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Allylation of Acid Chlorides by Allyltributyltin in the Presence of Catalytic Amounts of Dibutyltin Dichloride

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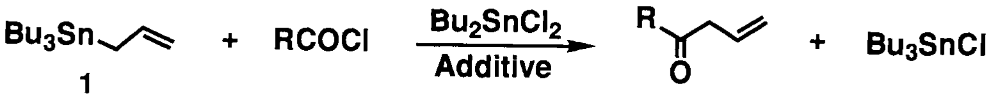
Redistribution of allyltributyltin and dibutyltin dichloride into allyldibutyltin chloride and tributyltin chloride is enhanced by coordinative compounds such as phosphine oxide and ammonium chloride. This redistribution is applied to the reaction of allyltributyltin and acid chlorides promoted by catalytic amounts of dibutyltin dichloride - tetraethylammonium chloride.

The palladium-[1] and rhodium-catalyzed[2] coupling of acid chlorides with allyltributyltin (**1**) has been ardently investigated to present a potential route to allylketones. On the other hand, allyldibutyltin halide (**3**) has been reported to effect the allylation without catalysts.[3] Although **3** is readily available by redistribution of **1** and dibutyltin dihalide (**2**),[4] requirement of excess amounts of **2**, a stronger Lewis acid, would considerably prevent a synthetic application of this active reagent. We wish to report our success in the effective redistribution promoted by the addition of coordinative compounds and its catalytic application to the coupling of **1** with acid chlorides.



The redistribution of **1** and **2** was strikingly promoted by the addition of coordinative compounds. As shown in Table 1, 20% of **1** unreacted even after 3 h in the absence of additives. Contrarily, the addition of ammonium halides or HMPA completed the redistribution within 10 min. Triethylamine was less effective. This order accords with the order of their coordination ability toward tin halides. Ammonium halides have been known to form a complex with tin halides in which the halide of the former strongly coordinates to the tin atom.[5] It is noteworthy that the use of catalytic amounts of additives was sufficient for this redistribution (entries 5, 6). This result is explainable as follows. Of the four tin compounds shown in equation 1, the dihalide **2** would be most subject to coordination due to its strong acidity. The coordination increases the polarity of the tin - halogen bond to enhance the nucleophilic addition of the halogen to **1**, furnishing **3** and tributyltin halide.[4,6] Then, the additive coordinates to alternative **2** and finally acts as a catalyst. In the case of the chloro derivative a similar result was observed though the redistribution was very fast even without additives.

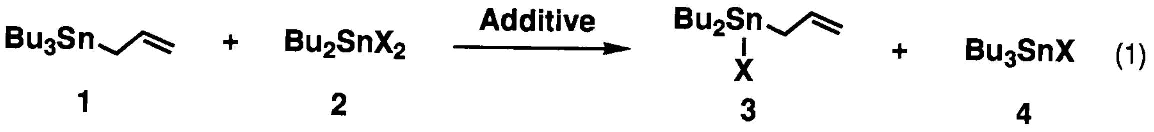


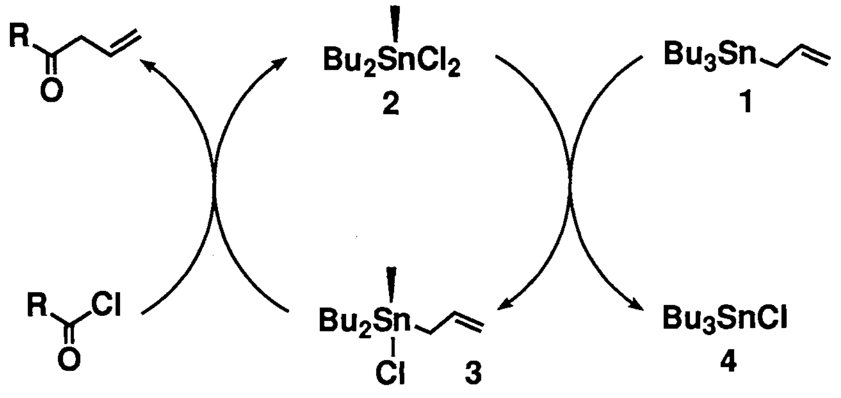
Table 1. Redistribution of allyltributyltin (**1**) and dibutyltin dihalide (**2**) [a]

Entry	Bu_2SnX_2 (X=)	Solv.	Additive	Conversion of **1** / % [b]
1	I	-	-	25(80) [c]
2	I	-	Bu_4NI	98
3	I	-	HMPA	100
4	I	-	Et_3N	42
5	I	-	Bu_4NI [d]	100
6	I	-	HMPA [d]	100
7	Cl	PhH	-	49 (100) [e]
8	Cl	PhH	HMPA	81
9	Cl	PhH	Bu_4NI	78
10	Cl	PhH	Et_4NCl	66

a)**1**/**2**/Additive = 1/1/1 mmol, 10 min. 20 °C, Solv. 1 ml. b)Determined by GC. c)3 h. d)0.1 mmol. e)Without solvent, 5 min.

The above results prompted us to attempt the catalytic allylation of acid chlorides as depicted in Scheme 1, where the active allyldibutyltin chloride **3** is constantly supplied by the redistribution. This method has some advantages over the allylation using stoichiometric 3. The former gives Bu_3SnCl which is a weak Lewis acid and its readily removed by ammonium fluoride. Contrarily, Bu2SnCl2 produced in the latter reaction is apt to cause undesired rearrangement due to its, stronger Lewis acidity.[7]

Table 2 summarizes the allylation of acid chlorides utilizing the redistribution. The use of catalytic amounts of additives is crucial, since without them, only a 35% yield of benzylallylketone



Scheme 1.

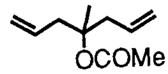
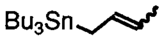
was obtained in spite of complete consumption of phenylacetyl chloride (entry 3). No reaction, of course, took place in the absence of Bu_2SnCl_2 (entry 2). The efficiency of these additives is noteworthy in connection with the fact that Gambaro et al. reported a low reactivity of allyldibutyltin chloride complexated with HMPA. The regeneration of Bu_2SnCl_2 may be accelerated by the coordination[8] to give allylketones in the last step of the catalytic cycle (Scheme 1).

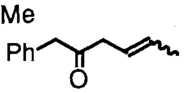
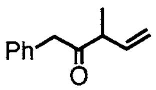
Table 2. Reaction of allyltributyltin (**1**) with acid chlorides [a]

Entry	RCOCl(R=)	Additive	Time / h	Yield / % [b]
1	$PhCH_2$	Et_4NCl	0.5	82
2 [c]	$PhCH_2$	Et_4NCl	5	0
3	$PhCH_2$	-	3.5	35
4	$PhCH_2$	$Bu_3P{=}O$	3.5	53
5	$PhCH_2$	HMPA	3	75
6	*n*-Bu	Et_4NCl	3.5	52
7	*t*-Bu	Et_4NCl	21	61
8 [d]	Me	Et_4NCl	24	trace (62) [e]
9 [f]	$PhCH_2$	Et_4NCl	2	75 [g]

a)**1**/RCOCl/Bu_2SnCl_2/Additive = 2.2/2/0.2/0.3 mmol, 60 °C.

b)Determined by GC. c)Without Bu_2SnCl_2. d)20 °C

e)  f)  was used instead of **1**.

g)Mixture of  (31%) and  (44%).

Tetraethylammonium chloride showed a fine effect more than phosphine oxides in contrast to the redistribution, furnishing benzylallylketone in 82% yield within 30 min at 60 °C (entry 1). This result indicates that the coordination of additives plays an important role in the coupling of **3** and acid chlorides as well as in the redistribution. Though requiring longer reaction times, *n*-valeroyl chloride and pivaloyl chloride also gave the corresponding allylketones in good yields (entries 6, 7). In the case of acetyl chloride, however, a further allylation of the produced allylketone was predominant (entry 8). Crotyltributyltin was also applicable though producing a mixture of products (entry 9). As a result, this reaction may be value in an allylation with allyltributyltin under nearly neutral conditions in the absence of transition metal catalysts.

A typical experiment is as follows: Allyltributyltin (2.2 mmol) and phenylacetyl chloride (2 mmol) were successively added to the mixture of Et_4NCl (0.3 mmol) and Bu_2SnCl_2 (0.2 mmol), and the resulting solution was stirred at 60 °C for 30 min. After the reaction, 50 ml of ether and aqueous ammonium fluoride (10%, 50 ml) were added for removal of Bu_3SnCl. The ether layer was dried over Mg_2SO_4, and benzylallylketone was obtained by distillation; bp 60 °C/0.1 mmHg; IR 1720 (C=O), 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) $\delta = 3.24$ (2H, d, J = 7.5 Hz), 3.77 (2H, s), 5.04 - 5.26 (2H, m), 5.73 - 6.11 (1H, m), 7.20 - 7.40 (5H, m); ^{13}C NMR ($CDCl_3$) $\delta = 46.75$ (t), 49.50 (t), 118.83 (t), 126.94 (d), 128.61 (d), 129.35 (d), 130.29 (d), 133.89 (s) 205.63 (s).

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