



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.

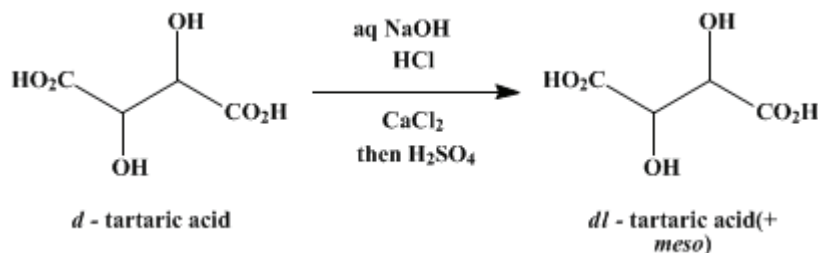
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.497 (1941); Vol. 6, p.82 (1926).

dl-TARTARIC ACID

[By-product, *meso*-Tartaric Acid]



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1. Procedure

In a copper or iron kettle of 4-l. capacity is placed a solution of 200 g. (1.33 moles) of *d*-tartaric acid and 700 g. of sodium hydroxide in 1400 cc. of water. A 12-l. flask through which cold water is run is placed in the mouth of the kettle in order to prevent loss of water vapor, and the mixture is boiled gently over an open flame for four hours. The solution is now transferred to a 12-l. flask or crock and partially neutralized with 1400 cc. of commercial hydrochloric acid (sp. gr. 1.19). To the still alkaline solution is now added just enough sodium sulfide to precipitate all the iron or copper which has been dissolved from the kettle (Note 1). The filtered solution is then just acidified with hydrochloric acid, boiled to expel all hydrogen sulfide, and made very faintly alkaline to phenolphthalein with sodium hydroxide solution. To the hot solution is then added a concentrated solution of 300 g. of anhydrous calcium chloride which causes an immediate precipitation of calcium *dl*-tartrate and *meso*-tartrate.

The mixture is allowed to stand for one week (Note 2) and the precipitate filtered, washed with cold water until free of chlorides, and dried at 40–50°. The yield is 246–315 g. The product is found on analysis to consist principally of the tetrahydrate, C₄H₄O₆Ca·4H₂O (Note 3). It is suspended in 800 cc. of water and treated with the calculated quantity (0.4 g. for every 1.0 g.) of concentrated (95–96 per cent) sulfuric acid. The mixture is warmed on the steam bath, with occasional shaking, or mechanical stirring, for thirty to forty hours (Note 4), filtered hot, and the calcium sulfate washed well with hot distilled water.

The united filtrate is evaporated on the steam bath until the volume amounts to 200 cc., at which point crystals should have already begun to separate from the hot solution. After standing at room temperature for twenty-four hours or longer, the crystals are filtered by suction as free from mother liquor as possible and recrystallized from an equal weight of distilled water (Note 5). The filtrate from this recrystallization is evaporated on the steam bath and the second crop of *dl*-tartaric acid filtered and recrystallized as before. The yield is 65–75 g. (29–33.4 per cent of the theoretical amount).

The sirupy filtrate from the *dl*-tartaric acid, which consists principally of *meso*-tartaric acid together with a small amount of unchanged *d*-tartaric acid, is diluted with its own volume of water and divided into two equal parts; one part is exactly neutralized with potassium hydroxide, using phenolphthalein, and the second part is added. After standing for twenty-four hours the potassium hydrogen *d*-tartrate is filtered off. The filtrate is neutralized with ammonia, then just acidified with acetic acid, and treated with an excess of calcium chloride solution (about 500 cc. of a 25 per cent solution). After standing for a week (Note 2) the precipitated calcium *meso*-tartrate is filtered and washed with cold distilled water. It may, if desired, be recrystallized from boiling water. The yield is 42–55 g. (corresponding to 13–17 per cent of the original *d*-tartaric acid). The sirupy free acid may be prepared from this salt by treatment with sulfuric acid as above.

2. Notes

1. If [iron](#) is not removed at this point it separates with the calcium salt and contaminates the final product. If desired, [copper](#) can be removed at a later stage by passing [hydrogen sulfide](#) through the acid solution.
2. The calcium salts, in particular that of [meso-tartaric acid](#), separate very slowly, and the yield is appreciably lower if the mixture is allowed to stand only eighteen hours.
3. The calcium salt of the principal product, [dl-tartaric acid](#), crystallizes with four molecules of water; the secondary product, [meso-tartaric acid](#), forms a calcium salt which crystallizes with three molecules of water. The amount of [sulfuric acid](#) actually required may readily be calculated from the percentage of [calcium](#) found on analysis in the regular way; or it may be estimated by igniting a sample, and titrating the residue with standard acid.
4. This long treatment is necessary since, on the one hand, the calcium salts tend to be protected by the [calcium sulfate](#) which crystallizes on them, and, on the other hand, it is important to allow all the free [sulfuric acid](#) to react.
5. A very complete separation of the [calcium sulfate](#) may be effected by adding to the concentrated solution 1000 cc. of [alcohol](#), allowing the mixture to stand for twenty-four hours, and filtering. The alcohol is then distilled from the filtrate and the procedure followed as indicated above.

3. Discussion

[dl-Tartaric acid](#) can be prepared by racemization of [d-tartaric acid](#) by heating to 175° with a small amount of water¹ or by boiling with a large excess of concentrated alkali;² and by the oxidation of [fumaric acid](#).³

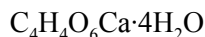
References and Notes

1. Jungfleisch, Compt. rend. **75**, 439 (1872); Bull. soc. chim. (2) **18**, 201 (1872).
2. Meissner, Ber. **30**, 1574 (1897); Holleman, Rec. trav. chim. **17**, 66 (1898); Campbell, Slotin, and Johnston, J. Am. Chem. Soc. **55**, 2604 (1933).
3. Kekulé and Anschütz, Ber. **13**, 2150 (1880); Hofmann, Ehrhart, and Schneider, Ber. **46**, 1667 (1913); Milas and Terry, J. Am. Chem. Soc. **47**, 1412 (1925); Standard Brands, U. S. pat. 2,000,213 [C. A. **29**, 4027 (1935)]; Milas and Sussman, J. Am. Chem. Soc. **58**, 1302 (1936).

Appendix

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

calcium salt



calcium salts

[alcohol](#) (64-17-5)

[calcium chloride](#) (10043-52-4)

[sulfuric acid](#) (7664-93-9)

hydrochloric acid (7647-01-0)
acetic acid (64-19-7)
ammonia (7664-41-7)
sodium hydroxide (1310-73-2)
iron (7439-89-6)
hydrogen sulfide (7783-06-4)
copper (7440-50-8)
calcium sulfate (7778-18-9)
potassium hydroxide (1310-58-3)
calcium (7440-70-2)
dl-tartaric acid (87-69-4)
sodium sulfide (1313-82-2)
Fumaric acid (110-17-8)
phenolphthalein (77-09-8)
D-tartaric acid (147-71-7)
meso-Tartaric Acid (147-73-9)
calcium dl-tartrate (3164-34-9)
meso-tartrate
potassium hydrogen d-tartrate
calcium meso-tartrate