



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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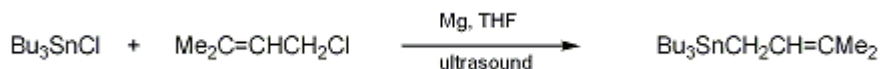
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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 9, p.707 (1998); Vol. 71, p.118 (1993).

TRIBUTYL(3-METHYL-2-BUTENYL)TIN

[Stannane, tributyl(3-methyl-2-butenyl)-]



Submitted by Yoshinori Naruta, Yutaka Nishigaichi, and Kazuhiro Maruyama¹.
Checked by Bruce M. Branan and Leo A. Paquette.

1. Procedure

CAUTION! This experiment should be performed with gloves in an efficient hood in order to avoid the contact of toxic tributyltin derivatives with the skin and to avoid their unpleasant odor. One should wear earmuffs during operation of an ultrasound processor.

A dry, 500-mL, three-necked flask appropriately shaped to accommodate the horn of an ultrasonic processor is equipped with a thermometer and a pressure-equalizing dropping funnel to which a nitrogen inlet is attached. A nitrogen atmosphere is established in the flask, which is charged with 100 mL of anhydrous tetrahydrofuran (THF) (Note 1), 3.04 g (0.125 mol) of magnesium (Mg) turnings (Note 2), 32.5 g (0.100 mol) of tributyltin chloride (Note 2), and a small piece of iodine (optional), and then immersed in an ice-salt bath. After the temperature of the solution falls below 15°C, 13.4 mL (0.120 mol) of 1-chloro-3-methyl-2-butene (Note 3) in 50 mL of THF is added dropwise over 30–60 min while maintaining the temperature at less than 20°C (Note 4) under sonication at an output power of 30–75W (Note 5). After the addition is complete, sonication is continued for a further 30–45 min (Note 6) to complete the reaction. The reaction mixture is poured into 400 g of ice water and the mixture is extracted with three 100-mL portions of ether. The combined ethereal solutions are washed with 50 mL of water and 50 mL of brine, dried over anhydrous magnesium sulfate, and evaporated under aspirator pressure to yield a colorless oil. This oil is further evacuated (1 mm) at room temperature for 1 hr (Note 7) to give 36 g (100%) of tributyl(3-methyl-2-butenyl)tin. This material is sufficiently pure for direct use in most reactions, but can be purified by distillation to afford 33.2 g (92%) of colorless oil, bp 105–107°C (0.01 mm) (Note 8),(Note 9),(Note 10).

2. Notes

1. THF is distilled from benzophenone ketyl and stored over sodium wire under a nitrogen atmosphere. For the drying procedure and caution, see *Org. Synth., Coll. Vol. VII 1990*, 451 and *Org. Synth., Coll. Vol. V 1973*, 976, respectively.
2. Magnesium turnings were purchased from Wako Pure Chemical Industries and the Aldrich Chemical Company, Inc. Tributyltin chloride was obtained from Tokyo Kasei Kogyo and the Aldrich Chemical Company, Inc. They were used without further purification.
3. As purchased from the Aldrich Chemical Company, Inc., this chloride contains 5–10% of 3-chloro-3-methyl-1-butene. Contamination by this isomeric chloride does not affect the yield of tributyl(3-methyl-2-butenyl)tin.
4. The reaction temperature should be kept below 20°C to prevent side reactions. If the temperature exceeds 20°C, one should stop both the addition of the prenyl chloride and the ultrasound irradiation, and wait for the reaction temperature to fall below 15°C.
5. The submitters used Heat Systems-Ultrasonics Model W-220 (maximum output power 200W) with a standard horn. The checkers used a Sonics and Materials Inc. Vibra-Cell High Intensity Ultrasonic Processor (maximum power outlet 600W) fitted with a 13-in extender probe. If the applied ultrasonic processor does not have a power meter, one can judge the applied power by the occurrence of vigorous stirring of the Mg turnings around the immersed ultrasonic horn. If the Mg turnings settle to the bottom of the flask, the applied sonication power is insufficient.

For reaction on a 10-mmol scale, an ultrasonic cleaner with sufficient output power (e.g., Branson Model B-220) can be used for external irradiation.

6. After completion of the reaction, ultrasonic irradiation for an unnecessarily long period causes decomposition of the allyltributyltin. The end of the reaction can be determined by a faint turbidity in the solution and by darkening of the brilliant Mg surface.

7. Through this treatment, most of the low-boiling impurity can be removed.

8. Good purity (95–98%) is observed by GLC (glass capillary column, OV-101, 0.33 mm × 25 m) at an oven temperature of 200°C.

9. Because of modest thermal instability of the material, one should distill at a bath temperature below 150°C. When the bath temperature exceeds 150°C, considerable decomposition of the allylic tributyltin occurs and a poorer yield is realized. The checkers measured a bp of 100°C at 0.1 mm.

10. The spectrum is as follows: ¹H NMR (400 MHz, CDCl₃) δ: 0.83 (m, 6 H, SnCH₂), 0.89 (t, 9 H, J = 7, CH₃ of Bu), 1.29 (m, 6 H, SnCH₂CH₂), 1.47 (m, 6 H, CH₂CH₃), 1.57 (s, 3 H, cis-CH₃), 1.64 (d, 2 H, J = 9, CH₂CH=C), 1.67 (s, 3 H, trans-CH₃), 5.28 (broad t, 1 H, J = 9, CH=C); ¹³C NMR (75 MHz, CDCl₃) δ: 9.4, 10.7, 13.7, 17.4, 25.5, 27.4, 29.3, 123.0, 125.3; ¹¹⁹Sn NMR (120 MHz, CDCl₃) δ: -13.4.

Waste Disposal Information

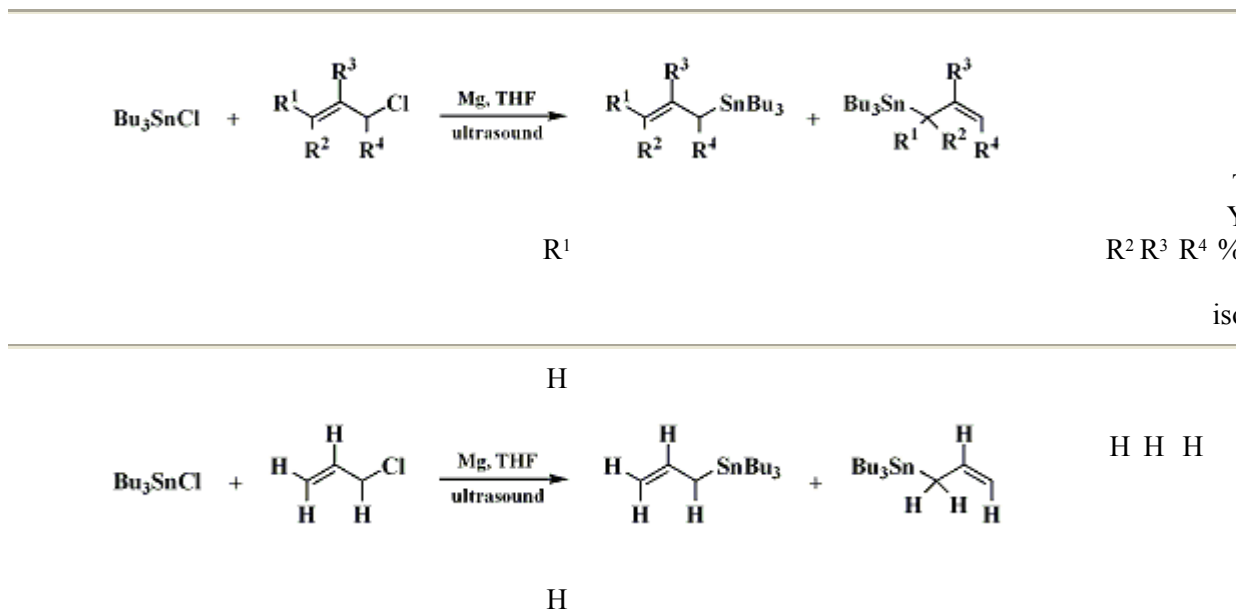
All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

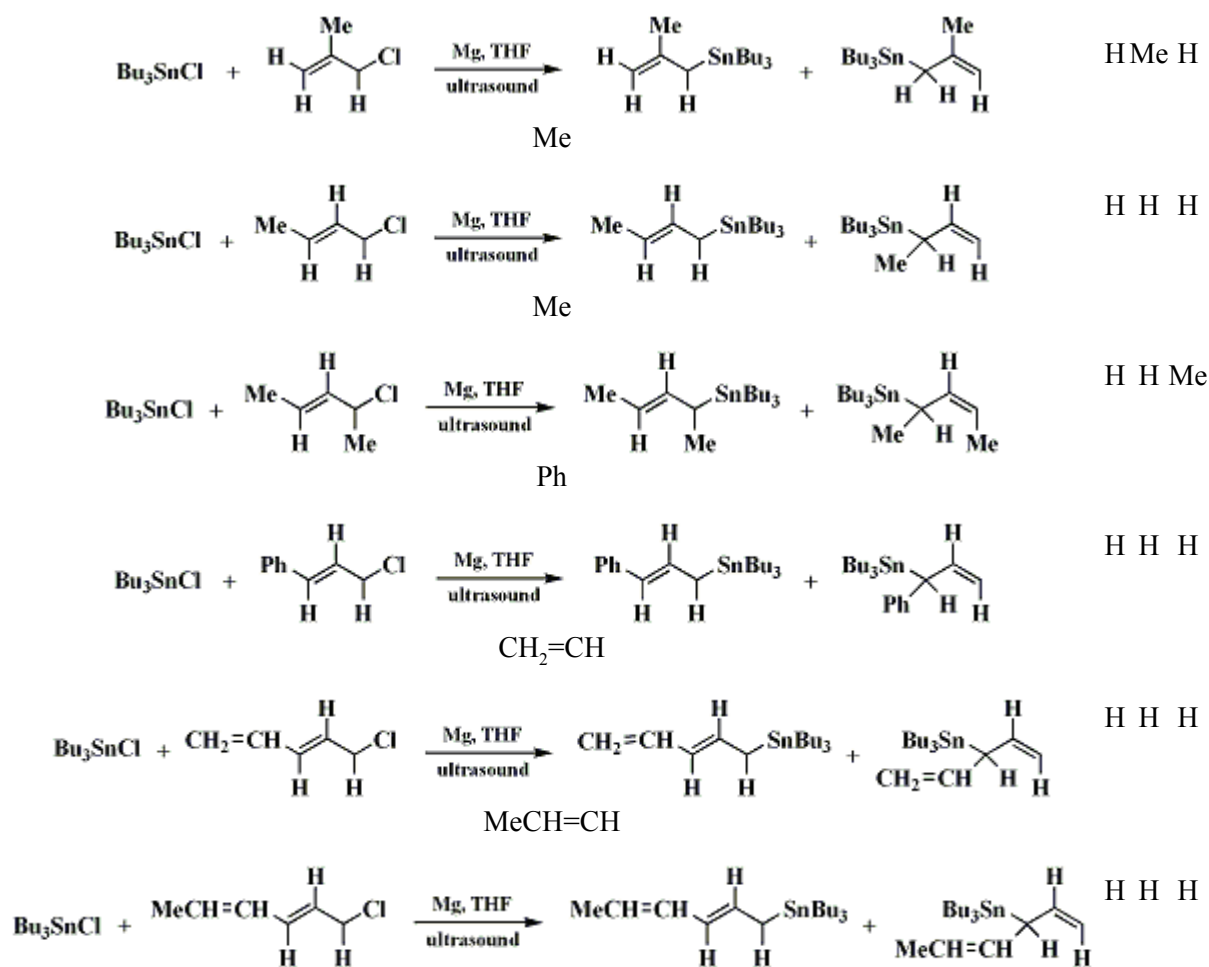
3. Discussion

This procedure describes ultrasound-promoted Barbier-type cross coupling of an allylic chloride with tributyltin chloride.² Allylic trialkyltin derivatives have also been prepared by (i) a coupling reaction of a trialkyltin chloride with an allyl Grignard reagent^{3,4,5} or allyllithium,^{6,7} and allyl derivatives with stannyl metals,^{8,9,10,11,12} (ii) stannylation of allylic sulfides,¹² sulfones,^{13,14} selenoxides,¹⁵ alcohols,¹⁶ and allyl palladium.^{17,18,19} The method with an allylic Grignard reagent prepared in advance of the coupling reaction is an alternative to this method, but the ultrasonic procedure is more convenient and effective. For the preparation of simple allyltributyltin or its homologues, the present method has advantages over other methods, especially because of easy manipulation and scale-up, reproducibility, and yield.

This procedure is representative of a general and versatile method for the preparation of allylic tributyltins. Other allylstannanes prepared using this method are shown in the Table.

TABLE
COUPLING OF ALLYLIC HALIDES WITH TRIBUTYLTIN CHLORIDE^a





^aAll reactions were performed on a 10-mmol scale.

^bThe α -adduct is a mixture of trans:cis = 55:45.

^cPure [trans-2-chloro-3-pentene](#) was used. The α -adduct is a mixture of trans:cis = 55:45.

^dNo cis isomer is formed.

^eThe stereoisomer ratio is trans:cis = 92:8.

^fThe trans,trans-isomer is obtained in >90% purity.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 9, 741](#)
- [Org. Syn. Coll. Vol. 10, 632](#)

References and Notes

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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

benzophenone ketyl

brine

magnesium (Mg) turnings

Mg turnings

ether (60-29-7)

magnesium turnings (7439-95-4)

nitrogen (7727-37-9)

iodine (7553-56-2)

sodium (13966-32-0)

magnesium sulfate (7487-88-9)

Tetrahydrofuran (109-99-9)

tributyltin (688-73-3)

Tributyl(3-methyl-2-butenyl)tin,
Stannane, tributyl(3-methyl-2-butenyl)- (53911-92-5)

1-chloro-3-methyl-2-butene,
prenyl chloride (503-60-6)

3-chloro-3-methyl-1-butene (2190-48-9)

trans-2-chloro-3-pentene

tributyltin chloride (1461-22-9)

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