



Allylic Tin(IV)—Tin(II) Chloride—Acetonitrile as a Novel System for Allylation of Carbonyls or Imines

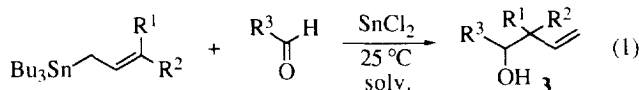
Makoto Yasuda, Yoshihiro Sugawa, Akihiro Yamamoto,
Ikuya Shibata, and Akio Baba*

Department of Applied Chemistry, Faculty of Engineering, Osaka University.

2-1 Yamadaoka, Suita, Osaka 565, Japan

Abstract: Effective allylation of aldehydes, ketones and imines was accomplished by allylic tributyltins **1** in the presence of SnCl₂ in an acetonitrile solution. In this reaction system, Sn(IV)-Sn(II) transmetalation must play a key role, generating the allylic tin(II) reagents as a novel reacting species. Acetonitrile effectively promoted the transmetalation to give *anti*-adducts in the reaction with cinnamyltin **1c**, whereas dichloromethane disturbed the transmetalation to produce *syn*-adducts.
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Allylation of carbonyl groups by allylic metals is a highly efficient tool for selective functionalization.¹ One of the most fundamental and important methods is allylation by four-valent allylic tin compounds which are easily available for the selective reactions. However, the allylation commonly requires some activators, for example, strong Lewis acids² or electronegative ligands to tin atoms.³ Recently, the transmetalation from allylic tins into other metallic species has been also utilized.⁴ In this communication, we report our examination of carbonyl or imino allylations by allylic tributyltins in the presence of SnCl₂ as an effective activator which is classified as a weak Lewis acid (eq. 1). In this reaction system, Sn(IV)-Sn(II) transmetalation plays a key role, generating the allylic tin(II) reagents as a novel reacting species. This type of interaction between Sn(IV) and Sn(II) compounds, which includes transmission of active substituents toward the electrophiles such as carbonyl moieties, has not been reported so far as we know, although divalent tin compounds⁵ have received much attention.



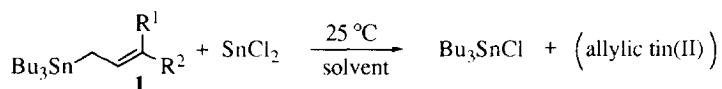
- 1a:** R¹ = R² = H **2a:** R³ = *n*-Bu
1b: R¹ = R² = Me **2b:** R³ = *i*-Pr
1c: R¹ = H, R² = Ph
1d: R¹ = H, R² = Me

It was noteworthy that the reaction between prenyltin **1b** and isobutyraldehyde **2b** was accelerated by SnCl₂ only in an acetonitrile solution as shown in Table 1 (entries 7-11), whereas the more reactive pair of **1a** and **2a** reacted even in other solvents such as dichloromethane and toluene. Of course, no reaction proceeded without SnCl₂ (entry 1). The interaction of allylic tins **1** with SnCl₂ was monitored by the amount of Bu₃SnCl formed in various solvents (Table 2). Only in acetonitrile, the color of the suspended mixture of **1** and SnCl₂ immediately turned dark brown, and the quantitative formation of Bu₃SnCl was monitored by GLC and ¹¹⁹Sn NMR. This result strongly suggested the transmetalation between **1** and SnCl₂, and the generation of a new active species, perhaps a divalent allylic tin compound.

Table 1. Effect of Solvents in the SnCl₂-Mediated Reaction of Allylic Tin **1** with Aldehyde **2**^a

entry	allylic tin	aldehyde	solv.	time/h	yield/%
1 ^b	1a	2a	THF	2	0
2	1a	2a	CH ₂ Cl ₂	2	100
3	1a	2a	CHCl ₃	3	81
4	1a	2a	toluene	3	82
5	1a	2a	THF	2	100
6	1a	2a	MeCN	2	100
7	1b	2b	CH ₂ Cl ₂	6	2
8	1b	2b	CHCl ₃	6	2
9	1b	2b	toluene	10	1
10	1b	2b	THF	6	6
11	1b	2b	MeCN	2	95

^a Reactions were carried out in solvent (1.0 mL) using allylic tin **1** (1.0 mmol), SnCl₂ (1.0 mmol), and aldehyde **2** (1.0 mmol). ^b Without SnCl₂.

Table 2. Transmetallation of **1** with SnCl₂^a

entry	allylic tin	solvent	time/h	yield of Bu ₃ SnCl/% ^b
1	1a	THF	0.5	52
2	1a	CH ₂ Cl ₂	5	13
3	1a	MeCN	0.5	92
4	1b	THF	5	34
5	1b	CH ₂ Cl ₂	7	13
6	1b	MeCN	2	85
7	1c	MeCN	1	92


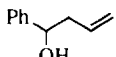
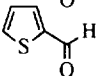
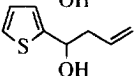

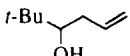
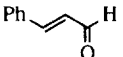
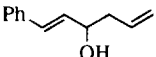

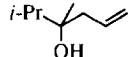

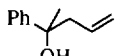
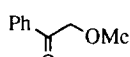
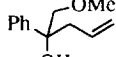
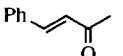
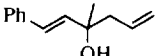

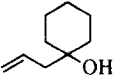

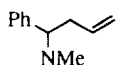

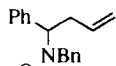
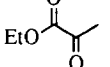
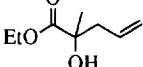
^a Allylic tin **1** (1.0 mmol), SnCl₂ (1.0 mmol), solvent (1.0 mL).

^b Determined by GLC.

A representative procedure for the allylation is as follows. An allyltributyltin **1a** (1.0 mmol) was added to a stirred suspended solution of SnCl₂ (1.0 mmol) and benzaldehyde **2c** (1.0 mmol) in dry MeCN (1.0 mL). The color of the suspension changed to dark brown in 30 min. No striking difference in the yield was observed in the case of the addition of aldehyde to a mixture of **1a** and SnCl₂. After stirring for 2 h, diethyl ether (100 mL) and aqueous NH₄F (15%; 40 mL) were added, the organic layer was washed with water, dried (MgSO₄) and evaporated. The homoallyl alcohol **3c** was purified by flash chromatography (hexane-diethyl ether, 9 : 1) on silica gel. In the ¹¹⁹Sn NMR examination⁶ of the mixture of allyltributyltin **1a** and SnCl₂ in acetonitrile, however, only signals for Bu₃SnCl and a trace amount of tetraallyltin were observed. An active allylic tin species could not be detected, perhaps because of the interruption of the precipitate. As a sluggish reaction was confirmed between aldehydes and tetraallyltin in the presence of tributyltin halide, tetraallyltin was clearly excluded from the candidates of the real species. Other possibilities of allylic tin(IV) as the active species, for example, chlorodibutylallyltin, dichlorobutylallyltin, trichloroallyltin were also omitted as no signals for them were confirmed in ¹¹⁹Sn NMR. These results strongly suggested that the allylic tin(II) species acted for carbonyl allylation.

Table 3 shows the effective allylation of various types of electrophiles including aldehydes, ketones and imines to the corresponding homoallyl alcohols or amines by the **1a**-SnCl₂-acetonitrile system. Both aryl and alkyl aldehydes were allylated in quantitative yields, while the sterically demanding aldehyde **2e** gave a little lower yield. Only 1,2-adducts were obtained in the reaction with α,β -unsaturated aldehyde **2f** or ketone **2j**. The selective allylation of the keto group was observed in the reaction of α -keto ester **2n**.

Table 3. Allylation of Carbonyls or Imines by Allyltributyltin **1a**-SnCl₂-MeCN System

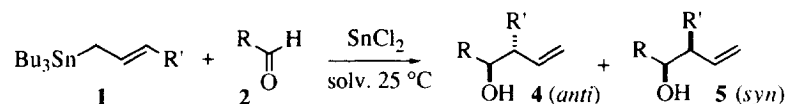
entry	no.	electrophile 2	product 3	time/h	yield/%
1	c			2	100
2	d			1	100
3	e			1	78
4	f			1	97
5	g			2	85
6	h			1	100
7	i			1	100
8	j			3	90
9	k			1	100
10	l			3	89
11	m			3	91
12	n			2	100

Next, we investigated the stereochemistry in the reactions of cinnamyltin **1c** and crotyltin **1d** with aldehydes as shown in Table 4. In the reaction with **1c**, *anti*-adducts **4** were produced in an acetonitrile solution in up to 100% selectivity (entries 1,2,4,5 and 6), whereas dichloromethane predominantly gave *syn*-isomer **5** (82% selec., entry 3). This stereochemical outcome⁷ strongly indicates that in acetonitrile, allyltin(II) was generated by transmetalation to give *anti*-isomer **4** via a cyclic transition state, and that in dichloromethane, SnCl₂ acted as a Lewis acid to activate the carbonyl group via an acyclic transition state because of the sluggish transmetalation in this solvent. These selectivities were achieved by only simply the choice of solvent, acetonitrile or dichloromethane. Thus, the transmetalation of **1c** with SnCl₂ found to be

crucial to the formation of *anti*-isomer **4**. In contrast, the ZnCl₂-mediated formation of *anti*-isomer **4** was not claimed to include the transmetallation.^{7c} The reactions of crotyl tin **1d** by the SnCl₂-mediated system, however, gave low *anti*-selectivities even in a nitrile solution, while *syn*-isomers were predominantly formed in dichloromethane.

The SnCl₂-promoted system examined here is very convenient and useful for stereoselective organic syntheses with the generation of divalent allylic tin(II) as a novel reagent, which would be stabilized by coordination of acetonitrile. We are now investigating the spectroscopic evidence for allylic tin(II) regarded as an active intermediate together with full details of its reactivities.

Table 4. Stereoselective Addition of Cinnamyltin **1c** or Crotyl tin **1d** to Aldehyde **2**



entry	allylic tin R'	aldehyde R	solv.	time/h	yield/%	4 : 5
1	1c Ph	2c Ph	MeCN	1	83	94:6
2	1c Ph	2o Me	MeCN	1	64	92:8
3	1c Ph	2o Me	CH ₂ Cl ₂	1	55	18:82
4	1c Ph	2p Et	MeCN	1	86	97:3
5	1c Ph	2b <i>i</i> -Pr	MeCN	1	77	100:0
6	1c Ph	2q MeCH=CH-	MeCN	1	89	97:3
7 ^a	1d Me	2c Ph	MeCN	4	69	52:48
8 ^b	1d Me	2c Ph	EtCN	6	50	64:36
9	1d Me	2c Ph	CH ₂ Cl ₂	3	92	18:82
10	1d Me	2r <i>cy</i> -Hex	MeCN	3	58	54:46
11	1d Me	2r <i>cy</i> -Hex	CH ₂ Cl ₂	5	61	21:79

^a -40 °C to 25 °C. ^b Sn(OTf)₂ was used instead of SnCl₂ at -78 °C to 25 °C.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan. Thanks are due to Mrs. Y. Miyaji and Mr. H. Moriguchi, Faculty of Engineering, Osaka University, for their assistance in obtaining NMR and MS spectra.

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(Received in Japan 17 May 1996; revised 24 June 1996; accepted 28 June 1996)