
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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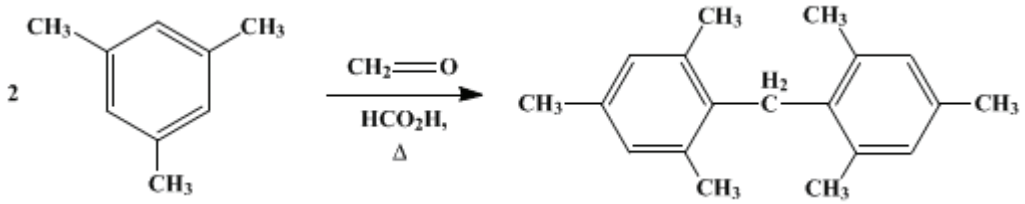
# DIMESITYLMETHANE

## [Methane, dimesityl-]




Submitted by John H. Cornell, Jr. and Morton H. Gollis[1].
Checked by William E. Parham and James Togeas.

## 1. Procedure

Into a 5-l. round-bottomed flask fitted with stirrer, thermometer, and reflux condenser are introduced 165 g. (5 moles) of 91% paraformaldehyde (Note 1) and 1250 g. (24 moles) of 88% formic acid (Note 2). The mixture is heated to 80° with stirring and is stirred until the paraformaldehyde has dissolved. To the stirred mixture is rapidly added 1.8 kg. (15 moles) of mesitylene and the whole heated under reflux for 6 hours (Note 3).

On cooling to room temperature, a large mass of dirty-yellow crystals separates. The liquid layers are decanted from the yellow solid, and the aqueous (lower) layer is separated and discarded. The solid is washed in the reaction flask by stirring with 500 ml. of benzene. This slurry of solid in benzene is filtered and the solid sucked dry on a Büchner funnel. This filtrate is combined with the upper organic layer from the original reaction mixture, and the combined benzene solution is washed with 500 ml. of water, 500 ml. of 2–3% aqueous sodium carbonate (Note 4), and 200 ml. of saturated sodium chloride solution. Benzene and water are removed from this solution by distillation at atmospheric pressure. The still residue is cooled to room temperature, and precipitated solid is removed by filtration and added to the large crop of solid from the original reaction mixture. The combined solids are washed twice with 300 ml. of water, once with 400 ml. of 2–3% aqueous sodium carbonate, and once with 300–400 ml. of water and sucked dry on a Büchner funnel.

The yield is 779 g. of crude dimesitylmethane (62% of theoretical) melting at 128.5–131°, uncor.; its purity as determined by vapor-phase chromatography is 99.9 mole per cent (Note 5).

## 2. Notes

1. The checkers used 150 g. (5 moles) of paraformaldehyde obtained from Eastman Organic Chemicals.
2. Contact with formic acid and inhalation of its vapors should be avoided.
3. When a smaller ratio of mesitylene to formaldehyde was used, a considerable amount of polymeric residue was formed and the yield was very much reduced.
4. It is advisable to add the sodium carbonate solution cautiously and with good agitation to avoid a violent evolution of carbon dioxide.
5. The crude product is pure enough for most purposes. However, for catalytic reduction to bis(2,4,6-trimethylcyclohexyl)methane, the residual acid must be removed by dissolving the solid in hot benzene and stirring or shaking with dilute aqueous sodium carbonate solution until the washings are basic; this is followed by a water wash and drying.
The solid can be recrystallized from boiling benzene and precipitated with about 0.15 part of boiling methanol to give white platelets (68%), m.p. 133–135°, plus a second, less pure crop (22%) melting at 128–133°. Reported for dimesitylmethane,[2] m.p. 134.4–135.4°, b.p. 212–213°/21 mm.
The reaction has been scaled up tenfold using a 50-l. flask without changes in procedure and in the same yield.

## 3. Discussion

Substituted diarylmethanes have been prepared from formaldehyde and a variety of its derivatives. Sulfuric acid is a common catalyst.[2,3] The procedure described is based on the general method of Gordon, May, and Lee.[4] Formic acid is preferable to sulfuric acid as a catalyst because it is capable of acting as a solvent as well, thus eliminating troublesome emulsions. Side reactions such as sulfonation are avoided.

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## References and Notes


1 Monsanto Chemical Company, Special Projects Department, Boston, Mass.

2 C. M. Welch and H. A. Smith, *J. Am. Chem. Soc.*, **73**, 4391 (1951).

3 I. G. Matveev, D. A. Drapkina, and R. L. Globus, *Trudy Vsesoyuz. Nauch.-Issledovatel, Inst. Khim. Reaktivov*, No. **21**, 83, (1956) [*C. A.*, **52**, 15474 (1958)].

4 L. B. Gordon, P. D. May, and R. J. Lee, *Ind. Eng. Chem.*, **51**, 1275 (1959).


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

sulfuric acid (7664-93-9)

Benzene (71-43-2)

methanol (67-56-1)

formaldehyde (50-00-0)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

formic acid (64-18-6)

carbon dioxide (124-38-9)

Mesitylene (108-67-8)

Dimesitylmethane,
Methane, dimesityl- (733-07-3)

bis(2,4,6-trimethylcyclohexyl)methane

paraformaldehyde (30525-89-4)