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.

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The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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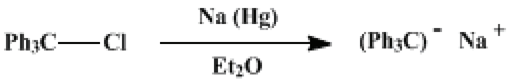
Organic Syntheses, Coll. Vol. 2, p.607 (1943); Vol. 19, p.83 (1939).

TRIPHENYLMETHYLSODIUM

[Sodium, triphenylmethyl-]



$$Ph_3C{-}Cl \xrightarrow[Et_2O]{Na(Hg)} (Ph_3C)^- \; Na^+$$

Submitted by W. B. Renfrow Jr and C. R. Hauser.
Checked by Lee Irvin Smith and E. C. Ballard.

1. Procedure

A solution of 63 g. (0.226 mole) of pure triphenylchloromethane (Note 1) in 1.5 l. of pure anhydrous ether is prepared in a 2-l. bottle provided with a tight ground-glass stopper, and 1150 g. of freshly prepared 1 per cent sodium amalgam (0.5 gram atom of sodium) is added (Note 2). The stopper is greased with a small amount of Lubriseal and the bottle is stoppered tightly. The bottle is clamped firmly in a mechanical shaker and shaken vigorously. The reaction is strongly exothermic, and the bottle should be cooled with wet towels during the shaking operation. A persistent blood-red color develops rapidly, generally within ten minutes. After shaking for three hours *the bottle is cooled to room temperature*, removed from the shaker, and allowed to stand undisturbed until the sodium chloride has settled (Note 3).

The ether solution of triphenylmethylsodium is separated from the sodium chloride and amalgan by the following procedure. The stopper of the reaction bottle is removed and replaced immediately by a closely fitting two-holed cork carrying a short glass tube that protrudes about 1 cm. into the bottle, and a long glass tube bent into an inverted U-shape. The short tube is connected through a drying train to a cylinder of nitrogen. One arm of the U-tube reaches to within about 4 cm. of the bottom of the bottle, and the other end extends just below the bottom of a two-holed cork that is fitted tightly into a 2-l. Erlenmeyer flask. The flask is filled with nitrogen and serves as receiver for the decanted solution. The cork of the Erlenmeyer flask is provided with a short-stemmed separatory funnel which serves to release nitrogen during the decantation and may be used subsequently to introduce reactants (Note 4). The corks are sealed by a coating of paraffin-wax. The stopcock of the dropping funnel is opened slightly, and the ether solution of triphenylmethylsodium is forced slowly and steadily into the nitrogen-filled flask by means of a small pressure of nitrogen from the cylinder. With proper adjustment of the height of the glass tube above the surface of the sodium chloride and amalgam, it is possible to remove all but 50 to 75 cc. of the ether solution.

If a good grade of triphenylchloromethane and freshly prepared amalgam are used the yield of triphenylmethylsodium is almost quantitative. The solution may be analyzed approximately, as follows: A 50-cc. aliquot portion is allowed to flow into 25 cc. of water in a separatory funnel. The aqueous layer is drawn off and the ether solution washed with three 25-cc. portions of water. The aqueous solutions are combined, boiled to expel ether, and titrated with 0.2 *N* sulfuric acid, methyl red being used as indicator.

2. Notes

1. A good grade of triphenylchloromethane, m.p. 112–113°, should be used. The commercial product may be recrystallized conveniently from a mixture of five parts of ligroin (b.p. 90–110°) and one part of acetyl chloride, using about 1.8 g. of solvent per gram of material. Directions for preparing triphenylchloromethane are given in Volume 23 of this series.
2. A 1 per cent sodium amalgam is prepared by cutting 11.5 g. (0.5 gram atom) of sodium into pieces about 5 mm. square and dissolving them, one at a time, in 1150 g. of purified mercury. A piece of sodium is speared on the sharpened end of a long glass rod and thrust quickly beneath the surface of the mercury, in a 500-cc. wide-mouthed Erlenmeyer flask. To avoid damage from flying pieces of sodium resulting from the vigorous reaction, the glass rod is inserted through a piece of heavy cardboard which

serves to cover the mouth of the flask during the reaction.

3. If solid 3 per cent sodium amalgam is used, solutions containing almost 0.67 mole of triphenylmethylsodium per liter—about five times as concentrated as the solution described in the procedure above—can be prepared.

One and seven-tenths kilograms of 3 per cent sodium amalgam (2.2 gram atoms of sodium) is prepared by adding 1649 g. of mercury to 51 g. of molten sodium under mineral oil—compare Org. Syn. Coll. Vol. I, **1941**, 554, Note 1. The amalgam while still hot is poured into a large evaporating dish and left to cool. It is then transferred to a large iron mortar, broken into pieces about 1 mm. on a side, washed free from oil with ligroin, and placed in a 2-l. glass-stoppered bottle. One and one-half liters of dry ether and 278 g. (1 mole) of triphenylchloromethane are added, and the glass stopper, greased with Lubriseal, is inserted. The bottle is shaken in a mechanical shaker until no solid amalgam remains, and then for two hours longer. If the shaker has a 4- to a 5-in. stroke and makes three to four strokes per second, the total time on the shaker is from five to eight hours. With less effective shaking, more time is required. The reaction is sufficiently slow so that cooling with towels is unnecessary. The rest of the procedure is the same as that on p. 608. (Private communication from Charles R. Hauser and Boyd E. Hudson, Jr. Checked by Lee Irvin Smith and R. W. Liggett.)

4. Triphenylmethylsodium is a useful reagent for the preparation of the sodium derivatives of very weak acids (aliphatic esters, acid anhydrides, etc.). An example of this procedure, using ethyl isobutyrate, is given on p. 268.

3. Discussion

The procedure described above is a modification of the method of Schlenk and Ochs.[1]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 268
- Org. Syn. Coll. Vol. 6, 461

References and Notes

1. Schlenk and Ochs, Ber. **49**, 608 (1916).

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

ligroin

Methyl Red

sulfuric acid (7664-93-9)

ether (60-29-7)

acetyl chloride (75-36-5)

sodium chloride (7647-14-5)

nitrogen (7727-37-9)

mercury (7439-97-6)

sodium (13966-32-0)

Triphenylchloromethane (76-83-5)

Triphenylmethylsodium,
Sodium, triphenylmethyl- (4303-71-3)

ethyl isobutyrate (97-62-1)

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