Organic Syntheses

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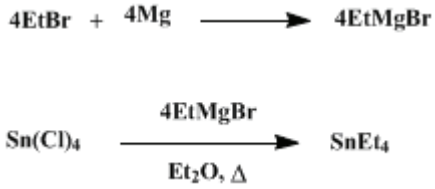
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI: 10.15227/orgsyn.036.0086

Organic Syntheses, Coll. Vol. 4, p.881 (1963); Vol. 36, p.86 (1956).

TETRAETHYLTIN

[Tin, tetraethyl-]



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Checked by M. S. Newman and L. L. Wood.

1. Procedure

A 2-l. three-necked flask is fitted with a reflux condenser (Note 1), a stirrer (Note 2), and a dropping funnel. The flask is suspended in a steam cone, which can also be used as a cooling bath. In the flask is placed 50 g. (2.05 g. atoms) of fine magnesium turnings (Note 3). In the dropping funnel is first introduced 5 ml. of a solution of 250 g. (175 ml., 2.3 moles) of ethyl bromide in 500 ml. of absolute ether. Three drops of bromine is mixed with the 5 ml., and the mixture is added to the magnesium. The Grignard reaction which starts at once (Note 4) is maintained by gradually adding the remainder of the ethyl bromide-ether solution. When the spontaneous reaction subsides, the mixture is heated gently under reflux with stirring for 30 minutes.

The flask is then cooled in ice, and in the course of about 20 minutes 83 g. of tin tetrachloride (37 ml., 0.32 mole) is added with vigorous stirring (Note 5). The mixture is heated at the reflux temperature for 1 hour, after which the condenser is set for distillation. During 1.5 hours the ether is removed by distillation while the flask is heated by an ample supply of steam (Note 6) and (Note 7).

The flask is again cooled in ice, the collected ether is returned to the reaction mixture, and the latter is decomposed by slowly adding first 85 ml. of ice water, then 400 ml. of ice-cold 10% hydrochloric acid. After stirring for some minutes, the contents of the flask are transferred to a separatory funnel. The layers are separated, and the ether layer is filtered through a folded filter and dried with calcium chloride (Note 8).

The ether is removed by distillation, and the crude tetraethyltin is distilled under water-pump vacuum, using a water bath for heating. The yield of tetraethyltin boiling at 63–65° /12 mm. is 67–72 g. (89–96%), n_D^{25} 1.4693–1.4699, d_4^{25} 1.1916 (Note 9).

2. Notes

1. A wide condenser must be employed to permit an ample reflux of ether.
2. A seal is recommended as described in *Org. Syntheses Coll. Vol.* **3**, 368 (1955), Note 1.
3. The submitters have carried out this preparation on a three-fold scale with comparable yields.
4. In general bromine starts Grignard reactions more quickly than the usually employed iodine.
5. For adding the tin tetrachloride it is advisable to use a dropping funnel which contains no ether vapor, since the latter gives troublesome formation of solid etherate.
6. The stirrer must be stopped at the beginning of the distillation or it will break, for the contents of the flask turn into a solid mass.
7. Removal of the ether is necessary to permit raising the reaction temperature. The temperature at the center of the mass reaches 60–65°. During the 1.5 hours of distillation, about 200 ml. of ether is collected, the remainder being firmly bound as etherates.
8. To obtain a product free from traces of triethyltin halide the dried ethereal solution is treated with dry ammonia, and the precipitate formed is removed by filtration.
9. The submitters report that the same yields in terms of percentages are obtained if the procedure is

applied to the preparation of tetra-*n*-propyltin and tetra-*n*-butyltin.

3. Discussion

Tetraethyltin has been prepared from tin-sodium alloy and ethyl iodide;[2] from tin-sodium-zinc alloy and ethyl bromide;[3,4] from tin tetrachloride and ethylmagnesium bromide;[5,6,7,8] or triethylaluminum;[9] from tin-magnesium alloy and ethyl bromide or chloride;[10,11,12] and from stannous chloride and ethyllithium.[13] The method described is essentially that of Pfeiffer and Schnurmann.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 4, 258

References and Notes

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

ethyl bromide or chloride

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

magnesium,
magnesium turnings (7439-95-4)

bromine (7726-95-6)

Ethyl bromide (74-96-4)

stannous chloride

iodine (7553-56-2)

ethylmagnesium bromide (925-90-6)

tin tetrachloride (7646-78-8)

Ethyl iodide (75-03-6)

Tetraethyltin,
Tin, tetraethyl- (597-64-8)

tin-sodium

tin-sodium-zinc

triethylaluminum (97-93-8)

tin-magnesium

ethyllithium

tetra-n-propyltin (2176-98-9)

tetra-n-butyltin (1461-25-2)