3 mmol) and allylic stannane (0.45 mmol) in acetonitrile (10 ml) were irradiated with 300 W high-pressure mercury arc lamp through Pyrex for 12-15 h. After evaporation of the solvent, the products were isolated by TLC (hexane/ether=7/3).

5) **8** : ^{1}H-NMR (270 MHz, $CDCl_3$) δ 0.88-2.43(m, 11H), 5.03(dd, 2H, $=CH_2$, J=10.3 and 15.9 Hz), and 5.72(m, 1H, -CH=); ^{13}C-NMR (270 MHz, $CDCl_3$) δ 25.19(t), 30.92(t), 38.80(d), 40.85 (t), 41.43(t), 47.92(t), 116.85(t), 135.73(d), and 211.76(s); IR (CCl_3) 3000, 2950, 1705, 1610, 1450, 1210, and 920 cm^{-1}. **12** : ^{1}H-NMR ($CDCl_3$) δ 2.29(m, 1H), 2.53(m, 1H), 2.90 (dd, 1H, J=5.4 and 14.0 Hz), 3.18(dd, 1H, J=8.7 and 14.0 Hz), 3.80(m, 1H), 5.05(m, 2H, CH_2=), 5.74(m, 1H, C=CH-), and 7.26-7.83(m, 9H); IR (CCl_3) 3000, 2900, 2250, 1700, 1200, 910 cm^{-1}. All other conjugate addition products (**9**, **13**, and **14-19**) exhibited satisfactory spectral data.

6) **10** : ^{1}H-NMR ($CDCl_3$) δ 0.03(s, 9H), 0.58(dd, 1H, J=5.0 and 14.0 Hz), 0.70(dd, 1H, J=14.0 and 16.0 Hz), 1.98(m, 1H), 2.65(m, 1H), 2.98(m, 1H), 4.15(m, 1H), 4.28(m, 1H), 7.20-7.90 (m, 10H). **11** : 1H-NMR ($CDCl_3$) δ 0.05(s, 9H), 1.00(dd, 1H, J=14.0 and 15.0 Hz), 1.21 (dd, 1H, J=5.0 and 16.0 Hz), 1.82(m, 1H), 2.65(m, 1H), 3.56(m, 1H), 4.79(m, 1H), and 7.29-7.90 (m, 10H). The NMR data for **10** and **11** might be vise versa.

7) It is well known that the possibility of electron transfer process can be estimated by Rehm-Weller equation, in which the oxidation and reduction potentials of electron donor and acceptor are important factors. D. Rehm and A. Weller, Isr. J. Chem., **8**, 259 (1970).

8) Ketyl or semiquinone radical attacks nucleophilically to allyltrialkylstannyl radical cation to generate allyl radical. See Ref. 3a and also K. Maruyama and Y. Matano, Bull. Chem. Soc. Jpn., **63**, 2218 (1990).

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