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.

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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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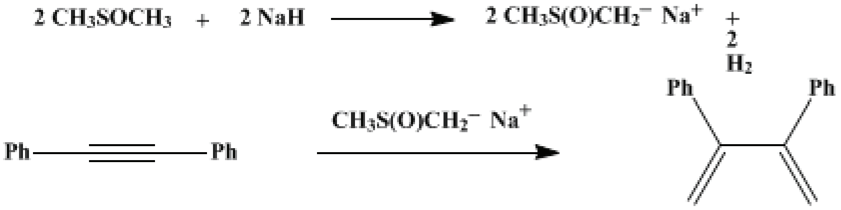
Organic Syntheses, Coll. Vol. 6, p.531 (1988); Vol. 50, p.62 (1970).

2,3-DIPHENYL-1,3-BUTADIENE

[1,3-Butadiene, 2,3-diphenyl]



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Checked by James B. Sieja and Richard E. Benson.

1. Procedure

A 300-ml., three-necked, round-bottomed flask is fitted with a sealed mechanical stirrer, a thermometer, and a reflux condenser to which is attached a T-tube connected to a source of pure nitrogen. The remaining joint of the T-tube is connected to a bubbling device so that the rate of nitrogen flow can be observed throughout the course of the reaction. The flask is flushed with nitrogen and charged with 30 ml. of anhydrous dimethyl sulfoxide (Note 1) and 2.4 g. of about 50% sodium hydride in oil (*ca.* 0.05 mole) (Note 2). Stirring is begun and the contents of the flask are heated to 75° for 30 minutes (Note 3) under a slight pressure of nitrogen. The flask is cooled in a water bath to 30°, before a solution of 4.45 g. (0.0250 mole) of diphenylacetylene in 20 ml. of anhydrous dimethyl sulfoxide is added dropwise with stirring to the dark-gray solution. During the addition, the temperature of the reaction mixture gradually rises until it approaches 40°. After the addition is completed, the reaction mixture is heated to 65° and held at this temperature for 2.5 hours. The resulting red-brown reaction mixture is cooled to room temperature and poured into 500 ml. of an ice and water mixture with stirring. After the ice has melted, the mixture is extracted with five 150 ml. portions of diethyl ether. The ether extracts are combined, washed with three 100-ml. portions of water, then dried over sodium sulfate. The ether is removed by distillation at reduced pressure, and the product (about 6.0 g.) is chromatographed on 180 g. of alumina (Note 5). Elution with 1:7 (v/v) benzene:*n*-hexane gives ten 50-ml. fractions, of which the first two contain nearly all the mineral oil from the sodium hydride reagent. Fractions 3 through 8 are combined, and the ether is removed by distillation, yielding 1.2–1.4 g. (22–25%) of slightly impure 2,3-diphenyl-1,3-butadiene (Note 6). Recrystallization from methanol gives 0.55–0.70 g. (10.7–13.6%) of pure 2,3-diphenyl-1,3-butadiene, m.p. 47–48° (Note 7).

The ^{1}H NMR spectrum (60 MHz., CCl_4) shows a complex multiplet centered at δ 7.2 attributable to the aromatic protons, and two doublets centered at δ 5.4 and 5.2, respectively, attributable to the olefinic protons.

2. Notes

1. Commercially available dimethyl sulfoxide was freshly distilled in the presence of calcium hydride, b.p. 56–57° (5 mm.).
2. Sodium hydride in oil (about 50%), available from Metal Hydrides Inc., Beverly, Massachusetts, was used.
3. The formation of dimsyl(methylsulfinyl) anion is essentially complete at this time.
4. The preparation of diphenylacetylene is described in *Org. Synth.*, **Coll. Vol. 3**, 350 (1955) and **Coll. Vol. 4**, 377 (1963). The checkers purchased it from Eastman Organic Chemicals.
5. Aluminum Oxide Woelm neutral, activity grade 1, available from M. Woelm, Eschwege, Germany, was used. The column dimensions were 2.9 cm. × 29 cm., and the alumina was packed with *n*-hexane.
6. This grade of 2,3-diphenyl-1,3-butadiene is satisfactory for most purposes.
7. Crude 2,3-diphenyl-1,3-butadiene is unstable. The pure product should be stored in the dark in a

refrigerator. The submitters have found it to be stable for at least one year under these conditions.

3. Discussion

This method provides a simple, one-step synthesis of 2,3-diphenyl-1,3-butadiene from the readily available diphenylacetylene and illustrates an unusual, relatively uninvestigated reaction. The scope of the reaction is unknown, but it appears that the procedure could be applied to disubstituted acetylenes having aryl substituents unaffected by the strong basic conditions of the reaction.

A conventional preparation of 2,3-diphenyl-1,3-butadiene involves dehydration of *meso*-2,3-diphenyl-2,3-butanediol by acidic reagents such as acetic anhydride,[2,3,4] acetyl bromide,[4] sulfanilic acid,[5] and potassium hydrogen sulfate.[6] Other procedures have been summarized[7] previously.

References and Notes

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4. C. F. H. Allen, C. G. Eliot, and A. Bell, *Can. J. Res.*, **B17**, 75 (1939).
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6. K. Alder and J. Haydn, *Justus Liebigs Ann. Chem.*, **570**, 201 (1950).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

alumina

Benzene (71-43-2)

methanol (67-56-1)

ether,
diethyl ether (60-29-7)

acetic anhydride (108-24-7)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

potassium hydrogen sulfate (7646-93-7)

sulfanilic acid (121-57-3)

aluminum oxide (1344-28-1)

acetyl bromide (506-96-7)

sodium hydride (7646-69-7)

Diphenylacetylene (501-65-5)

n-hexane (110-54-3)

dimethyl sulfoxide (67-68-5)

calcium hydride (7789-78-8)

2,3-Diphenyl-1,3-butadiene,
1,3-Butadiene, 2,3-diphenyl (2548-47-2)

meso-2,3-diphenyl-2,3-butanediol