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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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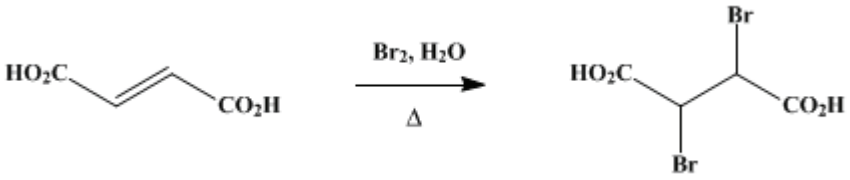
α,β-DIBROMOSUCCINIC ACID

[Succinic acid, α,β-dibromo-]



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1. Procedure

In a 2-l. three-necked, round-bottomed flask, equipped with a mechanical stirrer (Note 1), dropping funnel, and Friedrichs condenser[1] (Note 2), are placed 200 g. (1.7 moles) of fumaric acid (Note 3) and 400 g. of water (Note 4). The materials are thoroughly mixed until the fumaric acid has been completely wet by the water. The resulting thick, viscous mass is then stirred vigorously (Note 5) and brought to boiling by heating on a wire gauze with a Bunsen flame (Note 6).

Two hundred and seventy-six grams (94.3 cc., 1.7 moles) of bromine (Note 7) is now added as rapidly as possible through the dropping funnel, the rate of addition being so controlled that the Friedrichs condenser is continuously about half full of the refluxing liquid (Note 8). This operation takes about one hour (Note 9). After about 100 g. of bromine has been added, the dibromosuccinic acid forms rapidly and separates in tiny white needles. At the completion of the reaction there should be a slight excess of bromine, as indicated by the red color of the solution. Occasionally 5–10 g. of bromine has to be added at this point to ensure an excess.

The reaction flask is now surrounded with ice water and cooled to 10°, with stirring. The product is then collected on a large Büchner funnel, and washed with cold water to remove the bromine liquor. The filtrate may be discarded, as it contains only impurities. The material is dried overnight at room temperature and need not be recrystallized; the yield is 343–400 g. (72–84 per cent of the theoretical amount).

2. Notes

1. A heavy stirrer with as large a paddle as possible is used, in order to rotate the mass of crystals formed during the course of the reaction. A mercury seal is unnecessary, but it is advisable to have the stirrer bearing extend beneath the surface of the liquid.
2. Glass connections or rubber stoppers should be used throughout, as corks are rapidly disintegrated by the hot bromine.
3. Commercial fumaric acid ("practical") is sufficiently pure for this preparation. Directions for preparing fumaric acid are given on p. 302.
4. Any larger amount of water leads to the formation of monobromomalic acid, tartaric acid, and compounds of unknown composition.[2]
5. Vigorous stirring is essential to obtain good yields.
6. It is necessary to keep the reaction mixture boiling throughout the entire course of the reaction. During the addition of the bromine, however, the size of the flame should be reduced considerably, because the reaction is exothermic.
7. The apparatus should be set up under a hood, or the top of the condenser connected to a gas absorption trap for the removal of bromine vapor, small amounts of which escape continually under the conditions of the experiment.
8. By this procedure most of the unchanged bromine is washed back into the flask, so that the amount escaping from the top of the condenser is kept at a minimum.

9. If the bromine is added over a much longer period of time, the yield is materially decreased.

3. Discussion

α,β-Dibromosuccinic acid may be prepared by heating succinic acid with bromine and water in a closed tube at 180°;[3] by heating succinic acid, red phosphorus, and bromine in a closed tube at 140°;[4] by heating fumaric acid with 2 moles of bromine in acetic acid for seven hours in a sealed tube at 100°;[5] from fumaric acid, bromine, and water at 100° under pressure;[6] and by the method described above.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 10

References and Notes

1. Friedrichs, Z. angew. Chem. **33** (I) 30 (1920).
2. Kekulé, Ann. Spl. Bd. **1**, 338 (1861).
3. Kekulé, Ann. **117**, 120 (1861); Ann. Spl. Bd. **1**, 338 (1861); Bourgoin, Bull. soc. chim. (2) **19**, 148 (1873).
4. Gorodetzky and Hell, Ber. **21**, 1729 (1888).
5. Michael, J. prakt. Chem. (2) **52**, 289 (1895).
6. Kekulé, Ann. Spl. Bd. **1**, 129 (1861); Baeyer, Ber. **18**, 674 (1885).

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

red phosphorus

acetic acid (64-19-7)

bromine (7726-95-6)

Succinic acid (110-15-6)

tartaric acid (87-69-4)

Fumaric acid (110-17-8)

α,β-Dibromosuccinic acid,
Succinic acid, α,β-dibromo- (526-78-3)

dibromosuccinic acid

monobromomalic acid