



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.

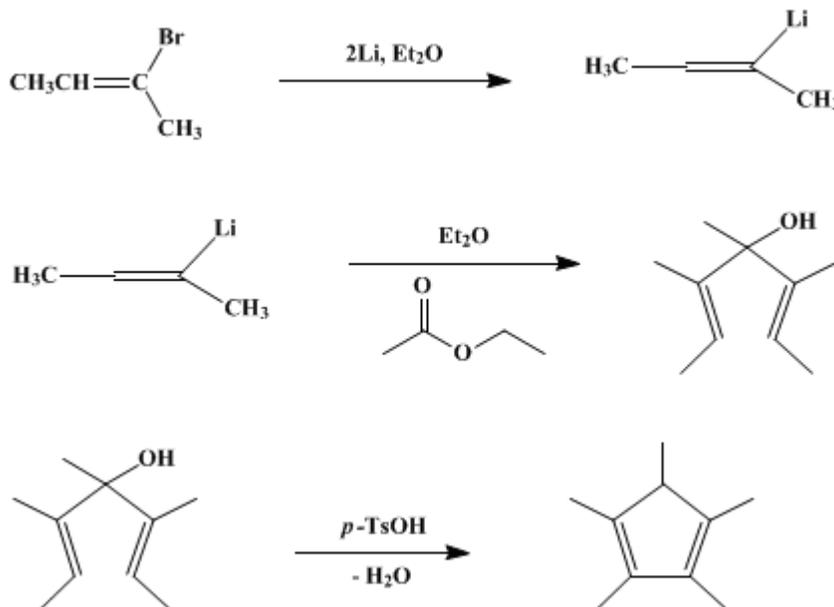
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1,2,3,4,5-PENTAMETHYLCYCLOPENTADIENE

[1,3-Cyclopentadiene, 1,2,3,4,5-pentamethyl-]



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1. Procedure

A. *3,4,5-Trimethyl-2,5-heptadien-4-ol*. Lithium wire (1/8 in.) is cut up into approximately 1-cm lengths and washed with hexane (Note 1). A mixture of the cut-up lithium (21 g, 3.0 mol) in 100 mL of diethyl ether from a freshly opened can is stirred well under argon in a 2-L, three-necked, round-bottomed flask equipped with a reflux condenser and a 250-mL addition funnel. 2-Bromo-2-butene (*cis-trans* mixture) is purified and dried by passing it through a 2×15 -cm column of basic alumina (Note 2). An addition funnel is charged with 2-bromo-2-butene (200 g, 1.48 mol) and a small amount of the alkene is added dropwise to the flask until reaction begins, as shown by warming of the reaction mixture and formation of bubbles on the surface of the lithium (Note 3). At this point the mixture is diluted with an additional 900 mL of fresh diethyl ether, and the remainder of the 2-bromo-2-butene is added at a rate sufficient to maintain gentle reflux. Stirring is continued for 1 hr following completion of this addition, after which ethyl acetate (66 g, 0.75 mol) diluted with an equal volume of fresh diethyl ether is added dropwise via the addition funnel. The reaction mixture turns from yellow-orange to milky-yellow with this addition. It is then poured into 2 L of saturated aqueous ammonium chloride. The ethereal layer is separated, and the aqueous layer is adjusted to approximately pH 9 with hydrochloric acid. The aqueous layer is extracted three times with diethyl ether. The combined ethereal layers are dried over magnesium sulfate, filtered, and concentrated to 100–200 mL by rotary evaporation.

B. *1,2,3,4,5-Pentamethylcyclopentadiene*. A mixture of 13 g (0.068 mol) of *p*-toluenesulfonic acid monohydrate and 300 mL of diethyl ether is stirred under argon in a 1-L, three-necked, round-bottomed flask equipped with a reflux condenser and a 250-mL addition funnel. The concentrate from above is added as quickly as possible to the flask from the addition funnel, maintaining a gentle reflux. As the reaction proceeds, a water layer separates. The mixture is stirred for 1 hr after the addition is completed and then washed with saturated aqueous sodium bicarbonate until the washings remain basic. The ethereal layer is separated, and the combined aqueous layers are extracted three times with diethyl ether. The combined ethereal layers are dried over sodium sulfate. Diethyl ether is removed by rotary

evaporation, and the crude product is distilled under reduced pressure (bp 55–60°C, 13 mm): yield 73–75 g (73–75%) (Note 4).

2. Notes

1. High-sodium lithium (1–2% sodium) is preferred in order to facilitate initiation of the reaction. (The checkers used 1% sodium in lithium wire purchased from Lithium Corporation of America, Bessemer City, NC.)
2. While published procedures have used samples of 2-bromo-2-butene as obtained from the supplier without further purification, impurities in some batches often make it difficult, if not impossible, to start the reaction safely.
3. *Caution! It is imperative to add only a few milliliters of the 2-bromo-2-butene and to patiently wait for the reaction with the lithium to begin. Addition of too much 2-bromo-2-butene too soon may lead to a violent reaction.*
4. Pentamethylcyclopentadiene has the following spectral properties; IR (neat) cm^{-1} : 2940, 2890, 2840, 2730, 1670, 1655, 1440, 1370; ^1H NMR (CDCl_3) δ : 1.00 (3 H, d, $J = 7.6$, CH_3CH), 1.8 (12 H, br s, $\text{CH}_3\text{C}=\text{C}$), 2.45 (1 H, q, $J = 6.5$, CHCH_3).

3. Discussion

The procedure described here is a modification of that previously published.³ Specifically, it is frequently insufficient to use the 2-bromo-2-butene as obtained from the supplier without purification using basic alumina I. Such purification assures facile reaction with lithium. Furthermore, the large volumes of diethyl ether used in the past are unnecessary and may inhibit initiation of the reaction of 2-bromo-2-butene with lithium. Finally, while dry solvents and reagents are required, diethyl ether from a freshly opened can is sufficiently free of water, and distillation from lithium aluminum hydride is unnecessary.

1,2,3,4,5-Pentamethylcyclopentadiene is a useful aromatic building block for the preparation of other compounds. It can be converted to many salts of its conjugate base with alkali metals or strong bases such as butyllithium.⁴ These pentamethylcyclopentadienyl anion salts as well as the diene itself can be transformed into η^5 -pentamethylcyclopentadienyl ligands of organotransition metal complexes by many known methods.⁴

References and Notes

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3. Threlkel, R. S.; Bercaw, J. E. *J. Organomet. Chem.* **1977**, *136*, 1.
4. Feitler, D.; Whitesides, G. M. *Inorg. Chem.* **1976**, *15*, 466; Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Dalton Trans.* **1979**, 355, and references cited therein.

Appendix

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

2-Bromo-2-butene (cis-trans mixture)

High-sodium lithium

hydrochloric acid (7647-01-0)

ethyl acetate (141-78-6)

diethyl ether (60-29-7)

ammonium chloride (12125-02-9)

sodium bicarbonate (144-55-8)

sodium sulfate (7757-82-6)

sodium (13966-32-0)

lithium (7439-93-2)

magnesium sulfate (7487-88-9)

butyllithium (109-72-8)

lithium aluminum hydride (16853-85-3)

hexane (110-54-3)

argon (7440-37-1)

pentamethylcyclopentadiene,
1,2,3,4,5-Pentamethylcyclopentadiene,
1,3-Cyclopentadiene, 1,2,3,4,5-pentamethyl- (4045-44-7)

p-toluenesulfonic acid monohydrate (6192-52-5)

2-Bromo-2-butene

3,4,5-Trimethyl-2,5-heptadien-4-ol (64417-15-8)