



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.

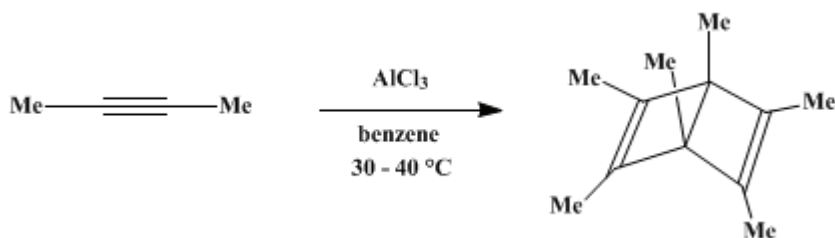
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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HEXAMETHYL DEWAR BENZENE

[Bicyclo[2.2.0]hexa-2,5-diene, 1,2,3,4,5,6-hexamethyl-]



Submitted by Sami A. Shama and Carl C. Wamser¹.

Checked by Reto Naef, Dieter Seebach, and Beat Weidmann.

1. Procedure

Caution! Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

A 250-mL, three-necked, round-bottomed flask containing a 2.5-cm magnetic stirring bar is equipped with a Dewar-type reflux condenser containing ice, a dropping funnel, and a gas inlet tube. A calcium chloride drying tube is attached to the condenser and the apparatus is flushed with dry deoxygenated nitrogen (Note 1). The gas inlet tube is then replaced by a thermometer, and a suspension of 5.0 g of aluminum trichloride in 50 mL of benzene is introduced into the flask (Note 2). A solution of 100 g (1.85 mol) of 2-butyne (Note 3) and (Note 4) in 50 mL of cold dry benzene is added, with vigorous stirring, through the dropping funnel, over a period of 1 hr. During the addition, the temperature of the reaction mixture is kept between 30 and 40°C through the use of a water bath. Stirring is continued for 5 hr at 30–40°C after the addition has been completed. The catalyst is then decomposed by pouring the mixture onto 50 g of crushed ice in a 500-mL separatory funnel, whereupon the dark brown color turns pale yellow. When the ice has melted completely, the organic layer is separated, washed with two 25-mL portions of cold water, dried over anhydrous potassium carbonate, and filtered. Benzene and unreacted butyne (Note 5) are removed in a rotary evaporator using a water bath at 40°C and a water aspirator vacuum. The residual liquid is distilled through a short-path distillation head under reduced pressure using a capillary. The yield is 38–50 g (38–50%) of hexamethyl Dewar benzene, bp 43°C/10 mm, mp 7–8°C, n_D^{20} 1.4480 (Note 6) and (Note 7).

2. Notes

- Commercial nitrogen is deoxygenated by bubbling it through a trap containing an alkaline pyrogallol solution.² The gas is then dried by passing it through a potassium hydroxide tower. The checkers used argon as an inert atmosphere.
- Aluminum trichloride is purified by sublimation under reduced pressure and the benzene is dried over sodium wire before use. The checkers used sublimed AlCl₃ as supplied by Merck (Darmstadt).
- 2-Butyne was purchased from Chemical Samples Company or from Fluka AG.
- The bottle containing 2-butyne (bp 27°C) should be chilled thoroughly before opening.
- About 20 g of 2-butyne may be collected in an ice-cooled receiver if the dried solution is concentrated by distillation through a 25-cm Vigreux column rather than by evaporation. The checkers do not recommend this mode of workup, nor did they use a column for distilling the Dewar benzene, to avoid prolonged heating of the bicyclic system.
- The spectral properties of hexamethyl Dewar benzene are as follows: ¹H NMR (CDCl₃) δ: 1.07 (s, 6 H), 1.58 (s, 12 H).

7. [Hexamethyl Dewar benzene](#) undergoes thermal isomerization^{3,4} and reacts with acids⁵ and transition-metal ions.⁶ It should be stored in a freezer in a tightly sealed bottle. [Hexamethyl Dewar benzene](#) is reportedly a carcinogen,⁷ and care must be taken to avoid contact with the skin or inhalation of its vapor.

3. Discussion

The present procedure is that of Schäfer^{8,9} and is the first method available for large-scale preparation of a Dewar benzene. Other syntheses of compounds containing the Dewar benzene skeleton have generally involved photochemical isomerization of the corresponding benzene isomer.¹⁰

The present procedure represents a novel reaction, bicyclo trimerization. The intermediate dimeric complex of AlCl_3 with [tetramethylcyclobutadiene](#) has been isolated, and addition of different alkynes to this complex provides a synthetic route to a variety of substituted Dewar benzenes.¹¹

References and Notes

1. Department of Chemistry, California State University, Fullerton, CA 92634. Present address: Department of Chemistry, Portland State University, Portland, OR 97207.
2. Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley-Interscience: New York, 1972; p. 438.
3. Oth, J. F. M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 646.
4. Adam, W.; Chang, J. C. *Int. J. Chem. Kinet.* **1969**, *1*, 487.
5. Hogeveen, H.; Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 385.
6. Bishop, K. C., III. *Chem. Rev.* **1976**, *76*, 461.
7. Dannenberg, H.; Brachmann, I.; Thomas, C. Z. *Krebsforsch.* **1970**, *74*, 100; *Chem. Abstr.* **1970**, *73*, 1933a.
8. Schäfer, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 669.
9. Schäfer, W.; Hellman, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 518.
10. van Tamelen, E. E. *Acc. Chem. Res.* **1972**, *5*, 186.
11. Rantwijk, S. Van; Timmermans, G. J.; Van Bekkum, H. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*(2), 39.

Appendix

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

AlCl_3

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

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

[nitrogen](#) (7727-37-9)

[aluminum trichloride](#) (3495-54-3)

[sodium wire](#) (13966-32-0)

[pyrogallol](#) (87-66-1)

[butyne](#) (107-00-6)

argon (7440-37-1)

2-butyne (503-17-3)

tetramethylcyclobutadiene

Hexamethyl Dewar benzene,
Bicyclo[2.2.0]hexa-2,5-diene, 1,2,3,4,5,6-hexamethyl- (7641-77-2)