A PALLADIUM-CATALYZED NOVEL ALLYLSTANNYLATION OF NORBORNENE

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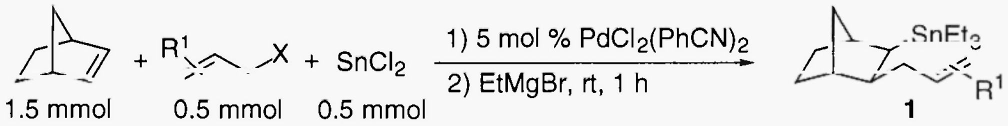
Abstract : Palladium-catalyzed reaction of norbornene with allylic halides, ester, or phenyl ether and tin(II) chloride provided allylstannylation products after a treatment of the reaction mixture with ethylmagnesium bromide solution.

Carbometallation of alkenes is a useful two-carbon homologation of organometallics.[1,2] Carbostannylation is relatively less explored among them, while it is desirable to construct carbon-tin bond according to this protocol. It was first developed by Himbert and then Yamaguchi *et al.*, employing combinations of nucleophilic organotin reagents and alkynes that possess π-accepting substituents.[3-5] Yamamoto *et al.* reported a Lewis acid promoted *trans*-allylstannylation of nonpolar terminal alkynes.[6] Recently, Shirakawa *et al.* developed transition metal-catalyzed carbostannylations of alkynes using alkynyl-[7] and allyltributyltin reagents.[8,9] Despite these studies, the scope of the reaction is still limited. Unlike alkyne-carbostannylations, the alkene-counterpart has seldom been explored.[4] We wish to report here a palladium-catalyzed novel allylstannylation of norbornene utilizing allylic halides and tin(II) chloride. The present reaction provides the first example of a palladium-catalyzed *cis*-carbostannylation of a non-polar carbon-carbon double bond (eq 1).[2]



(1)

The effects of solvent and reaction temperature were first examined using allyl bromide as the allylic compound. The results are indicated in Table I.

Table I. Palladium-catalyzed carbostannylation of norbornene with allyl bromide-tin(II) chloride.

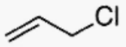
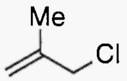
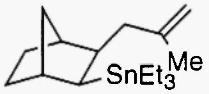
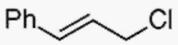
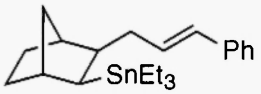
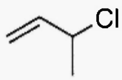
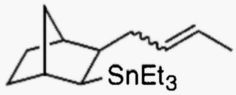
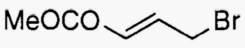
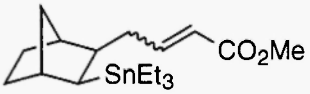
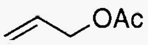
run	solvent	temperature (°C)	time (h)	yield[a] (%)
1	DMF	55	11.5	0
2	dioxane	55	11.5	31
3	CH_2Cl_2	55	11.5	85
4	toluene	55	3	quant
5	toluene	55	1	45
6	toluene	RT	11	56
7	toluene	RT	60	quant

[a] Isolated yields.

In a typical procedure, to a solution (3.0 cm^3) of dichlorobis(benzonitrile)palladium (0.025 mmol) were added successively allyl bromide (0.5 mmol), norbornene (1.5 mmol), and tin(II) chloride (0.5 mmol) in a 10 cm^3 tube under nitrogen, successively. The tube was cooled with a liquid nitrogen bath and sealed under vacuum, then heated at 55 °C. The reaction mixture was then treated with an ether solution of ethylmagnesium bromide (0.95 mol/dm^3, 4.5 mmol) at 0 °C and stirred at RT for 1 h. The crude product was obtained by treatment with 1 mol/dm^3 hydrochloric acid, extraction with ether, and drying the organic layer over anhydrous sodium sulfate. Silica-gel column chromatography after concentration afforded the desired product **1**. In contrast with Masuyama's carbonyl allylation and Kurosawa's generation of allyltin trichloride, that employed a similar reagent system[10] in strongly coordinating solvents such as *N*,*N*'-dimethylimidazolidin-2-one (DMI) and/or *N*,*N*-dimethylformamide (DMF),[11,12] the present reaction gave poor results in such solvents (runs 1 and 2). On the other hand, much better results were obtained when the reaction was performed in less coordinating solvents such as toluene and dichloromethane (runs 3 and 4).[13] Thus we chose toluene as the solvent for this reaction. The reaction could be performed at RT, although it took then a few days to go to completion.

Other representative results are summarized in Table II. The yields were excellent with allyl and β-methallyl chloride (runs 1 and 2) like in the case of allyl bromide. When allylic reagents with a substituent at 1- or 3-position of the allylic moiety were used (runs 3-5), carbon-carbon bond formation took place regioselectively at the unsubstituted end of the allylic moiety. Interestingly, an ester functionality of the allylic reagent remained intact after the Grignard treatment (run 5). Not only allylic halides but also allyl acetate and allyl phenyl ether gave the corresponding allylstannylation products in moderate yields (runs 6 and 7). On the other hand, no reaction was observed when iodobenzene was employed in place of allylic compounds. Both benzyl chloride and bromide gave 1,2-diphenylethane as a sole product.

Table II. Palladium-catalyzed carbostannylation of norbornene with allylic compounds.

run	allylic compound	time (h)	product	yield (%)[a]
1		3	**1**	quant
2		3		quant
3		3		51
4		11		49
5		10		50
6		3	**1**	56
7		3	**1**	33

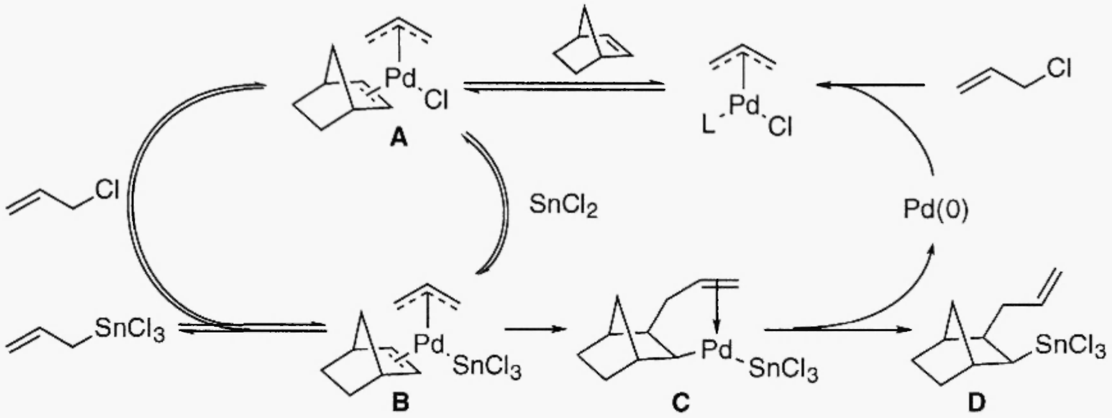
[a] Isolated yields.

We would propose a plausible reaction pathway as depicted in Scheme 1. The catalytic palladium(0) species reacts with allyl chloride and norbornene to form an intermediary complex

A.[14,15] Then it is transformed into the key intermediate **B** by tin(II) chloride. This process might be reversible.[12,16,17] π-Allylpalladium chloride is indeed reported to add to norbornene by means of allylpalladation.[18] The process is, however, reported not to be facile.[19] In order to obtain the adduct in good yield, it is necessary to replace an anionic ligand of a π-allylpalladium complex like chloride by an electron-accepting ligand as hexafluoroacetylacetonate or acetate.[12,19-26] Consequently, the smooth isomerization of the intermediate **B** into **C**, that is assumed to be the rate-determining step,[27] could be ascribable to a weak σ-donor and potential π-acceptor ability of the trichlorostannate ligand. Finally, reductive elimination provides the adduct **D** with a concomitant regeneration of the catalytic palladium(0) species.

The complex **B** may also be in equilibrium with allyltin trichloride under the reaction condition.[12] An almost homogeneous solution was formed[28] by the palladium-catalyzed reaction between allyl bromide and tin(II) chloride in toluene in the absence of norbornene. It would suggest the formation of allyltin trichloride, since tin(II) chloride appears insoluble in toluene. This result was surprising to us, because ultrasonic irradiation was necessary for Masuyama's carbonyl allylation in such solvents.[29]

Scheme 1 A Plausible Reaction Pathway



The present reaction brings about a novel method of not only promoting a norbornene allylation but also forming a carbon-tin bond that possesses a potential utility for further transformations using electrophiles.[30,31] Utilization of the intermediary trichlorotin species such as **D** is currently under investigation. Such a process would be valuable because it is free from generating toxic trialkyltin by-products that are currently suspected to be endocrine disrupters.

Acknowledgment.

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(28) ^{119}Sn NMR of the solution (JEOL α-500 spectrometer, Me_4Sn in $CDCl_3$ as an external standard, noise decoupling) showed a singlet at δ -25.9 ppm. On the other hand, the signal of a tetrahydrofuran solution of tin (II) chloride appeared at δ -206.0 ppm. A significant difference of the chemical shift from that reported by Masuyama[10,29] could be attributed to their use of such a strongly coordinating solvent as DMF that would form a hyper-valent tin complex with electron deficient allyltin species.

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