Organic Syntheses

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.

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.

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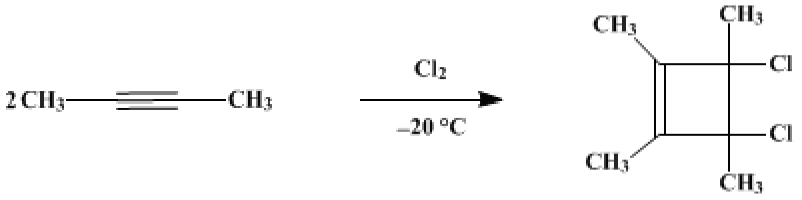
3,4-DICHLORO-1,2,3,4-TETRAMETHYLCYCLOBUTENE

[Cyclobutene, 1,2,3,4-tetramethyl-3,4-dichloro-]



Submitted by R. Criegee[1]
Checked by G. Brown and V. Boekelheide.

1. Procedure

A 400-ml. three-necked flask equipped with a mechanical stirrer, a gas dispersion tube, and a thermometer is charged with 216 g. (4 moles) of 2-butyne, 14 ml. of boron trifluoride etherate, and 1 ml. of water (Note 1). The mixture is stirred vigorously while the flask is partially immersed in a dry ice-acetone bath to maintain an internal temperature of −20°. Chlorine (195 g., 2.75 moles) is then added (Note 2) gradually over a period of 17–20 hours.

When all the chlorine has been added, the flask and contents (Note 3) are cooled to −78° and held at this temperature for 30 minutes. The white crystalline product which separates is collected on a sintered-glass funnel; 160–170 g. (45–48%) of crude crystals, m.p. 53–55°, is obtained. The crude product when stored at −20° takes on a reddish or blue color after a few days (Note 4).

Purification of the crude material is accomplished by dissolving it in petroleum ether (30–50°) or methylene chloride, shaking this solution three times with water, and passing the organic layer through a fluted filter paper. After the filtrate has been dried over anhydrous sodium sulfate, it is concentrated to a small volume and cooled to −78°. The perfectly white, crystalline product which separates is collected yielding 110–120 g. (30–33%) of crystals, m.p. 57–58° (Note 5).

2. Notes

1. The submitter reports that he and his colleagues have found since the procedure was submitted and checked that the yield and purity of the product is the same whether the preparation is carried out in the presence or absence of boron trifluoride etherate and water. Recommends that the 14 ml. of boron trifluoride etherate and 1 ml. of water *not* be added.
2. The chlorine is most conveniently added by liquefying the required amount in a gas trap. The gas trap is placed in an empty Dewar flask and covered with glass wool. While the liquid chlorine slowly warms up, the resulting gaseous chlorine is passed through a sulfuric acid wash bottle into the reaction mixture. The addition generally takes 17–20 hours.
3. The final reaction mixture is slightly yellow, but at times it can be reddish. During the reaction some white crystalline product collects at the walls of the reaction vessel.
4. It is important to purify the crude product as soon as possible since it decomposes readily in the impure state. Once decomposition has set in, purification is difficult.
5. A still purer product is obtained if the dried petroleum ether solution is evaporated to dryness with a water aspirator and the residual crude product distilled through a Vigreux column. After a small fore-run, pure tetramethyl-3,4-dichlorocyclobutene distils at 59–60° at 12 mm. The product melts at 58° and is more stable at room temperature than the recrystallized but undistilled material.

3. Discussion

The method used is that of Criegee and Moschel.[2] Smirnow-Samkow[3] made the same substance by the reaction of 2-butyne with sulfuryl chloride in 10–15% yield.

4. Merits of the Preparation

3,4-Dichloro-1,2,3,4-tetramethylcyclobutene is an unusually versatile intermediate.[4] The tertiary and allylic chlorine atoms undergo ready solvolysis. With lithium aluminum hydride the chlorine atoms are replaced by hydrogen. The resulting *cis, trans*-tetramethylcyclobutenes are starting materials for numerous transformations, *e.g.*, thermolysis leads to stereoiisomeric tetramethylbutadienes.[5] Lithium amalgam in ether results in the formation of octamethyltricyclooctadiene. With nickel carbonyl the nickel chloride complex of tetramethylcyclobutadiene is formed.[6] Ammonia transforms the dichloride into tetramethylpyrrole.[7] Other reactions have been reported.[8]

This method of preparation is simpler, more reproducible, and gives considerably better yields than the original one of Smirnow-Samkow.

References and Notes

1. Technische Hoschschule Karlsruhe, Institut für Organische Chemie, Karlsruhe, Germany.
2. R. Criegee and A. Moschel, *Ber.*, **92**, 2181 (1959).
3. J. W. Smirnow-Samkow, *Dokl. Akad. Nauk SSSR*, **83**, 869 (1952); J. W. Smirnow-Samkow and N. A. Kostromina, *Ukr. Khim. Zh.*, **21**, 233 (1955).
4. R. Criegee, *Angew. Chem.*, **74**, 703 (1962).
5. R. Criegee and K. Noll, *Ann.*, **627**, 1 (1959).
6. R. Criegee and G. Schröder, *Ann.*, **623**, 1 (1959).
7. R. Criegee and M. Krieger, *Ber.* **98**, 387 (1965).
8. R. Criegee, J. Dekker, W. Engel, P. Ludwig, and K. Noll, *Ber.*, **96**, 2362 (1963).

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

petroleum ether

octamethyltricyclooctadiene

nickel chloride complex of tetramethylcyclobutadiene

ammonia (7664-41-7)

ether (60-29-7)

sodium sulfate (7757-82-6)

sulfuryl chloride (7791-25-5)

chlorine (7782-50-5)

methylene chloride (75-09-2)

lithium (7439-93-2)

nickel carbonyl

lithium aluminum hydride (16853-85-3)

boron trifluoride etherate (109-63-7)

2-butyne (503-17-3)

3,4-Dichloro-1,2,3,4-tetramethylcyclobutene,
Cyclobutene, 1,2,3,4-tetramethyl-3,4-dichloro-,
tetramethyl-3,4-dichlorocyclobutene (1194-30-5)

tetramethylpyrrole (1003-90-3)