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Carbostannylation of Allenes Catalyzed by a Palladium Complex

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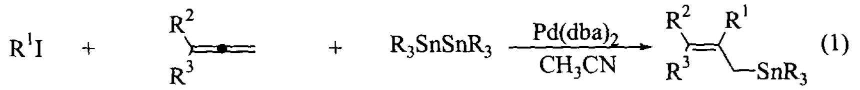
Abstract: Aryl or alkenyl iodides react regioselectively with allenes and hexaalkylditins in the presence of $Pd(dba)_2$ to give substituted allylstannanes.

Transformation of allenes into various organic reagents catalyzed by palladium complexes has continued to attract great attention.[1] Recently, we reported a palladium-catalyzed carbosilylation involving a three-component coupling reaction of an organic halide, allene and organosilylstannane to give an allylic silane.[2] The success of this carbosilylation and our continuing interest in allene chemistry prompted us to investigate the possibility of carbostannylation of allenes. To the best of our knowledge, the addition of an organic and a stannyl group to an allene is unknown. We wish to report that aryl or alkenyl iodides react smoothly with allenes and hexaalkylditins in the presence of a catalytic amount of palladium complex to give allylstannanes regioselectively (eq 1). It is interesting to note that the catalytic reaction is equivalent to addition of an $C(sp^2)\text{-}SnR_3$ bond to an allene molecule, although in reality this bond is too stable to be activated by the palladium complex under the reaction conditions. Allylstannanes are widely used in organic synthesis particularly in carbon-carbon bond formation.[3a] Several methods for the preparation of these reagents are known, but in general only simple allylstannanes are synthesized and more than two steps are required by these methods.[3] The present catalytic reaction provides a unique route for the introduction of various aryl or alkenyl substituents to allylstannanes at the olefinic β-carbon relative to the stannyl group. A wide range of highly substituted new allylstannanes can be conveniently prepared according to this methodology.



(1)

1a- 1i

2a: $R^2 = R^3 = Me$
2b: $R^2 = H, R^3 = cyclo\text{-}C_6H_{11}$
2c: $R^2 = H, R^3 = n\text{-}Bu$

3a: R = Me
3b: R = *n*-Bu

4: R = Me
5: R = *n*-Bu

Reaction of *p*-iodoacetophenone (**1a**), 1,1-dimethylallene (**2a**) and $Me_3SnSnMe_3$ (**3a**) catalyzed by $Pd(dba)_2$ (5 mol %) (dba = dibenzylideneacetone) in acetonitrile at 60 °C gave a trace of allylstannane **4a**. The main product observed is a coupling product *p*-acetylphenyltrimethylstannane from **1a** and **3a**.[4] This result is

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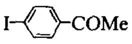
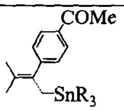
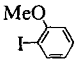
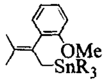
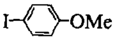
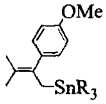
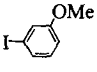
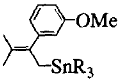
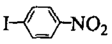
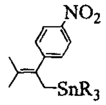
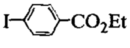
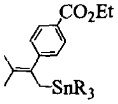
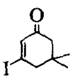
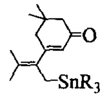
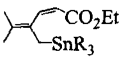
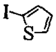
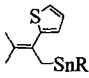
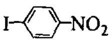
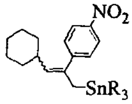
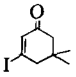
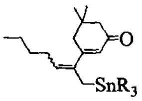
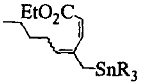
Table 1. Palladium-Catalyzed Coupling of Aryl or Alkenyl Iodides, Hexaalkylditins and Allenes.[a]

Entry	R^{1}I		Allene	Ditin	Product			E/Z [c]	Yield (%)[b]
1		**1a**	**2a**	**3a**		R = Me	**4a**		76
2		**1a**	**2a**	**3b**		R = Bu	**5a**		77
3		**1b**	**2a**	**3b**		R = Bu	**5b**		26
4		**1c**	**2a**	**3a**		R = Me	**4b**		35
5		**1c**	**2a**	**3b**		R = Bu	**5c**		40
6		**1d**	**2a**	**3b**		R = Bu	**5d**		55
7		**1e**	**2a**	**3a**		R = Me	**4c**		75
8		**1f**	**2a**	**3a**		R = Me	**4b**		69
9		**1f**	**2a**	**3b**		R = Bu	**5c**		80
10		**1g**	**2a**	**3a**		R = Me	**4e**		70
11		**1g**	**2a**	**3b**		R = Bu	**5g**		93
12		**1h**	**2a**	**3a**		R = Me	**4f**		40
13		**1h**	**2a**	**3b**		R = Bu	**5g**		81
14		**1i**	**2a**	**3a**		R = Me	**4g**		72
15		**1e**	**2b**	**3a**		R = Me	**4h**	25/75	73
16		**1g**	**2c**	**3b**		R = Bu	**5h**	31/69	98
17		**1h**	**2c**	**3b**		R = Bu	**5I**	32/62	98

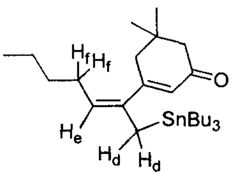
[a] General procedure. To a 25-ml sidearm flask were added aryl or alkenyl iodide (1.00 mmol), allene (2.00 mmol), Pd(dba)$_2$ (0.050 mmol, 5 mol%). The system was evacuated and purged with nitrogen three times. Acetonitrile (2.0 mL) was added to the system and the reaction mixture was stirred at 60 °C. To the reaction mixture was added (R$_3$Sn)$_2$ (1.20 mmol) in toluene (2.0 mL) *via* a syringe pump over a period of 2 h for (Me$_3$Sn)$_2$ and 4 h for (SnBu$_3$)$_2$. The reaction mixture was further stirred for 0.5 h at the same temperature and was filtered through Celite. The filtrate was concentrated on a rotary evaporator and then separated on a silica gel column to give the desired product. [b] Isolated yield. [c] Ratio was determined by ^{1}H NMR.

surprising in view of the known effective three-component coupling reaction of **1a**, **2a** and Bu$_3$SnSiMe$_3$ catalyzed by Pd(dba)$_2$ to give an allylsilane[2] in excellent yield. However, this carbostannylation is greatly improved and **4a** was obtained in 76 % yield (Table 1) when hexamethylditin was added to the reaction slowly over a period of 2 h *via* a syringe pump. Similarly, treatment of *p*-iodoacetophenone (**1a**) with 1,1-dimethylallene (**2a**) and $(n\text{-}Bu_3Sn)_2$ (**3b**) in the presence of $Pd(dba)_2$ affords allylstannane **5a** in 77 % yield. These reactions are regioselective, with the aryl group adding to the central carbon and the stannyl group to the nonsubstituted terminal carbon of the allene.

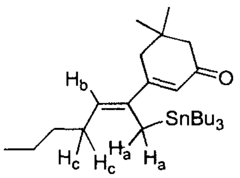
Other aryl iodides including *o*-, *p*- and *m*-iodoanisole (**1b**, **1c** and **1d**), *p*-iodonitrobenzene (**1e**) and ethyl *p*-iodobenzoate (**1f**) also react with dimethylallene (**2a**) and hexalkylditin (**3a** and **3b**) to give the corresponding allylstannanes in fair to excellent yields (Table 1). Based on the results shown in Table 1, it is clear that aryl iodides with an electron-withdrawing substituent such as an acetyl, an ester or a nitro group at the *para* position gives a higher yield of allylstannane than those with an electron-donating substituent such as a methoxy group. Moreover, aryl iodides bearing an *ortho* substituent generally give lower yields than those with the substituent at the *para* position. Bromobenzene and chlorobenzene do not react with **2a** and **3a** to afford the corresponding allylstannane **4a**.

In addition to aryl iodides, heteroaromatic and alkenyl iodides react with **2a** and **3** to afford the corresponding allylstannanes. Thus, 3-iodo-5,5-dimethylcyclohex-2-en-1-one (**1g**), ethyl (*Z*)-3-iodoacrylate (**1h**) and 2-iodothiophene (**1i**) gave the corresponding allylstannanes in 40 - 93 % yields (entries 10 - 14). For allylstananes **4f** and **5g**, the *cis* stereochemistry of the acrylate group remains the same as that of the original (*Z*)-3-iodoacrylate.

In addition to **2a**, mono-substituted allenes such as 1-cyclohexyl allene **2b** and 1-*n*-butylallene **2c** also undergo carbostannylation with aryl iodides and **3**, producing allylstannanes regioselectively in 73 - 98 % yields (entries 15 - 17). For the same aryl iodide and ditin used, mono-substituted allenes appear to afford higher yield of the allylstannanes than dimethylallene **2a**. However, two *E/Z* isomers of the products were obtained for the monosubstituted allenes. The stereochemistry of these products is determined by ^{1}H NMR NOE techniques. For example, the two isomers **5h** and **5h'** were isolated from the reaction of **2c** with **1g** and **3b**. The minor isomer **5h'** shows ^{1}H NMR signals at 1.78 and 5.06 ppm for the methylene (H_d) and olefin protons (H_e), respectively. Irradiation at the H_d signal led to increase of the intensity of H_e signal by 5.56 %. Similarly, irradiation at H_e signal resulted in increase of the intensity of H_d signal by 5.07 %. In contrast, NOE experiments of the major isomer **5h** reveal no change of the intensity of H_b and H_a signals on irradiation at H_a (1.88 ppm) and H_b (5.73 ppm) signals, respectively. These NOE results clearly establish that **5h** has *Z* geometry, while **5h'** is an *E* product. Other pairs of *E/Z* isomers are also determined by a similar technique.



5h'



5h

Based on the known palladium chemistry,[5] it is possible to propose a mechanism to account for the present palladium-catalyzed reaction. The initial step involves oxidative addition of the organic halide to a palladium(0) complex to give a palladium(II) intermediate, coordination of allene followed by insertion of allene into the Pd-carbon bond to give a π-allyl palladium(II) species.[6] Transmetallation between ditin and the palladium π -allyl complex followed by reductive elimination affords the final products and regenerates the palladium(0) species.

As indicated in Table 1, hexa-*n*-butylditin gives a higher yield of the allylstannane product than hexamethylditin in the present catalytic reaction. A possible reason for the low yield of hexamethylditin is its high reactivity toward the oxidative addition products[4, 7] of aryl (or alkenyl) iodides and Pd(0) leading only to two-component coupling products arylstannanes during the catalytic reaction. Hexa-*n*-butylditin is less reactive than hexamethylditin toward the oxidative addition products of aryl iodides and Pd(0) providing a higher probability for allenes to insert into the palladium-carbon bond, particularly when the concentration of hexa-*n*-butylditin in the solution is kept low by slow addition *via* a syringe pump.

We have demonstrated a new method for the regioselective synthesis of allylstannanes from allenes, aromatic or alkenyl iodides and ditins in the presence of a palladium complex. This reaction, which provides a convenient tool for the preparation of highly substituted allylstannanes at the β and γ carbons of the allylic groups, is complementary to other synthetic methods for allylstannanes.

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8. Selected spectral data of **4a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.0 Hz, 2 H), 7.17 (d, J = 8.0 Hz, 2 H), 2.57 (s, 3 H), 2.02 (s with Sn satellites, 2 H), 1.72 (s with Sn satellites, 3 H), 1.56 (s with Sn satellites, 3 H), -0.06 (s with Sn satellites, 9 H). HRMS: calcd for $C_{16}H_{24}OSn$ 352.0849, found 352.0850.
9. Selected spectral data of **5a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.0 Hz, 2 H), 7.20 (d, J = 8.0 Hz, 2 H), 2.57 (s, 3 H), 2.01 (s with Sn satellites, 2 H), 1.74 (s with Sn satellites, 3 H), 1.55 (s with Sn satellites, 3 H), 1.27 (m, 6 H), 1.84 (m, 6 H), 0.80 (t, J = 7.2 Hz, 9 H), 0.68 (m, 6 H). HRMS: calcd for $C_{25}H_{42}OSn$ 478.2257,found 478.2258.