



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.

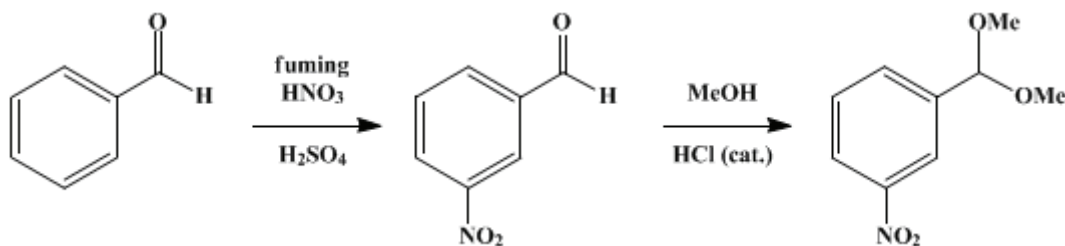
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.

Organic Syntheses, Coll. Vol. 3, p.644 (1955); Vol. 29, p.72 (1949).

***m*-NITROBENZALDEHYDE DIMETHYLACETAL**

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



Submitted by Roland N. Icke, C. Ernst Redemann, Burnett B. Wisegarver, and Gordon A. Alles.
Checked by H. R. Snyder and Frank X. Werber.

1. Procedure

A. *m*-Nitrobenzaldehyde. In a 3-l. three-necked flask provided with a dropping funnel, a thermometer, and an efficient mechanical stirrer is placed 1.25 l. of technical concentrated sulfuric acid (sp. gr. 1.84). The acid is stirred during the fairly rapid addition of 167 ml. (250 g., 4 moles) of technical fuming nitric acid (sp. gr. 1.49–1.50), with sufficient cooling by an ice bath so that the temperature of the mixed acids does not exceed 10°. The mixture is maintained at 5–10° while 213 g. (2 moles) of U.S.P. benzaldehyde (Note 1) is added with good stirring over a period of 2–3 hours. At the end of the addition the ice bath is removed and the mixture is allowed to stand overnight at room temperature.

The mixture is poured carefully onto about 3.25 kg. of cracked ice in a 2-gal. crock (Note 2) with manual stirring. The yellow precipitate is collected on a large Büchner funnel, washed with cold water, and pressed as dry as possible (Note 3). Further removal of water is accomplished by dissolving the moist product in about 100 ml. of warm benzene and separating the water layer in a separatory funnel. The benzene solution is filtered (Note 4) into a 1-l. distilling flask and concentrated on a steam bath. Distillation is discontinued when benzene no longer comes over or when nitrous fumes (from incompletely removed nitric acid) appear. The residual *m*-nitrobenzaldehyde is sufficiently pure for use in the next step (Note 5).

B. *m*-Nitrobenzaldehyde dimethylacetal. The above crude product is dissolved in 750 ml. of technical anhydrous methanol, 1 ml. of concentrated hydrochloric acid is added if necessary (Note 6), and the solution is allowed to stand at room temperature for 5 days (Note 7). A solution of sodium methoxide in methanol is added until the solution is just alkaline to moistened litmus paper. The methanol is removed by distillation on a steam bath; the residue is cooled to room temperature and treated with cool water to dissolve the inorganic salts. The aqueous solution is extracted with two 50-ml. portions of ether, and the extracts are added to the crude acetal. The solution is subjected to a preliminary drying over anhydrous magnesium sulfate (or sodium sulfate), filtered, and then dried for at least 12 hours over anhydrous sodium carbonate. After the ether has been removed by distillation on a steam bath the residue is distilled under reduced pressure from a 500-ml. Claisen flask. The yield of the light-yellow liquid acetal, boiling at 141–143°/8 mm. (Note 8), is 300–335 g. (76–85%) (Note 9).

2. Notes

- Commercial benzaldehyde may contain some benzoic acid. When taken from a previously unopened bottle, U.S.P. benzaldehyde usually is quite satisfactory. If there is any doubt concerning its purity, the aldehyde may be washed with dilute sodium carbonate solution, dried over anhydrous sodium carbonate, and distilled under diminished pressure just before use.
- Two 4-l. beakers may be used.
- A small amount of an oily liquid passes through the filter; this material is a mixture of the *ortho* and *meta* isomers. If a very pure product is desired, this oil may be discarded, although some of the *meta*

isomer will be lost. It is usually satisfactory to combine it with the solid material, the *m*-nitro acetal being obtained in a state of purity sufficient for most purposes in the final distillation.

4. A small amount of a solid by-product is removed.

5. If pure *m*-nitrobenzaldehyde is desired, the benzene solution is diluted with additional benzene and is washed well with aqueous sodium bicarbonate solution until the washings are alkaline. (*Warning! It has been reported [K. Ueno] that incomplete washing of the product in solution may result in an explosion during the distillation; all remaining acids must be removed before distillation is attempted.*) The solution is dried (with anhydrous sodium or magnesium sulfate), and the solvent is removed. The aldehyde is distilled under reduced pressure from a Claisen flask connected to an air-cooled condenser. The yield of product boiling at 119–123°/4 mm. is 226–254 g. (75–84%). The product readily crystallizes in the receiver.

6. When nitrous fumes are observed, there usually is enough acid present to catalyze the acetal formation.

7. The yield is not increased by extending the reaction period beyond 5 days.

8. The acetal boils at 116–119°/1 mm., 122–126°/2 mm., 130–132°/3 mm. The boiling range depends somewhat upon the rate of distillation.

9. The submitters obtained yields in the upper part of this range from runs twice the size described. They have stored samples of the product for as long as 4 years without deterioration.

3. Discussion

The only satisfactory method for the preparation of *m*-nitrobenzaldehyde is the direct nitration of benzaldehyde with a mixture of nitric and sulfuric acids. The procedure described is essentially that of Baker and Moffitt.¹

m-Nitrobenzaldehyde dimethylacetal has been prepared from the aldehyde and methanol in the presence of formiminomethyl ether hydrochloride² or Twitchell's reagent³ as the acid catalyst.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 59

References and Notes

1. Baker and Moffitt, *J. Chem. Soc.*, **1931**, 314.
 2. Claisen, *Ber.*, **31**, 1016 (1898).
 3. Zaganianis, *Ber.*, **71**, 2002 (1938).
-

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

m-nitro acetal

ACETAL (105-57-7)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

sodium bicarbonate (144-55-8)

nitric acid (7697-37-2)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

Benzoic acid (65-85-0)

benzaldehyde (100-52-7)

sodium methoxide (124-41-4)

sodium (13966-32-0)

magnesium sulfate (7487-88-9)

formiminomethyl ether hydrochloride

m-Nitrobenzaldehyde (99-61-6)

m-nitrobenzaldehyde dimethylacetal (3395-79-7)

Benzaldehyde, m-nitro-, dimethylacetal