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.

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.

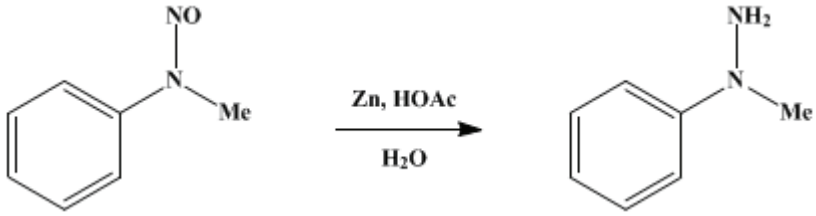
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.013.0066

Organic Syntheses, Coll. Vol. 2, p.418 (1943); Vol. 13, p.66 (1933).

α-METHYL-α-PHENYLHYDRAZINE

[Hydrazine, 1-methyl-1-phenyl-]



Submitted by W. W. Hartman and L. J. Roll.
Checked by Louis F. Fieser and J. T. Walker.

1. Procedure

A mixture of 200 g. (3.1 gram atoms) of zinc dust and 300 cc. of water is placed in a 2-l. three-necked flask equipped with an efficient mechanical stirrer, a thermometer, and a dropping funnel. The suspension is then stirred vigorously while a solution of 100 g. (0.73 mole) of N-nitrosomethylaniline (p. 460) in 200 cc. (210 g., 3.5 moles) of glacial acetic acid is added in a slow stream. The temperature is maintained between 10° and 20° by external cooling or by the addition of finely crushed ice. When all the acid solution has been added (about one and one-half to two hours is required, depending upon the rate of cooling) the mixture is stirred for an hour longer at room temperature and then warmed to 80° on the steam bath. The hot solution is filtered from the unreacted zinc, which is washed with three 100-cc. portions of a warm 5 per cent hydrochloric acid solution. The combined filtrate and washings are cooled and treated with sufficient 40 per cent sodium hydroxide solution to redissolve the zinc hydroxide precipitated. (About 1.2 l. is required.) The oily layer is separated and the aqueous layer extracted with two or three 100-cc. portions of ether. The combined oil and extracts are distilled from a steam bath until the ether is removed; the residue is then distilled under reduced pressure. The yield of colorless (Note 1) α-methyl-α-phenylhydrazine boiling at 106–109° 13 mm. is 46–50 g. (52–56 per cent of the theoretical amount).

2. Notes

1. α-Methyl-α-phenylhydrazine darkens on standing.

3. Discussion

α-Methyl-α-phenylhydrazine has been obtained by reducing nitrosomethylaniline with zinc and acetic acid[1] or electrolytically;[2] by reducing N-methylnitroformaldehyde phenylhydrazone with zinc and acetic acid;[3] by heating methylbenzoylphenylhydrazine with concentrated hydrochloric acid;[4] and by methylating phenylhydrazine with sodamide and methyl iodide.[5]

References and Notes

1. Fischer, Ann. **190**, 152 (1878); **236**, 198 (1886).
2. Wells, Babcock, and France, J. Am. Chem. Soc. **58**, 2630 (1936).
3. Bamberger and Schmidt, Ber. **34**, 591 (1901).
4. Tafel, ibid. **18**, 1744 (1885).
5. Grammaticakis, Compt. rend. **210**, 303 (1940).

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

α-Methyl-α-phenylhydrazine

N-methylnitroformaldehyde phenylhydrazone

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

Phenylhydrazine (100-63-0)

zinc (7440-66-6)

Methyl iodide (74-88-4)

Hydrazine, 1-methyl-1-phenyl- (618-40-6)

N-Nitrosomethylaniline,
nitrosomethylaniline

zinc hydroxide (20427-58-1)

methylbenzoylphenylhydrazine

sodamide (7782-92-5)