



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.

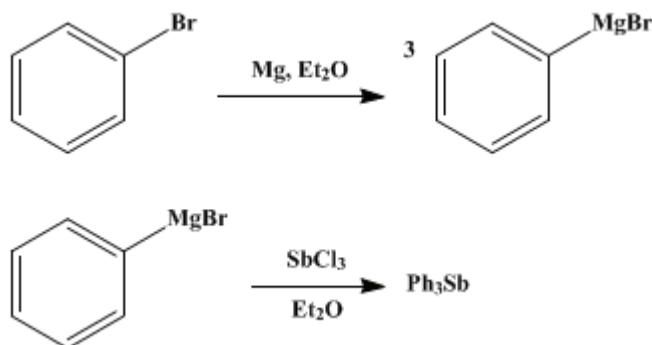
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.550 (1941); Vol. 7, p.80 (1927).

TRIPHENYLSTIBINE

[Stibine, triphenyl-]



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1. Procedure

In a 2-l. round-bottomed, three-necked flask fitted with a mercury-sealed mechanical stirrer, a reflux condenser, and a separatory funnel is placed 40 g. (1.65 atoms) of [magnesium turnings](#) ([Note 1](#)). This is covered with 200 cc. of dry [ether](#), and there is then added 100 cc. of a mixture of 260 g. (1.65 moles) of dry [bromobenzene](#) and 800 cc. of dry [ether](#). As soon as the reaction starts, 200 cc. more of dry [ether](#) is added and the remainder of the [bromobenzene](#) solution at such a rate as to cause gentle boiling (about two hours). With external cooling, the time may be shortened.

When all the [bromobenzene](#) has been added, there is added slowly through the separatory funnel a solution of 114 g. (0.5 mole) of freshly distilled [antimony trichloride](#) (m.p. 67–73°) in 300 cc. of dry [ether](#). The reaction proceeds smoothly and even briskly with the freshly distilled chloride. However, if the latter has not been freshly prepared, gentle warming may be required to start the reaction. When all the [antimony trichloride](#) has been added (one to two hours), the mixture is heated on the steam bath for one hour longer.

When cool, the reaction mixture is poured slowly with stirring into 1 l. of ice and water ([Note 2](#)). If the stirring is thorough, most of the [triphenylstibine](#) is to be found in the ether layer. The hydrolysis mixture is filtered through a Büchner funnel and the residue on the filter extracted three times ([Note 3](#)) with 100-cc. portions of [ether](#). The aqueous layer is separated and extracted twice with 200-cc. portions of [ether](#). The combined ether portions are evaporated slowly on a steam bath to remove the ether, and there remains behind a yellow semi-solid which crystallizes to a white solid on cooling ([Note 4](#)). The yield of crude product melting at 49° is 145–160 g. (82–90 per cent of the theoretical amount). For purification from a small amount of [biphenyl](#) which is present in the crude product, 90 g. of [triphenylstibine](#) is dissolved in 200 cc. of petroleum ether (b.p. 40–50°) by warming on a steam bath. There is generally a small amount of insoluble residue which is filtered and the filtrate cooled in a freezing mixture. The [triphenylstibine](#) separates as small prisms and weighs 58–65 g.; by further concentration of the filtrate to an approximate volume of 50 cc. and then cooling again, an additional 15–20 g. of product separates. Both portions melt at 50°.

2. Notes

1. The excess of the Grignard reagent insures the complete removal of all the halogen from the [antimony](#).
2. During the hydrolysis the use of acids to dissolve the [magnesium hydroxide](#) must be avoided, for the presence of acid tends to decompose the antimony compound.
3. During the filtration some other evaporates and the stibine compound is left on the filter with the

magnesium hydroxide. Extraction is necessary to remove this product.

4. The same method may be used for the preparation of *tri-p-tolylstibine*. Starting with 282 g. (1.65 moles) of *p*-bromotoluene (p. 136) and proceeding in the same manner as described there was secured 150–157 g. (77–80 per cent of the theoretical amount) of crude *tri-p-tolylstibine*. This product purified by recrystallization from methyl alcohol or ether melts at 125–126°. The reaction is somewhat more vigorous, and sometimes cooling is necessary at first.

3. Discussion

Triphenylstibine can be prepared from the interaction of chlorobenzene and antimony trichloride with sodium,¹ from antimony trichloride and phenylmagnesium bromide,² and from antimony and phenyllithium.³

References and Notes

1. Michaelis and Reese, Ann. **233**, 42 (1886); Morgan and Vining, J. Chem. Soc. **117**, 777 (1920).
 2. Pfeiffer and Heller, Ber. **37**, 4621 (1904).
 3. Talalaeva and Kocheshkov, J. Gen. Chem. (U.S.S.R.) **8**, 1831 (1938) [C. A. **33**, 5819 (1939)].
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

petroleum ether

antimony compound

stibine compound

methyl alcohol (67-56-1)

ether (60-29-7)

magnesium turnings (7439-95-4)

chlorobenzene (108-90-7)

sodium (13966-32-0)

bromobenzene (108-86-1)

Biphenyl (92-52-4)

antimony trichloride (7647-18-9)

magnesium hydroxide

Phenylmagnesium bromide (100-58-3)

Triphenylstibine,

[Stibine, triphenyl- \(603-36-1\)](#)

[antimony \(7440-36-0\)](#)

[Phenyllithium \(591-51-5\)](#)

[p-Bromotoluene \(106-38-7\)](#)

[Tri-p-tolylstibine](#)