



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](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.

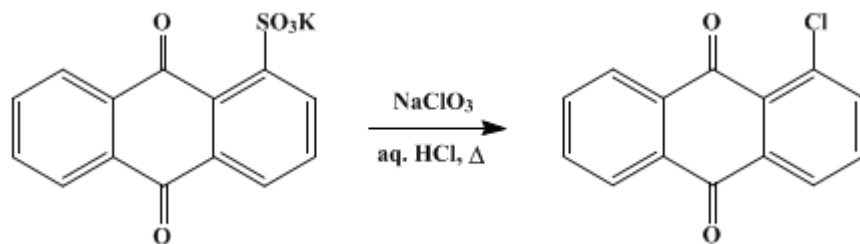
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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.128 (1943); Vol. 18, p.15 (1938).*

## **$\alpha$ -CHLOROANTHRAQUINONE**

[Anthraquinone, 1-chloro-]



Submitted by W. J. Scott and C. F. H. Allen.  
Checked by Louis F. Fieser and E. B. Hershberg.

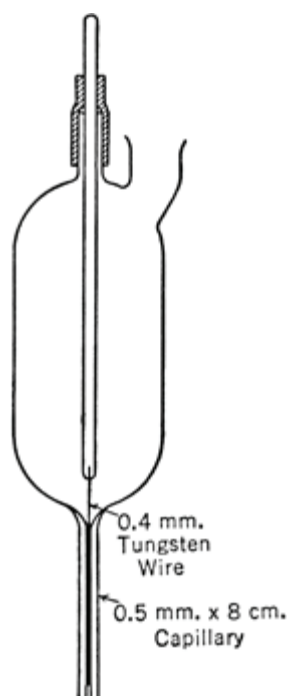
### 1. Procedure

A 2-l. three-necked flask fitted with a stirrer (Note 1) and (Note 2), condenser, and dropping funnel (Note 3) is mounted in the hood, and in it are placed 20 g. (0.061 mole) of potassium anthraquinone- $\alpha$ -sulfonate (p. 539), 500 cc. of water, and 85 cc. (1 mole) of concentrated hydrochloric acid. The solution is heated to boiling and stirred, while a solution of 20 g. (0.19 mole) of sodium chlorate (Note 4) in 100 cc. of water is added dropwise over a period of three hours (Note 5). The mixture is refluxed very slowly for an additional hour before the precipitated  $\alpha$ -chloroanthraquinone is collected by suction filtration and washed free from acid with hot water (about 350 cc.). After drying *in vacuo* at 100°, the bright yellow product melts at 158–160° (corr.) and weighs 14.6–14.7 g. (97–98 per cent of the theoretical amount) (Note 6) and (Note 7).

### 2. Notes

1. Since the mixture tends to foam toward the end of the reaction, it is advisable to use an effective stirrer. A Hershberg stirrer (p. 117) of tantalum wire gave good service in the hands of the checkers; the metal was not appreciably attacked after repeated use.
2. Although a glass sleeve for the stirrer is fairly satisfactory, it is better to use a seal of the conventional type (Org. Syn. Coll. Vol. I, 1941, 33, Fig. 2a) filled with water rather than mercury.
3. Since the usual dropping funnel has the disadvantage of requiring considerable attention from the operator, the checkers found it much more convenient to employ the device (of E. B. H.) shown in Fig. 5.

Fig. 5



4. [Potassium chlorate](#) is less satisfactory because of its lower solubility.
5. If the addition is too rapid or the boiling too vigorous, chlorinating gases are lost through the condenser.
6. Crystallization of the product from 200 cc. of *n*-butyl alcohol gives 13.4 g. of material in the form of yellow needles, m.p. 161–162° (corr.). Larger amounts are conveniently crystallized from [toluene](#), using 2 cc. per gram.
7. The melting point given for highly purified [α-chloroanthraquinone](#) is 162.5° (corr.). The possible contaminants include the β-isomer, 1,5-, and 1,8-dichloroanthraquinone, all of which melt at higher temperatures but depress the melting point of the α-monochloro compound.

### 3. Discussion

[α-Chloroanthraquinone](#) has been prepared from [α-aminoanthraquinone](#) by the diazo reaction,<sup>1</sup> by the action of [thionyl chloride](#) on [potassium anthraquinone-α-sulfonate](#) under pressure,<sup>2</sup> and by the above process.<sup>3</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 539](#)
- [Org. Syn. Coll. Vol. 3, 573](#)
- [Org. Syn. Coll. Vol. 4, 68](#)
- [Org. Syn. Coll. Vol. 4, 746](#)
- [Org. Syn. Coll. Vol. 4, 840](#)

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### References and Notes

1. Bayer and Company, Ger. pat. 131,538 [Frdl. **6**, 311 (1900–02)]; Groggins, "Unit Processes in Organic Syntheses," p. 175, McGraw-Hill Book Company, New York, 1935.
2. Meister, Lucius, and Brüning, Ger. pat. 267,544 (Chem. Zentr. **1914**, I, 89).
3. Bayer and Company, Ger. pat. 205,195 (Chem. Zentr. **1909**, I, 414); Badische Anilin- und Soda-Fabrik, Ger. pat. 228,876 (Chem. Zentr. **1911**, I, 102); Ullmann and Ochsner, Ann. **381**, 1 (1911).

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

1,5-, and 1,8-dichloroanthraquinone

hydrochloric acid (7647-01-0)

thionyl chloride (7719-09-7)

mercury (7439-97-6)

n-butyl alcohol (71-36-3)

toluene (108-88-3)

sodium chlorate (7775-09-9)

potassium chlorate (3811-04-9)

$\alpha$ -Chloroanthraquinone,  
Anthraquinone, 1-chloro- (82-44-0)

Potassium anthraquinone- $\alpha$ -sulfonate (30845-78-4)

$\alpha$ -aminoanthraquinone (82-45-1)