Organic Syntheses

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.

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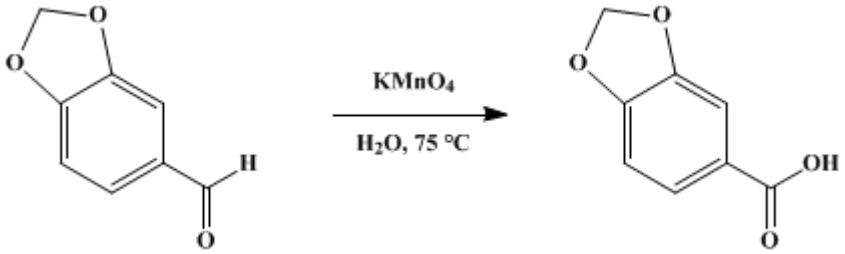
PIPERONYLIC ACID



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1. Procedure

Sixty grams (0.4 mole) of piperonal (Note 1) and 1.5 l. of water are placed in a 5-l. flask fitted with an efficient mechanical stirrer. The flask is placed on a steam bath, heated to 70–80°, and the stirrer started (Note 2). A solution of 90 g. (0.56 mole) of potassium permanganate in 1.8 l. of water is allowed to flow into the emulsion of piperonal and water over a period of forty to forty-five minutes (Note 3). The stirring and heating are continued for an hour longer, at the end of which time the permanganate is reduced. Enough 10 per cent potassium hydroxide solution is added to make the solution alkaline. The mixture is filtered while hot, and the manganese dioxide is washed with three 200-cc. portions of hot water. The combined filtrate and washings are cooled. At this point any unreacted piperonal that separates must be filtered (Note 4). The solution is now acidified with hydrochloric acid, the acid being added until no further precipitate forms. The resulting piperonylic acid is filtered, washed with cold water until free of chlorides, and dried. The yield is 60–64 g. (90–96 per cent of the theoretical amount) of a colorless product melting at 224–225° (corr.). For most purposes the crude material is pure enough, but it may be crystallized from ten times its weight of 95 per cent ethyl alcohol, yielding 52–56 g. (78–84 per cent of the theoretical amount) of needles melting at 227–228° (corr.).

2. Notes

1. The commercial grade of piperonal, m.p. 36°, may be used without purification.
2. The stirring must be sufficiently vigorous to emulsify the molten piperonal thoroughly with the water.
3. Addition of the piperonal to the permanganate lowers the yield to 50 per cent.
4. If the temperature of the reaction mixture is kept between 70° and 80° and the permanganate is added at the rate stated, the piperonal will be entirely oxidized.

3. Discussion

Piperonylic acid has been made by the oxidation of piperic acid,[1] piperonal,[1] safrole,[2] and isosafrole[2] with potassium permanganate. It has also been prepared by the action of methylene iodide on protocatechuic acid[3] in the presence of alkali.

References and Notes

1. Fittig and Mielck, Ann. **152**, 40 (1869).
2. Ciamician and Silber, Ber. **23**, 1160 (1890).
3. Fittig and Remsen, Ann. **168**, 94 (1873).

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

piperic acid

ethyl alcohol (64-17-5)

hydrochloric acid (7647-01-0)

potassium permanganate (7722-64-7)

potassium hydroxide (1310-58-3)

safrole (94-59-7)

manganese dioxide (1313-13-9)

Methylene iodide (75-11-6)

Piperonylic acid (94-53-1)

piperonal (120-57-0)

isosafrole (120-58-1)

protocatechuic acid (99-50-3)