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.

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.
PYROGALLOL 1-MONOMETHYL ETHER

Submitted by Alexander R. Surrey
Checked by Lee Irvin Smith and Chien-Pen Lo.

1. Procedure

The apparatus consists of a 1-l. three-necked flask fitted with a gas inlet tube extending about 3 cm. into the flask and connected to the flask through a bubbler, a thermometer extending to the bottom, a mechanical stirrer, and a reflux condenser connected at the upper end with an exit tube leading to the hood. The reaction is carried out in an atmosphere of illuminating gas (Note 1).

In the flask are placed 60.8 g. (0.4 mole) of 2-hydroxy-3-methoxybenzaldehyde (Note 2) and 200 ml. of 2 N sodium hydroxide (0.4 mole). The mixture is stirred until almost all the solid has dissolved. The stirrer is replaced by a dropping funnel which contains 284 ml. (0.5 mole) of 6% hydrogen peroxide (Note 3). With occasional shaking, the hydrogen peroxide is added in portions of 20–25 ml. About 1 hour is required for the addition; the temperature is kept between 40° and 50°. After the addition of the first portion of hydrogen peroxide, the temperature rises to about 45° and a dark solution results. The temperature is allowed to fall to 40° before the next portion of the peroxide is added.

After all the hydrogen peroxide is added, the reaction mixture is allowed to cool to room temperature and is then saturated with sodium chloride, after which it is extracted four times with 100-ml portions of ether. The combined extracts are dried over sodium sulfate. The ether is removed by distillation on a steam bath, and the residue is then distilled under reduced pressure. Pyrogallol monomethyl ether is collected at 136–138°/22 mm. The yield is 38–44.5 g. (68–80%) of a colorless to light yellow oil which solidifies on standing (Note 4).

2. Notes

1. Nitrogen can be used in place of illuminating gas. The gas is introduced at the rate of about 3 bubbles per second.
2. Practical 2-hydroxy-3-methoxybenzaldehyde (Eastman Kodak Company) was used in this preparation. Care should be taken when working with this material as its vapors are irritating and will cause sneezing.
3. The hydrogen peroxide solution was prepared by diluting 63 g. of a solution containing 27% hydrogen peroxide with water to 284 ml.
4. The procedure described is similar to that of Dakin1 for the preparation of catechol.2 The reaction has been carried out using four times the quantities specified here; the yield was 81% (C. F. H. Allen, private communication).

3. Discussion

Pyrogallol monomethyl ether has been prepared by the methylation of pyrogallol with dimethyl sulfate3 or methyl iodide;4 by the decarboxylation of 2,3-dihydroxy-4-methoxybenzoic acid;5 and by the methylation of pyrogallol carbonate with diazomethane and subsequent hydrolysis.6 The method described is taken from the improved procedure of Baker and Savage7 for the preparation of pyrogalol monomethyl ether from o-vanillin by oxidation with hydrogen peroxide.
This preparation is referenced from:


References and Notes


Appendix

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

- o-vanillin (60-29-7)
- ether (60-29-7)
- sodium hydroxide (1310-73-2)
- sodium chloride (7647-14-5)
- sodium sulfate (7757-82-6)
- nitrogen (7727-37-9)
- dimethyl sulfate (77-78-1)
- Catechol (120-80-9)
- hydrogen peroxide (7722-84-1)
- Methyl iodide (74-88-4)
- Diazomethane (334-88-3)
- pyrogallol (87-66-1)
- pyrogallol monomethyl ether,
  Pyrogallol 1-monomethyl ether (934-00-9)
- 2-hydroxy-3-methoxybenzaldehyde (148-53-8)
- 2,3-dihydroxy-4-methoxybenzoic acid (3934-81-4)
pyrogallol carbonate

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