



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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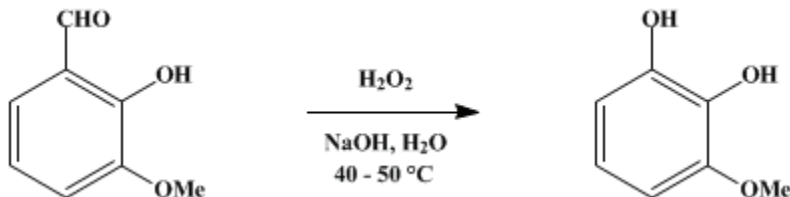
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.759 (1955); Vol. 26, p.90 (1946).

PYROGALLOL 1-MONOMETHYL ETHER



Submitted by Alexander R. Surrey
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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 pyrogallol monomethyl ether from *o*-vanillin by oxidation with hydrogen peroxide.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 753](#)

References and Notes

1. Dakin, *Am. Chem. J.*, **42**, 477 (1909).
 2. Dakin, *Org. Syntheses Coll. Vol. 1*, 149 (1941).
 3. Graebe and Hess, *Ann.*, **340**, 232 (1905).
 4. Herzig and Pollak, *Monatsh.*, **25**, 811 (1904).
 5. Herzig and Pollak, *Monatsh.*, **25**, 507 (1904).
 6. Hillemann, *Ber.*, **71**, 41 (1938).
 7. Baker and Savage, *J. Chem. Soc.*, **1938**, 1607.
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Appendix

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

[o-vanillin](#)

[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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