



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.

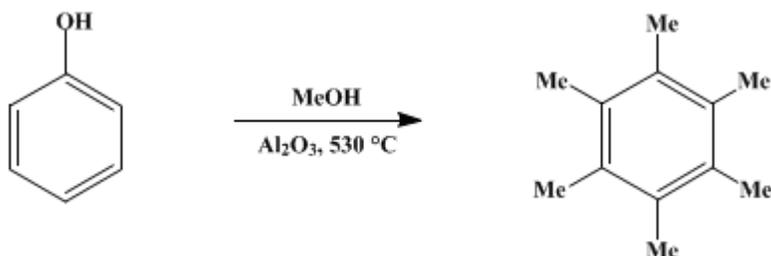
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.520 (1963); Vol. 35, p.73 (1955).*

## HEXAMETHYLBENZENE

[Benzene, hexamethyl-]



Submitted by N. M. Cullinane, S. J. Chard, and C. W. C. Dawkins<sup>1</sup>.  
Checked by T. L. Cairns and D. C. England.

### 1. Procedure

A solution of 100 g. (1.06 moles) of **phenol** in 1 l. of **methanol** is allowed to drop at a rate of 110 ml. per hour (**Note 1**) over an activated alumina catalyst (**Note 2**) heated to 530° (**Note 3**). The exit from the hot tube is attached to a receiver arranged to lead by-product gases to an efficient hood (**Note 4**). After addition of the **methanol** solution is finished, the pale yellow product is transferred to a Büchner funnel and washed with **methanol**. The yield of crude product melting at 135–145° is 112–115 g. (65–67%). Recrystallization from **ethanol** (50 g. in 650 ml.) gives 85% recovery or from **benzene** (50 g. in 130 ml.) gives 60% recovery of colorless **hexamethylbenzene**, m.p. 165–166°.

### 2. Notes

1. The submitters used a rate of 250 ml. per hour with a 2-in.-diameter tube, 16 in. long, packed with 300 g. of alumina, and a temperature in the catalyst bed about 370–380°. The checkers used 34 g. of alumina packed in a 7/8-in.-diameter tube 13 in. long.
2. The submitters used 4- to 8-mesh alumina from Peter Spence and Sons, Widnes, Lancashire, England. The checkers used 8- to 14-mesh Alorco H-41 obtained from the Aluminum Company of America, 1200 Alcoa Building, Pittsburgh 19, Pennsylvania.
3. Automatically controlling the outside of the catalyst tube to 370–400° gives a hot spot in the catalyst bed of 530° at the rate specified in equipment used by the checkers.
4. Gases formed in the reaction included **carbon monoxide**, **methane**, and **hydrogen**. The exact equation for the reaction is not known.

### 3. Discussion

**Hexamethylbenzene** has been prepared by passing the mixed vapors of **acetone** and **methanol** over alumina at 400°.<sup>2</sup> Briner, Plüss, and Paillard<sup>3</sup> have obtained it by passing different phenols mixed with **methanol** in an atmosphere of dry **carbon dioxide** over alumina at 410–440°. **Hexamethylbenzene** also has been prepared by the trimerization of **dimethylacetylene** in the presence of **triethylchromium**,<sup>4</sup> or a mixture of **triisobutylaluminum** and **titanium tetrachloride**.<sup>5</sup> The present method is based upon that of Cullinane and Chard.<sup>6</sup>

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### References and Notes

1. University College, Cardiff, Wales.
2. Reckleben and Scheiber, *Ber.*, **46**, 2363 (1913).
3. Briner, Plüss, and Paillard, *Helv. Chim. Acta*, **7**, 1046 (1924).
4. Zeiss and Herwig, *J. Am. Chem. Soc.*, **80**, 2913 (1958).

5. Franzus, Canterino, and Wickliffe, *J. Am. Chem. Soc.*, **81**, 1514 (1959).
  6. Cullinane and Chard, *J. Chem. Soc.*, **1945**, 821.
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

alumina

phenols

activated alumina

ethanol (64-17-5)

Benzene (71-43-2)

methanol (67-56-1)

hydrogen (1333-74-0)

carbon monoxide (630-08-0)

phenol (108-95-2)

carbon dioxide (124-38-9)

acetone (67-64-1)

methane (7782-42-5)

Hexamethylbenzene,  
Benzene, hexamethyl- (87-85-4)

titanium tetrachloride (7550-45-0)

dimethylacetylene (503-17-3)

triethylchromium

triisobutylaluminum (100-99-2)