



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. 4, p.484 (1963); Vol. 38, p.32 (1958).*

## 5-FORMYL-4-PHENANTHROIC ACID

[4-Phenanthrenecarboxylic acid, 5-formyl-]



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### 1. Procedure

*Caution! Ozone is extremely toxic and can react explosively with certain oxidizable substances. Ozone also reacts with some compounds to form explosive and shock-sensitive products. Ozone should only be handled by individuals trained in its proper and safe use and all operations should be carried out in a well-ventilated fume hood behind a protective safety shield. [Note added September 2009].*

A solution of 25 g. (0.125 mole) of [pyrene](#) ([Note 1](#)) in 100 ml. of [dimethylformamide](#) ([Note 2](#)) and ([Note 3](#)) is treated with a 50% excess of [ozone](#) ([Note 4](#)). The solution of the ozonide is added at a moderate rate, with stirring, to 500 ml. of 1% aqueous [acetic acid](#). The suspension is allowed to stand overnight ([Note 5](#)), and the resulting solid is collected by filtration and washed with water.

The moist solid is suspended in 200 ml. of 10% aqueous [potassium hydroxide](#) solution, and the suspension is boiled for 5 minutes. The hot solution is filtered, and the remaining solid is again extracted, using 100 ml. of [potassium hydroxide](#) solution.

To the dark-brown combined filtrates is added 100 ml. of [potassium hypochlorite](#) solution ([Note 6](#)), and the resulting solution is permitted to stand overnight. The mixture is then heated on a steam bath for 4 hours. The resulting orange solution is filtered while hot, and 100 ml. of 35% [sodium hydroxide](#) solution is added. The solution is cooled to 5°, the resulting solid is collected by filtration and washed with a small amount of saturated [sodium chloride](#) solution.

The moist sodium salt is digested with 50 ml. of cold 6*N* [hydrochloric acid](#), and after several hours the mixture is filtered and the resulting solid acid dried.

The crude acid is dissolved in 100 ml. of boiling [dimethylformamide](#), and 100 ml. of hot glacial [acetic acid](#) is added. Water is added to the hot solution until it becomes cloudy, and then just enough [dimethylformamide](#) is added to render the solution clear again. It is cooled to 5°, and the resulting acid collected by filtration and washed with glacial [acetic acid](#). Upon drying, 10–11.5 g. (32–38%) of [5-formyl-4-phenanthroic acid](#) ([Note 7](#)), melting at 272–276° ([Note 8](#)), is obtained.

### 2. Notes

1. Technical [pyrene](#), Reilly Tar and Chemical Corp., was employed. Purification did not improve the over-all yield, and purer [pyrene](#) is not sufficiently soluble in [dimethylformamide](#).

2. Freshly distilled [dimethylformamide](#) should be employed. The yields with the technical grade solvent were very erratic.

3. Complete solution is attained by heating the mixture for 5 minutes on a steam bath.

4. An ozonizer similar to that described by Henne and Perilstein<sup>2</sup> was employed. At an [oxygen](#) flow rate of 30 l./hr. it produced about 30 millimoles of O<sub>3</sub> per hour (3% conversion). Under these conditions the ozonization of 25 g. of [pyrene](#) requires about 6 hours.

5. Filtration of the hydrolyzate immediately after decomposition is difficult because of the fine nature of the solid. Upon standing, coagulation takes place to yield a granular brown solid.

6. The [potassium hypochlorite](#) solution was prepared<sup>3</sup> from the [calcium hypochlorite](#) sold by Mathieson Chemical

Corporation under the trade name HTH. If the HTH reagent used is not fresh, it is found that subsequent heating of the filtrate with the [potassium hypochlorite](#) solution does not result in an orange solution. The solution remains dark brown, and the product is distinctly brown. The yield is not affected.

7. Unpublished experiments indicate that [5-formyl-4-phenanthroic acid](#) exists mainly in the cyclic hydroxylactone form.

8. The checkers found that the melting point depends on the rate of heating. A reproducible melting point was obtained if the sample was placed in the bath at 270° and the temperature raised at the rate of two degrees per minute.

### 3. Discussion

The only reported method of preparation of [5-formyl-4-phenanthroic acid](#) is by the reaction described here.<sup>4</sup>

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#### References and Notes

1. Ohio State University, Columbus, Ohio.
2. Henne and Perilstein, *J. Am. Chem. Soc.*, **65**, 2183 (1943).
3. *Org. Syntheses Coll. Vol. 2*, 429 (1943).
4. Vollmann, Becker, Corell, and Streeck, *Ann.*, **531**, 65 (1937).

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#### Appendix

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

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

[acetic acid](#) (64-19-7)

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

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

[oxygen](#) (7782-44-7)

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

[potassium hypochlorite](#)

[ozone](#) (10028-15-6)

[calcium hypochlorite](#) (7778-54-3)

[pyrene](#) (129-00-0)

[dimethylformamide](#) (68-12-2)

[5-Formyl-4-phenanthroic acid](#),  
[4-Phenanthrenecarboxylic acid, 5-formyl-](#) (5684-15-1)