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.

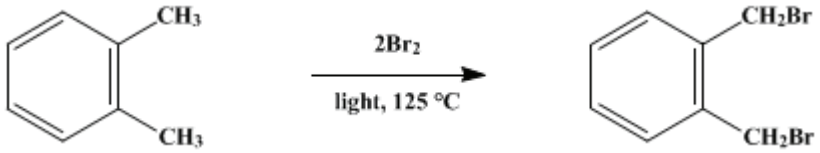
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.034.0100

Organic Syntheses, Coll. Vol. 4, p.984 (1963); Vol. 34, p.100 (1954).

o-XYLYLENE DIBROMIDE

[*o*-Xylene, α,α'-dibromo-]



Submitted by Emily F. M. Stephenson[1]
Checked by William S. Johnson, C. W. Taylor, and William DeAcetis.

1. Procedure

Caution! o-Xylylene dibromide is a powerful and persistent lachrymator. The preparation and all subsequent handling of this substance should, therefore, be carried out in an efficient hood with adequate protection by rubber gloves. A gas mask should be at hand for emergency. All apparatus coming in contact with the dibromide should be immersed in alcoholic alkali contained in a large crock with a lid. A period of 24 hours is sufficient for decontamination. Waste substances such as filter paper and corks usually require several days of such soaking before they can be safely discarded.

A 1-l. three-necked round-bottomed flask is fitted with a rubber slip-sleeve-sealed stirrer, a dropping funnel with the tip extended to reach almost to the bottom of the flask (Note 1), and an efficient condenser leading to a gas absorption trap.[2] *o*-Xylene (106 g., 1 mole) (Note 2) is placed in the flask, which is heated with an oil bath and illuminated with a sun lamp (Note 3) placed 1–5 cm. from the upper portion of the flask. When the temperature of the *o*-xylene reaches 125°, the dropwise addition of 352 g. (2.2 moles) of bromine is commenced with stirring. The rate of addition is regulated so that all the bromine is introduced in 1.5 hours. The mixture is stirred at 125° under illumination for an additional 30 minutes. It is then allowed to cool to 60° and poured into 100 ml. of boiling 60–68° petroleum ether contained in a beaker, the transfer being assisted with small amounts of warm solvent. As the homogeneous solution cools slowly to room temperature it is stirred frequently to prevent caking of the brown crystalline product that separates. After the mixture is cool and the bulk of the dibromide has crystallized, the beaker is placed in a refrigerator for 12 hours (Note 4). The product is then separated by suction filtration, washed twice with 25-ml. portions of cold petroleum ether, and then pressed on the filter until nearly dry. Final drying is effected in a vacuum desiccator containing solid potassium hydroxide. The brown crystalline product amounts to 123–140 g. (48–53% yield), the melting point ranging between 89° and 94° (Note 5).

2. Notes

1. It is convenient to seal a short inner tube inside the stem of the dropping funnel so that the rate of addition can be observed readily. The introduction of the bromine below the surface of the *o*-xylene through an extended stem, about 4-mm. inside diameter, results in better mixing of reactants and less loss of bromine vapors.
2. The submitter used *o*-xylene obtained from Light and Company, Wraysbury, Middlesex, England. It was refluxed with sodium, then distilled from sodium, b.p. 144–144.5°, and stored over sodium.
The checkers employed the white label grade of *o*-xylene supplied by Eastman Kodak Company without further purification.
3. The submitter employed a 600-watt lamp, and the checkers used a 275-watt General Electric sun lamp.
4. Occasional stirring during the first 3–4 hours of this chilling period helps to prevent caking of the product on the side of the beaker.
5. This product is satisfactory for most preparative work. Further purification may be effected by recrystallization from 95% ethanol (3 ml./g.), to give material melting at 93–94° in 80–85% recovery.

Other solvents that have been used for recrystallization are petroleum ether (British Drug House, "Analar," b.p. 60–80°) (19 ml./g.), and chloroform (1 ml./g.).

3. Discussion

o-Xylylene dibromide has been prepared from *o*-xylene by direct bromination[3] or by treatment with N-bromosuccinimide;[4] by the direct bromination of *o*-xylyl bromide;[5] and by the action of concentrated hydrobromic acid on the monophenyl ether of α,α'-dihydroxy-*o*-xylene.[6] The present procedure is essentially that of Perkin[3] as modified by Cope and Fenton.[7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 1064

References and Notes

1. University of Melbourne, Melbourne, Australia.
2. *Org. Syntheses Coll. Vol.* **2**, 4 (1943).
3. Perkin, *J. Chem. Soc.*, **1888**, 5; Atkinson and Thorpe, *J. Chem. Soc.*, **1907**, 1695.
4. Wenner, *J. Org. Chem.*, **17**, 523 (1952).
5. von Braun and Cahn, *Ann.*, **436**, 262 (1924).
6. von Braun and Zobel, *Ber.*, **56**, 2142 (1923).
7. Cope and Fenton, *J. Am. Chem. Soc.*, **73**, 1668 (1951).

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

petroleum ether

ethanol (64-17-5)

chloroform (67-66-3)

HYDROBROMIC ACID (10035-10-6)

bromine (7726-95-6)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

monophenyl ether (101-84-8)

N-bromosuccinimide (128-08-5)

o-Xylylene dibromide,
o-Xylene, α,α'-dibromo- (91-13-4)

α,α'-dihydroxy-o-xylene (612-14-6)

o-Xylene (95-47-6)

o-xylyl bromide (576-23-8)