CHEMISTRY LETTERS, pp. 133-136, 1991.

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Coupling Reaction of Allylstannanes with Arenes

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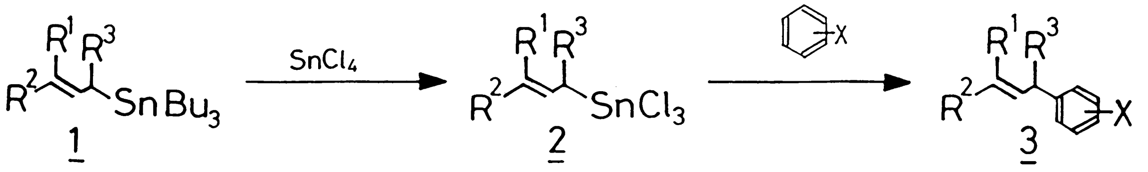
The tin(IV) chloride promoted coupling reaction of allylstannanes with various arenes proceeded to give the allylated arenes in good yields. It was also found that tin(II) bromide was an effective catalyst for Friedel-Crafts allylation using allylic bromides.

Recently we reported that allylated ketones were obtained by the reaction of allylstannanes with trimethylsilyl enol ethers in the presence of copper(II) or tin(IV) salts.[1] These results showed that the allylstannane activated by copper(II) or tin(IV) salt acts as an electrophile. However, the structure and reactivity of the active species formed from allylstannanes were still uncertain. Therefore we have investigated the application of the above species to the typical reactions which proceed via carbocation intermediates.

In this communication, we summarize the tin(IV) chloride promoted electrophilic aromatic substitution using allylstannanes (1) (Eq. 1).



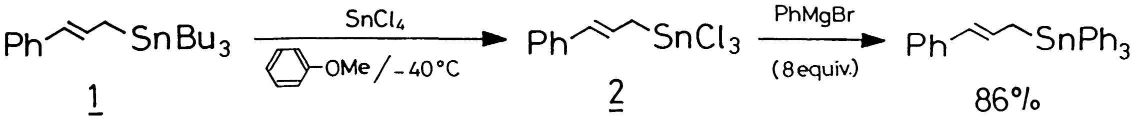
(1)

When the primary allylstannanes (1) were treated with tin(IV) chloride in refluxing aromatic solvents, the corresponding allylated aromatic compounds (3) were produced in good yields. The results of the reaction of tributylcinnamylstannane with anisole carried out in the presence of various amounts of tin(IV) chloride indicated that 0.6 equivalents of tin(IV) chloride were much enough to complete the reaction. The secondary allylstannanes (1) seemed to be more reactive than the primary ones, because their coupling reactions with anisole proceeded even at 0 °C. In one case, isomerization of the product (3) to the olefin conjugated with the benzene ring was observed (entry 10).

As shown in Table 1, the coupling products (3) were obtained with excellent regioselectivity. In all the reactions examined, arenes always attacked the carbon α to the tributylstannyl group. However, the distribution of position isomers was largely affected by substituents on allylstannanes (1).

The typical experimental procedure is as follows: To a m-xylene (3 ml) solution of tributylcinnamylstannane (204 mg, 0.5 mmol) was added a CH_2Cl_2 solution of $SnCl_4$ (0.5 ml, 0.5 mmol) at r.t. Then the reaction mixture was refluxed for 4 h. The reaction was quenched by addition of water and the organic material was extracted with CH_2Cl_2. The extract was washed with 10% KF aqueous solution and water successively, dried (Na_2SO_4), and condensed under reduced pressure. The residue was purified by PTLC (hexane : AcOEt = 95 : 5) to give 1-cinnamyl-2,4-dimethylbenzene (101 mg, 91%).

Since the intermediates of the present reaction were assumed to be allyltrichlorostannanes (2),2) the following experiment was performed. A mixture of tributylcinnamylstannane (1) and an equimolar amount of $SnCl_4$ in anisole was treated with phenylmagnesium bromide (8 equiv.) at -40 °C to afford cinnamyltriphenylstannane in 86% yield (Eq. 2). This fact firmly supports the above assumption. Although the process of the regeneration of tin(IV) chloride is not wholly clear at present, it is reasonable to speculate that the present reaction is the electrophilic substitution of arenes with allyltrichlorostannanes (2) in which the trichlorostannyl group serve as a leaving group.



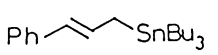
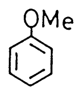
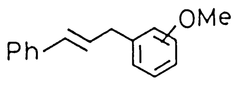
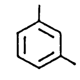
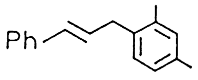
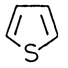
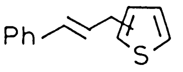
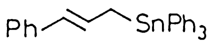
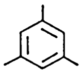
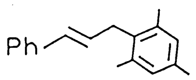
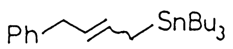
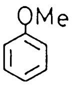
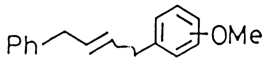
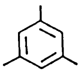
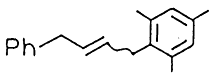
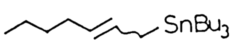
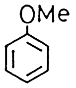
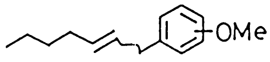
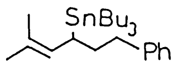
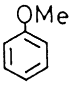
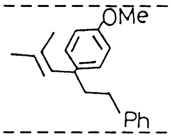
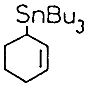
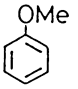
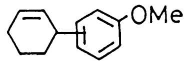
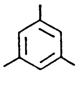
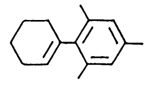
(2)

Since allylstannanes are prepared by various methods including desulfurizative stannylation of allyl sulfides,3) the present reaction provides a useful method for the introduction of a substituted allyl group to aromatic compounds. Although Ochiai and Fujita have already reported the similar transformation using thallium(III) trifluoroacetate,4) it should be pointed out that the reagent employed in their reaction was a strongly oxidizing agent and must be handled with the special caution.

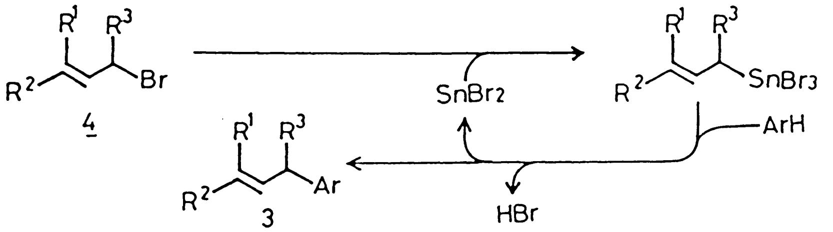
It is well known that the direct allylation of aromatic compounds by electrophilic aromatic substitution using allylic halides or alcohols are always complicated owing to the intervention of redox reaction and the instability of the products under the reaction conditions employed.5)

On the basis of the results obtained in the above study, we next examined the tin(II) bromide catalyzed Friedel-Crafts allylation using allylic bromides (4) as outlined in Eq. 3.

Table 1. The allylation of arenes with allylstannanes (1)[a]

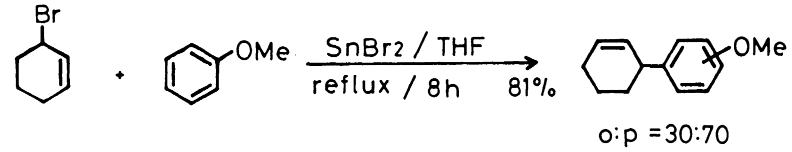
Entry	1	Arene	SnCl$_4$ equiv.	Temp °C	Time h	Product (3)	Yield[b] %	o : p[c]
1			0.2	reflux	4		22	7 : 93[d]
			0.6	r.t.	24		78	9 : 91
			1.0	reflux	2		68	7 : 93[d]
2			1.0	reflux	4		91	e)
3			0.6	reflux	3		54	f)
4			1.1	reflux	3		82	-
5			0.6	reflux	2.5		74	44 : 56
6			0.6	reflux	2.5		78	-
7			0.6	reflux	2.5		72	29 : 71
8			0.6	0	2		62	e)
9			0.8	0	2		78[g]	32 : 68
10			1.1	r.t.	overnight		56[g]	-

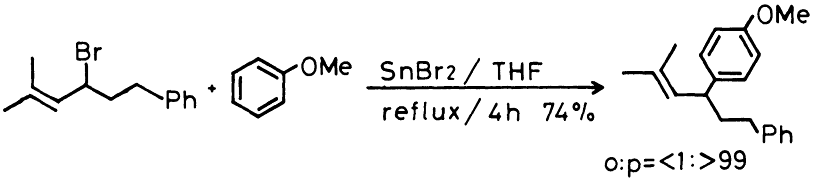
a) All reactions were performed with a similar procedure as described in the text, unless otherwise noted. b) The structures of these compounds were supported by IR and NMR spectra. c) The two isomers were separated from each other by PTLC. d) Determined by HPLC analysis (Merck Si60, solvent; Hexane : AcOEt = 95 : 5). e) Only the indicated product was formed. f) The ratio of position isomers was not determined. g) In the presence of powdered molecular sieves 4 A (1.1 g / 0.5 mmol of 1).



(3)

As was expected, the allylated arenes (3) were obtained in good yields by the treatment of allylic bromides (4) with anisole in the presence of tin(II) bromide at elevated temperatures.[6)]





Further investigation is now in progress.

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3) T. Takeda, S. Ogawa, N. Ohta, and T. Fujiwara, Chem. Lett., 1987, 1967, and references cited therein.
4) M. Ochiai, M. Arimoto, and E. Fujita, Tetrahedron Lett., 22, 4491(1981); M. Ochiai, E. Fujita, M. Arimoto, and H. Yamaguchi, Chem. Pharm. Bull., 30, 3994 (1982); M. Ochiai, E. Fujita, M. Arimoto, and H. Yamaguchi, ibid., 31, 86 (1983).
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6) The reaction was carried out by refluxing a THF (2 ml) solution of the allylic bromide (4) (1 mmol) and anisole (2 ml) in the presence of tin(II) bromide (0.6 mmol).

(Received October 17, 1990)