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.

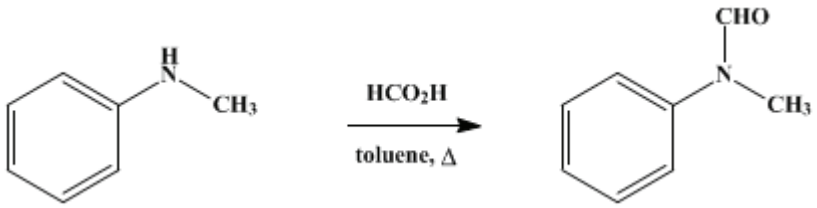
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.020.0066

Organic Syntheses, Coll. Vol. 3, p.590 (1955); Vol. 20, p.66 (1940).

N-METHYLFORMANILIDE

[Formanilide, N-methyl-]



Submitted by L. F. Fieser and J. E. Jones.
Checked by C. F. H. Allen and J. VanAllan.

1. Procedure

In a 3-l. round-bottomed flask fitted with a 3-ft. indented column to which is attached a condenser set for downward distillation are placed 321 g. (3 moles) of methylaniline, 300 g. of formic acid (85–90%), and 1.8 l. of toluene (Note 1). The solution is distilled slowly. As long as the azeotrope containing water is present, the temperature of the vapor is 87–88°; when the water has been removed, the temperature rises to 108–110° (Note 2). The distillation is continued until approximately 1.5 l. of toluene has been collected (5–6 hours). The residue is then transferred to a modified Claisen flask and distilled under reduced pressure, the portion boiling at 114–121°/8 mm. being collected. This has a freezing point of 13.6–13.7°; n_D^{29} 1.553–1.555. The yield is 380–393 g. (93–97%). This product is satisfactory for the preparation of aldehydes. Upon redistillation it boils at 117–121°/8 mm., 130–132°/22 mm. The freezing point and refractive index are unchanged (Note 3).

2. Notes

1. The toluene serves to remove the water and minimize side reactions.
2. The water layer of the distillate is separated; it amounts to 140–150 ml.
3. If a water separator with a stopcock is employed, in such a way that the organic solvent is returned to the reaction flask, it is possible to use 200 ml. of benzene in place of the 1.8 l. of toluene (J. Meek, private communication).

3. Discussion

N-Methylformanilide has been obtained in a yield of 67.5% by heating methylaniline with formamide in glacial acetic acid solution.[1] The method above is a modification of that of Morgan and Grist,[2] who heated the amine and formic acid in the absence of a solvent or water-carrier (the present authors obtained a yield of only 40–50% by that procedure).

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 98
- Org. Syn. Coll. Vol. 4, 915

References and Notes

1. Hirst and Cohen, *J. Chem. Soc.*, **67**, 830 (1895).
2. Morgan and Grist, *J. Chem. Soc.*, **113**, 690 (1918).

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

acetic acid (64-19-7)

Benzene (71-43-2)

formamide (75-12-7)

formic acid (64-18-6)

toluene (108-88-3)

methylaniline (100-61-8)

N-methylformanilide,
Formanilide, N-methyl- (93-61-8)