



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.

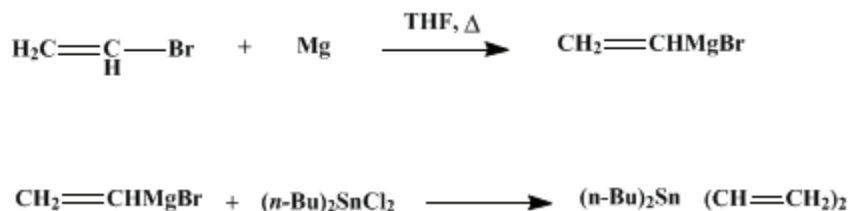
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.258 (1963); Vol. 39, p.10 (1959).

DI-*n*-BUTYLDIVINYLTIN

[Tin, dibutyldivinyl-]



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1. Procedure

In a 2-l. three-necked flask, equipped with a Dry Ice-acetone reflux condenser, a mechanical stirrer, and a 250-ml. dropping funnel, is placed 29.2 g. (1.2 g. atoms) of [magnesium turnings](#). Enough [tetrahydrofuran](#) (THF) ([Note 1](#)) to cover the [magnesium](#) is added, stirring is begun, and about 5 ml. of [vinyl bromide](#) ([Note 2](#)) is added. After the reaction has started ([Note 3](#)), an additional 350 ml. of the THF is added. The rest of the [vinyl bromide](#) (140 g., 1.3 moles, total), dissolved in 120 ml. of THF, is added at such a rate that a moderate reflux is maintained. After the addition has been completed, the solution is refluxed for 30 minutes ([Note 4](#)). The Grignard solution is then cooled to room temperature, and the Dry Ice-acetone condenser is replaced with a water condenser which is fitted with a Drierite-filled drying tube. A solution of 135 g. (0.44 mole) of [di-*n*-butyltin dichloride](#) ([Note 5](#)) in 250 ml. of THF ([Note 6](#)) is then added, with stirring, at such a rate that a moderate reflux is maintained. After the addition has been completed, the reaction mixture is refluxed for 20 hours. The mixture is cooled to room temperature and is hydrolyzed by the slow addition of 150 ml. of a saturated [ammonium chloride](#) solution ([Note 7](#)). The organic layer is then decanted and the residual salts are washed thoroughly with 3 portions of [ether](#), the washings being added to the organic layer. The [ether](#) and the THF are stripped off at atmospheric pressure; a Claisen distillation head is used. The residue is distilled at reduced pressure using a vacuum-jacketed Vigreux column equipped with a total-reflux partial take-off head to give 95–116 g. (74–91%) of [di-*n*-butyldivinyltin](#), b.p. 60° /0.4 mm., n_D^{25} 1.4797 ([Note 8](#)) and ([Note 9](#)).

2. Notes

1. [Tetrahydrofuran](#), obtained from the Electrochemicals Department of E. I. du Pont de Nemours & Co., was distilled from [lithium aluminum hydride](#) prior to use. It is not advisable to leave THF purified in this manner standing around for longer periods, since, in the absence of the inhibitor present in the commercial material, peroxides form fairly rapidly. (See also [p. 793, Note 2](#)).
2. [Vinyl bromide](#), obtained from the Matheson Company, was redistilled prior to use. The distillate was collected in a receiver cooled with a Dry Ice-acetone mixture and protected from day-light.
3. In most cases the formation of the Grignard reagent began in the absence of any initiator. In cases where the reaction did not begin within a few minutes, 0.5 ml. of [methyl iodide](#) served to initiate attack on the [magnesium](#).
4. In small-scale preparations of [vinylmagnesium bromide](#) it is advisable to carry out the reaction in an atmosphere of dry [nitrogen](#) in order to prevent hydrolysis and oxidation of the Grignard reagent. In larger-scale preparations such as the one described here, where a considerable excess of Grignard reagent is used, such precautions are not necessary.
5. [Di-*n*-butyltin dichloride](#) is a commercial product of Metal and Thermit Corporation, Rahway, New Jersey.
6. The checkers found that 250 ml. of dry [ether](#) was equally effective.
7. Enough saturated [ammonium chloride](#) solution is added to cause coagulation of the inorganic salts to a particle size of about 2–5 mm. in diameter; the volume of solution required varies but averages about

100–120 ml. per mole of Grignard reagent. If the hydrolysis is stopped at this point, a clear, essentially dry organic layer results, and in most instances no further drying is required before distillation.

8. This general procedure has been used to prepare^{2,3} a large number of vinyltin compounds, including:

$\text{CH}_2=\text{CHSnR}_3$ (R = CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$, C_6H_5)

$(\text{CH}_2=\text{CH})_2\text{SnR}_2$ (R = CH_3 , $n\text{-C}_4\text{H}_9$, $(\text{CH}_3)_3\text{SiCH}_2$, C_6H_5)

$(\text{CH}_2=\text{CH})_3\text{SnR}$ (R = $n\text{-C}_4\text{H}_9$, C_6H_5)

$(\text{CH}_2=\text{CH})_4\text{Sn}$

9. Grignard reagents other than [vinylmagnesium bromide](#) may be used in this general procedure. The initial use of a Dry Ice-acetone condenser, is then not required. Use of the [THF](#) solvent provides a distinct advantage over the method recently described in detail (p. 881), in which [ether](#) is used as a solvent, since fewer steps are required.

3. Discussion

The above procedure is essentially that described previously by the author.² [Di-*n*-butylvinyltin](#) has been prepared by the reaction between [vinylmagnesium chloride](#) with either [di-*n*-butyltin dichloride](#) or [di-*n*-butyltin oxide](#).⁴ The preparation of [vinylmagnesium bromide](#) was first described by Normant.⁵

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 83](#)
- [Org. Syn. Coll. Vol. 6, 488](#)

References and Notes

1. Massachusetts Institute of Technology, Cambridge, Massachusetts.
 2. Seyferth and Stone, *J. Am. Chem. Soc.*, **79**, 515 (1957).
 3. Seyferth, *J. Am. Chem. Soc.*, **79**, 2133 (1957).
 4. Rosenberg, Gibbons, and Ramsden, *J. Am. Chem. Soc.*, **79**, 2137 (1957).
 5. Normant, *Compt. rend.*, **239**, 1510 (1954).
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Appendix

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

[ether](#) (60-29-7)

[ammonium chloride](#) (12125-02-9)

[magnesium](#),
[magnesium turnings](#) (7439-95-4)

[nitrogen](#) (7727-37-9)

[Methyl iodide](#) (74-88-4)

[Tin, dibutyldivinyl-](#),
[DI-*n*-BUTYLDIVINYLTIN](#) (7330-43-0)

[vinyl bromide](#) (593-60-2)

[vinylmagnesium bromide \(1826-67-1\)](#)

[vinylmagnesium chloride \(3536-96-7\)](#)

[Tetrahydrofuran,
THF \(109-99-9\)](#)

[lithium aluminum hydride \(16853-85-3\)](#)

[di-n-butyltin oxide \(818-08-6\)](#)

[di-n-butyltin dichloride \(683-18-1\)](#)

[Di-n-butylvinyltin](#)