



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

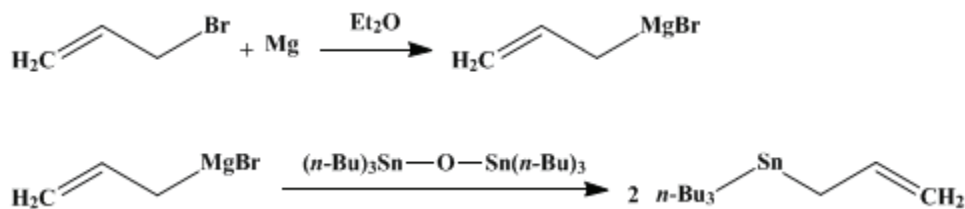
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 8, p.23 (1993); Vol. 68, p.104 (1990).

ALLYLTRIBUTYLTIN

[Stannane, tributyl-2-propenyl-]



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1. Procedure

Magnesium turnings (72.6 g, 3 g-atom) and 1000 mL of anhydrous ethyl ether are placed under argon in a dry, 3-L, three-necked flask equipped with a mechanical stirrer, a 500-mL pressure-equalizing dropping funnel, a Claisen adapter, a thermometer, an ice-water-cooled condenser, and an argon inlet. The dropping funnel is charged with allyl bromide (158 mL, 1.8 mol) (Note 1) in 150 mL of anhydrous ether. Stirring is initiated and a 10–12-mL portion of the allyl bromide solution is run into the reaction flask. The resulting mixture is treated with a few crystals of iodine, whereupon a rise in temperature and clouding of the reaction mixture occurs, indicating that the reaction has begun (Note 2). The remainder of the allyl bromide solution is added dropwise with continued stirring at such a rate as to maintain a gentle reflux. The addition requires approximately 1.5 hr. The mixture is then refluxed for an additional 1.5 hr.

While the Grignard solution is being refluxed, the dropping funnel is charged with bis(tributyltin) oxide (371 g, 0.62 mol) (Note 1) in 150 mL of anhydrous ether. After the reflux, heating is stopped and the bis(tributyltin) oxide solution is added at such a rate as to maintain a reaction temperature of 36–38° C. The addition requires approximately 1 hr. After the addition is complete, the reaction mixture is refluxed for 1.5 hr and then stirred overnight at room temperature.

The reaction mixture is cooled in a water-ice bath, and a saturated aqueous ammonium chloride solution is added at such a rate as to maintain the temperature below 35°C. Ammonium chloride solution is added in portions until addition produces no further exothermic reaction (Note 3). The supernatant solution is decanted through glass wool onto 400 g of ice in a 4-L separatory funnel. The residual solids are washed with three portions of hexane, approximately 1000 mL total, and the washes are decanted into the separatory funnel. After the phases are separated, the aqueous phase is washed with an additional 500-mL portion of hexane. The combined organic extracts are washed with 500 mL of saturated ammonium chloride, and then with 500 mL of brine. The organic layer is dried over anhydrous magnesium sulfate and filtered. Most of the solvent is removed by a rotary evaporator and the residual oil is distilled at reduced pressure using an ice-water-cooled fraction cutting head. After a small forerun, approximately 390–392 g (94% of theory) is collected as a colorless oil, bp 116°C at 1.6 mm (lit. 155°C at 17 mm).²

2. Notes

1. Allyl bromide and bis(tributyltin) oxide were obtained from Aldrich Chemical Company, Inc.
2. Initiation of the reaction required about 1 min of sonication in an ordinary laboratory cleaner.
3. Approximately 190 mL of saturated aqueous ammonium chloride is required.

3. Discussion

Within the last decade, organotin chemistry has become a major source of new and highly selective

reagents for effecting carbon–carbon bond formation. Transmetalation, nucleophilic substitution, stereoselective carbonyl addition, and transition-metal- or radical-mediated substitution reactions have all been accomplished using [allyltributyltin](#). Because of the broad range of selective reactivities under which the synthetically versatile allyl group may be transferred to a highly functionalized substrate, allyltin compounds have secured a position on the modern chemist's list of indispensable reagents.

Transmetalation of [allyltributyltin](#) with organolithium species³ has been used for the generation of [allyllithium](#) solutions free of the coupling by-products that often result from reduction of allylic halides with [lithium](#) metal. These solutions may then be used directly for the preparation of Gilman reagents and other reactive modifications of the parent [allyllithium](#).

The use of [allyltributyltin](#) in combination with a Lewis acid has been used to effect both nucleophilic substitution⁴ and stereoselective carbonyl addition⁵ reactions. These reactions occur with a high degree of selectivity because of the reagent's nucleophilic, completely nonbasic character in the presence of a sufficiently reactive carbon electrophile. [Allyltin](#) reagents appear to be more useful than the corresponding allylsilanes for these purposes.

By far the most generally useful synthetic application of [allyltributyltin](#) is in the complementary set of transition-metal- and radical-mediated substitution reactions. When the halide substrates are benzylic, allylic, aromatic, or acyl, transition-metal catalysis⁶ is usually the method of choice for allyl transfer from [tin](#) to [carbon](#). When the halide (or halide equivalent) substrate is aliphatic or alicyclic, radical chain conditions⁷ are appropriate, as β -hydrogen elimination is generally not a problem in these cases.

Allyltrioorganotin compounds have been prepared by the reaction of allyl Grignard⁸ or [allyllithium](#) reagents with triorganotin halides as well as by the procedure described. This procedure is an adaptation of that used by Rosenberg⁹ for the preparation of vinyltrialkyltin compounds. Allyltrioorganotin compounds in which the allyl group bears complex substituents can be prepared by desulfurization of allylic sulfides, sulfoxides, or sulfones with triorganotin hydrides.¹⁰

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 9, 707](#)
- [Org. Syn. Coll. Vol. 10, 632](#)

References and Notes

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(Registry Number)

brine

ether,
ethyl ether (60-29-7)

ammonium chloride (12125-02-9)

magnesium turnings (7439-95-4)

Allyl bromide (106-95-6)

tin (7440-31-5)

iodine (7553-56-2)

carbon (7782-42-5)

lithium (7439-93-2)

magnesium sulfate (7487-88-9)

hexane (110-54-3)

allyltin

Allyllithium

Allyltributyltin,
Stannane, tributyl-2-propenyl- (24850-33-7)

bis(tributyltin) oxide (56-35-9)