A Highly Stereospecific Allylation of Benzil by Using (*E*)-and (*Z*)-Allylic Stannanes *via* Photoinduced Electron Transfer

Akio Takuwa,* Yutaka Nishigaichi, Takashi Yamaoka and Kenji Iihama

Department of Chemistry, Faculty of Science, Shimane University, Matsue 690, Japan

Irradiation of benzil in acetonitrile in the presence of (*E*)- and (*Z*)-but-2-enyl-, pent-2-enyl-, and hex-2-enyl-tributylstannanes afforded the corresponding (*E*)- and (*Z*)-homoallylic alcohols, respectively, with complete retention of the original double bond configuration in good yields.

The carbonyl compound–allylic stannane condensation reaction is well known to give the branched homoallyl alcohol (γ-adduct) in the presence of Lewis acid with a high *erythro* diastereoselectivity.[1] However, little is known about the method for introducing the allylic moiety of the organotin reagent at the α-position to the carbonyl carbon.[2] In recent years, photoinduced single electron transfer (SET) processes using allyltrialkylstannanes as electron donors have provided reasonably efficient carbon–carbon bond formations through ion radical fragmentations followed by radical coupling,[3–5] and we reported that irradiation of aromatic ketones in the presence of 3-methylbut-2-enyl- or 3-phenylprop-2-enyl-trialkylstannane yielded the linear homoallylic alcohols (α-adduct) *via* a SET mechanism.[6] The stereochemical fate of the introduced allylic groups is an important problem to be solved. In this communication we describe a highly regioselective and stereospecific allylation of benzil with (*E*)- and (*Z*)-allylic stannanes *via* SET. The allylic stannanes chosen for the present study are (*E*) and (*Z*) isomers of but-2-enyl- **1a**, pent-2-enyl- **1b**, and hex-2-enyl-tributylstannane **1c**.†

Irradiation of an acetonitrile solution containing benzil **2** (0.5 mmol) and (*E*)- or (*Z*)-allylic stannane (**1a–c**; 1 mmol) with a 300 W high-pressure mercury lamp at 20 °C through a solution filter of $CuSO_4$ and $NaNO_2$ in NH_4OH (transmitted light: λ = 400–480 nm) for 5 h afforded a regioisomeric mixture of the linear homoallylic alcohols **3** and the branched ones **4** in excellent to high yields.‡ The results are summarized in Table 1. In all cases, the allylic groups were introduced preferentially at the α-position in contrast to the Lewis acid ($TiCl_4$)-induced reaction which yielded **4** exclusively.§

Turning attention to the alkene geometry of **3**, the (*E*)-allylic groups of (*E*)-**1a–c** were introduced with almost complete retention of the original double bond configuration. When (*Z*) compounds (*Z*)-**1a–c** were used, the alkene

Table 1 Photoallylation of benzil **2** with (*E*)- and (*Z*)-allylic stannanes **1a–c** in acetonitrile

Allylic stannane	*E*:*Z* ratio of **1**	Irradn. temp./°C	Regioisomer ratio **3**:**4**[a,b]	*E*:*Z* ratio of **3**[a]	Total yield (%)[c]
(*E*)-**1a**	89:11	20	68:32	89:11	89
(*Z*)-**1a**	36:64	−30	64:36	43:57	94
		20	65:35	47:53	94
(*E*)-**1b**	95:5	20	77:23	92:8	94
		70	78:22	75:25	92
(*Z*)-**1b**	7:93	−30	67:33	9:91	81
		20	70:30	17:83	88
		70	78:22	73:27	84
(*E*)-**1c**	100:0	20	77:23	95:5	97
(*Z*)-**1c**	5:95	−30	66:34	5:95	96
		20	70:30	17:83	96

[a] Determined by ^1H NMR spectroscopy. [b] The products **4** were composed of a 1:1 mixture of *syn*- and *anti*-isomers. [c] Isolated yields based on quantity of **2** used.

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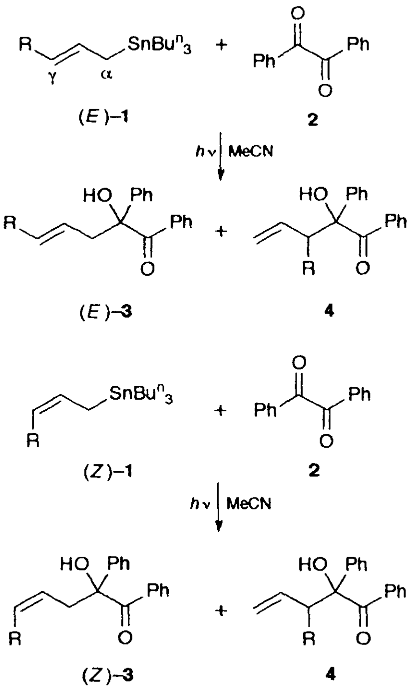
† The *E*:*Z* compositions of the allylic stannanes were determined from the relative integration of the alkenic carbons by ^{13}C NMR resonances (A. Gambaro, P. Ganis, D. Marton, V. Peruzzo and G. Tagliavini, *J. Organomet. Chem.*, 1982, **231**, 307).

‡ All new compounds gave satisfactory spectral data. The regioisomeric homoallyl alcohols could be separated into individual isomers by TLC (silica gel).

§ The reaction was carried out as follows: to a CH_2Cl_2 solution of **2** (0.5 mmol) $TiCl_4$ (1 mmol) was added under N_2 at −78 °C, and then (*E*)-**1a** (1 mmol) was added dropwise. After stirring at this temperature for 20 min, the reaction was quenched and worked up. The γ-adduct **4a** (96%; diastereoisomer ratio, 62:38) was the sole product.



a, R = Me; **b**, R = Et; **c**, R = Pr^n

Scheme 1

geometry was partially lost (Scheme 1, Table 1).¶ Both the *E* : *Z* ratios of **3** and the regioisomer ratios **3** : **4** in each reaction were independent of irradiation time (0.5, 1, 2 and 5 h), and no isomerization was observed in the recovered allylic stannanes. These results suggest that the *E*-configuration of the allylic radicals produced by the cleavage of the tributylstannyl cation[3–6] from (*E*)-**1**$^{+\cdot}$ is retained, and the *Z*-configuration of the radicals generated from (*Z*)-**1**$^{+\cdot}$ is also, to our surprise, appreciably retained,|| during the course of the reaction under the present, neutral, experimental conditions.

In order to attain the completely stereospecific introduction of (*Z*)-allylic groups, the temperature effect on the reaction was examined (Table 1). Upon irradiation at −30 °C, the *Z*-configuration of the original double bond in (*Z*)-**1b** and (*Z*)-**1c** was perfectly maintained in the products [(*Z*)-**3b** and (*Z*)-**3c**]. In the case of the reaction with (*Z*)-**1a**, decreasing irradiation-temperature tended to cause an increase in the retention of the alkene geometry. On the contrary, independent irradiation at elevated temperature (70 °C) using (*E*)-**1b** and (*Z*)-**1b** produced **3b** of the same *E* : *Z* ratio. This indicates that the *E* : *Z*-isomerisation between the (*E*)- and (*Z*)-pent-2-enyl radicals has reached equilibrium at this temperature†† before the coupling with the semidione radical [PhCO$\dot{\mathrm{C}}$(OSnBu$_3$)Ph].[5,6]

So far as we know this is the first example of addition of allylic stannanes to carbonyls which shows complete retention of the alkene geometry of the tin reagents.

We thank the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

Received, 12th July 1991; Com. 1/03552E

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[¶] The assignments of the double bond configurations for (*E*)-**3** and (*Z*)-**3** were established from the *J*-values of the alkenic protons [*J* 15.4 Hz for (*E*)-**3**; *J* 10.0–11.0 Hz for (*Z*)-**3**].

[||] It has been reported that allylic radicals are configurationally stable in the chlorination of alkenes with Bu^{t}OCl by a photoinduced radical chain process (C. Walling and W. Thaler, *J. Am. Chem. Soc.*, 1961, **83**, 3877). The barrier to rotation in allyl radicals has also been reported (see A. E. Dorigo, Y. Li and K. N. Houk, *J. Am. Chem. Soc.*, 1989, **111**, 6942).

[††] No isomerization between (*E*)-**3b** and (*Z*)-**3b** was observed at this temperature.