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.*

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# TRIPHENYLALUMINUM

## [Aluminum, triphenyl-]

$$3\ (C_6H_5)_2Hg + 2\ Al \xrightarrow{\text{xylene, }\Delta} 2\ (C_6H_5)_3Al + 3\ Hg$$

Submitted by T. A. Neely, William W. Schwarz, and Herbert W. Vaughan, Jr.[1].
Checked by R. D. Lipscomb and B. C. McKusick.

## 1. Procedure

*Caution! Triphenylaluminum and its etherate undergo decomposition in the presence of air and moisture. Upon contact with water, vigorous heat evolution and sparking have been observed.*

A 500-ml. one-necked flask with a side arm to admit nitrogen is fitted with a reflux condenser protected at the top by a T-tube through which nitrogen is slowly passed during the entire reaction (Note 1). In the flask there is placed 12 g. (0.44 g. atom) of aluminum wool (Note 2), and the system is thoroughly dried by flaming (Note 3) and then cooled to room temperature. A positive pressure of nitrogen is maintained in the system by admission of the gas through the side arm while the flask is detached from the condenser, stoppered, and transferred to a nitrogen-filled dry box. To the flask there is added 80 g. (0.23 mole) of diphenylmercury (Note 4) which is spread evenly on top of the aluminum wool, followed by 340 ml. of sodium-dried xylene. The flask is stoppered, returned to the condenser, and immersed in a preheated oil bath, which is maintained at 140–150°. The reaction mixture is allowed to reflux for 24 hours, the water drained from the condenser, and the top of the condenser is connected to a vacuum system through a trap cooled in dry ice. The xylene is distilled by gradually reducing the pressure to 20–30 mm. The flask is cooled to room temperature and nitrogen readmitted.

The flask is returned to the dry box, and the nearly dry solid that remains in it is transferred to an extraction thimble (123 mm. × 43 mm.) previously dried in a vacuum oven. The product is extracted in a dried Soxhlet apparatus (250 mm. × 50 mm.) with 250 ml. of dry ether (Note 5) in a carefully dried 300-ml. flask. The extraction is continued for 15–20 hours (Note 6), during which time white crystals of triphenylaluminum etherate form in the flask. The flask and its contents are placed in a dry box, the ether is decanted, and the crystals are washed several times by decantation with small portions of dry ether. The triphenylaluminum etherate is dried at 25° under reduced pressure; m.p. 126–130°. The ether of crystallization is removed by heating the etherate at 150° (0.1 mm.) for about 13 hours (Note 7). Pure triphenylaluminum, m.p. 229–232°, is obtained; yield 23–27 g. (59–70%).

## 2. Notes

1. All operations are conducted in an atmosphere of prepurified nitrogen or in a nitrogen-filled dry box. A positive nitrogen pressure is maintained in the flask during all transfers and additions. Prepurified nitrogen is available from Matheson Co., East Rutherford, New Jersey.
2. Suitable aluminum wool is available from Custom Scientific Instrument Inc., Kearney, New Jersey. It is thoroughly cleaned with both methylene chloride and ether and dried before use.
3. All glassware used in this preparation must be dry. Flaming out while purging with prepurified nitrogen is sufficient.
4. Suitable diphenylmercury is available from Orgmet, Hampstead, New Hampshire, or it can be prepared by the procedure of Gilman and Brown.[2]
5. A new container of anhydrous ether from Mallinckrodt Chemical Works or Merck and Co. is satisfactory.
6. At the end of the extraction the residual aluminum wool should be disposed of very carefully because it is in a highly reactive condition. As the ether evaporates, the aluminum wool oxidizes rapidly and becomes quite hot. In one run, 84% of the theoretical amount of metallic mercury was liberated during

this oxidation.

The checkers evaporated the ether in a stream of nitrogen, then allowed air to diffuse in gradually through a small opening during 2 days. The residue was then inert.

7. During this operation the etherate melts, effervesces, and then solidifies. The etherate sublimes to a small extent; this can be counteracted by immersing the flask in an oil bath only part way during the first half of the heating, and finally immersing it to the bottom of its neck.

## 3. Discussion

The general procedure for this reaction, which was first reported by Friedel and Crafts,[3] is essentially that of Hilpert and Grüttner[4] as modified by Gilman and Marple.[5] Upon laboratory examination of these methods, only water-reactive gums and tars were isolated. Nesmeyanov and Novikova[6] reported the preparation of triphenylaluminum by a similar method, but worked on a test-tube scale and did not report a yield. Wittig and Wittenberg[7] prepared crystalline triphenylaluminum in 43% yield by the action of phenyllithium on aluminum chloride. In most of the procedures found, the triphenylaluminum was used in solution; hence crystalline material was not isolated.

When aluminum wool was substituted for strips of aluminum foil, a 20% yield of triphenylaluminum was obtained. This yield was increased to 70% by the extractive isolation described above. An alternative method of isolation and purification, that of Krause and Polack,[8] was not attempted because of the lack of experimental detail and the complexity of the apparatus.

## 4. Merits of the Preparation

Triphenylaluminum is useful as a component of catalyst systems for ionic or coordination polymerization of vinyl compounds. This preparation of the material in solid form enables the purity of the compound to be easily determined. The availability of solid triphenylaluminum permits the user a choice of solvents for a reaction, and a variety of concentrations of the reagent. Storage and dispensation of the reagent are more convenient in the solid form.

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## References and Notes

1. Thiokol Chemical Corporation, Huntsville, Alabama. This work was supported by the United States Army Ordnance Corp.; Contract DA-01-021-ORD-5314, Mod. 3.
2. H. Gilman and R. E. Brown, *J. Am. Chem. Soc.*, **52**, 3314 (1930).
3. C. Friedel and J. M. Crafts, *Ann. Chim. et Phys.*, [6] **14**, 460 (1888).
4. S. Hilpert and G. Grüttner, *Ber.*, **45**, 2828 (1912).
5. H. Gilman and K. E. Marple, *Rec. Trav. Chim.*, **55**, 133 (1936).
6. A. N. Nesmeyanov and N. N. Novikova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 372 (1942).
7. G. Wittig and D. Wittenberg, *Ann.*, **606**, 13 (1957).
8. E. Krause and H. Polack, *Ber.*, **59**, 777, 1428 (1926).

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

sodium-dried xylene

ether (60-29-7)

nitrogen (7727-37-9)

aluminum (7429-90-5)

mercury (7439-97-6)

aluminum chloride (3495-54-3)

xylene (106-42-3)

Diphenylmercury (587-85-9)

methylene chloride (75-09-2)

Phenyllithium (591-51-5)

Triphenylaluminum,
Aluminum, triphenyl- (841-76-9)

triphenylaluminum etherate