



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.

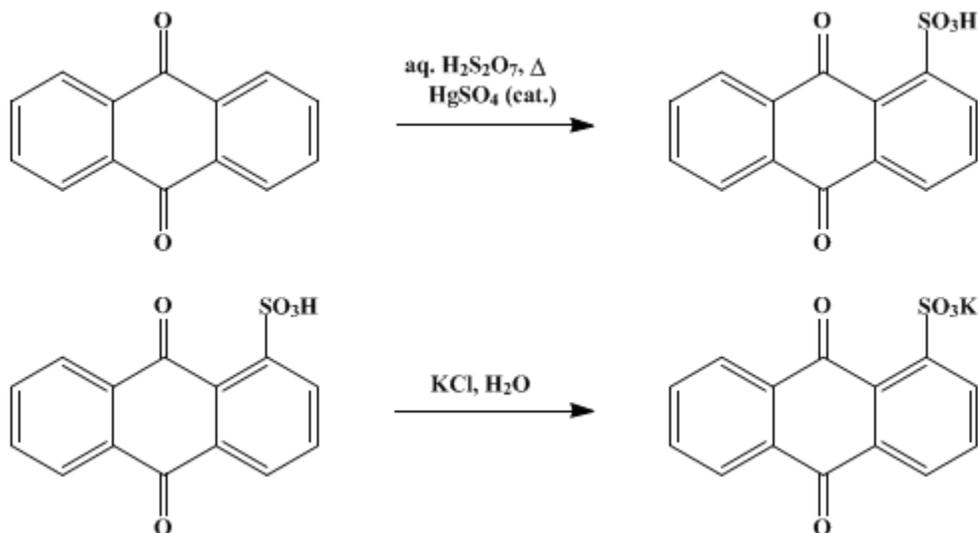
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.539 (1943); Vol. 18, p.72 (1938).

POTASSIUM ANTHRAQUINONE- α -SULFONATE

[1-Anthraquinonesulfonic acid, potassium salt]



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1. Procedure

A 500-cc. three-necked flask fitted with a mechanical stirrer (Note 1) and a thermometer is half immersed in an oil bath mounted in a hood. In the flask are placed 120 g. of 19–22 per cent oleum and 1 g. of yellow mercuric oxide, the bath is warmed to 100° , and 100 g. (0.48 mole) of anthraquinone (Note 2) is added through a powder funnel attached by a piece of wide rubber tubing. The mixture is stirred vigorously and heated at 147 – 152° for forty-five to sixty minutes, after which the bath is removed and the flask is lowered from the stirrer and replaced by a 2-l. beaker containing 1 l. of hot water. While the water is being stirred, the hot acid solution is poured cautiously down the inner wall of the beaker; the mixture is then boiled for five minutes longer with stirring. After the unchanged anthraquinone (53–59 g.) (Note 3) is collected by suction on a 20-cm. Büchner funnel provided with a cotton filter cloth, it is washed with 200 cc. of hot water. The light brown filtrate, together with the wash water, is heated to 90° , and a solution of 32 g. of potassium chloride in 250 cc. of water is added. After cooling to room temperature (Note 4), the potassium salt, which crystallizes in the form of pale yellow leaflets, is collected on a large Büchner funnel (filter paper) and washed with 200 cc. of cold water. The yield of product, dried at 100° *in vacuo*, is 57–55 g. (Note 5) (77–86 per cent of the theoretical amount based on the anthraquinone converted) (Note 6) and (Note 7).

2. Notes

1. It is necessary to provide an efficient stirrer driven by a powerful motor. The yields reported were obtained using a Hershberg Chromel wire stirrer (p. 117); with other stirrers the yields were about 10 per cent lower.
2. The anthraquinone employed melted at 284.5 – 285.5° (corr.). It may be prepared conveniently by oxidation of anthracene (p. 554).
3. The recovered material contains mercury and other impurities and melts at 265 – 275° . When this is used as such in a second run, there is considerably more disulfonation than with pure anthraquinone.
4. Under the conditions specified very little disulfonation occurs, so that the crystallizing mixture may be allowed to cool to 25° without danger of contamination of the product with disulfonates. When recovered anthraquinone is employed, it is advisable to collect the product when the mixture has cooled

to 60°, for the disulfonates present are then retained in the mother liquor. The solubilities of the 1,5- and 1,8-disulfonates increase more rapidly with increasing temperature than does the solubility of the α -monosulfonate.

5. The 57-g. yield refers to the experiment in which 53 g. of starting material was recovered; the percentage yield improves with increase in the amount of [anthraquinone](#) recovered.

6. The purity of the product may be checked by converting a sample to [\$\alpha\$ -chloroanthraquinone](#) (p. 128) and taking the melting point; that from the above salt melted at 158–160° (corr.).

7. The conditions adopted in this procedure favor the production of the α -monosulfonate in a state of high purity at the expense of a high conversion of [anthraquinone](#). A better conversion can be achieved by conducting the sulfonation at a higher temperature, or by using more oleum, but in either case there is a considerable increase in the amount of disulfonic acids formed. The extent of β -sulfonation is not influenced greatly by the temperature but is dependent chiefly on the amount of mercuric salt present in the solution. The amount specified corresponds approximately to the limit of solubility of the salt in the acid employed, and very little of the β -acid is formed. As the potassium β -sulfonate is more soluble than the α -salt, traces of this isomer are easily eliminated by crystallization.

3. Discussion

The only practical method for the preparation of anthraquinone- α -sulfonates is based upon the discovery¹ that in the presence of a small amount of mercuric salt anthraquinone is sulfonated chiefly in the α -rather than in the β -position. Detailed procedures are described by Fierz-David,² by Lauer,³ and by Groggins;⁴ the above directions are based largely upon the observations of Lauer.³

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 128](#)
- [Org. Syn. Coll. Vol. 3, 573](#)

References and Notes

1. Iljinsky, *Ber.* **36**, 4194 (1903); Schmidt, *ibid.* **37**, 66 (1904).
2. Fierz-David, *Helv. Chim. Acta* **10**, 197 (1927).
3. Lauer, *J. prakt. Chem. (2)* **130**, 185 (1931); *ibid.* (2) **135**, 164 (1932).
4. Groggins, "Unit Processes in Organic Synthesis," pp. 268–269, McGraw-Hill Book Company, New York, 1935.

Appendix

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

oleum

anthraquinone- α -sulfonates

[mercury](#) (7439-97-6)

[mercuric oxide](#) (21908-53-2)

[Anthraquinone](#) (84-65-1)

[anthracene](#) (120-12-7)

potassium chloride (7447-40-7)

α -Chloroanthraquinone (82-44-0)

Potassium anthraquinone- α -sulfonate,
1-Anthraquinonesulfonic acid, potassium salt (30845-78-4)