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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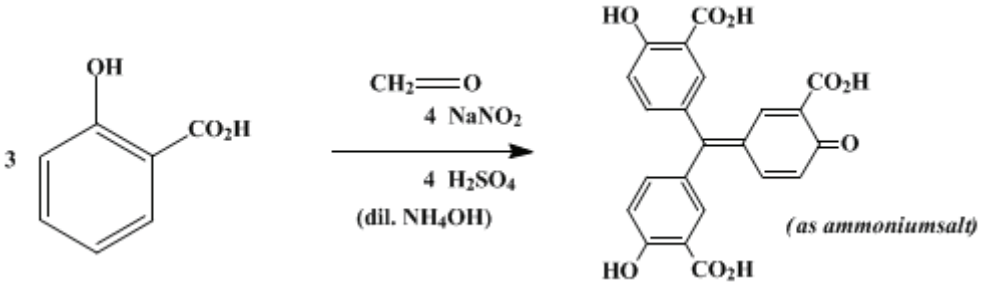
AMMONIUM SALT OF AURIN TRICARBOXYLIC ACID



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1. Procedure

To 70 cc. of concentrated sulfuric acid (Note 1) in a 1-l. short-necked flask fitted with a mechanical stirrer and immersed in an ice-water bath is added, with vigorous stirring, 10 g. (0.145 mole) of solid sodium nitrite in small portions. The addition is made at such a rate that only a very small amount of nitrogen oxide is evolved. When solution is complete, 20 g. (0.145 mole) of salicylic acid is added in small portions with stirring; about fifteen minutes is required. The mixture is stirred at 20° until all the solid is in solution (Note 2). The mixture should then be light red to brown in color, very viscous, and quite homogeneous. It is surrounded by an ice-salt bath, and, when the temperature reaches 0°, 5 cc. (0.065 mole) of a 35–40 per cent solution of formaldehyde (formalin) (see Note 1 on p. 378) is slowly added with extremely vigorous stirring, at such a rate that the temperature does not rise above 5° (Note 3). The reaction is complete a few minutes after all the formaldehyde has been added. About 100 g. of finely crushed ice is then added, followed by 500 cc. of ice water; the stirring should be vigorous during the addition (Note 4). The contents of the flask are stirred until the aurin tricarboxylic acid has disintegrated into small pieces.

The solid is washed several times by decantation, using cold water, and finally filtered with suction. It is then dissolved in dilute ammonia (1 volume of concentrated ammonia with 2 volumes of water) while it is still on the filter paper in the suction funnel (Note 5). The filtrate is evaporated to dryness on a steam bath. The resulting glassy, light yellowish-brown ammonium salt, which weighs 19–22 g. (83–96 per cent of the theoretical amount) is sufficiently pure (Note 6) for use as a test for aluminum.[1]

2. Notes

1. The reaction may be carried out somewhat less satisfactorily with the use of 55 cc. of sulfuric acid.
2. If solution is not complete, unchanged salicylic acid will be present in the final product.
3. If the stirring is quite violent, the temperature may be allowed to rise somewhat higher, say to 15–20°, but if the temperature is allowed to rise with only moderate stirring, the yield is lowered, owing to the formation of tars.
4. Foaming may occur during the addition of the water but this can be controlled by adding a few drops of ether.
5. The purification of the crude aurin tricarboxylic acid by extracting with hot water[1] is undesirable, for the hot water causes the acid to soften, and results in the formation of large viscous semiliquid masses which cannot be washed readily.
6. The method suggested by Caro[2] for the purification of aurin tricarboxylic acid seems to be unnecessary when the dye is to be used as a test for aluminum.[1] In the method the crude product is dissolved in sodium hydroxide, sodium bisulfite is added until the solution is decolorized, and the addition compound of the free acid is precipitated by adding hydrochloric acid.

3. Discussion

The preparation of aurin tricarboxylic acid was first described in a patent[3] granted to Geigy, in which the foregoing method is embodied in one of the examples; another method, involving the action of sodium nitrite upon a warm solution of salicylic acid in a mixture of methyl alcohol and sulfuric acid, is also described in the same patent. It can also be prepared[2] by the action of sulfuric acid and nitrite upon a mixture of salicylic acid and 3,3'-dicarboxy-4,4'-dihydroxydiphenylmethane ("methylene disalicylic acid"), which is formed from salicylic acid with formaldehyde in presence of hydrochloric acid.

References and Notes

1. Hammett and Sottery, J. Am. Chem. Soc. **47**, 142 (1925).
2. Caro, Ber. **25**, 939 (1892).
3. Geigy, Ger. pat. 49,970 [Frdl. **2**, 50 (1891)]; Holaday, J. Am. Chem. Soc. **62**, 989 (1940).

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

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

methyl alcohol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

formaldehyde,
formalin (50-00-0)

sodium nitrite (7632-00-0)

nitrite (14797-65-0)

AMMONIUM SALT OF AURIN TRICARBOXYLIC ACID (569-58-4)

nitrogen oxide

salicylic acid

aurin tricarboxylic acid

aluminum (7429-90-5)

sodium bisulfite (7631-90-5)

3,3'-dicarboxy-4,4'-dihydroxydiphenylmethane

methylene disalicylic acid