



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.

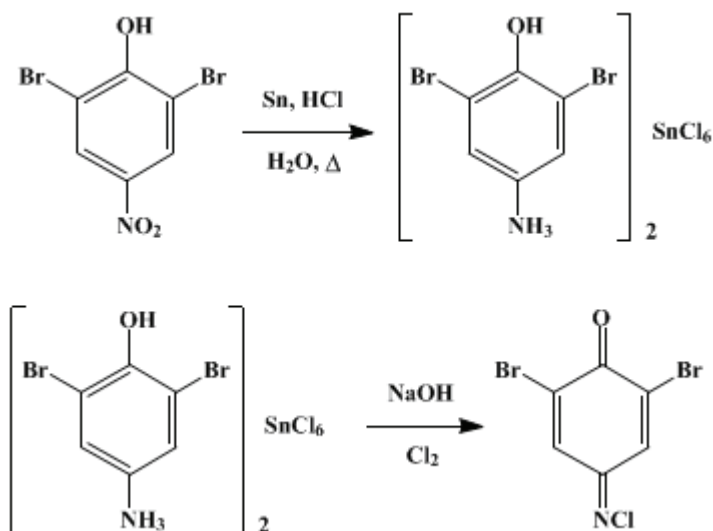
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.175 (1943); Vol. 15, p.8 (1935).

2,6-DIBROMOQUINONE-4-CHLOROIMIDE

[Quinonimine, 2,6-dibromo-N-chloro-]



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1. Procedure

(A) *2,6-Dibromo-4-aminophenol Chlorostannate*.—In a 5-l. round-bottomed flask is placed 148.5 g. (0.5 mole) of 2,6-dibromo-4-nitrophenol (p. 173) with 300 cc. (3.7 moles) of concentrated hydrochloric acid (sp. gr. 1.19), 300 cc. of water, and 185 g. (1.56 gram atoms) of mossy tin. Three cubic centimeters of capryl alcohol is added to control the foaming, and the mixture is heated in the open flask with stirring on the steam bath until the reaction starts. The reaction may proceed vigorously at the outset, and it is well to heat cautiously during the initial stages. Hydrochloric acid and water are added from time to time, and foaming can be controlled by the addition of a part of the water. A total of 520 cc. (6.4 moles) of concentrated hydrochloric acid and 900 cc. of water are added during the course of the reaction. When the first, vigorous reaction is over the mixture is heated strongly until all the dibromonitrophenol has dissolved, and the hot solution (at about 85°) is filtered through a layer of Norite on a hot Büchner funnel. The filtrate, which usually is colorless, is cooled to 0° with stirring for two hours, or allowed to stand in a cool place overnight. The product, which separates in the form of colorless or slightly yellow needles, is collected on a Büchner funnel and washed with cold dilute hydrochloric acid (one volume of concentrated acid to one volume of water). The material is usually colorless and may be used directly for the reaction which follows (Note 1). After drying in an oven at 50–60°, or in a vacuum desiccator over sodium hydroxide, the tin salt weighs 214–220 g. The theoretical weight, based on the formula assumed above, is 217 g.

(B) *2,6-Dibromoquinone-4-chloroimide*.—The chlorostannate is conveniently oxidized in two batches (Note 2). In a 3-l. flask is placed a solution of 115 g. (2.9 moles) of sodium hydroxide in 175 cc. of water, 1 kg. of cracked ice is added, and 108 g. (1.52 moles) of chlorine gas is passed into the mixture. About 80 per cent of the ice is melted by the operation. In a 5-l. flask 110 g. (0.127 mole) of the tin salt of 2,6-dibromo-4-aminophenol is dissolved in 1.2 l. of water and 12 cc. of concentrated hydrochloric acid. Solution is effected by warming the mixture to 40–50°, after which it is cooled to 15–17° and 600 g. of ice is added. The sodium hypochlorite solution is then added all at once with vigorous stirring (Hood). A yellow precipitate of 2,6-dibromoquinone-4-chloroimide separates immediately, and chlorine is evolved. As soon as the sodium hypochlorite solution has been stirred in, 120 cc. of concentrated hydrochloric acid is added in order to keep the tin salts in solution (Note 3). The fine,

yellow precipitate is filtered under the hood on a Büchner funnel (Note 4) and washed with 1.5 l. of 5 per cent hydrochloric acid to remove tin salts and chlorine. The product is dried on a glass tray at 30–40° (Note 5), or in a vacuum desiccator over sodium hydroxide. From two such batches the yield of chloroimide melting at 80–82° is 126–130 g. (84–87 per cent of the theoretical amount based on the weight of 2,6-dibromo-4-nitrophenol used in Part A).

2. Notes

1. If the product has an appreciable yellow color, it should be recrystallized from a mixture of 150 cc. of concentrated hydrochloric acid and 375 cc. of water, heating to 85–90°. The yield of recrystallized product is 180–190 g. By evaporating the mother liquor to one-third the original volume under reduced pressure, an additional 15–25 g. of tin salt can be recovered.
2. As much as 700 g. of tin salt can be oxidized in one run by using a 70-l. crock for the reaction vessel.
3. The particle size of the chloroimide can be increased by stirring for one hour at this point.
4. The first liter of filtrate is refiltered until it is clear.
5. Care must be taken in drying as one larger run decomposed violently in an open tray when the temperature was about 60°.

3. Discussion

2,6-Dibromoquinone-4-chloroimide has been prepared by the action of sodium hypochlorite on 2,6-dibromo-4-aminophenol in the form of the chlorostannate¹ or as the hydrochloride.²

References and Notes

1. Möhlau, Ber. **16**, 2845 (1883); Friedländer and Stange, *ibid.* **26**, 2262 (1893); Möhlau and Uhlmann, Ann. **289**, 94 (1896); Mikhailov, Trans. Inst. Pure Chem. Reagents No. **16**, 83 (1939) [C. A. **34**, 3707 (1940)].
 2. Gibbs, J. Biol. Chem. **72**, 653 (1927).
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Appendix

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

hydrochloric acid (7647-01-0)

sodium hydroxide (1310-73-2)

tin (7440-31-5)

Norite (7782-42-5)

chlorine (7782-50-5)

sodium hypochlorite (7681-52-9)

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

2,6-Dibromoquinone-4-chloroimide (537-45-1)

Quinonimine

capryl alcohol (111-87-5)

dibromonitrophenol

2,6-dibromo-4-aminophenol (609-21-2)

tin salt of 2,6-dibromo-4-aminophenol

2,6-Dibromo-4-aminophenol chlorostannate