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.

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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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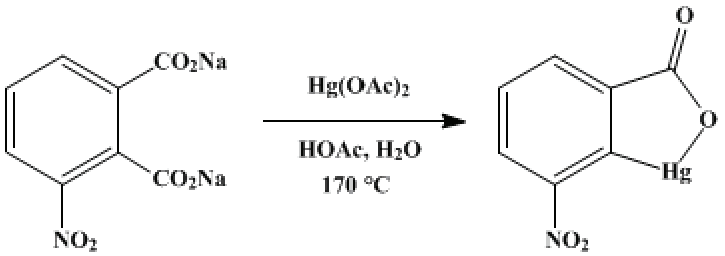
Organic Syntheses, Coll. Vol. 1, p.56 (1941); Vol. 7, p.1 (1927).

ANHYDRO-2-HYDROXYMERCURI-3-NITROBENZOIC ACID

[Benzoic acid, anhydro-2-hydroxymercuri-3-nitro-]



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1. Procedure

A solution of 80 g. (2 moles) of sodium hydroxide in 800 cc. of water is prepared in a 2-l. beaker. To the warm solution is added 211 g. (1 mole) of 3-nitrophthalic acid (p. 408) (Note 1). A small amount of insoluble material is removed by filtration through a large preheated Büchner funnel (Note 2). A solution of 350 g. (1.1 moles) of mercuric acetate (Note 3) in a mixture of 50 cc. of glacial acetic acid and 700 cc. of water is prepared by heating and filtering while hot (Note 4). The two hot solutions are poured into a 3-l. long-necked flask and mixed by shaking. No precipitate should separate (Note 5). The flask is clamped in a large oil bath (Note 6) with the level of the oil almost to the neck of the flask. It is fitted with a reflux condenser provided with a tube leading to a large beaker placed on the desk (Note 7).

The temperature of the oil bath is raised to 170° over a period of about one hour. If any considerable amount of material is driven through the condenser, it is poured back through the top of the condenser as soon as the reaction slackens. The heating at 165–175° is continued for about seventy hours. After about sixty hours the end of the tube leading from the top of the condenser is introduced below the surface of about 1 cc. of mercury in a small test tube. The evolution of carbon dioxide can be followed by observing the bubbles which pass through the mercury. When not more than one or two bubbles escape per minute, the heating is discontinued (Note 8).

The product is allowed to settle and the hot supernatant liquid is poured through a preheated suction filter. The filtrate deposits less than 10 g. of crude product on cooling. The product in the flask is shaken with several 100-cc. portions of water, and all the fine material is transferred to the filter. Some lumpy material is usually left in the flask. This is transferred to a large mortar and ground to a paste with a little water and then transferred to the filter. After sucking as dry as possible, the suction is shut off, and 100 cc. of alcohol is poured over the material on the filter. After standing a few minutes, suction is again applied. The product is then dried to constant weight (Note 9). The yield of anhydro-2-hydroxymercuri-3-nitrobenzoic acid is 300–330 g. (82–90 per cent of the theoretical amount based on the 3-nitrophthalic acid used). It is a cream-colored powder which dissolves in an excess of dilute sodium hydroxide, leaving only a slight turbidity (Note 10) and (Note 11).

2. Notes

1. 3-Nitrophthalic acid melting above 200° (sealed tube) is pure enough for this preparation.
2. Although the insoluble material is very small in amount, filtration without suction is too slow.
3. Commercial mercuric acetate, about 90 per cent pure, was used. The equivalent amounts of mercuric oxide and acetic acid may be used if the acetate is not available.
4. A small amount of mercurous compounds is removed by the filtration.
5. If more concentrated solutions are used, the mercuric salt precipitates and the reaction runs less

smoothly.
6. A large galvanized pail containing extra heavy lubricating oil was used. This oil does not fume even after heating for long periods.
7. This beaker serves to catch any material which is carried over during a slightly violent reaction which sometimes takes place at the beginning.
8. If a more accurate indication of the end of the reaction is desired, a tube containing mercury may be inverted in a small beaker of mercury and any gas evolved during the later stages of the reaction may be collected over the mercury.
9. The wet material may be used without drying for the preparation of 2-bromo-3-nitrobenzoic acid (p. 125).
10. To dissolve the mercury compound it should be dusted into boiling sodium hydroxide solution.
11. By a similar procedure phthalic anhydride may be converted into anhydro-*o*-hydroxymercuribenzoic acid. Thus, 300 g. (2 moles) of phthalic anhydride and 750 g. (2.2 moles) of commercial mercuric acetate (Note 3) give 550 g. of the mercury compound (85 per cent of the theoretical amount). With phthalic anhydride the reaction is complete in six to ten hours.

3. Discussion

Anhydro-2-hydroxymercuri-3-nitrobenzoic acid has been prepared only in accordance with the procedure described.[1]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 125

References and Notes

1. Whitmore and Culhane, J. Am. Chem. Soc. **51**, 602 (1929).

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

Anhydro-2-hydroxymercuri-3-nitrobenzoic acid

Benzoic acid, anhydro-2-hydroxymercuri-3-nitro-

mercurous compounds

mercuric salt

mercury compound

Anhydro-o-hydroxymercuribenzoic acid

alcohol (64-17-5)

acetic acid (64-19-7)

sodium hydroxide (1310-73-2)

3-Nitrophthalic acid (603-11-2)

mercuric acetate (1600-27-7)

mercury (7439-97-6)

carbon dioxide (124-38-9)

mercuric oxide (21908-53-2)

acetate

2-Bromo-3-nitrobenzoic acid (573-54-6)

phthalic anhydride (85-44-9)