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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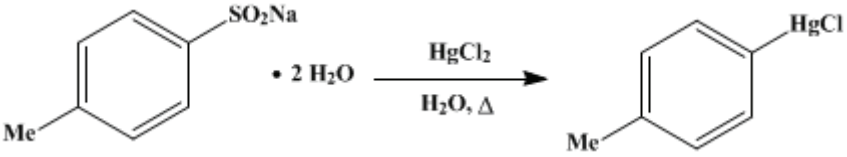
p-TOLYLMERCURIC CHLORIDE

[Mercury compounds. *p*-Tolylmercuric chloride]



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1. Procedure

To 1 l. of boiling water in a 3-l. beaker or large evaporating dish (Note 1) is added 150 g. (0.55 mole) of mercuric chloride; to this mixture is then added, with good stirring, 116 g. (0.54 mole) of sodium *p*-toluenesulfinate (p. 492). A thick, white, curdy precipitate forms at once (Note 2), and in a short time sulfur dioxide is evolved copiously. The heating and stirring are continued until no more sulfur dioxide is evolved, which requires about two hours.

The mixture is then filtered by suction, and the precipitate dried in an oven at about 80° for twelve hours. The dry precipitate is then placed in a 1-l. round-bottomed flask with reflux condenser, and covered with 800 cc. of xylene. The mixture is agitated by shaking, the xylene heated to boiling for five to ten minutes, and the solution filtered through a hot funnel to remove the calomel which is formed during the reaction (Note 2). The filtrate is cooled, the *p*-tolylmercuric chloride filtered off, and the undissolved portion extracted again with the filtrate (Note 3). This is repeated twice. In this way 90–100 g. (51–57 per cent of the theoretical amount) of a product which melts at 233° is obtained.

2. Notes

1. It is essential that the vessel employed should be of at least 3-l. capacity. If it is smaller, the contents will probably overflow during the first evolution of sulfur dioxide.
2. A large amount of calomel is formed in this reaction owing to the reduction of the mercuric chloride by the sulfurous acid formed. This reduction produces hydrochloric acid which probably changes some of the mercury compound to toluene and mercuric chloride. An attempt was made to avoid this action by adding sodium hydroxide slowly during the process to keep the solution from becoming strongly acid, but the yield was increased only slightly. The yield was not increased by adding the sulfinate to the mercuric chloride gradually or by reversing this process.
3. There is always a considerable amount of inorganic mercury left in the filtrate, which gives very little more of the *p*-tolylmercuric chloride when treated with more of the sulfinate. This may be present largely in the form of the mercuric salt of *p*-toluenesulfonic acid produced by the oxidation of some of the sulfinic acid liberated in a side-reaction.

3. Discussion

p-Tolylmercuric chloride can be prepared from *p*-toluenesulfinic acid and mercuric chloride,[1] from *p*-toluenesulfonyl chloride and diphenylmercury at 120°,[2] by treating *p*-tolylboric acid with mercuric chloride, [3] by the direct mercuration of toluene with mercuric acetate,[4] from *p*-tolylmercuric nitrate and hydrochloric acid,[5] from hydrochloric acid and *p*-tolylmercuric hydroxide formed by the oxidation of di-*p*-tolylmercury,[6] from di-*p*-tolylmercury by heating with mercuric chloride in alcohol, [7] by heating the double salt of *p*-toluenediazonium chloride and mercuric chloride in acetone with copper powder,[8] and from *p*-toluenediazonium chloride and finely divided mercury.[9]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 159
- Org. Syn. Coll. Vol. 1, 231

References and Notes

1. Peters, Ber. **38**, 2569 (1905).
2. Otto, Ber. **18**, 249 (1885).
3. Michaelis, Ber. **15**, 185 (1882).
4. Dimroth, Ber. **32**, 761 (1899); Steinkopf, Ann. **413**, 329 (1917).
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6. McGowan, J. prakt. Chem. (2) **29**, 138 (1884).
7. Otto, ibid. (2) **1**, 185 (1870).
8. Nesmejanov, Ber. **62**, 1010 (1929).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sulfinic acid

calomel

inorganic mercury

double salt of p-toluenediazonium chloride

alcohol (64-17-5)

hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

sulfur dioxide (7446-09-5)

mercuric acetate (1600-27-7)

mercury (7439-97-6)

copper powder (7440-50-8)

acetone (67-64-1)

toluene (108-88-3)

mercuric chloride (7487-94-7)

p-tolylmercuric chloride (539-43-5)

xylene (106-42-3)

Diphenylmercury (587-85-9)

sulfurous acid (7782-99-2)

p-Toluenesulfonyl chloride (98-59-9)

p-Toluenesulfinic acid (536-57-2)

Sodium p-toluenesulfinate

DI-p-TOLYLMERCURY (537-64-4)

mercuric salt of p-toluenesulfonic acid

p-tolylboric acid

p-tolylmercuric nitrate

p-tolylmercuric hydroxide

p-toluenediazonium chloride