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THE TIN(IV) CHLORIDE-PROMOTED CROSS-COUPLING REACTION OF ALLYLSTANNANES WITH ALLYLSILANES

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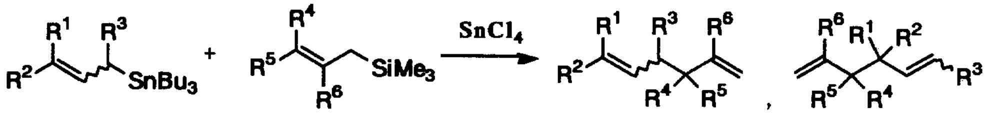
Abstract: The cross-coupling reaction of allylstannanes with allylsilanes selectively proceeded in the presence of tin(IV) chloride to give 1,5-dienes. It was found that the substitution of a phenylthio group at γ-position remarkably increased the reactivity of allylstannanes.

The coupling reaction between organometals is one of the most useful methods for the preparation of symmetric compounds, and various reactions such as the oxidative coupling reactions promoted by copper salts,1) silver(I) oxide,2) and palladium(II) acetate-*t*-butylhydroperoxide3) have been reported. The thermal4) and transition metal-catalyzed5) reductive coupling reactions were also reported. Although the selective cross-coupling reaction of allylstannanes with vinylstannanes was achieved,3) it is well known that the cross-coupling of two different organometallic compounds is generally difficult. Recently, we showed that allylstannanes react with the nucleophilic reagents, such as enol silyl ethers6) and arenes7), in the presence of tin(IV) chloride. We expected that tin(IV) chloride was also effective for the cross-coupling of two different allylic organometalloides. In this communication, we wish to report the tin(IV) chloride-promoted selective cross-coupling reaction of allylstannanes with allylsilanes.

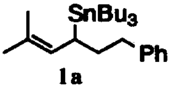
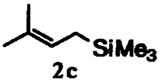
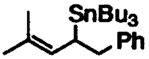
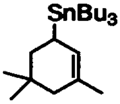
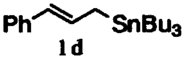
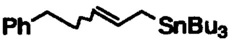


1 + 2 → α-3, γ-3 (1)

A simple treatment of the mixture of 2-methyl-6-phenyl-4-tributylstannyl-2-hexene (**1a**) and an equimolar amount of 2-methyl-4-trimethylsilyl-2-butene (**2c**) with tin(IV) chloride in CH_2Cl_2 at -78 °C gave the cross-coupling products **3** selectively, and the formation of any self-coupling product was not observed. The yield of **3** increased when two equivalents of the allylsilane were employed (run 2 in Table 1). In a similar manner, the reactions of various allylstannanes **1** with allylsilanes **2** were examined. As the results listed in Table 1 show, the coupling products **3** were obtained in good yields by the reactions of secondary allylstannanes. On the contrary, the primary allylstannanes were less reactive than secondary ones; cinnamyltributylstannane (**1d**) gave the 1,5-dienes **3** only in moderate yields (runs 8 and 9). Furthermore, no formation of the coupling product was observed in the reaction of **1e** (run 10).

The regiospecific transposition in the allylsilane was observed in the present reaction similarly to the reaction of allylsilanes and allylstannanes with allylic ethers and halides reported by Hosomi *et al.*8) With respect to the allylic system originated in allylstannanes, however, it was found that the regioselectivity of these reactions varied according to the substituents on both allylstannanes and allylsilanes.

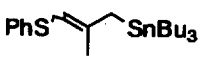
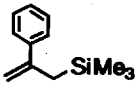
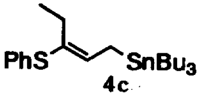
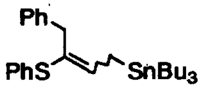
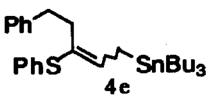
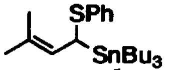
Table 1. The reaction of allylstannanes **1** with allylsilanes **2**[a]

Run	Allylstannane 1	Allylsilane 2	Temp ℃	Time h	Yield[b] %	α : γ
1	 **1a**	 **2a**	-78	1	76	76 : 24[c]
2		 **2b**	-78	1	83(65)[d]	36 : 64[c]
3		 **2c**	-78	1	87	100 : 0[c]
4	 **1b**	**2a**	-78	1	71	56 : 44[c]
5		**2b**	-78	1	71	27 : 73[c]
6	 **1c**	**2a**	-78	2	63	100 : 0[e]
7		**2c**	-78	2	69	100 : 0[e]
8	 **1d**	**2a**	r.t.	1	35	80 : 20[f]
9		**2b**	r.t.	1	47	44 : 56[f]
10	 **1e**	**2b**	reflux	4	-	

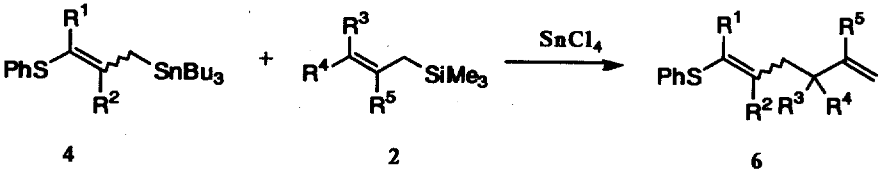
a) All reactions were performed using 2 equiv. of the allylsilane **2** with a similar procedure as described in the text, unless otherwise noted. b) The structures of these compounds were supported by IR and NMR spectra. c) Determined by HPLC analysis (Merck Si 60, hexane). d) The reaction was carried out using 1 equiv. of **2b**. e) Determined by GLC analysis (SE-30) and NMR spectrum. f) Determined by NMR spectrum.

A typical experimental procedure is as follows: A CH_2Cl_2 stock solution of 2-methyl-4-trimethylsilyl-2-butene (**2c**) (0.6 ml, 1 mmol) was added to a CH_2Cl_2 (3 ml) solution of 2-methyl-6-phenyl-4-tributylstannyl-2-hexene (**1a**) (232 mg, 0.5 mmol) and the reaction mixture was cooled to -78 °C. Then a CH_2Cl_2 (0.5 ml) solution of $SnCl_4$ (0.5 mmol) was added to the mixture. After being stirred for 1 h, the reaction was quenched by addition of water and the organic materials were extracted with CH_2Cl_2. The extract was washed with 10% KF aqueous solution, dried (Na_2SO_4), and condensed under reduced pressure. The residue was chromatographed on silica gel (hexane) to give 3,3,6-trimethyl-4-(2-phenylethyl)-1,5-heptadiene (**3**) (106 mg, 87%).

Table 2. The reaction of γ-phenylthioallylstannanes 4 with allylsilanes 2a)

Run	γ-Phenylthioallylstannane 4	Allylsilane 2	Temp °C	Time h	Yieldb) %
1	 4a	2b	r.t.	1	51
2	 4b	2b	r.t.	0.6	53
3		 2d	r.t.	0.8	57
4	 4c	2a	r.t.	1	34c)
5		2b	r.t.	1	80d)
6e)		2c	r.t.	1	50
7		2d	r.t.	1	84
8	 4d	2b	r.t.	1	75
9	 4e	2b	r.t.	1	79
10		2d	r.t.	0.9	88
11	 5	2b	-45	4	74

a) All the reactions were performed using 2 equiv. of the allylsilane 2 with a similar procedure as described in the text, unless otherwise noted. b) All compounds gave satisfactory spectral data. c) E : Z = 55 : 45. d) E : Z = 73 : 27. e) The reaction was carried out using the stereoisomeric mixture of 4c.



(2)

As noted above, the reactivity of primary allylstannanes **1** was insufficient for the present reaction. Then we examined the use of phenylthio group substituted primary allylstannanes **4**[9] which were expected to be more reactive than simple allylstannanes (Eq 2). As was expected, the coupling reactions of **4** proceeded at room temperature to afford the 1,5-dienes in good yields (Table 2). The regioselectivity of this reaction was excellent, and the only the regioisomer **6**, which resulted by the attack of allylsilane at the α-position to tributylstannyl group, was produced. The stereoselectivity of the reaction, however, was found to depend on the structures of reactants even when the stereoisomeric pure starting material was employed (see runs 4 and 5). The similar reaction of α-phenylthioallylstannane **5** with **2b** also proceeded to give 2,6-dimethyl-4-phenylthio-1,5-heptadiene regioselectively (run 11).

Since the phenylthio group of alkenyl sulfide **6** can be reductively removed[10] or replaced by an alkyl group[11], it should be noted that the present reaction is useful for the regioselective preparation of 1,5-dienes.

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