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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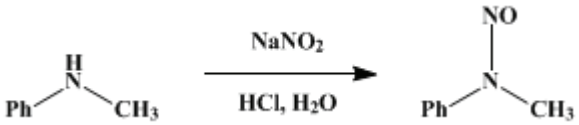
Organic Syntheses, Coll. Vol. 2, p.460 (1943); Vol. 13, p.82 (1933).

N-NITROSOMETHYLANILINE

[Aniline, N-methyl-N-nitroso-]



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1. Procedure

A mixture of 107 g. (1 mole) of methylaniline (Note 1), 145 cc. of concentrated hydrochloric acid, and 400 g. of ice is placed in a 3-l. flask equipped with a mechanical stirrer. The mixture is stirred vigorously, and the temperature is maintained at 10° or below by the addition of more ice as required, while a solution of 70 g. (1 mole) of sodium nitrite in 250 cc. of water is added during the course of five or ten minutes. Stirring is then continued for one hour more. The oily layer is separated, and the aqueous portion is extracted with two 100-cc. portions of benzene. The benzene is removed by distillation at ordinary pressure, and the residue is fractionated under reduced pressure. The main fraction of the nitrosomethylaniline distils as a light yellow liquid boiling at 135–137°/13 mm. The yield (Note 1) is 118–127 g. (87–93 per cent of the theoretical amount).

2. Notes

1. The yield is dependent upon the quality of the methylaniline used. The higher yield reported was obtained with pure material, b.p. 81–82°/14 mm.

3. Discussion

N-Nitrosomethylaniline was first prepared by the action of nitrous acid on methylaniline.[1] It has been obtained also by the action of methyl iodide on the sodium salt of benzene diazoic acid followed by reduction;[2] by treating dimethylaniline with tetranitromethane,[3] or with phenylnitrocarbinol;[4] by the acid hydrolysis of nitrosophenylglycine;[5] and by oxidizing dimethyldiphenylhydrazine with nitric oxide.[6]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 418

References and Notes

1. Hepp, Ber. **10**, 329 (1877).
2. Bamberger, ibid. **27**, 373 (1894).
3. Schmidt and Fischer, ibid. **53**, 1538 (1920).
4. Cohen and Calvert, J. Chem. Soc. **73**, 164 (1898).
5. Fischer, Ber. **32**, 249 (1899).
6. Wieland and Fressel, Ann. **392**, 148 (1912).

Appendix

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

sodium salt of benzene diazoic acid

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

sodium nitrite (7632-00-0)

nitrous acid (7782-77-6)

dimethylaniline (121-69-7)

Methyl iodide (74-88-4)

nitric oxide

N-Nitrosomethylaniline,
nitrosomethylaniline

Aniline, N-methyl-N-nitroso- (614-00-6)

methylaniline (100-61-8)

tetranitromethane (509-14-8)

phenylnitrocarbinol

nitrosophenylglycine (6415-68-5)

dimethyldiphenylhydrazine