



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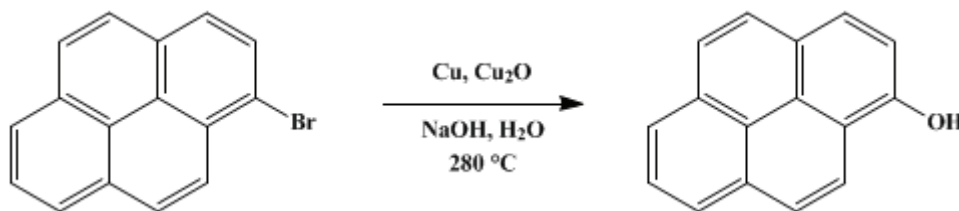
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.632 (1973); Vol. 48, p.94 (1968).

3-HYDROXYPYRENE

[1-Pyrenol]



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Checked by William G. Dauben, John R. Wiseman, and Michael H. McGann.

1. Procedure

Caution! Many pyrene derivatives are carcinogens. Contact of the skin with these materials should be avoided.

In a 100-ml. pressure vessel (Note 1) are placed 14.0 g. (0.050 mole) of 3-bromopyrene (Note 2), 0.5 g. of copper bronze powder (Note 3), 1.5 g. of cuprous oxide (Note 4), and 60 ml. of 10% aqueous sodium hydroxide (Note 5). The vessel is sealed, heated rapidly with shaking to 275–280°, and maintained at this temperature for 3 hours. The vessel is allowed to cool and is opened, and the contents are poured into a 500-ml. beaker containing 200 ml. of water (Note 6). The mixture is filtered, and the filter cake is washed with water until the washings become neutral to pH paper. The combined filtrate and washings, which show a blue fluorescence, are made acid to Congo red paper with 20% aqueous sulfuric acid. The precipitate is collected by filtration, washed free of acid with water, and dried in an oven at 100° to give *ca.* 9 g. of a gray solid.

The solid is boiled under reflux with *ca.* 175 ml. of benzene for 1 hour, and the benzene-insoluble material is removed from the hot mixture by filtration through a medium-grade sintered-glass funnel (Note 7). Small portions of activated alumina are added to the hot filtrate until a strong green fluorescence develops; 20–25 g. is needed (Note 8). The mixture is boiled (Note 9) under reflux for 15 minutes and filtered hot. On concentration and cooling, the fluorescent, lemon-yellow filtrate yields 3-hydroxypyrene as light yellow needles, m.p. 179–181°. An additional quantity of equally pure product is obtained by further concentration of the mother liquor. The total yield is 5.5–6.0 g. (50–55%) (Note 10).

2. Notes

1. Stainless steel and Hastelloy-C vessels were used with equivalent results.
2. This material, m.p. 93–95°, is readily prepared in high yields (78–86%) from commercial pyrene by the method of the submitter,² who used pyrene, m.p. 151–153°, obtained from Chemicals Division, Union Carbide Corp.
3. Copper bronze, type 3310, obtained from U.S. Bronze Powder Works, Inc., Flemington, New Jersey, was used. The use of some grades of copper powder leads to a considerably lower yield.
4. Technical grade cuprous oxide obtained from Baker and Adamson Products, General Chemical Division, Allied Chemical Corp., was used.
5. The amount of sodium hydroxide used does not affect the yield, provided that it is present in a quantity well in excess of that required by the stoichiometry.
6. The sodium salt of 3-hydroxypyrene is somewhat insoluble in the reaction mixture. Dilution before filtration ensures its removal from the copper residues.
7. The funnel should be preheated to prevent crystallization of the product in its pores. The filtration

process can be accelerated by scraping the muddy cake from the funnel surface.

8. The use of a larger quantity reduces the yield with no significant improvement in quality.

9. The presence of the alumina causes the mixture to bump violently. Agitation of the boiling mixture with a magnetically driven stirring bar helps to alleviate this problem. The vessel should be securely clamped.

10. The submitter obtained 25–29 g. (57–67%) of product when the reaction was run with 56.2 g. (0.20 mole) of the bromide in a 400-ml. pressure vessel.

3. Discussion

This procedure is based on the method of Smith, Opie, Wawzonek, and Prichard³ for the preparation of 2,3,6-trimethylphenol. 3-Hydroxypyrene has been prepared by fusion of pyrene-3-sulfonic acid with sodium hydroxide⁴ and by desulfonation of 3-hydroxypyrene-5,8,10-trisulfonic acid with hot, dilute sulfuric acid.⁵

4. Merits of the Preparation

It has been shown⁶ that two mechanisms, elimination-addition (benzyne) and S_N2 displacement, are operative in the liquid-phase hydrolysis of halogenated aromatic compounds. The formation of isomeric phenols as a result of the availability of the benzyne route makes the reaction of limited synthetic value. The incorporation of the copper-cuprous oxide system suppresses reaction via the benzyne route, so that the present method has general utility for the preparation of isomer-free phenols. For example, *p*-cresol is the only cresol formed from *p*-bromotoluene under the conditions of this preparation.

The methods previously reported for the preparation of 3-hydroxypyrene have been found to be unsatisfactory, because of both very poor yields and difficulties in operation.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 147](#)

References and Notes

1. Contribution No. 300 from the Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19899.
2. [W. H. Gumprecht, this volume. p. 147.](#)
3. L. I. Smith, J. W. Opie, S. Wawzonek, and W. W. Prichard, *J. Org. Chem.*, **4**, 318 (1939).
4. H. Vollmann, H. Becker, M. Corell, and H. Streeck, *Ann.*, **531**, 1 (1937); W. Kern, U. S. Patent 2,018,792 (1935) [*C.A.*, **30**, 112 (1936)].
5. E. Tietze and O. Bayer, *Ann.*, **540**, 189 (1939).
6. A. T. Bottini and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 1458 (1957).

Appendix

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

alumina

copper bronze

copper bronze powder

sulfuric acid (7664-93-9)

Benzene,
benzyne (71-43-2)

sodium hydroxide (1310-73-2)

bromide (24959-67-9)

copper,
copper powder (7440-50-8)

cuprous oxide

cresol (95-48-7)

pyrene (129-00-0)

3-Bromopyrene (1714-29-0)

3-Hydroxypyrene,
1-Pyrenol (5315-79-7)

2,3,6-trimethylphenol (2416-94-6)

pyrene-3-sulfonic acid (26651-23-0)

3-hydroxypyrene-5,8,10-trisulfonic acid

copper-cuprous oxide

p-Bromotoluene (106-38-7)

p-CRESOL (106-44-5)

sodium salt of 3-hydroxypyrene