



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.

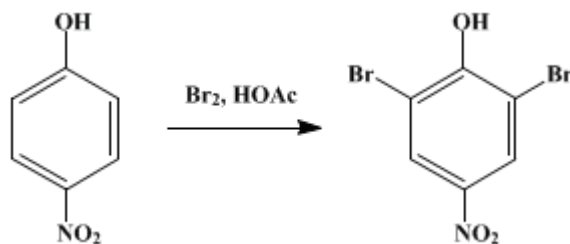
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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2,6-DIBROMO-4-NITROPHENOL

[Phenol, 2,6-dibromo-4-nitro-]



Submitted by W. W. Hartman and J. B. Dickey.
Checked by Louis F. Fieser and C. H. Fisher.

1. Procedure

In a 5-l. round-bottomed flask, fitted with a liquid-sealed mechanical stirrer, a dropping funnel, and a tube leading to a gas trap to carry off the hydrogen bromide, 278 g. (2 moles) of *p*-nitrophenol (m.p. 112–113°) is dissolved in 830 cc. of glacial acetic acid. To this solution at room temperature is added, dropwise with stirring during the course of three hours, a solution of 750 g. (240 cc., 4.7 moles) of bromine in 700 cc. of glacial acetic acid. After the addition of the bromine the reaction mixture is stirred for one-half hour and then warmed on the steam bath (internal temperature about 85°) for one hour in order to remove as much of the excess bromine as possible. The last traces of bromine are removed by passing a stream of air into the reaction mixture, which then has a yellow or brown color. The mixture is treated with 1.1 l. of cold water, stirred until cool (Note 1), and allowed to stand in ice, or in an ice chest, overnight. The pale yellow crystalline product is collected on a 19-cm. Büchner funnel and washed first with 500 cc. of 50 per cent aqueous acetic acid and then thoroughly with water. It is dried in an oven at 40–60° or in a vacuum desiccator over sodium hydroxide. The yield is 570–583 g. (96–98 per cent of the theoretical amount) of a nearly colorless product melting with decomposition at 138–140° (Note 2).

2. Notes

1. If the solution is stirred during cooling the product is less likely to cake on the walls of the flask and the resulting crystals are easier to wash.
2. This material is sufficiently pure for most purposes, and the quality is not greatly improved by recrystallization from 50 per cent acetic acid. Samples prepared by bromination, even after purification, invariably decompose at the melting temperature, which is somewhat dependent upon the rate of heating. The material obtained by nitration has been found to melt without decomposition at 144–145°.¹

3. Discussion

2,6-Dibromo-4-nitrophenol has been prepared by the nitration of 2,6-dibromophenol¹ or of dibromophenolsulfonic acid,² and by the action of nitric acid on 2,6-dibromo-4-nitrosophenol³ or on 2,4,6-tribromophenol.⁴ It has been obtained from the corresponding ethyl ether⁵ and by the action of bromine on *p*-nitrosophenol,⁶ 4,6-dibromo-2-nitrophenol,⁷ 5-nitro-2-hydroxybenzoic acid,⁸ and 5-nitro-2-hydroxybenzene-sulfonic acid.⁹ The dibromination of *p*-nitrophenol^{10, 11} has been carried out in sulfuric acid solution¹² and in the presence of aluminum chloride.¹³ The method described here is essentially that of Möhlau and Uhlmann.¹¹

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 2, 175*

References and Notes

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Appendix

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

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

sodium hydroxide (1310-73-2)

nitric acid (7697-37-2)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

aluminum chloride (3495-54-3)

2,6-Dibromo-4-nitrophenol,
Phenol, 2,6-dibromo-4-nitro- (99-28-5)

2,6-dibromophenol (608-33-3)

dibromophenolsulfonic acid

2,6-dibromo-4-nitrosophenol

2,4,6-tribromophenol (118-79-6)

4,6-dibromo-2-nitrophenol

5-nitro-2-hydroxybenzoic acid (96-97-9)

5-nitro-2-hydroxybenzene-sulfonic acid

p-nitrophenol (100-02-7)

p-nitrosophenol (104-91-6)