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.

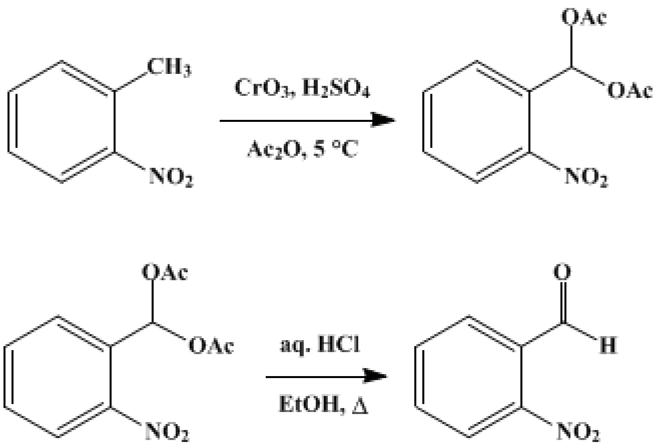
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.024.0075

Organic Syntheses, Coll. Vol. 3, p.641 (1955); Vol. 24, p.75 (1944).

o-NITROBENZALDEHYDE

[Benzaldehyde, *o*-nitro-]



Submitted by S. M. Tsang, Ernest H. Wood, and John R. Johnson.
Checked by Lee Irvin Smith and J. W. Opie.

1. Procedure

A. *o-Nitrobenzaldiacetate.* In a 2-l. three-necked round-bottomed flask equipped with an effective mechanical stirrer and a thermometer, and surrounded by an ice bath, are placed 600 g. (570 ml.) of glacial acetic acid, 565 ml. (612 g., 6 moles) of acetic anhydride, and 50 g. (0.36 mole) of *o*-nitrotoluene. To this solution is added slowly, with stirring, 156 g. (85 ml., 1.5 moles) of concentrated sulfuric acid. When the mixture has cooled to 5°, 100 g. (1 mole) of chromium trioxide is added in small portions at such a rate that the temperature does not rise above 10°; about 2 hours is required for the addition (Note 1). Stirring is continued for 5 hours after the chromium trioxide has been added (Note 2). The reaction mixture is poured into a large jar two-thirds filled with chipped ice, and cold water is added until the total volume is about 6 l. The mixture is then stirred vigorously for at least 15 minutes to promote solidification of the oily layer (Note 3). The oily solid is filtered with suction on a Büchner funnel, washed with cold water, and then stirred mechanically with 500 ml. of cold 2% sodium carbonate solution. The solid is then collected on a filter, washed with cold water, and dried in the air. The crude substance is digested with 150 ml. of petroleum ether (b.p. 60–70°) for 30 minutes, cooled, and filtered (Note 4). After having been dried in a vacuum desiccator, the product weighs 21–22 g. (23–24%) and melts at 87–88° (Note 5).

B. *o-Nitrobenzaldehyde.* A suspension of 51.6 g. of the diacetate in a mixture of 500 g. (272 ml.) of concentrated hydrochloric acid, 450 ml. of water, and 80 ml. of ethanol is stirred and refluxed for 45 minutes. The mixture is then cooled to 0°, and the solid is filtered with suction and washed with water (Note 6) and (Note 7). The crude product is purified by rapid steam distillation through a 100-cm. Allihn condenser into a cooled receiver. About 3.5 l. of distillate is collected during 30 minutes; the cooled distillate is filtered, and the *o*-nitrobenzaldehyde is dried in a desiccator over calcium chloride. It weighs 23.7 g. (74%) and melts at 44–45°.

2. Notes

1. Proper control of the temperature is very important during addition of the chromium trioxide. If the temperature rises very much, the reaction may become violent.
2. A hard, tarry mass forms during the later stages of this oxidation. For this reason stirring becomes increasingly difficult and a rather powerful motor must be used. After decantation of the liquid portion of the reaction mixture, ice and a little water (total volume 1 l. for the amounts of materials specified)

are added to the reaction flask, and the mass is broken up with a spatula. The suspension is then combined with the mixture in the large jar.

3. It is essential that the oily layer should be stirred vigorously until it has solidified; otherwise large losses will be incurred during the subsequent filtration.

4. This treatment removes unchanged *o*-nitrotoluene.

5. The checkers have carried out this preparation using three times the amounts of material specified here. The percentage yields were the same.

6. In one run, the submitters substituted an equivalent amount of sulfuric acid for the hydrochloric acid, omitted the filtration, and steam-distilled the mixture directly. The yield of *o*-nitroaldehyde was 74.7%; this product also melted at 44–45°.

7. The crude aldehyde may be dried and then purified by distillation under reduced pressure. For this purpose, an ordinary Claisen flask is used. No fractionation is necessary; the distillation serves only to remove a small amount of tarry material. The boiling range is rather wide (120–144°/3–6 mm.), but the entire distillate (30 g. from 66 g. of the diacetate) solidifies and melts at 44–45°. The aldehyde may also be recrystallized, although with some loss. For this purpose 11 g. of the solid is dissolved in toluene (2–2.5 ml. per gram) at room temperature, the solution is diluted with petroleum ether (b.p. 30–60°; 7 ml. per ml. of solution) and cooled to −10° or below. The pale yellow needles weigh 9 g. and melt at 44–45°.

3. Discussion

o-Nitrobenzaldehyde has been prepared by action of oxides of nitrogen upon *o*-nitrobenzyl alcohol;[1] by oxidation of *o*-nitrocinnamic acid or ester with permanganate or nitrous acid;[2] by oxidation of *o*-nitrophenylpyruvic acid with permanganate;[3] and from *o*-nitrotoluene by a number of methods. These include: action of isoamyl nitrite and sodium ethoxide, followed by hydrolysis of the resulting *o*-nitrobenz-*anti*-aldoxime with concentrated hydrochloric acid;[4] direct action of a number of oxidizing agents including potassium dichromate and sulfuric acid,[5] manganese dioxide,[6] nickel oxide,[7] and cerium oxide;[8] action of mercury oxide in the presence of alkali, followed by hydrolysis of the resulting *o*-nitrobenzalmercurioxide with nitrous or nitric acid;[9] and action of chromic acid in acetic acid and acetic anhydride, followed by hydrolysis of the resulting *o*-nitrobenzaldiacetate.[10] *o*-Nitrobenzaldehyde is also formed, along with much *m*-nitrobenzaldehyde, by direct nitration of benzaldehyde.[11]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 56
- Org. Syn. Coll. Vol. 4, 713
- Org. Syn. Coll. Vol. 4, 730
- Org. Syn. Coll. Vol. 5, 825

References and Notes

1. Cohen and Harrison, *J. Chem. Soc.*, **71**, 1057 (1897).
2. Friedländer and Henriques, *Ber.*, **14**, 2803 (1881).
3. Reissert, *Ber.*, **30**, 1042 (1897).
4. Lapworth, *J. Chem. Soc.*, **79**, 1274 (1901); Farbwerke vorm. Meister, Lucius, and Brüning, Ger. pat. 107,095 (*Chem. Zentr.*, **1900**, I, 886).
5. Lauth, *Bull. soc. chim. France*, (3) **31**, 133 (1904).
6. Gilliard, Monnet, and Cartier, Ger. pat. 101,221 (*Chem. Zentr.*, **1899**, I, 959); Badische Anilin- u. Sodafabr., Ger. pat. 175,295 (*Chem. Zentr.*, 1906, II, 1589).
7. Badische Anilin- u. Sodafabr., Ger. pat. 127,388 (*Chem. Zentr.*, **1902**, I, 150).
8. Farbwerke vorm. Meister, Lucius, and Brüning, Ger. pat. 174,238 (*Chem. Zentr.*, **1906**, II, 1297).
9. Reissert, *Ber.*, **40**, 4216, 4220 (1907); Ger. pat. 186,881 (*Chem. Zentr.*, **1907**, I, 1295).
10. Thiele and Winter, *Ann.*, **311**, 356 (1900).
11. Friedländer and Henriques, *Ber.*, **14**, 2801 (1881).

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

petroleum ether

o-nitroaldehyde

o-nitrobenzalmercurioxide

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

acetic anhydride (108-24-7)

nitric acid (7697-37-2)

sodium carbonate (497-19-8)

nitrogen (7727-37-9)

nitrous acid (7782-77-6)

mercury oxide (21908-53-2)

benzaldehyde (100-52-7)

toluene (108-88-3)

sodium ethoxide (141-52-6)

chromic acid (7738-94-5)

manganese dioxide (1313-13-9)

permanganate

potassium dichromate (7778-50-9)

o-nitrotoluene (88-72-2)

chromium trioxide (1333-82-0)

Isoamyl nitrite (110-46-3)

o-Nitrobenzaldehyde,
Benzaldehyde, o-nitro- (552-89-6)

nickel oxide

cerium oxide

o-Nitrobenzaldiacetate (6345-63-7)

m-Nitrobenzaldehyde (99-61-6)

o-nitrobenz-anti-aldoxime

o-nitrobenzyl alcohol (612-25-9)

o-nitrocinnamic acid

o-nitrophenylpyruvic acid (5461-32-5)