



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.

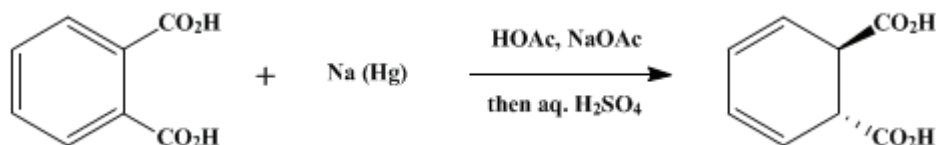
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.461 (1988); Vol. 50, p.50 (1970).

***trans*-1,2-DIHYDROPHthalic ACID**

[3,5-Cyclohexadiene-1,2-dicarboxylic acid, *trans*-]



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Checked by Herbert A. Kirst and E. J. Corey.

1. Procedure

A vigorously stirred, particle-free (Note 1) solution of 170 g. (1.02 moles) of phthalic acid and 281 g. of sodium acetate in 1.7 l. of water is cooled in an ice bath while a total of 3400 g. of 3% sodium amalgam (Note 2) is added in 50–100 g. portions (Note 3). With each portion of added amalgam there is also added 10–20 ml. (500 ml. total) of 50% acetic acid. The total addition time required is 4–5 hours. The solution is decanted from the mercury onto a Buchner funnel and filtered with suction through a layer of Celite 545. The cold filtrate is treated with 1.7 l. of cold 20% sulfuric acid; the acid begins to crystallize immediately. After standing for 4 hours at 20–22°, the acid is collected by suction filtration, washed well with ice-cold water, removing excess sulfuric acid, and dried in a vacuum desiccator over sulfuric acid, giving 124 g. (72%) of crystalline product, m.p. 210–213°. A purer product can be obtained by recrystallization. For minimum losses during recrystallization, the crude acid is divided into two portions, and each is added to 1.2–1.5 l. of rapidly stirred, boiling water to effect as rapid a solution as possible. When almost all of the solids have dissolved *ca.* 1 g. of activated charcoal (Norit) is added, the solution is filtered through a fluted filter, and the filtrate is cooled in ice to induce rapid crystallization (Note 4). The colorless crystals are collected by filtration and dried under reduced pressure, yielding 93–107 g. (54–62%) of the acid, m.p. 212–214°.

2. Notes

1. If any crystals of phthalic acid are present, crystallization will occur on cooling.
2. The 3% sodium amalgam was prepared by the procedure in *Org. Synth., Coll. Vol. 2*, 609, (1943), (Note 3), with the following explanation. The mineral oil and sodium are placed in a 1-l. heavy-wall filter flask and heated on a hot plate until the sodium is molten. To this hot, strongly swirled mixture is added mercury from a 1-l. separatory funnel. The initial amounts of mercury (about $\frac{1}{4}$ the total) are added in a fine steady stream, gradually increasing the rate of flow as the initial crackling ceases. Fire flashes can be observed if the initial addition is too rapid. Once the initial reaction subsides, the mercury should be added as rapidly as possible, and about the last third can be essentially poured in. The molten amalgam is *immediately* poured into a shallow, porcelainized, metal pan and stirred with a wide spatula so that large chunks are not allowed to form as the amalgam cools. Once cool, the amalgam pieces are washed repeatedly with petroleum ether, removing the mineral oil.
3. Another portion of amalgam and one of acid are added as soon as the gas evolution from the previous addition subsides.
4. The submitters report that treatment with decolorizing carbon may not be necessary. Although the crude product is invariably colorless, a yellow color develops during recrystallization. The checkers found that without decolorization a yellow product of somewhat lower m.p. was obtained.

3. Discussion

The present method, based on a recent publication,² is a modification of that previously reported.³ *trans*-1,2-Dihydrophthalic acid has been converted to the *cis*-anhydride by heating in acetic anhydride,² which on photolysis (Hanovia, type L mercury lamp) yields the photo-anhydride, bicyclo[2.2.0]hex-5-

ene-2,3-dicarboxylic anhydride.^{2,4} The photoanhydride has been converted to bicyclo[2.2.0]hexa-2,5-diene,⁴ bicyclo[2.2.0]hex-2-ene,² and *exo*-bicyclo[2.2.0]hexan-2-ol² as well as certain derivatives of the alcohol. The present procedure also gives a more complete preparation of 3% sodium amalgam.

References and Notes

1. Department of Chemistry, Kansas State University, Manhattan, Kansas 66502.
 2. R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967).
 3. B. R. Landau, Ph.D. Thesis, Harvard University, 1950.
 4. E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85**, 3297 (1963)
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Appendix

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

petroleum ether

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

acetic anhydride (108-24-7)

sodium acetate (127-09-3)

mercury (7439-97-6)

decolorizing carbon (7782-42-5)

sodium (13966-32-0)

phthalic acid (88-99-3)

bicyclo[2.2.0]hex-5-ene-2,3-dicarboxylic anhydride

bicyclo[2.2.0]hexa-2,5-diene

bicyclo[2.2.0]hex-2-ene

trans-1,2-Dihydrophthalic acid,
3,5-Cyclohexadiene-1,2-dicarboxylic acid, trans- (5675-13-8)

exo-bicyclo[2.2.0]hexan-2-ol