# Stereoretentive introduction of (*E*)- and (*Z*)-γ-alkoxyallyl groups into carbonyl compounds *via* light-promoted reaction with γ-alkoxyallylstannanes

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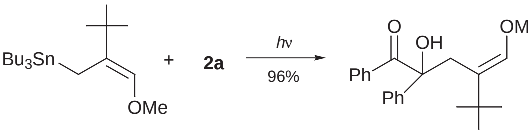
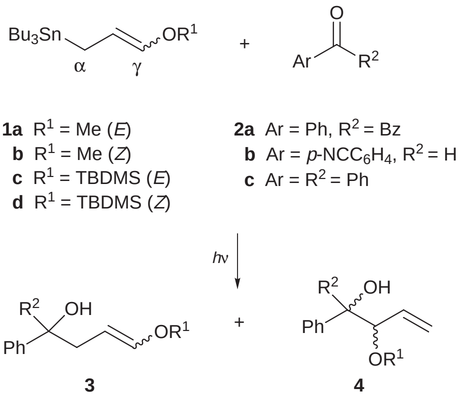
**The light-promoted condensation between carbonyl compounds and (*E*)- or (*Z*)-γ-alkoxyallylstannanes affords predominantly the linear homoallylic alcohols, with retention of the double bond geometry of the γ-alkoxyallyl moieties.**

It is well-known that both (*E*)- and (*Z*)-γ-methoxyallylstannanes add to aldehydes at the γ-position in the presence of $BF_3 \bullet OEt_2$ to produce the vicinal diol monomethyl ether (γ-product).[1] The α-ethoxyallylstannane also afforded the γ-product *via* a double allylic shift (one at the reagent level and the second in the addition reaction).[2] In addition, Thomas,[3] Marshall[4] and Gung[5] have reported that α-alkoxy or α-silyloxy substituted crotylstannanes also reacted at the γ-position with aldehydes or ketones under both thermal and Lewis acid-promoted conditions to afford the homoallyl alcohols having an alkoxy or silyloxy group at the terminus of the allylic carbon (*i.e.* vinyl ethers) and that the geometry of the vinyl ether unit in the products is generally *Z* or an *E*/*Z* mixture depending on the reaction conditions and on the substrates. Thus, the stereoretentive introduction of (*E*)- and (*Z*)-γ-alkoxyallyl groups at the α-position of carbonyl compounds has yet to be developed. We[6] and Fukuzumi[7] have found recently that the light-promoted reaction between Group 14 organometallic compounds and electron accepting carbonyl compounds is one of the most useful methodologies for selective carbon–carbon bond forming reactions. In connection with our interest in the light-promoted reaction of allylstannane, we studied the photoallylation of carbonyl compounds with γ-methoxy- and γ-siloxy-allylstannanes. Reported here is the first example of the regioreversed and stereoretentive introduction of (*E*)- and (*Z*)-γ-alkoxyallyl groups *via* light-promoted reaction (Scheme 1).

Irradiation ($h\nu$ > 400 nm) of an MeCN solution containing (*E*)-γ-(methoxyallyl)tributylstannane [(*E*)-**1a**, 24 mmol $dm^{-3}$] and benzil (**2a**, 20 mmol $dm^{-3}$) for 2 h at 0 °C gave two addition products. These were identified as the desired α-product (*E*)-**3a** (74%) and the regioisomeric γ-product **4a** (18%) (Table 1, entry 1). Irradiation of the diketone **2a** with the geometrically isomeric tin reagent (*Z*)-**1a** under the same conditions afforded the α-product (*Z*)-**3a** (66%) and the regioisomer **4a** (23%) (entry 2). The *E*/*Z* olefin geometry of α-product **3a** could be deduced from the 12.7 and 6.3 Hz coupling constants of the vicinal vinyl protons in the $^1H$ NMR spectrum.‡ Double allylation of the two carbonyl groups in the diketone **2a** did not occurred even under prolonged irradiation. The photoallylation also proceeded even in less polar solvents such as benzene and hexane, but slightly less efficiently. (*E*)- and (*Z*)-γ-[(*tert*-Butyldimethylsiloxy)allyl]tributylstannanes [(*E*)- and (*Z*)-**1b**] also reacted photochemically with **2a** to give again the desired α-products predominantly, with complete retention of the double bond geometry of the allylic moiety of the tin reagent **1b** in both cases (entries 3 and 4). When the γ-methoxyallylstannane had a bulky *tert*-butyl group at the β-position (**1c**), it showed complete α-regioselectivity [eqn. (1)]. Thus, the α-regioselectivity depended upon the steric crowding around the γ-position of the allylic stannanes.



(1)



**Scheme 1**

The photoallylation of *p*-cyanobenzaldehyde **2b** with γ-alkoxyallylstannanes was also examined. Irradiation of the absorption band of aldehyde **2b** in MeCN containing (*E*)- or (*Z*)-**1a** with light of wavelength longer than 320 nm for 5 h at 0 °C gave two regioisomeric homoallylic alcohols in which the γ-methoxyallyl group was again introduced preferentially at the α-position (entries 5 and 7). Similar but higher α-regioselectivity was observed in the photoallyltion with the siloxyallyltin reagents (*E*)- and (*Z*)-**1b**. However, the γ-alkoxyallylic groups in both the tin reagents **1a**,**b** were

**Table 1** Light-promoted condensation of (*E*)- and (*Z*)-γ-alkoxyallyltributylstannanes with carbonyl compounds

| Entry | **1** | **2** | *T*/°C | Products (% yield; *E*:*Z*)[a,b] |
|---|---|---|---|---|
| 1 | (*E*)-**1a** | **2a** | 0 | **3a** (74; 98:2), **4a** (18) |
| 2 | (*Z*)-**1a** | **2a** | 0 | **3a** (66; 2:98), **4a** (21) |
| 3 | (*E*)-**1b** | **2a** | 0 | **3b** (78; 99:1), **4b** (9) |
| 4 | (*Z*)-**1b** | **2a** | 0 | **3b** (74; 1:99), **4b** (14) |
| 5 | (*E*)-**1a** | **2b** | 0 | **3c** (36; 91:9), **4c** (14) |
| 6 | (*E*)-**1a** | **2b** | −78 | **3c** (37; 96:4), **4c** (13) |
| 7 | (*Z*)-**1a** | **2b** | 0 | **3c** (32; 14:86), **4c** (17) |
| 8 | (*Z*)-**1a** | **2b** | −78 | **3c** (42; 8:92), **4c** (21) |
| 9 | (*E*)-**1b** | **2b** | 0 | **3d** (39; 88:12), **4d** (8) |
| 10 | (*E*)-**1b** | **2b** | −78 | **3d** (37; 92:8), **4d** (6) |
| 11 | (*Z*)-**1b** | **2b** | 0 | **3d** (36; 13:87), **4d** (12) |
| 12 | (*Z*)-**1b** | **2b** | −78 | **3d** (47; 8:92), **4d** (15) |
| 13 | (*E*)-**1a** | **2c** | −78 | **3e** (52; 96:4), **4e** (15) |
| 14 | (*Z*)-**1a** | **2c** | −78 | **3e** (46; 9:91), **4e** (19) |

[a] *E*:*Z* ratios were determined by $^1H$ NMR analysis of the crude mixture. [b] The γ-products consisted of a 1:1 mixture of *syn* and *anti* diastereomers.

introduced with partial loss of the geometry of the allylic double bond. On the other hand, when the irradiation was carried out at −78 °C in propionitrile, the geometry of the γ-alkoxyallylic group of the tin reagents **1a**,**b** was almost completely maintained in the α-products (entries 6 and 8). Benzophenone **2c** could also be allylated with (*E*)- and (*Z*)-**1a** to give preferentially the α-product with retention of the geometry of the γ-methoxyallyl moiety (entries 13 and 14).

The present allylation is initiated by an electron transfer from the tin reagent **1** to the photoexcited carbonyl compound **2** to give the γ-alkoxyallyltributyltin radical cation ($\mathbf{1}^{\bullet+}$)-ketyl radical anion pair ($\mathbf{2}^{\bullet-}$), followed by the dissociation of the (γ-alkoxyallyl) C–Sn bond of $\mathbf{1}^{\bullet+}$ into a γ-alkoxyallyl radical and a tributyltin cation.[6,7] The resulting γ-alkoxyallyl radical couples with $\mathbf{2}^{\bullet-}$ preferentially at the less crowded α-position to yield the linear homoallylic alcohol. The configuration of the γ-alkoxyallyl unit is maintained without *E*/*Z*-isomerization during all these processes to give the α-product stereospecifically.

When the $BuSnCl_3$-mediated transmetallation method[8] was employed for the reaction of the tin reagents (*E*)- and (*Z*)-**1a** with aldehyde **2b**, the α-product **3a** was also produced from both the tin reagents, but the olefin geometry of the product **3a** was *Z* regardless of the geometry of the starting tin reagents.§ In addition, it has been reported that alkoxyallyl carbanion reagents ($ROCH{=}CHCH_2M$: R = alkyl or $SiMe_3$; M = Li) react with electrophiles including carbonyl compounds to afford (*Z*)-linear vinyl ethers.[9]

In conclusion, we have found that the present light-promoted reaction provides the first example of a stereoretentive introduction of (*E*)- and (*Z*)-γ-alkoxyallyl groups from γ-alkoxyallylstannanes into carbonyl compounds at the α-position.

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## Notes and References

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‡ After irradiation, the products were separated into individual regioisomers (**3a** and **4a**) by TLC ($SiO_2$, hexane–$Et_2O$, 1:1, v/v). Each geometrical isomer could be purified by carefully repeating the TLC separation (hexane–$CH_2Cl_2$, 1:2, v/v). *Selected data* for α-product (*E*)-**3a**: oil; $\delta_H(CDCl_3$, 270 MHz) 2.7 (dd, *J* 7.7, 15.2, 1H), 3.0 (dd, *J* 7.7, 13.2, 1H), 3.4 (s, 3H), 4.1 (s, 1H), 4.4 (ddd, *J* 12.7, 13.2, 15.2, 1H), 6.2 (d, *J* 12.7, 1H), 7.2–7.8 (m, 10H); $\nu_{max}(CHCl_3)/cm^{-1}$ 3534 (OH), 1679 (C=O). For α-product (*Z*)-**3a**: oil; $\delta_H(CDCl_3$, 270 MHz) 2.9 (dd, *J* 7.0, 14.4, 1H), 3.2 (dd, *J* 7.0, 15.4, 1H), 3.4 (s, 3H), 4.4 (ddd, *J* 6.3, 14.4, 15.4, 1H), 4.5 (s, 1H), 6.0 (d, *J* 6.3, 1H), 7.2–7.8 (m, 10H); $\nu_{max}(CHCl_3)/cm^{-1}$ 3542 (OH), 1673 (C=O). All other compounds gave satisfactory spectral data. The γ-product **4a** consisted of a 1:1 mixture of *syn* and *anti* diastereomers, which supports the proposed reaction mechanism showing the products being formed by the combination of allylic and ketyl radicals.

§ To a solution of the tin reagent (*E*)- or (*Z*)-**1a** (0.3 mmol) in $CH_2Cl_2$ (6 ml) under $N_2$ at −78 °C was added $BuSnCl_3$ (0.3 mmol) in $CH_2Cl_2$ (3 ml). After stirring the mixture at that temperature for 10 min, the substrate **2b** (0.2 mmol) was added slowly and the resulting mixture was stirred for 2 h at that temperature. The reaction mixture was quenched with a 10% aq. KF and worked up as usual. The (*Z*)-α-product was obtained in 19 and 71% yield, respectively, along with a very small amount of γ-product [(*Z*)-**3a**:**4a** = 91:9 from (*E*)-**1a**; 99:1 from (*Z*)-**1a**].

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