



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.

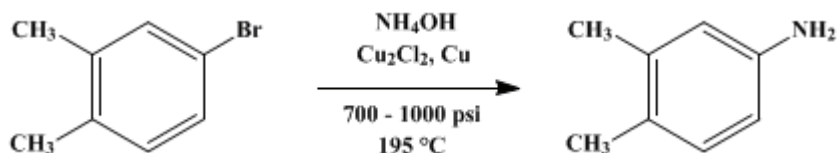
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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3,4-DIMETHYLANILINE

[Xylidine, 3,4-]



Submitted by W. A. Wisansky and S. Ansbacher.

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1. Procedure

In a 1.1-l. steel reaction vessel (Note 1) are placed 200 g. (1.08 moles) of 4-bromo-*o*-xylene (p. 138), 14 g. copper wire, and 600 ml. (540 g., 9.0 moles) of 28% ammonia containing 12 g. of cuprous chloride. The steel reaction vessel is heated and rocked at 195° (thermostatic control) (Note 2) for 14 hours (Note 3); the pressure rises to 700–1000 lb. After cooling, the bomb is emptied and the two layers are separated; 40 ml. of 40% sodium hydroxide is added to the organic layer, and the mixture is steam-distilled. The amine distils and crystallizes when the distillate is cooled. It is separated from the water and dissolved in 500 ml. of 8% hydrochloric acid; the acid solution is extracted with two 100-ml. portions of ether (Note 4). The ether extracts are discarded, and the acid solution is made alkaline with 160 ml. of 40% sodium hydroxide. The resulting mixture is steam-distilled (Note 5). The distillate is cooled, most of the water is decanted, and the crystalline xylidine is dissolved by shaking with two 250-ml. portions of ether. The combined ether solutions are dried over calcium chloride and concentrated by distillation at a steam bath. The residue is distilled under reduced pressure from a Claisen flask. The yield of 3,4-dimethylaniline, boiling at 116–118°/22–25 mm., is 103 g. (79%). This crude product is recrystallized from 200 ml. of petroleum ether (b.p. 60–80°); the hot solution is placed in a refrigerator, and the crystallization is allowed to proceed overnight. The yield of recrystallized 3,4-dimethylaniline is 86 g. (66%) (Note 6); it melts at 47.3–49.2° (Note 7).

2. Notes

1. A hydrogenation vessel supplied by the American Instrument Company is satisfactory. A certain amount of copper plates out on the walls of the bomb during the reaction, but most of it is removed when the apparatus is cleaned.
2. The heating and rocking are carried out in a hydrogenation assembly. The temperature must not be allowed to exceed 200°; at higher temperatures decomposition occurs and the yield suffers.
3. The optimum reaction time may vary slightly with apparatus of different types.
4. The crude product contains a small amount of unchanged 4-bromo-*o*-xylene which is removed by the ether extraction.
5. Caution must be exercised because a considerable amount of ether is present; it distils first and may be only partially condensed. A preliminary heating of the mixture on a steam bath does not remove the ether completely.
6. In an alternative method of purification the submitters collected the amine from the second steam distillation on a suction filter, pressed out the oily materials on the filter, and distilled the resulting crystalline product under diminished pressure; the distillate was not recrystallized. The checkers found it difficult to effect complete removal of oils by filtration; they preferred to omit this step and to recrystallize the distilled amine.
7. The reported melting point of 3,4-dimethylaniline varies from 47–48°¹ to 48.5–49°.²

3. Discussion

3,4-Dimethylaniline has been prepared by reduction of the corresponding nitro compound, either

chemically^{2,3} or catalytically using platinum,⁴ Raney nickel,⁵ or molybdenum^{6,7} or tungsten sulfide⁶ catalysts. It has been prepared from 3,4-dimethylphenol by heating with ammonia, ammonium bromide, and zinc bromide;⁸ from *m*-toluidine hydrochloride by alkylation with methanol at high temperature,^{1,9} from anhydro-4-amino-2-methylbenzyl alcohol by dry distillation from calcium hydroxide;¹⁰ from 2-methyl-5-aminobenzyl alcohol by reduction with sodium; from 2-methyl-5-nitrobenzyl acetate by catalytic reduction;¹¹ from 2-methyl-5-nitrobenzyl or -benzal chloride (prepared from dichloromethyl ethyl ether¹² or bis-chloromethyl ether¹³ and *p*-nitrotoluene) by catalytic,^{12,13} chemical,¹³ or electrochemical^{12,14} reduction; from *o*-xylene by direct amination with hydroxylamine hydrochloride in the presence of aluminum chloride;¹⁵ and from 3,4-dimethylacetophenone by Beckmann rearrangement of the oxime^{16,17} or by reaction with hydrazoic acid in the presence of concentrated sulfuric acid.¹⁸ The present method has been published.¹⁹

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 138

References and Notes

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Appendix

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

petroleum ether

oxime

anhydro-4-amino-2-methylbenzyl alcohol

3,4-dimethylacetophenone

hydrazoic acid

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

methanol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

ammonium bromide (12124-97-9)

platinum (7440-06-4)

Raney nickel (7440-02-0)

aluminum chloride (3495-54-3)

sodium (13966-32-0)

cuprous chloride (7758-89-6)

calcium hydroxide

Hydroxylamine hydrochloride (5470-11-1)

3,4-Dimethylaniline,
Xylidine, 3,4- (95-64-7)

xylidine (95-68-1)

molybdenum (7439-98-7)

tungsten sulfide

3,4-dimethylphenol (95-65-8)

zinc bromide (7699-45-8)

2-methyl-5-aminobenzyl alcohol

2-methyl-5-nitrobenzyl acetate

dichloromethyl ethyl ether

bis-chloromethyl ether

4-Bromo-o-xylene (583-71-1)

o-Xylene (95-47-6)

p-nitrotoluene (99-99-0)

m-toluidine hydrochloride (638-03-9)

2-methyl-5-nitrobenzyl chloride

2-methyl-5-nitrobenzal chloride