The Copper(I) Iodide-promoted Allylation of Vinylstannanes with Allylic Halides

Takeshi Takeda,* Ko-ichi Matsunaga, Yuki Kabasawa, and Tooru Fujiwara
Department of Applied Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184

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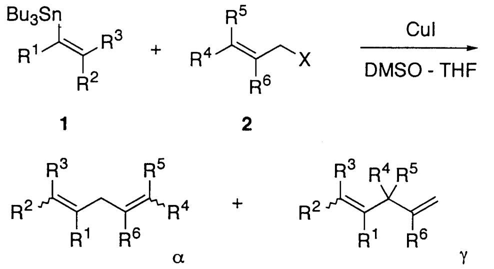
The stereospecific allylation of vinylstannanes with allylic halides proceeded in the presence of copper(I) iodide in DMSO-THF at room temperature. The stereospecificity of the reaction was dependent on the structures of vinylstannanes and allylic halides, and also the leaving group of allylic halides employed. Concerning the regioselectivity regarding allylic system, higher α-regioselection was observed in the reactions of allylic chlorides than in those of the corresponding iodides.

The palladium-catalyzed allylation of vinylstannanes has been studied as a useful method for the stereoselective preparation of substituted olefins.[1] In the course of the study on the palladium-catalyzed transformation of β-tributylstannyl-α,β-unsaturated ketones,[2] however, it became apparent that allylation of such vinylstannanes using allylic halides was complicated and the allylation products were obtained in only poor yields even when copper(I) iodide was employed as a co-catalyst.[3] This result prompted us to investigate an alternative method of allylation, and we found that copper(I) iodide promotes the reaction of various vinylstannanes with allylic halides *in the absence of palladium catalyst* in dipolar aprotic solvents such as DMSO-THF to give allylation products in good to high yields (eq. 1). In this communication, we summarize the characteristics of this allylation including its regioselectivity and stereospecificity.[4]

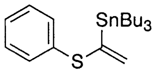
When 1-phenylthio-1-tributylstannylethylene (**1a**) was treated with 4-chloro-2-methyl-2-butene (**2a**) in the presence of a catalytic amount of copper(I) iodide in DMSO-THF, the allylation product was obtained in a moderate yield (run 1). The yield was increased by the use of 0.5 or 1 equiv. of copper(I) iodide (runs 2 and 3). The typical experimental procedure is as follows: To a flask charged with copper(I) iodide (48 mg, 0.25 mmol) was added a THF (1.5 ml) solution of **1a** (213 mg, 0.5 mmol) and a DMSO (4.3 ml) solution of **2a** (105 mg, 1 mmol) successively at room temperature. After being stirred for 2 h, the reaction mixture was diluted with ether and washed with 3.5% NH_3 aqueous solution and then water. The organic layer was dried (Na_2SO_4) and condensed. The residue was purified by silica-gel chromatography (hexane) to give a mixture of 5-methyl-2-phenylthio-1,4-hexadiene and 3,3-dimethyl-2-phenylthio-1,4-pentadiene (85 mg, 83%).

It was found that DMSO is indispensable as a co-solvent (run 4), and DMF is less suitable for the present reaction (run 5). The regioselectivity regarding the allylic system was found to be dependent on the leaving group of allylic halides; the allylations of **1** with allylic chlorides occur with excellent α-regioselection whereas the reactions of allylic iodides prepared *in situ* by the treatment of the chlorides with NaI was less regioselective (runs 6 and 9). On the other hand, the reaction of 3-chloro-2-methylpropene (**2d**) was less stereospecific than that of the corresponding iodide **2c** or **2c** prepared *in situ* from **2d** (see runs 10, 11, and 12). However, the high stereospecificity was achieved by the use of an equimolar amount of LiCl as a co-catalyst even in the reaction using allylic chloride **2d** (run 13). Other metal salts such as $MgCl_2$ and $CaCl_2$ were also found to be effective to improve the stereospecificity. It was observed that the use of Na_2CO_3 as an additive in the reaction of **2a** suppressed the formation of protodestannylated compound (run 7). Since the allylation of vinylstannanes **1d-g** bearing a carbonyl, hydroxyl, or methoxy group at γ to tributylstannyl group with allylic chloride **2d** proceeded with complete retention of configuration (runs 16-19), it is obvious that the stereospecificity of the reaction is also affected by the structures of vinylstannanes **1**.

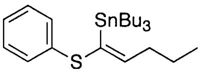
Concerning the copper(I) salt promoted reactions of vinylstannanes, Piers and Wong described the copper(I) chloride-mediated intramolecular coupling with vinyl halides[6] and intramolecular conjugate addition to α,β-unsaturated ketones.[7] Recently the intermolecular homocoupling of vinylstannanes under the similar reaction conditions was reported by Quayle *et al.*[8] Tanaka, Torii, and their co-workers also reported the copper(I) chloride-promoted Michael type addition of vinylstannanes to allenecarboxylates derived from penicillin.[9] Further they recently reported that copper(I) chloride promotes the reaction of 3-chloromethylcephem with vinylstannanes to give the corresponding allylation products and suggested the intermediary of vinylcopper species.[10] As for the possibility of the formation of such a species, Liebeskind *et al.* have suggested that vinyltributylstannane reacts with copper(I) iodide in highly dipolar solvents such as 1-methyl-2-pyrrolidinone and in the absence of



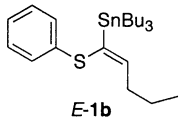
(1)



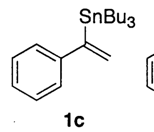
1a



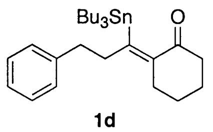
Z-**1b**



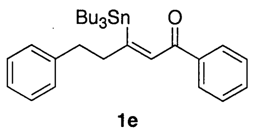
E-**1b**



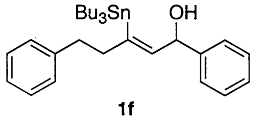
1c



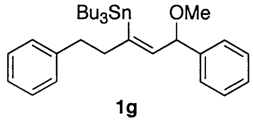
1d



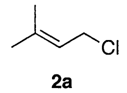
1e



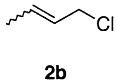
1f



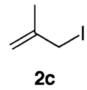
1g



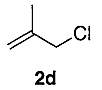
2a



2b



2c



2d

Table 1. The copper(I) iodide promoted allylation of vinylstannanes[a]

Run	Vinylstannane[5] 1	Allylic Halide 2	Additive (equiv.)	CuI / equiv.	Time / h	Yield[b] / %	*E* : *Z*[c]	α : γ[c]
1	**1a**	**2a**	-	0.1	10	68		96 : 4
2	**1a**	**2a**	-	0.5	2	83		96 : 4
3	**1a**	**2a**	-	1.0	2	81		97 : 3
4[d]	**1a**	**2a**	-	0.5	6 days	21		83 : 17
5[e]	**1a**	**2a**	-	0.5	7	43		94 : 6
6	**1a**	**2a**	NaI (2.0)	1.0	2	78		79 : 21
7	**1a**	**2a**	Na_2CO_3 (0.1)	0.5	2.5	88		96 : 4
8	**1a**	**2b**	-	1.0	2	76		88 : 12
9	**1a**	**2b**	NaI (2.0)	1.0	6	87		64 : 36
10	*Z*-**1b**	**2d**	-	1.0	14	77	69 : 31	
11	*Z*-**1b**	**2c**	-	1.0	0.5	86	93 : 7	
12	*Z*-**1b**	**2d**	NaI (2.0)	1.0	16	88	95 : 5	
13[f]	*Z*-**1b**	**2d**	LiCl (1.0)	1.0	16	83	92 : 8	
14	*E*-**1b**	**2d**	NaI (2.0)	1.0	26	86	3 : 97	
15	**1c**	**2a**	-	1.0	1	60		99 : 1
16	**1d**	**2d**	-	1.0	3	87	*Z* only[g]	
17	**1e**	**2d**	-	1.0	3	74	*Z* only[g]	
18	**1f**	**2d**	-	0.5	31	80	*Z* only[g, h]	
19	**1g**	**2d**	-	0.5	35	93	*Z* only[i]	

[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] Determined by NMR spectrum. [d] THF (3 ml / 1 mmol of **1**) was used as a solvent. [e] DMF (3 ml / 1 mmol of **1**) was used as a solvent. [f] DMSO (6 ml / 1 mmol of **1**) was used as a co-solvent. [g] No signal corresponding to the *E* isomer was observed. [h] The NMR spectrum contained some unidentified signals. [i] The NMR spectrum suggested that the product consisted of a single stereoisomer.

strong ligands to yield an organocopper species.[11]

The role of copper(I) iodide in the present allylation is not clear at present. Although it is presumed that the allylation proceeds *via* the vinylcopper intermediate, another possible reaction pathway in which copper(I) iodide activates allylic halide to form the carbocation-like intermediate[12] should be also considered.

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References and Notes

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3 It is well known that Stille-type reactions are facilitated by the use of copper(I) iodide as a co-catalyst; see references cited in ref. 2.

4 A part of the results described here has been reported; the 67th Annual Meeting of the Chemical Society of Japan, Tokyo, 1994, Abstr., 3K113; the 69th Annual Meeting of the Chemical Society of Japan, Kyoto, 1995, Abstr., 2H531.

5 The vinylstannane **1a** was prepared by the method reported by Harirchian and Magnus. B. Harirchian and P. Magnus, *J. Chem. Soc., Chem. Commun.*, **1977**, 522. The vinylstannanes *Z*-**1b** was stereoselectively prepared by the stannylation of 1-(phenylthio)vinyllithium reagent, and *E*-**1b** was synthesized by the photoisomerization of *Z*-**1b**. T. Takeda, F. Kanamori, M. Masuda, and T. Fujiwara, *Tetrahedron Lett.*, **32**, 5567 (1991). The details of preparation of **1d** and **1e** were described in ref. 2. The hydroxyvinylstannane **1f** was prepared by the reduction of **1e** with $LiAlH_4$ (1 equiv.) in Et_2O at -78 °C in 83% yield, and methylation of **1f** (NaH (2 equiv.) / MeI (5 equiv.) / THF / 0 °C then room temperature) gave the methoxyvinylstannane **1g** in 96% yield.

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