



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.

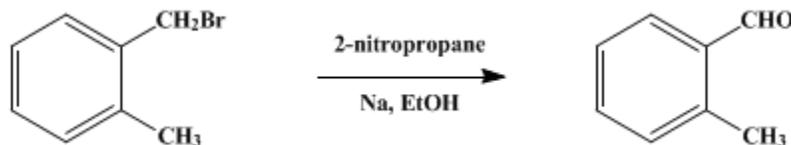
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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. 4, p.932 (1963); Vol. 30, p.99 (1950).

***o*-TOLUALDEHYDE**



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1. Procedure

Eleven and one-half grams (0.5 g. atom) of sodium is dissolved in 500 ml. of absolute ethanol in a 1-l. round-bottomed flask. Forty-six grams (0.52 mole) of 2-nitropropane is added, then 92.5 g. (0.50 mole) of *o*-xylyl bromide (Note 1). The flask is attached to a reflux condenser connected to a drying tube and shaken at intervals for 4 hours. The reaction mixture, originally at room temperature, becomes warm spontaneously, and a white precipitate of sodium bromide forms (Note 2).

After a reaction period of 4 hours the sodium bromide is separated by filtration and the ethanol is removed by distillation on a steam bath. The residue of product and sodium bromide is dissolved in 100 ml. of ether and 150 ml. of water. The ether layer is washed with two 50-ml. portions of 10% sodium hydroxide solution to remove any acetoxime and excess 2-nitropropane and is then washed with 50 ml. of water. The ether layer is separated and is dried with 15 g. of anhydrous sodium sulfate, and the ether is removed by distillation on a steam bath.

The crude product is distilled from a Claisen flask under reduced pressure. The yield of *o*-tolualdehyde boiling at 68–72°/6 mm., n_D^{25} 1.5430, is 41–44 g. (68–73%) (Note 3).

2. Notes

1. *o*-Xylyl bromide may be obtained from the Eastman Kodak Company or may be prepared by the light-catalyzed bromination of *o*-xylene.²
2. The solution is originally supersaturated with the sodium salt of 2-nitropropane, and a precipitate of this salt may be mistaken for sodium bromide.
3. This is a general method for the preparation of substituted benzaldehydes. The following aldehydes have been prepared by the same general procedure.³

Aldehyde	Yield, %
<i>p</i> -Bromobenzaldehyde	75
Benzaldehyde	73
<i>p</i> -Carbomethoxybenzaldehyde	72
<i>p</i> -Cyanobenzaldehyde	70
<i>p</i> -Trifluoromethylbenzaldehyde	77

3. Discussion

A procedure for the preparation of *o*-tolualdehyde from *o*-toluanilide by the Sonn-Müller method has been published in *Organic Syntheses*.⁴ In addition to the alternative methods of preparation listed there, *o*-tolualdehyde has been prepared from *o*-xylyl bromide⁵ or chloride⁶ and hexamethylenetetramine; by the Stephen reduction of *o*-tolunitrile;⁷ by the reduction of the latter with lithium triethoxyaluminumhydride⁸ or sodium triethoxyaluminumhydride;⁹ by the condensation of crotonaldehyde with barium or calcium oxide at 300°;¹⁰ by the oxidation of *o*-methylbenzyl alcohol with *N*-chlorosuccinimide;¹¹ by the reaction of ethyl orthoformate with *o*-tolylmagnesium bromide;¹² by the

reaction of the *o*-tolylmagnesium chloride-tetrahydrofuran complex with [methyl formate](#);¹³ and by the procedure of the present preparation.³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 818](#)

References and Notes

1. Purdue University, Lafayette, Indiana.
 2. Cumming, Hopper, and Wheeler, *Systematic Organic Chemistry*, p. 351, Constable and Company, London, 1937 (description of a procedure for light-catalyzed bromination which is applicable to *o*-xylene).
 3. Hass and Bender, *J. Am. Chem. Soc.*, **71**, 1767 (1949).
 4. [Org. Syntheses Coll. Vol. 3, 818 \(1955\)](#).
 5. Sommelet, *Compt. rend.*, **157**, 852 (1913).
 6. Shacklett and Smith, *J. Am. Chem. Soc.*, **75**, 2654 (1953).
 7. Stephen, *J. Chem. Soc.*, **127**, 1874 (1925).
 8. Brown, Shoaf, and Garg, *Tetrahedron Letters*, **3**, 9 (1959).
 9. Hesse and Schrödel, *Angew. Chem.*, **68**, 438 (1956); *Ann.*, **607**, 24 (1957).
 10. Wiemann, Martineau, and Tiquet, *Compt. rend.*, **241**, 807 (1955).
 11. Hebbelynck and Martin, *Bull. soc. chim. Belges*, **60**, 54 (1951) [*C. A.*, **46**, 7051 (1952)].
 12. Gibson, *J. Chem. Soc.*, **1956**, 808.
 13. Ramsden (to Metal & Thermit Corp.), Brit. pat. 806,710 [*C. A.*, **54**, 2264 (1960)].
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

barium or calcium oxide

o-tolylmagnesium chloride-tetrahydrofuran complex

[ethanol \(64-17-5\)](#)

[ether \(60-29-7\)](#)

[sodium hydroxide \(1310-73-2\)](#)

[sodium bromide \(7647-15-6\)](#)

[sodium sulfate \(7757-82-6\)](#)

[benzaldehyde \(100-52-7\)](#)

[sodium \(13966-32-0\)](#)

[Ethyl orthoformate](#)

[N-chlorosuccinimide \(128-09-6\)](#)

ACETOXIME

methyl formate (107-31-3)

hexamethylenetetramine (100-97-0)

o-Tolunitrile (529-19-1)

chloride

crotonaldehyde (123-73-9)

2-nitropropane (79-46-9)

sodium triethoxyaluminumhydride

lithium triethoxyaluminumhydride

o-Xylene (95-47-6)

p-Bromobenzaldehyde (1122-91-4)

p-cyanobenzaldehyde (105-07-7)

o-Tolualdehyde (529-20-4)

o-toluanilide

o-tolylmagnesium bromide

o-Methylbenzyl alcohol (89-95-2)

o-xylyl bromide (576-23-8)

p-Carbomethoxybenzaldehyde (1571-08-0)

p-Trifluoromethylbenzaldehyde (455-19-6)