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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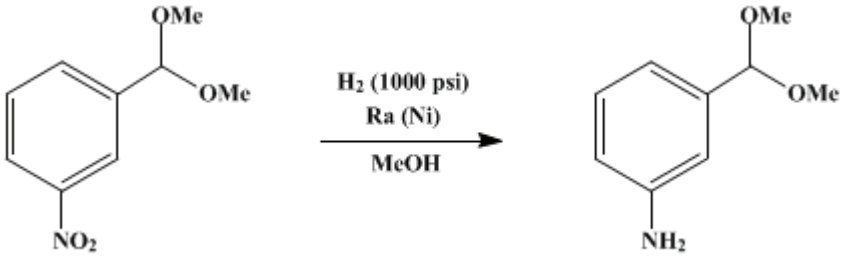
m-AMINOBENZALDEHYDE DIMETHYLACETAL

[Benzaldehyde, *m*-amino-, dimethylacetal]



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1. Procedure

In a 1-l. steel bomb are placed 295 g. (1.5 moles) of *m*-nitrobenzaldehyde dimethylacetal (p. 644), 250 ml. of technical anhydrous methanol, and 1 tablespoon of Raney nickel catalyst. Hydrogen is introduced until the pressure is about 1000 lb. (Note 1). The bomb is heated to about 40°, at which point the heating is discontinued and the shaker is started. The hydrogenation soon becomes rapid as the temperature rises to about 70° (Note 2). The bomb is refilled with hydrogen as many times as necessary (Note 3). The theoretical amount of hydrogen (4.5 moles) is absorbed in about 1.5 hours.

The bomb is cooled, the remaining hydrogen is discharged, and the bomb is opened. The solution is transferred to a beaker, and the bomb is rinsed with a little methanol which is added to the solution. The catalyst is removed by filtration *(Caution! The catalyst may be pyrophoric)*, and most of the filtrate is transferred to a 500-ml. Claisen flask set on a steam bath for distillation of the methanol; the remainder of the filtrate is introduced into the Claisen flask when the volume of the first portion has been reduced sufficiently by distillation. After all the methanol has been removed the aminoacetal is distilled under diminished pressure. The yield of *m*-aminobenzaldehyde dimethylacetal, a light-yellow liquid boiling at 123–124°/4 mm. or 110–112°/1.5 mm., is 168–196 g. (67–78%).

2. Notes

1. The hydrogenation is similar to one described on p. 63. As the bomb does not contain enough hydrogen to complete the reduction, more hydrogen should be admitted whenever the pressure drops below 300 lb.
2. Because of the high heat capacity of the bomb the internal temperature continues to rise (to about 70°) after the heater is turned off. As the exothermic hydrogenation begins the temperature rises to about 80°. The temperature should be kept below 85° to prevent hydrogenolysis of the acetal.
3. If the hydrogenation is started at a pressure of about 1500 lb. in a 2.5-l. bomb it will not be necessary to introduce more hydrogen. However, it may be necessary to stop the shaker occasionally to prevent a temperature rise beyond 85°.

3. Discussion

This acetal has not been described previously. The corresponding diethylacetal has been prepared by the reduction of *m*-nitrobenzaldehyde diethylacetal with sodium sulfide[1] and by the reaction of the anhydro compound of *m*-aminobenzaldehyde with ethanolic hydrogen chloride and ethyl orthoformate.[2]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 564

References and Notes

1. Haworth and Lapworth, *J. Chem. Soc.*, **121**, 76 (1922).
2. Bottomley, Cocker, and Nanney, *J. Chem. Soc.*, **1937**, 1891.

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

Aminoacetal

diethylacetal

ACETAL (105-57-7)

hydrogen chloride (7647-01-0)

methanol (67-56-1)

hydrogen (1333-74-0)

nickel (7440-02-0)

sodium sulfide (1313-82-2)

Ethyl orthoformate

m-aminobenzaldehyde (1709-44-0)

m-Aminobenzaldehyde dimethylacetal (53663-37-9)

m-nitrobenzaldehyde dimethylacetal (3395-79-7)

m-nitrobenzaldehyde diethylacetal

Benzaldehyde, m-amino-, dimethylacetal