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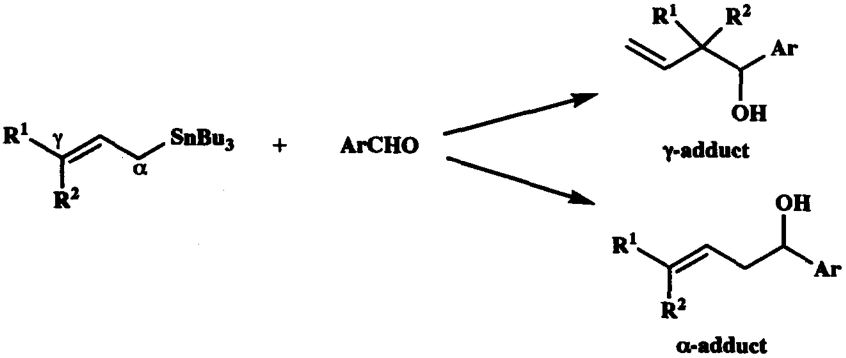
α-Regioselective and Stereospecific Addition of Allylic Tins to Aldehydes via Photoinduced Electron Transfer

Akio Takuwa,* Junji Shiigi and Yutaka Nishigaichi
Department of Chemistry, Faculty of Science, Shimane University, Matsue 690, Japan

Abstract: *(E)- and (Z)-Allylic tributyltins add to aromatic aldehydes to afford regioreversed α-adduct predominantly with almost complete retention of the stereochemistry of the allylic groups under photochemical conditions. The photoinduced single electron transfer mechanism is proposed.*

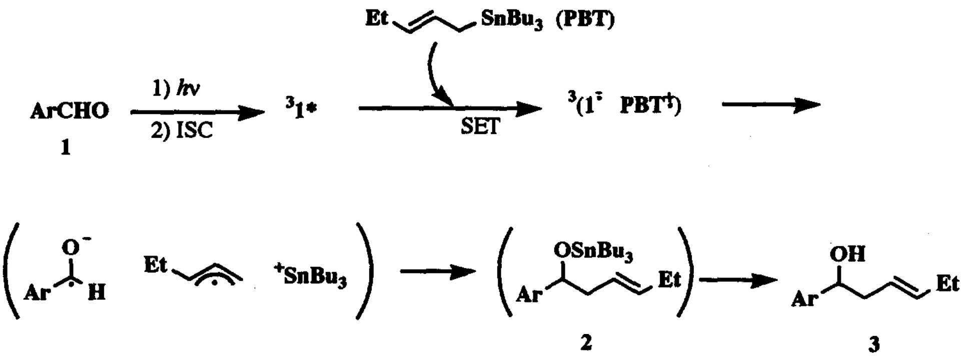
The addition of allyltin reagents to aldehydes has been extensively developed for the useful carbon-carbon bond construction in organic synthesis over the past decade.[1] The addition reaction has been promoted by Lewis acids,[2] heat,[3] and high pressure.[4] In general, the reaction of aldehydes with the substituted allylic stannanes under these conditions results in the products in which the allylic group is attached at the more highly substituted position (γ-adduct). On the other hand, the regioreversed addition of the allylic stannanes to aldehydes to produce linear homoallylic alcohols (α-adduct) has been scarcely studied,[5] but the stereoselective addition with retention of the double-bond geometry of the allylic group in the tin reagents is totally unprecedented despite their great potential importance in organic synthesis.[6] Recently, we found that the addition reaction of allyltrialkyltins to carbonyl compounds such as benzophenone, enone, and benzil could be also promoted by light.[7] Herein, we report that the photoinduced α-regioselective and stereospecific allylation of aromatic aldehydes using (*E*)- and (*Z*)-allylic tributyltins.



A representative experimental procedure is given by the reaction of *p*-cyanobenzaldehyde with (*E*)-2-pentenyltributyltin (PBT; *E*/*Z* = 95:5): A N_2-purged propionitrile solution (10 mL) of the aldehyde (52.4 mg, 0.4 mmol) and the PBT (215.6 mg, 0.6 mmol) was irradiated at -78 °C with a light (>320 nm) from a 300 W high-pressure Hg arc lamp through a saturated solution of $CuSO_4$. After being irradiated for 5 h, the reaction mixture was concentrated, and the crude products were purified by preparative TLC on silica gel (hexane-ether, 7:3) to afford homoallylic alcohols (51 mg, 63% yield); the α:γ and *E*:*Z* ratios of the alcohols were determined to be 73:27 and 91:9, respectively, by ^1H NMR analysis. Unreacted (*E*)-PBT was recovered without isomerization (*E*:*Z* = 96:4). The results of regio- and stereochemistry of the homoallylic alcohols for the present photoallylation are summarized in Table 1.

As is apparent from Table 1, α-adduct is obtained with 62-91% regioselectivity[8] with retention of the stereochemistry of the double-bond in the original allyltin reagents. The α-regioselectivity was affected by the bulkiness of the substituent at the γ-position of the allyl group. The stereospecificity of (*E*)-allylic tins was higher than that of (*Z*)-allylic tins. The most remarkably high regioselectivity and stereospecificity were observed in the reactions with geranyl- and neryltributyltins. The polar substituents, chloro and cyano groups, on aldehyde were inert to this allylation.

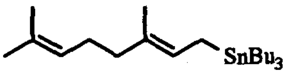
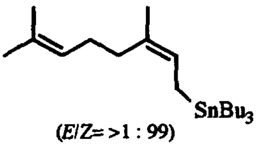
A plausible reaction mechanism for the photoreaction between *p*-cyanobenzaldehyde (**1**) and (*E*)-PBT is proposed as in equation 1. The photoexcited triplet state of **1** (E^{red}= -1.38V) could oxidize (*E*)-PBT (E^{ox}= +0.95V vs. Ag/AgCl) to give a triplet ion radical pair via single electron transfer (SET). Cation radical of (*E*)-PBT undergoes facile C-Sn bond cleavage to produce pentenyl radical and tributylstannyl cation as previously demonstrated in SET reactions with electron acceptors.[9] The resulting pentenyl radical would be coupled with ketyl radical preferentially at its less hindered site with retaining configuration to give **2** which is hydrolyzed to the final product, (*E*)-1-(4-cyanophenyl)-3-hexen-1-ol (**3**), during work-up.



(1)

As mentioned above, no *E*-*Z* isomerization of (*E*)- or (*Z*)-PBT in the photoreaction with **1** was observed. In addition, (*E*)-**3** did not isomerize to (*Z*)-**3** under the present photoreaction conditions. These results strongly suggested that the partial loss of the double-bond stereochemistry in homoallylic alcohol compared with that in the starting allylic stannanes is due to the isomerization of allylic radicals. This was supported by the following evidences. When the photoreactions of **1** with (*E*)- and (*Z*)-PBT were carried out at 20 °C, the *E*/*Z* ratios of α-adduct were 88:12 and 28:72, respectively. On the other hand, the photoreactions at more elevated temperature (70 °C) showed the same *E*/*Z* ratio (*E*:*Z* = 78:22) for both (*E*)- and (*Z*)-PBT. These results clearly indicate that 2-pentenyl radical retains its configuration even at 20 °C, but thermodynamic equilibrium is reached at 70 °C.

Table 1. Photochemical Reaction of Allylic Tins with Aldehydes[a]

Allylic tins	Aldehydes	Yield/%[b,c]	α : γ[d,e]	E : Z[d]
(*E*)-$C_2H_5CH=CHCH_2SnBu_3$ (*E*/*Z*=95 : 5)	PhCHO	48	70 : 30	86 : 14
	p-ClC_6H_4CHO	59	73 : 27	92 : 8
	p-NCC_6H_4CHO	63	73 : 27	91 : 9
		55[f]	70 : 30[f]	88 : 12[f]
		48[g]	68 : 32[g]	72 : 28[g]
(*Z*)-$C_2H_5CH=CHCH_2SnBu_3$ (*E*/*Z*=6 : 94)	PhCHO	45	66 : 34	18 : 82
	p-ClC_6H_4CHO	58	65 : 35	15 : 85
	p-NCC_6H_4CHO	64	65 : 35	13 : 87
		67[f]	64 : 36[f]	28 : 72[f]
		50[g]	65 : 35[g]	72 : 28[g]
(*E*)-${}^nC_3H_7CH=CHCH_2SnBu_3$ (*E*/*Z*=97 : 3)	*p*-NCC_6H_4CHO	58	78 : 22	87 : 13
(*Z*)-${}^nC_3H_7CH=CHCH_2SnBu_3$ (*E*/*Z*=5 : 95)	*p*-NCC_6H_4CHO	49	70 : 30	12 : 88
(*E*)-$CH_3CH=CHCH_2SnBu_3$ (*E*/*Z*=93 : 7)	PhCHO	40	62 : 38	86 : 14
	p-ClC_6H_4CHO	60	63 : 37	88 : 12
	p-NCC_6H_4CHO	56	62 : 38	90 : 10
 (*E*/*Z*= >99 : 1)	*p*-ClC_6H_4CHO	44	91 : 9	99 : 1
	p-NCC_6H_4CHO	45	90 : 10	99 : 1
 (*E*/*Z*= >1 : 99)	PhCHO	33	82 : 18	1 : 99
	p-ClC_6H_4CHO	41	84 : 16	1 : 99
	p-NCC_6H_4CHO	49	85 : 15	1 : 99

[a] Allylation was carried out by irradiation (>320 nm) of allylic tin and aldehyde (1 and 1.5 equiv., respectively) in propionitrile for 5 h at -78 °C. [b]Isolated yield based on aldehyde used. [c]Benzopinacol was also obtained in 17-23% yield. [d]Determined by ^1H NMR and/or GC analysis. [e]Erythro : threo = 1:1 in γ-adduct. [f]Irradiation temperature: 20 °C. [g]Irradiation temperature: 70 °C.

The present photoallylation of aldehyde using allylic tin reagents provides a new route to α-regioselective and stereocontrolled linear homoallyl alcohols. Further mechanistic studies and extension of this interesting reaction are now under way.

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