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Extremely Facile and Stereoselective Preparation of Allylstannanes with Use of Ultrasound

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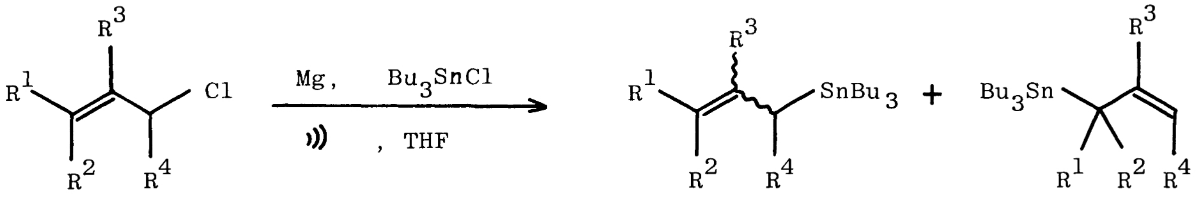
Various allylstannanes are conveniently prepared in quantitative yields by means of ultrasound-promoted Barbier-type reaction from chlorotributylstannane and allyl halides in a stereoselective manner.

Allylstannanes have been recognized as useful synthetic reagents. Especially, since Lewis acid mediated addition reaction of allylstannanes to various carbonyl compounds was established,[1)] they have been frequently utilized in organic synthesis.[2)] Allylstannanes can be prepared by several reported methods, i.e. coupling reaction of allylmetals and stannyl halide[3)] or allyl derivatives and stannyl metals,[4)] stannylation of allyl sulfides,[5)] and elimination of selenoxides.[6)] The reported procedures, however, are not suitable for the synthesis of them in quantity. Even in the most conventional method, due to their instability under acidic conditions considerable amount of decomposition causes decreasing of their yields during isolation.[3)]

We report herein a new and convenient method of the allylstannane preparation by means of ultrasound-promoted Barbier-type reaction.[7,8)] This is the first example of the ultrasound-promoted cross coupling reaction between two halides, each of which can afford self-coupling products under the applied reaction conditions.[9)] This method provides various kinds of allylstannanes in almost quantitative yield from the corresponding allyl chloride and chlorotributylstannane.

Preparation of allyltributylstannane is shown as a typical example of this method. To a THF solution (15 ml) of chlorotributylstannane (10.0 mmol), magnesium turnings (13.0 mmol), and a piece of iodine, allyl chloride (12.0 mmol) was added dropwise at 0 °C under a nitrogen atmosphere with external irradiation of ultrasound[10)] in the course of 45 min. After aqueous workup and ether extraction, allyltributylstannane (2a) was obtained in quantitative yield without contamination of any by-products.[11,12)] The obtained allylstannane possessed enough purity for allylation reaction without further purification. This method is superior to the reported ones in its simplicity of manipulation and its excellent yield. Especially, allyl halides were efficiently converted to the corresponding stannyl compounds without formation of their Wurtz-type coupling products, which were frequently observed in the course of the preparation of allylic Grignard



1 2 3

Table 1. Synthesis of Allyltributylstannanes

	R^1	R^2	R^3	R^4	Allylstannane, Isolated yield/ % **2** + **3**	Isomeric ratio **2** / **3**
a	H	H	H	H	100	-
b	H	H	Me	H	96	-
c	Me	H	H	H	100	≈1[a)]/ 1
d	Me	Me	H	H	100	100 / 0
e	Me	H	H	H	52[b)]	-
f	Ph	H	H	H	100[c)]	100 / 0
g	CH_2=CH	H	H	H	96[d)]	100 / 0
h	MeCH=CH	H	H	H	100[e)]	100 / 0

[a)] Stereoisomeric ratio of **2c** was trans/cis=55/45. [b)] Pure trans isomer **1e** was used. The isomeric ratio of the obtained **2e** was trans/cis=55/45. [c)] No cis isomer was detected by means of ^{1}H NMR. [d)] Trans isomer **2g** was selectively obtained (trans/cis=92/8). [e)] Trans, trans isomer was selectively obtained in >90% purity.

reagents. In the similar manner, various substituted allylic tributylstannanes were successfully synthesized in nearly quantitative yield as shown in Table 1. In the cases of 1f-1h, the corresponding trans- or trans,trans-isomers (2f-2h) were obtained in good to excellent isomeric purity (>90%) with preservation of the original stereochemistry.12) On the other hand, a mixture of their stereoisomers (trans/cis=69/31) was given by the coupling reaction of penta- or hexadienyl lithium with trimethylstannyl halide.13)

This method is also applicable to the preparation of the related stannyl compounds. Benzyltributylstannane and tetraallylstannane were prepared both in quantitative yield by the combination of benzyl chloride-Bu_3SnCl and allyl chloride-$SnCl_4$, respectively.

In contrast to chlorostannanes, chlorotrimethylsilane did not afford the expected allylsilane under the similar conditions, presumanbly because of the preferential formation of the corresponding disilane.11)

References

1) K. Maruyama and Y. Naruta, J. Org. Chem., 43, 3796 (1978); Y. Naruta, S. Ushida, and K. Maruyama, Chem. Lett., 197, 919; Y. Naruta and K. Maruyama, ibid., 1979, 881 and 885; Y. Naruta, J. Am. Chem. Soc., 102, 3774 (1980); idem., J. Org. Chem., 45, 4097 (1980).

2) For examples, Y. Yamamoto, H. Yatagai, Y. Naruta, and K. Maruyama, J. Am. Chem. Soc., 48, 1559 (1983); B.M. Trost and P.J. Bonk, J. Am. Chem. Soc., 107, 1778 (1985); V.J. Jephcote, A.J. Pratt, and E.J. Thomas, J. Chem. Soc., Chem. Commun., 1984, 800; A.J. Pratt and E.J. Thomas, ibid., 1982, 1115; G.E. Keck and E.P. Boden, Tetrahedron Lett., 25, 1879 (1984); M. Shimagaki, H. Takubo, and T. Oishi, ibid., 26, 6235 (1985).

3) E. Abel and R.J. Rowley, J. Organomet. Chem., 84, 199 (1975); M. Andrianome and B. Delmond, Tetrahedron Lett., 26, 6341 (1985).

4) E. Matarasso-Tchiroukhine and P. Cadiot, J. Organomet. Chem., 121, 155 (1976).

5) Y. Ueno and M. Okawara, J. Am. Chem. Soc., 101, 1893 (1979); Y. Ueno, S. Aoki, and M. Okawara, ibid., 101, 5415 (1979); Y. Ueno, M. Ohta, and M. Okawara, J. Organomet. Chem., 197, C1 (1980).

6) V.J. Jephcote and E.J. Thomas, Tetrahedron Lett., 26, 5327 (1985).

7) On recent reports in this field, see; J.-L. Luche and J.-C. Damiano, J. Am.

Chem. Soc., 102, 7926 (1980); A.V. Kuchin, R.A. Nurnshev, and G.A. Tolstikov, Zh. Obsh. Khim., 53, 2519 (1983); C. Petrier, J. Einhorn, and J.-L. Luche, Tetrahedron Lett., 26, 1449 (1985); C. Petrier, J.C.de S. Barbosa, C. Dupuy, and J.-C. Luche, J. Org. Chem., 50, 5761 (1985); T. Kitazume and N. Ishikawa, J. Am. Chem. Soc., 107, 5186 (1985); H.C. Brown and U.S. Racherla, J. Org. Chem., 51, 427 (1986).

8) The rate of the cross coupling reaction without the ultrasound irradiation was generally lower than that of the ultrasound-promoted reaction. The amount of moisture in the reaction system and the activity of the applied magnesium surface affected to the reproducability of the time requrired for the compleation of the coupling reaction. Especially, the unsonicated reactions of 1e, 1g, and 1f afforded the comparable amount of the corresponding homocoupling products.

9) Treatment of chlorotributylstannane with Mg in THF affords hexabutyldistannane. This reaction was also accelerated by ultra-sound irradiation, while in the presence of allyl chloride any distannane was not detected. cf. H.Shirai, Y. Sato, and M. Niwa, Yakugaku Zasshi, 90, 59 (1970).

10) Branson model B-220 (output power 100W) was used.

11) B.H. Han and P. Boudjouk, Tetrahedron Lett., 22, 2757 and 3813 (1981).

12) Purity was determined by means of ^{1}H NMR. 3c and 3e gradually isomerized at -20 °C to 2c and 2e, respectively.

13) Y. Naruta, N. Nagai, Y. Arita, and K. Maruyama, Chem. Lett., 1983, 1683.

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