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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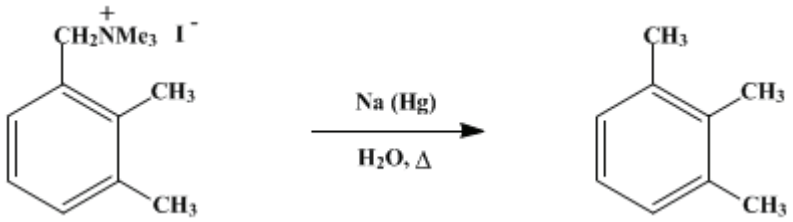
HEMIMELLITENE

[Benzene, 1,2,3-trimethyl-]



Submitted by W. R. Brasen and C. R. Hauser[1].
Checked by William S. Johnson, Donald W. Stoutamire, and A. L. Wilds.

1. Procedure

A 3-l. round-bottomed three-necked flask, fitted with a reflux condenser and a sealed stirrer, is charged with 2 l. of hot water and 100 g. (0.33 mole) of 2,3-dimethylbenzyltrimethylammonium iodide (Note 1). The stirred suspension is heated on the steam bath, and 2760 g. of 5% sodium amalgam (Note 2) is added in 200- to 250-g. portions over a period of 45 minutes. Stirring and heating are continued for 24 hours; then the mixture is steamdistilled until no more oily material comes over. The distillate (1–1.5 l.) is extracted with three 50-ml. portions of ether. The combined extracts are washed with 50 ml. of 10% hydrochloric acid and 50 ml. of saturated sodium chloride solution, and dried over anhydrous calcium chloride. After removal of the ether by distillation, the residue is distilled from a Claisen flask, giving 33.5–35.5 g. (85–90% yield) of colorless hydrocarbon, b.p. 171–174°. On redistillation 85–90% of the material distils at 173–174°, n_D^{25} 1.5116–1.5120.

2. Notes

1. The methiodide is prepared from 2,3-dimethylbenzyldimethylamine according to the procedure for producing the lower homolog (p. 587, Notes 5 and 8).
2. The sodium amalgam is prepared in a 1-l. filter flask fitted with a two-hole rubber stopper carrying a dropping funnel and an outlet tube. The flask is charged with 138 g. (6 g. atoms) of sodium and 300 ml. of mineral oil. With a stream of nitrogen passing through the side arm of the flask, the flask is heated on a hot plate covered with an asbestos pad until the sodium melts, and then 2622 g. of mercury is added rapidly from the dropping funnel over a 1–2 minute period with swirling. The whole operation is carried out in a large pan to catch material in case of breakage. A vigorous exothermic reaction occurs, and the hands must be adequately protected with several layers of cloth or heavy gloves as the temperature approaches 400°. If the addition is rapid enough, the amalgam will be a liquid; otherwise the material will be partially solid and must be heated vigorously to produce a homogeneous melt. The mineral oil is decanted from the molten amalgam, which is poured into a shallow metal pan while still warm and is cut or broken (with a hammer) into small pieces as it solidifies. It is finally washed with petroleum ether and stored in a tightly stoppered bottle or under petroleum ether.

3. Discussion

Hemimellitine has been prepared by the action of sodium on 2,3-dimethyliodobenzene and methyl iodide,[2] by the reduction of the chloromethylation product of *o*-xylene,[3] by the catalytic hydrogenolysis of 2,3-dimethylbenzyl alcohol,[4] and by treatment of 1,5,5,6-tetramethyl-1,3-cyclohexadiene with a catalyst prepared from sodium and *o*-chlorotoluene.[5] The present procedure is based on the method of Kantor and Hauser.[6]

References and Notes

1. Duke University, Durham, North Carolina. Work supported by the Office of Ordnance Research.
2. von Auwers, *Ann.*, **419**, 116 (1919).
3. von Braun and Nelles, *Ber.*, **67**, 1094 (1934).
4. Smith and Spillane, *J. Am. Chem. Soc.*, **62**, 2639 (1940).
5. Pines and Eschinazi, *J. Am. Chem. Soc.*, **78**, 5950 (1956).
6. Kantor and Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951).

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

petroleum ether

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium chloride (7647-14-5)

nitrogen (7727-37-9)

mercury (7439-97-6)

sodium (13966-32-0)

o-Chlorotoluene (95-49-8)

Methyl iodide (74-88-4)

Hemimellitene,
Benzene, 1,2,3-trimethyl-,
Hemimellitine (526-73-8)

2,3-dimethylbenzyltrimethylammonium iodide

2,3-dimethylbenzyldimethylamine (15848-75-6)

2,3-dimethyliodobenzene (31599-60-7)

2,3-dimethylbenzyl alcohol (13651-14-4)

1,5,5,6-tetramethyl-1,3-cyclohexadiene

o-Xylene (95-47-6)