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Carbonyl allylations by 3-halopropenes or 2-propenyl mesylate with tin(IV) chloride and tetrabutylammonium iodide

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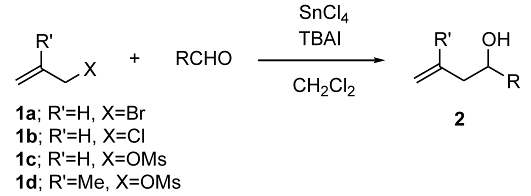
Abstract—2-Propenyl tin species, prepared from 3-halopropenes or 2-propenyl mesylate with tin(IV) chloride and tetrabutylammonium iodide in dichloromethane, causes nucleophilic addition to aldehydes to produce the corresponding homoallylic alcohols. © 2003 Elsevier Science Ltd. All rights reserved.

Allylic tin is one of the most convenient allylating agents in carbonyl allylations.[1,2] Allylic trihalotins, derived from starting allylic compounds such as allylic halides,[3] alcohols[4] and esters[4b,5] with tin(II) halides in situ, namely under Barbier conditions, especially have the advantage of the availability and tractability of both the starting allylic compounds and tin(II) halides. The reactivity in the carbonyl allylation by (*E*)-but-2-en-1-ol with tin(II) chloride is dependent upon the solubility of tin(II) chloride, while the regioselectivity is dependent upon the dielectric constants of the solvents;[4,6] polar solvents such as 1,3-dimethylimidazolidin-2-one, DMF and THF–H_2O let the allylation proceed smoothly for obtaining high yields with γ-*anti* selectivity, while nonpolar solvents such as diethyl ether and dichloromethane lead to unusual α-regioselection[7] without practical yields because of the insolubility of tin(II) chloride. The carbonyl allylation in the nonpolar solvents needs special conditions such as ultrasonic[6] or biphasic[3i] systems to dissolve tin(II) chloride. A new synthetic methodology will be required for preparing allylic tin species in the nonpolar and low-boiling solvents under general Barbier conditions.[8] Since tin(IV) chloride is soluble in nonpolar solvents such as dichloromethane and benzene, in contrast to tin(II) chloride, finding a reducing method of tin(IV) chloride to tin(II) species will make it possible to prepare allylic tins from the usual starting allylic compounds in nonpolar solvents. Here, we report on (1) a novel preparation of 2-propenyltin species from 3-halopropenes or 2-propenyl mesylate with tin(IV) chloride and tetrabutylammonium iodide (TBAI)[9] in dichloromethane and carbonyl allylations by the 2-propenyltin species, and (2) an application of the carbonyl allylation to γ-*syn* selection, rather than the α-regioselection in dichloromethane and *anti*-diastereoselection in polar solvents in the previous carbonyl allylation with tin(II) chloride.[3–5]

The allylation of benzaldehyde by 2-propenyl bromide (**1a**), chloride (**1b**), or mesylate (**1c**) with tin(IV) chloride and TBAI was investigated under various conditions (Scheme 1). The results are summarized in Table 1 (entries 1–5 and 13). An optimum experiment is as follows (entry 13): To the solution of **1c** (2 mmol), benzaldehyde (1 mmol) and TBAI (6 mmol) in dichloromethane (3 ml) was added a one-molar dichloromethane solution of tin(IV) chloride (2 ml) on an ice-bath for 10–15 min, and then the solution was stirred at room temperature for 44 h. After usual work-up and purification by column chromatography,



Scheme 1.

Keywords: nucleophilic additions; allylations; allylic tins; homoallylic alcohols; tin(IV) chloride.

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1-phenyl-3-buten-1-ol (**2**, R = Ph) was obtained in 71% yield. In the allylation by **1b**, 3 mmol of **1b**, 3 mmol of tin(IV) chloride and 9 mmol of TBAI each to 1 mmol of benzaldehyde were needed for obtaining almost the same yield as that obtained by **1c** (entry 5). Tin(IV) chloride and TBAI each can be saved by the use of **1c** that itself is also saved. Thus, mesylate **1c** is superior to halides **1a** and **1b** in the carbonyl allylations. The allylations may require more than three equimolar amounts of TBAI to tin(IV) chloride. No pinacol coupling product was obtained under these conditions, in contrast to the $\mathrm{TiCl_4}$–TBAI reducing system for pinacol coupling.[9] No allylation took place at temperatures below −20°C. Carbonyl allylations using **1b** and **1c** were carried out with various aldehydes under the optimum conditions of benzaldehyde (entries 5 and 13, respectively). Benzaldehydes bearing an electron-donating or electron-withdrawing group, α,β-unsaturated aldehydes, and aliphatic aldehydes can be employed for the carbonyl allylations (Table 1).[10]

Some selectivity in carbonyl allylation was demonstrated with $\mathrm{SnCl_4}$–TBAI: (1) Chemoselective allylations of aldehydes using **1b** and **1c** can be realized in the presence of ketones; the allylation of benzaldehyde in the presence of acetophenone and the allylation of heptanal in the presence of 2-heptanone (Scheme 2).[10] No allylation of ketones occurred under these conditions. (2) 2-Phenylpropanal bearing a stereocenter at the 2-position underwent Felkin-Anh-type allylation by **1c** to produce 2(*anti*)-phenyl-5-hexen-3-ol as a major product (Scheme 3).[10] (3) The carbonyl allylation by 1-chloro-2-butene (**3**)[†] with $\mathrm{SnCl_4}$-TBAI under the same conditions as those of **1b** γ-regioselectively occurred with *syn*-diastereoselection (Scheme 4).[10,11]

This carbonyl allylation is outlined in Scheme 5, by reference to the pinacol coupling with $\mathrm{TiCl_4}$-TBAI reagent.[9] Iodide ion probably serves as a reducing agent for preparing trichlorostannate(II) ion ($^-\mathrm{SnCl_3}$) from $\mathrm{SnCl_4}$ via the formation of pentacoordinate stannate(IV) ion ($^-\mathrm{SnCl_4I}$) followed by the reductive elimination of iodine monochloride (I-Cl). The trichlorostannate(II) ion may cause nucleophilic substitution to allyl substrates **1** to prepare allyltrichlorotin that functions as an allylic nucleophile for carbonyl allylation. I-Cl may react with two equimolar amounts of TBAI to produce TBACl and tetrabutylammonium triiodide ($\mathrm{TBAI_3}$).[12] Since excess tin(IV) species are present in the reaction system, the carbonyl allylation with **3** probably proceeds via an acyclic antiperiplanar transition state between 2-butenyltrichlorotin and aldehyde coordinating another tin(IV) to exhibit γ-*syn*-selectivity.[1] In contrast to $\mathrm{TiCl_4}$–TBAI, $\mathrm{SnCl_4}$–TBAI is a useful reagent for Barbier-type carbonyl allylation because it lacks the ability to reduce aldehydes.

Table 1. Carbonyl allylations by **1** with $\mathrm{SnCl_4}$ and TBAI[a]

Entry	Substrate	R	Time (h)	**2**, Yield (%)[b]
1	**1a**	Ph	48	41
2[c]	**1a**	Ph	48	45
3[d]	**1a**	Ph	48	8
4	**1b**	Ph	24	29
5[e]	**1b**	Ph	24	72
6[e]	**1b**	$4\text{-MeC}_6\text{H}_4$	48	52
7[e]	**1b**	$4\text{-ClC}_6\text{H}_4$	24	76
8[e]	**1b**	PhCH=CH	48	23
9[e]	**1b**	$\mathrm{PhCH_2CH_2}$	48	37
10[e]	**1b**	$\mathrm{H_2C{=}CH(CH_2)_8}$	48	31
11[e]	**1b**	$\mathrm{C_6H_{13}}$	48	62
12[e]	**1b**	$c\text{-C}_6\text{H}_{11}$	48	45
13	**1c**	Ph	24	71
14	**1c**	$4\text{-MeC}_6\text{H}_4$	48	68
15	**1c**	$4\text{-ClC}_6\text{H}_4$	24	65
16	**1c**	$4\text{-MeOOCC}_6\text{H}_4$	24	88
17	**1c**	$\mathrm{PhCH_2CH_2}$	48	50
18	**1c**	$\mathrm{C_6H_{13}}$	48	55
19	**1c**	$c\text{-C}_6\text{H}_{11}$	48	61
20	**1d**	Ph	48	49
21	**1d**	$\mathrm{C_6H_{13}}$	48	34

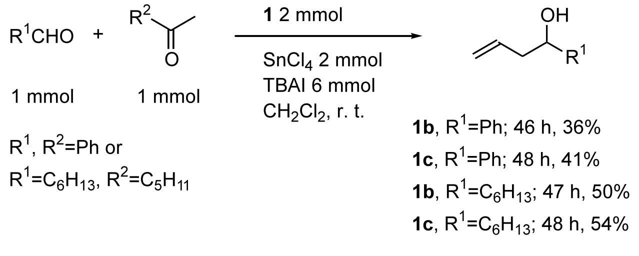
[a] After adding a one-molar dichloromethane solution of tin(IV) chloride (2 ml) to the solution of **1a**, **1b**, **1c** or **1d** (2 mmol), aldehydes (1 mmol) and TBAI (6 mmol) in dichloromethane (3 ml) on an ice-bath for 10–15 min, the reaction was carried out at room temperature.

[b] Isolated yields.

[c] The reaction was carried out at 40°C.

[d] The reaction was carried out at 0°C.

[e] Aldehydes (1 mmol), **1b** (3 mmol), TBAI (9 mmol), and a one-molar dichloromethane solution of $\mathrm{SnCl_4}$ (3 ml) were used.



Scheme 2.

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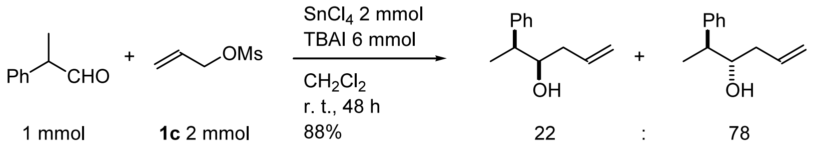
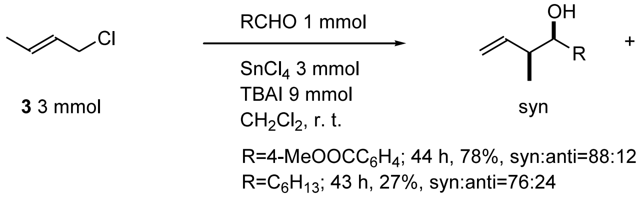
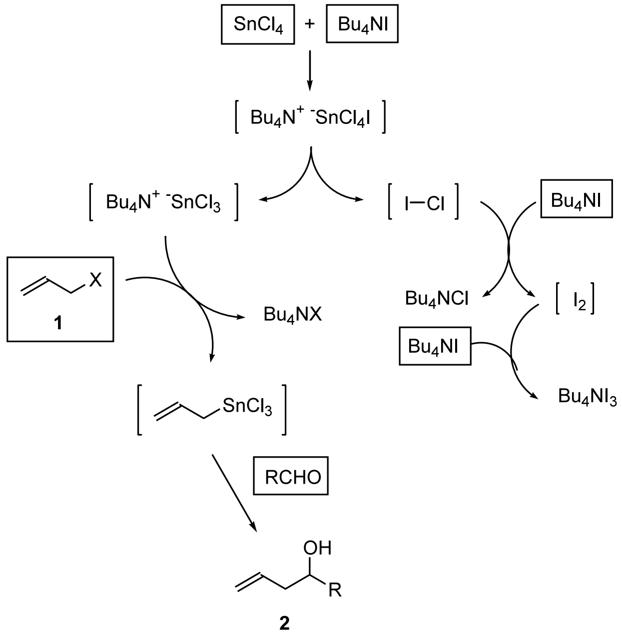
[†] 1-Chloro-2-butene was purchased from Aldrich Chemical Co., Inc.



Scheme 3.



Scheme 4.



Scheme 5. A plausible mechanism.

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12. $TBAI_3$ was identified by direct comparison of UV–vis, ^1H NMR, and ^{13}C NMR spectra with those of an authentic sample prepared from tetrabutylammonium iodide and iodine, similarly to Ref. 9.