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.

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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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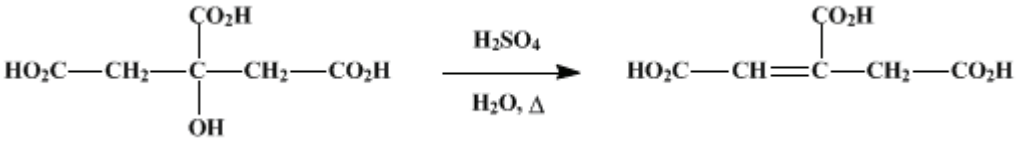
# ACONITIC ACID

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## 1. Procedure

In a 1-l. round-bottomed flask equipped with a reflux condenser (Note 1) are placed 210 g. (1 mole) of powdered citric acid monohydrate and a solution of 210 g. (115 cc., 2 moles) of concentrated sulfuric acid in 105 cc. of water. The mixture is heated in an oil bath kept at a temperature of 140–145° for seven hours. The light brown solution is poured into a shallow dish, and the flask is rinsed with 10 cc. of hot glacial acetic acid. The liquid is allowed to cool slowly to 41–42° (Note 2), with occasional stirring to break up the solid mass of aconitic acid which separates, and the solid is collected on a suction funnel (Note 3). The material is pressed and drained thoroughly until practically dry, when it is removed and stirred to a homogeneous paste with 70 cc. of concentrated hydrochloric acid, cooled in an ice bath. The solid is collected on a suction funnel (Note 3), washed with two 10-cc. portions of cold glacial acetic acid, sucked thoroughly, and spread out in a thin layer on porous plate or paper for final drying (Note 4). This product contains practically no sulfate and is pure enough for most purposes. It is colorless, and when dry weighs 71–77 g. (41–44 per cent of the theoretical amount) (Note 5). The point of decomposition determined under controlled conditions (Note 6) varies from 180° to 200°.

For purification the acid is crystallized from about 150 cc. of glacial acetic acid, using an acid-resistant filter for the hot solution (Note 7). Aconitic acid separates as small, colorless needles weighing 50–60 g., and about 10 g. more can be secured by concentrating the mother liquor under reduced pressure to one-third of its volume. The material is dried in the air and then in a desiccator containing sodium hydroxide in order to remove all traces of acetic acid. One crystallization usually is sufficient to bring the point of decomposition to 198–199° (Note 6).

## 2. Notes

1. A ground-glass connection is highly desirable.
2. By filtering at this point rather than at a lower temperature, a separation from a small amount of low-melting material is accomplished without much loss of aconitic acid.
3. This material may be filtered conveniently by means of a sintered glass funnel, or by using a pad of pure wool flannel in an 8-cm. Büchner funnel.
4. In humid weather the solid often deliquesces, and this necessitates drying in a desiccator. The material retains acetic acid very tenaciously, and drying should be continued until the odor of the solvent no longer can be noticed.
5. A determination by the method of Pucher, Vickery, and Leavenworth[1] showed that 26 g. of citric acid remained in the sulfuric acid solution. It is inadvisable to use this solution for another run; the accumulation of water and by-products reduces the yield and the quality of the product considerably.
6. When heated in a capillary tube aconitic acid decomposes rather suddenly with vigorous gas evolution at a temperature which is closely dependent upon the rate of heating and the temperature at which the sample is introduced. In the literature[2] "melting points" ranging from 182.5° to 194.5° are recorded. The uncrystallized aconitic acid, when introduced at 180° into a small bath provided with mechanical agitation and heated at the rate of 2–3° per minute, usually decomposed at 189–190°. The once recrystallized material, introduced at 190°, decomposed at 198–199°; introduced at 195°, it decomposed at 204–205°. A determination on the Dennis bar,[3] the most reliable method for this type of compound, showed a decomposition point of 209°. The sample must be thoroughly dry to obtain the highest figures.

7. The hot solution is very destructive to filter paper. A convenient filter is made by preparing a 1–2 mm. mat of asbestos in a 6-cm. Büchner funnel, dusting onto this a 2–3 mm. layer of Norite, washing by suction, and heating the unit, together with a suction flask, in an oven at 120°. When dry and hot, the apparatus is ready for use.

## 3. Discussion

Aconitic acid has been prepared from citric acid by the action of sulfuric acid[4] or hydrogen chloride,[5] or by heating.[6] It has been prepared also from methyl acetylcitrate[7] and from acetylcitric anyhdride.[8] The method described is essentially that of Hentschel.[4] Phosphoric acid (85 per cent) can be used in place of sulfuric acid, but much closer regulation of the conditions seems necessary and the yield is not greatly improved.

The effects of acid strength and temperature on the reaction between sulfuric acid and citric acid have been reported by Quartaroli and Belfiori: the use of pyrosulfuric acid, cold, or sulfuric acid of less than 94 per cent strength, hot, leads to the formation of aconitic acid.[9]

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## References and Notes


1. Pucher, Vickery, and Leavenworth, Ind. Eng. Chem., Anal. Ed. **6**, 190 (1934).
2. Malachowski and Maslowski, Ber. **61**, 2521 (1928).
3. Dennis and Shelton, J. Am. Chem. Soc. **52**, 3128 (1930).
4. Hentschel, J. prakt. Chem. (2) **35**, 205 (1887).
5. Hunäus, Ber. **9**, 1751 (1876).
6. Pawolleck, Ann. **178**, 153 (1875).
7. Anschütz and Klingemann, Ber. **18**, 1953 (1885).
8. Easterfield and Sell, J. Chem. Soc. **61**, 1007 (1892).
9. Quartaroli and Belfiori, Ann. chim. applicata **28**, 297 (1938) [C. A. **33**, 1669 (1939)].


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

acetylcitric anyhdride

pyrosulfuric acid

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

sodium hydroxide (1310-73-2)

citric acid (77-92-9)

Norite (7782-42-5)

phosphoric acid (7664-38-2)

Aconitic acid (499-12-7)

citric acid monohydrate (5949-29-1)

methyl acetylcitrate