



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.

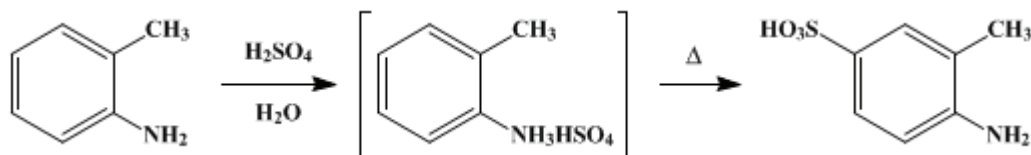
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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***o*-TOLUIDINESULFONIC ACID**

[*m*-Toluenesulfonic acid, 6-amino-]



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1. Procedure

In a 500-ml. three-necked round-bottomed flask, fitted with a stirrer, thermometer, and 250-ml. dropping funnel, are placed 19 ml. of water and 27.8 ml. (0.5 mole) of concentrated **sulfuric acid** (sp. gr. 1.84), and the whole is warmed to 70°. From the dropping funnel is added, dropwise, over a 30-minute period, 53.5 g. (0.5 mole) of ***o*-toluidine** (Note 1). The temperature is allowed to reach about 85° in order to prevent the separation of solid before all the amine has been added. When addition is complete, the temperature is raised to 100–105° for 5 minutes. The flask is then placed on a steam bath, the stirrer and dropping funnel are removed, and the flask is evacuated by means of a water pump to about 15 mm. (Note 2); after 21 hours all the water has been removed. The flask is then immersed in an oil bath, and the internal temperature is raised to 180° over a period of 2 hours and kept at 180–195° (bath temperature about 190–205°) for 7 hours while the same diminished pressure is maintained (Note 3). The crude product is dissolved in 1.3 l. of boiling water, and 99 g. of **barium hydroxide octahydrate** is added with stirring; the solution is now alkaline to litmus. After the addition of 3 g. of **Norit**, the solution is heated for 1.5 hours on a steam bath, and 17.5 ml. of concentrated **sulfuric acid** (sp. gr. 1.84) diluted with 20 ml. of water is added with good stirring. The solution is heated to 96° and filtered through a large, preheated Büchner funnel; the filter cake is rinsed with 100 ml. of boiling water (Note 4).

The filtrate is transferred to a 3-l. round-bottomed flask and concentrated under a pressure of about 50 mm. to a volume of 200 ml. (Note 5). After the mixture has been chilled overnight in a refrigerator, the crystalline acid (68–74 g.) is filtered by suction and dried (Note 6). An additional small amount (5–8 g.) can be obtained by evaporating the filtrate to dryness. This residue is allowed to remain in contact with 75 ml. of **methanol** for about an hour with occasional shaking. The solid is filtered, dried, and weighed. The total yield of ***o*-toluidinesulfonic acid** is 74–79 g. (79–83%) (Note 7) and (Note 8).

2. Notes

1. The amine used should boil over a range of not more than 2°.
2. If time is an important consideration, and a smaller yield (60%) is acceptable, the procedure may be modified: the acid sulfate is heated for 1 hour under reduced pressure; the temperature is then raised to 180° for 1 hour and finally to 180–190° for 3 hours. The solid residue is taken up in 1 l. of hot water and 55 ml. of 40% **sodium hydroxide**, a small amount of unchanged amine is distilled with steam, and the clear solution is treated with **Norit** and filtered as above. The acid is then precipitated by adding 65 ml. of concentrated **hydrochloric acid**.
3. During this time the amine acid sulfate melts and loses water, and the product solidifies to a white crystalline mass.
4. Low yields may result from crystallization of some of the acid in the funnel at this point if the funnel is preheated insufficiently. Some acid may also be lost in the large bulk of inorganic solid. Filtration through the finely divided filter cake is often so slow that the under side and stem of the funnel collect large amounts of crystalline acid which is not rinsed out by the 100 ml. of boiling water. The use of a steam-heated Büchner funnel or prolonged preheating of an ordinary Büchner funnel does not seem to

minimize this effect. It is advisable to remove the funnel after filtration is complete, and to take out the filter cake and rinse the funnel with two 100-ml. portions of boiling water. The combined washings are heated to boiling and filtered, and the filtrate is added to that obtained in the original filtration.

5. The flask should be equipped with a still head to prevent carry-over of the solution during distillation; a capillary jet is also an aid in this evaporation. Much of the acid separates during this concentration; the crystals are easily filterable.

6. The acid was spread out on a large filter paper and dried above a steam radiator for 48 hours. The literature reports the acid to be a monohydrate which loses its water of crystallization by drying at 120° for 3 hours. However, titration of the air-dried acid showed that it was not hydrated. A sample of the acid heated to 120° for 3 hours showed no change in neutral equivalent.

7. This aminosulfonic acid has no definite melting point. On a Maquenne block a decomposition range of 335–380° was observed.

8. The product secured by this procedure is free from [sodium sulfate](#) and isomeric sulfonic acids. Titrations of the first crop of crystals gave neutral equivalents ranging from 187.0 to 187.6; the calculated neutral equivalent is 187.2. The second crop is less pure since it had a neutral equivalent of about 177.

3. Discussion

[o-Toluidinesulfonic acid](#) has been obtained by a variety of reactions. Of these the ones of preparative value are the sulfonation of [o-toluidine](#) by fuming [sulfuric acid](#),^{1,2,3} the rearrangement of the amine sulfate or acid sulfate,^{4,5} and the reduction of the corresponding nitrotoluenesulfonic acid.⁶ The above procedure is based on the directions of Huber,⁵ who has described the preparation of ten aminoarylsulfonic acids by this method.

References and Notes

1. Gerver, *Ann.*, **169**, 374 (1873).
 2. Claus and Immel, *Ann.*, **265**, 72 (1891).
 3. Schultz and Lucas, *J. Am. Chem. Soc.*, **49**, 299 (1927).
 4. Neville and Winther, *Ber.*, **13**, 1941 (1880).
 5. Huber, *Helv. Chim. Acta*, **15**, 1372 (1932).
 6. Foth, *Ann.*, **230**, 306 (1885).
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Appendix

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

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

[hydrochloric acid](#) (7647-01-0)

[methanol](#) (67-56-1)

[sodium hydroxide](#) (1310-73-2)

[sodium sulfate](#) (7757-82-6)

[Norit](#) (7782-42-5)

[barium hydroxide octahydrate](#) (12230-71-6)

[o-toluidine \(95-53-4\)](#)

[o-Toluidinesulfonic acid \(98-33-9\)](#)

[m-Toluenesulfonic acid, 6-amino- \(88-44-8\)](#)