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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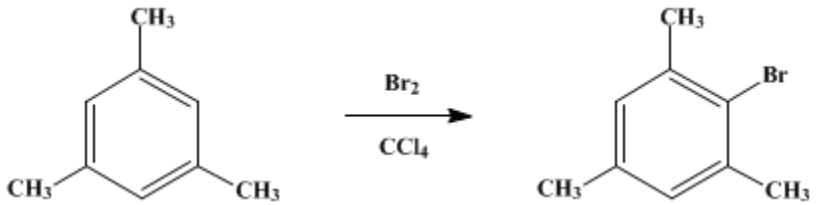
Organic Syntheses, Coll. Vol. 2, p.95 (1943); Vol. 11, p.24 (1931).

BROMOMESITYLENE

[Mesitylene, 2-bromo-]



Submitted by Lee Irvin Smith
Checked by Roger Adams and H. A. Stearns.

1. Procedure

In a 3-l. three-necked flask, provided with a short reflux condenser, a mechanical stirrer, and a separatory funnel, is placed a solution of 636 g. (5.3 moles) of mesitylene (Note 1) in 375–440 cc. of carbon tetrachloride. The flask is placed in an ice-salt bath, and when the temperature of the reaction mixture is below 10° a solution of 900 g. (288 cc., 5.6 moles) of bromine in 565 cc. of carbon tetrachloride is added to the well-stirred solution. The bromination proceeds very readily, and the hydrogen bromide which is evolved is led off through the condenser and absorbed in water. The addition of the bromine solution requires about three hours, during which time the temperature is maintained at 10–15°.

After the addition of the bromine is complete, the reaction mixture is allowed to stand at room temperature for about one hour. It then has a light yellow color. The solution is washed with water and then with two 500-cc. portions of 20 per cent sodium hydroxide solution to remove any dissolved hydrobromic acid. The solution is dried over calcium chloride and filtered. The carbon tetrachloride is distilled through a good column until the temperature at the top of the column reaches about 120°. When the carbon tetrachloride has distilled, the oil is likely to turn dark and give off fumes.

The residue is added to a solution of 50 g. of sodium in about a liter of 95 per cent alcohol. The solution is boiled under a reflux condenser for about one hour (Note 2) and then allowed to stand overnight. The reaction mixture is diluted with about 6 l. of water and the two layers are separated. The aqueous layer is extracted with three or four 500-cc. portions of carbon tetrachloride (Note 3), and the extracts are added to the bromomesitylene. This solution is then washed thoroughly with water. The carbon tetrachloride solution is separated, dried over calcium chloride, and distilled. After the carbon tetrachloride is removed the bromomesitylene is fractionated carefully under reduced pressure from a modified Claisen flask. The fraction boiling at 105–107°/16–17 mm. (Note 4) is bromomesitylene. The yield is 840–870 g. (79–82 per cent of the theoretical amount). There is a small low-boiling portion (about 25 g.) and also a small high-boiling residue. The bromomesitylene obtained in this way gives no precipitate on standing twenty-four hours with alcoholic silver nitrate solution. It has a melting point of −1° to +1°.

2. Notes

1. The mesitylene was prepared as described in Org. Syn. Coll. Vol. I, **1941**, 341, and boiled at 58–59°/15 mm.
2. The treatment with sodium ethoxide removes any traces of side-chain halogen derivatives. Some care has to be exercised at this point as the solution may foam at the beginning of the heating period.
3. The carbon tetrachloride distilled from the crude bromomesitylene may be used for this purpose. The total volume of solution should be about 2 l.
4. Boiling points of bromomesitylene observed at different pressures were as follows: 132°/62 mm.; 139°/70 mm.; 146°/78 mm.; 157°/100 mm.

3. Discussion

Bromomesitylene is always prepared by brominating mesitylene—a reaction that can be run in the dark,[1] or in daylight,[2] or using sulfur bromide and nitric acid,[3] or with metallic manganese as a catalyst in the absence of any solvent.[4]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 360
- Org. Syn. Coll. Vol. 3, 848
- Org. Syn. Coll. Vol. 5, 706

References and Notes

1. Schramm, Ber. **19**, 212 (1886).
2. Fittig and Storer, Ann. **147**, 6 (1868); Smith and MacDougall, J. Am. Chem. Soc. **51**, 3002 (1929).
3. Kalle and Company, Ger. pat. 123,746 [Frdl. **6**, 53 (1900–02)].
4. Duke, Lewis, and Dunbar, Proc. S. Dakota Acad. Sci. **15**, 21 (1935) [C. A. **30**, 2556 (1936)].

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

metallic manganese

alcohol (64-17-5)

calcium chloride (10043-52-4)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

silver nitrate (7761-88-8)

HYDROBROMIC ACID,
hydrogen bromide (10035-10-6)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

Mesitylene (108-67-8)

Bromomesitylene (27129-86-8)

Mesitylene, 2-bromo- (576-83-0)

sulfur bromide