



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.

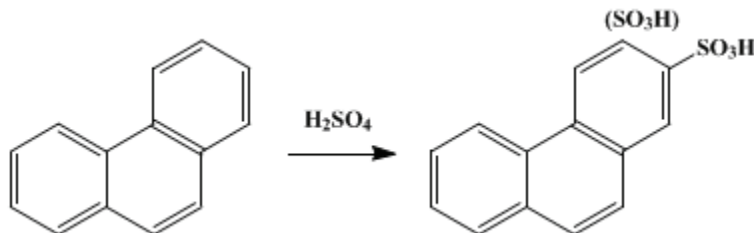
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.482 (1943); Vol. 16, p.63 (1936).

2- AND 3-PHENANTHRENESULFONIC ACIDS



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1. Procedure

The sulfonation is carried out in a 2-l. round-bottomed, three-necked flask fitted with a thermometer, a dropping funnel, and a stirrer (Note 1). Five hundred grams (2.8 moles) of pure phenanthrene (Note 2) is melted in the flask, which is clamped in an oil bath heated to 110°. Mechanical stirring is started, and 327 cc. (600 g., 5.8 moles) of concentrated sulfuric acid is run in at such a rate that the internal temperature does not rise above 120° (ten to fifteen minutes). The reaction mixture is stirred and maintained at a temperature of 120–125° for three and one-half hours, when a test portion should give a nearly clear solution in water. The reaction is exothermic, and the bath must be kept at a temperature 5–10° below that of the mixture. Some sulfur dioxide is given off, and the mixture becomes green.

The viscous solution, while still hot, is dissolved in 4 l. of water, and a solution of 400 g. of sodium hydroxide in 600–800 cc. of water is added. After thorough cooling in an ice bath, the precipitated sodium salt is collected on a large funnel, pressed well, and washed thoroughly with 1 l. of half-saturated sodium chloride solution (about 180 g. per liter). The precipitate contains chiefly the sodium 2- and 3-sulfonates. The filtrate contains a mixture of disulfonates and is discarded (Note 3). In order to effect a preliminary concentration of the less-soluble 2-isomer, the sodium salt mixture is dissolved in 7–8 l. of boiling water containing 100 cc. of concentrated hydrochloric acid (Note 4), and the filtered solution is then neutralized with sodium hydroxide and allowed to crystallize. After separating the mother liquor (A), which is saved, the crystals (consisting largely of the sodium 2-sulfonate) are dissolved in about 8 l. of boiling water (Note 5), and 100 g. of solid barium chloride dihydrate is added to the hot solution. The fine white precipitate of barium 2-phenanthrenesulfonate which forms is digested at the boiling point for a short time and then brought onto a 20-cm. Büchner funnel, preheated on the steam bath. The mother liquor (B) is saved.

The precipitated barium 2-sulfonate always retains a certain quantity of the 3-sulfonate, which must be extracted with hot water. The precipitate is digested at the boiling point with 6-l. portions of boiling water until the residual salt is found to be free from isomers. The purity is determined from the melting point of the *p*-toluidine salt, in the manner described below. Usually two or three such washings are required. The mother liquor (B) from the barium 2-sulfonate is combined with the various washings, and the whole is boiled down to a volume of about 6 l. Sulfuric acid (25–30 cc. of concentrated acid, diluted with water) is then added to precipitate the barium; the filtered solution (Note 6) is concentrated to about 2 l. and neutralized with potassium hydroxide to bring down a mixture of potassium sulfonates (C). The filtrate from the potassium salts may be boiled down further and treated with potassium chloride to ensure complete recovery of the potassium sulfonates, and then discarded. The potassium salt mixture collected in these operations is set aside. (C).

The mother liquor (A) from the sodium salt crystallization is boiled down to a volume of about 2–3 l., and 200 g. of potassium chloride is added to the hot solution. The potassium salt mixture which separates on cooling is collected and combined with the potassium salts (C) described in the preceding paragraph; the filtrate is discarded. The combined material is dissolved in the minimum amount of hot

water, and the filtered solution is heated to boiling and allowed to cool without disturbance. It deposits a large crop of the potassium 3-sulfonate in a very pure condition (180–210 g.). The mother liquor, containing more of the 3-sulfonate together with some of the 2-sulfonate, is concentrated to a small volume; the product is salted out with potassium chloride and washed free of sulfate ion with potassium chloride solution. A hot aqueous solution of this material is then treated with 10 g. of barium chloride dihydrate, and the precipitated barium 2-sulfonate (5–10 g.) is washed free of isomers. The original filtrate is reserved, but the washings are discarded. From the original filtrate, by evaporation, precipitation of the barium with sulfuric acid, neutralization with potassium hydroxide, and crystallization of the product, there is obtained an additional quantity of the pure potassium 3-sulfonate (50–70 g.).

The yields are: barium 2-phenanthrenesulfonate, 150–200 g. (17–21 per cent); potassium 3-phenanthrenesulfonate, 200–220 g. (24–26 per cent) (Note 7) and (Note 8).

Identification and Test of Purity.—The method¹ consists in the preparation and examination of a test sample of the *p*-toluidine salt of the sulfonic acid (Note 9). An aqueous solution of the free sulfonic acid (or of the sodium or potassium salt) is treated with an excess of *p*-toluidine and hydrochloric acid, enough water is added to bring all the material into solution at the boiling point, and crystallization is allowed to take place. The crystals should be washed well with water. A barium salt should be boiled with dilute sulfuric acid, a little decolorizing carbon added, and the filtered solution treated with *p*-toluidine. If the amine salt separates in an oily condition, the walls of the vessel should be scratched, for the *p*-toluidine salt, particularly that of the 3-acid, may remain as an oil for a short time, even when nearly pure. On the other hand, a rather impure acid gives a *p*-toluidine salt which remains as an oil almost indefinitely. This property characterizes a mixture of isomers nearly as definitely as the depression in the melting point, though this is large. In determining the melting point of an amine salt, the sample may be dried by pressing the material on a filter paper, but the capillary should be placed in the bath when the temperature is below 130°. The preliminary heating gives ample provision for thorough drying, without which the material may melt twenty to thirty degrees below the true melting point.

The *p*-toluidine salt of 2-phenanthrenesulfonic acid forms flat needles or plates melting at 282° (291° corr.); that of the 3-acid forms thick needles melting at 217° (222° corr.).

2. Notes

1. A convenient form of stirrer is made by bending a glass rod to an angle of 45° about 4 cm. from the end. This type of stirrer can be used to dislodge material adhering to the walls of the flask.
2. A pure grade of phenanthrene should be used. Technical 70 per cent phenanthrene may be purified by the method of Cohen and Cormier.² It is important to note that the presence of more than about 2 per cent of anthracene in phenanthrene raises the melting point.
3. It is estimated that no less than twelve isomeric disulfonates are present. No useful products have been obtained from the mixture.
4. The solubility of the sulfonates is increased appreciably by the presence of a mineral acid.
5. A 10-l. enameled pail heated with a ring burner serves as a convenient, if not very durable, vessel for boiling and evaporating the large volumes of solution involved. The contents may be ladled out with a casserole.
6. The addition of a little decolorizing carbon greatly facilitates the coagulation of barium sulfate and aids in retaining it on the filter.
7. The low yield of the monosulfonates is due in large part to the fact that disulfonic acids are invariably formed along with the mono acids.
8. For some reactions, such as alkali fusion, the barium salt of the 2-phenanthrenesulfonic acid is suitable. For conversion into the potassium salt, it is highly advisable to use the barium salt in the moist and finely divided condition in which it is first obtained. Since the reaction is slow at best, several fresh portions of sulfuric acid should be employed for precipitating the barium.
9. This is recommended as a general method of identifying sulfonates. In economy of time and material it is superior to the preparation of the free acid, the acid chloride, the ester, the amide, or the phenol. By this method one can identify quickly a few milligrams of an acid or of any of its metal salts, whether it

is in the solid state or in solution.

3. Discussion

The sulfonation of [phenanthrene](#) has been studied by Werner and his students,³ by Sandqvist,⁴ by Fieser,¹ and by Ioffe.⁵

References and Notes

1. Fieser, J. Am. Chem. Soc. **51**, 2460, 2471 (1929).
 2. Cohen and Cormier, *ibid.* **52**, 4363 (1930).
 3. Werner *et al.*, Ann. **321**, 248 (1902).
 4. Sandqvist, *ibid.* **392**, 76 (1912).
 5. Ioffe, J. Gen. Chem. (U.S.S.R.) **3**, 448 (1933) [C. A. **28**, 1694 (1934)].
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

2- AND 3-PHENANTHRENESULFONIC ACIDS

barium salt of the 2-phenanthrenesulfonic acid

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

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

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

[sodium chloride](#) (7647-14-5)

[sulfur dioxide](#) (7446-09-5)

[barium sulfate](#) (7727-43-7)

[decolorizing carbon](#) (7782-42-5)

[potassium hydroxide](#) (1310-58-3)

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

[barium](#) (7440-39-3)

[potassium chloride](#) (7447-40-7)

[barium chloride dihydrate](#) (10326-27-9)

[phenanthrene](#) (85-01-8)

Barium 2-phenanthrenesulfonate

Potassium 3-phenanthrenesulfonate

p-toluidine (106-49-0)

p-toluidine salt of 2-phenanthrenesulfonic acid