



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.

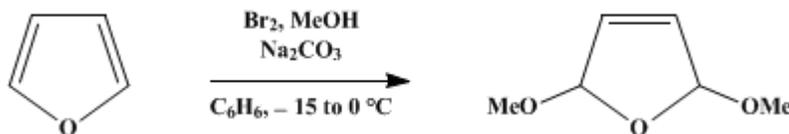
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.403 (1973); Vol. 40, p.29 (1960).

2,5-DIHYDRO-2,5-DIMETHOXYFURAN

[Furan, 2,5-dihydro-2,5-dimethoxy-]



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Checked by Alan E. Black and Henry E. Baumgarten.

1. Procedure

In a 3-l., three-necked flask equipped with a stirrer, thermometer, drying tube filled with Drierite, and a dropping funnel are placed 500 ml. of **methanol**, 500 ml. of **benzene**, 380 g. of anhydrous **sodium carbonate**, and 155 ml. (2.15 moles) of distilled **furan** (Note 1). The slurry is cooled to $< -5^\circ$ with a dry ice-acetone bath (maintained at -10 to -15° during the addition), and an ice-cold solution of 106 ml. (2.0 moles) of **bromine** in 1.0 l. of **methanol** (Note 2) is added dropwise or at such a rate as to maintain a reaction temperature of 0 to -5° . This requires about one hour; the mixture is stirred for an additional 2 hours at $< 0^\circ$ and filtered. The solids collected are washed in the funnel with two 100-ml. portions of **benzene**. The filtrate is stirred for 30 minutes with 100 g. of anhydrous **magnesium sulfate** and refiltered. The solvent is removed at reduced pressure (Note 3) to a volume of about 300 ml. Filtration and washing with **benzene** is repeated (Note 4), the filtrate is stirred for 15–20 minutes with anhydrous **potassium carbonate**, filtered, and distilled through a short packed column to give 195–205 g. (75–79%) of a clear oil, b.p. 80 – 82° (50 mm.), n_D^{25} 1.4333 (Note 5) and (Note 6).

2. Notes

1. The **furan** was distilled from anhydrous **potassium carbonate**. Use of undistilled **furan** gives a lower yield (8–10%).
2. The **methanol** is cooled to about 0° before adding the **bromine**, and the solution is kept cold during the addition.
3. An aspirator, water bath, and short packed column are used, and distillation is continued until the temperature of the distillate begins to rise about 30° . Good stirring is needed here to prevent bumping and local superheating. The pot temperature never exceeds 25 – 30° .
4. If an additional 500 ml. of **methanol** is used in lieu of the recommended 500 ml. of **benzene**, a small, heavier second phase, consisting mostly of **methanol**, water, and salts, may separate at this point. This is removed before drying the filtrate. Later, in the early stages of distillation of the product, if drying has not been thorough enough, water may appear in the distillate. This necessitates further drying, preferably by azeotropeing with **benzene**.
The checkers observed a separation into two layers in some runs even in the absence of added **methanol**. The layers were filtered together and any solids in the funnel were washed with two 100-ml. portions of **benzene**. The combined filtrates were dried with a second 100 g. of anhydrous **magnesium carbonate**.
5. The product from this procedure is yellow, due to **maleic dialdehyde**, and occasionally gives a positive Beilstein test for **bromine**, although its purity is better than 99.5% by glpc. A colorless product is reported² to be obtained by treatment with **sodium methoxide** before the final distillation. Activated alumina treatment of the distillate is also effective.
6. If the product is not used promptly a peroxidation inhibitor should be used. *t*-Butyl catechol (0.01%) is recommended.²

3. Discussion

Numerous 2,5-dialkoxy-2,5-dihydrofurans have been prepared by electrolytic oxidation of **furan** and

substituted furans in alcoholic ammonium bromide^{3,4,5} or by bromine^{6,7} or chlorine⁸ oxidation in the appropriate alcohol. The present method is a modification of the halogen oxidation procedures cited. It is more convenient and gives better yields (~5%) than with chlorine, and halogen-containing byproducts are eliminated in the distillation.

The 2,5-dialkoxy-2,5-dihydrofurans are cyclic acetals of unsaturated dicarbonyl compounds and as such serve as sources thereof. They are also valuable intermediates in the synthesis of numerous types of heterocyclic compounds including those of the tropinone series.³

Hydrogenation of the described product to tetrahydro-2,5-dimethoxyfuran is best accomplished with Raney nickel catalyst at 80–100° and 1700–2000 p.s.i. in 45–60 minutes.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 716](#)

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References and Notes

1. Eastman Kodak Co., Rochester, N.Y. 14650.
2. F. A. Senour, private communication.
3. N. Elming, in R. A. Raphael, E. C. Taylor, and H. Wynberg, "Advances in Organic Chemistry," Vol. 2, Interscience Publishers, New York, 1960, pp. 67–115.
4. N. L. Weinberg and H. R. Weinberg, *Chem. Rev.*, **68**, 449 (1968).
5. S. D. Ross and M. Finkelstein, *J. Org. Chem.*, **34**, 1018 (1969).
6. N. Clauson-Kaas, F. Limborg, and J. Fakstorp, *Acta Chem. Scand.*, **2**, 109 (1950).
7. J. Fakstorp, D. Raleigh, and L. E. Schniepp, *J. Am. Chem. Soc.*, **72**, 869 (1950).
8. D. G. Jones, U. S. Pat., 2,475,097, July 5, 1949.
9. J. F. Stenberg and R. W. Ryan, private communication.

Appendix

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

alumina

[potassium carbonate \(584-08-7\)](#)

[Benzene \(71-43-2\)](#)

[methanol \(67-56-1\)](#)

[ammonium bromide \(12124-97-9\)](#)

[sodium carbonate \(497-19-8\)](#)

[bromine \(7726-95-6\)](#)

[Raney nickel \(7440-02-0\)](#)

[sodium methoxide \(124-41-4\)](#)

chlorine (7782-50-5)

Furan (110-00-9)

magnesium sulfate (7487-88-9)

2,5-Dihydro-2,5-dimethoxyfuran,
Furan, 2,5-dihydro-2,5-dimethoxy- (332-77-4)

magnesium carbonate

maleic dialdehyde

tropinone (532-24-1)

tetrahydro-2,5-dimethoxyfuran (696-59-3)

t-Butyl catechol