



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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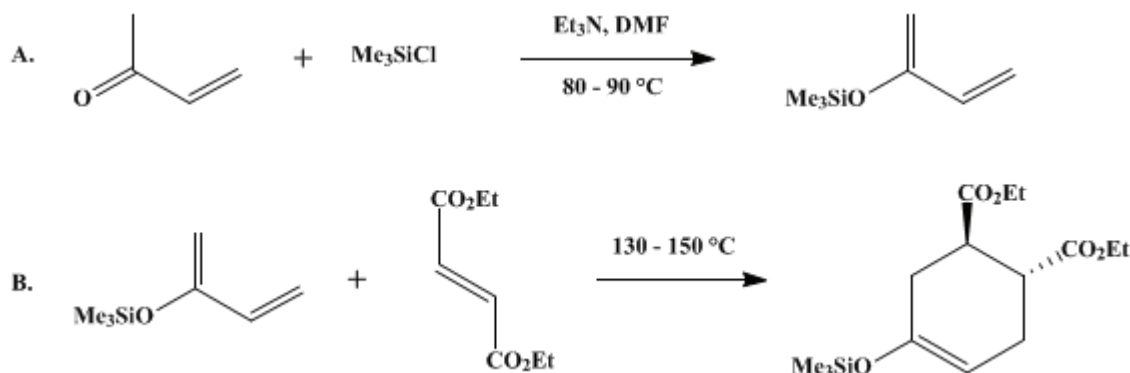
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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2-TRIMETHYLSILYLOXY-1,3-BUTADIENE AS A REACTIVE DIENE: DIETHYL *trans*-4-TRIMETHYLSILYLOXY-4-CYCLOHEXENE-1,2-DICARBOXYLATE

[4-Cyclohexene-1,2-dicarboxylic acid, 4-trimethylsilyloxy-, diethyl ester, *trans*-]



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Checked by Ping Sun Chu and George H. Büchi.

1. Procedure

Caution! Part A should be carried out in a hood, since the reagents are noxious.

A. *2-Trimethylsilyloxy-1,3-butadiene* (**1**). An oven-dried, 500-ml., three-necked, round-bottomed flask is fitted with two oven-dried addition funnels, a glass stopper, and magnetic stirrer, and placed in a 80–90° oil bath. Under an inert atmosphere, *methyl vinyl ketone* (25.0 g., 0.357 mole) in 25 ml. of *N,N*-dimethylformamide and *chlorotrimethylsilane* (43.4 g., 0.400 mole) in 25 ml. of *N,N*-dimethylformamide are added over 30 minutes to a magnetically stirred solution of *triethylamine* (40.5 g., 0.400 mole) in 200 ml. of *N,N*-dimethylformamide (Note 1). The reaction gradually darkens from colorless to yellow or dark brown, and supports a white precipitate of *triethylamine hydrochloride*. The reaction is set up to run overnight, or *ca.* 14 hours.

The reaction is cooled to room temperature, filtered (Note 2), and transferred to a 2-l. separatory funnel containing 300 ml. of *pentane*. To this solution is added 1 l. of *cold* 5% *sodium hydrogen carbonate* solution to facilitate the separation of phases and remove the *N,N*-dimethylformamide. The *pentane* layer is separated, and the aqueous layer extracted twice with 300-ml. portions of *pentane*. The *pentane* extracts are combined, washed with 200 ml. of *cold* distilled water (Note 3), dried over powdered anhydrous *sodium sulfate*, and filtered into a 2-l., round-bottomed flask.

The *pentane* and other volatiles are removed by fractional distillation, using a 5-cm., steel wool-packed column and heating the pot in a 70° oil bath (Note 4). A water aspirator vacuum is applied, and 18.2–22.9 g. (36–45%) of the diene **1** is distilled as a colorless oil, b.p. 50–55° (50 mm.) (Note 5). On a smaller scale, yields of up to 50% have been obtained.

B. *Diethyl trans-4-trimethylsilyloxy-4-cyclohexene-1,2-dicarboxylate* (**2**). A 25-ml., round-bottomed flask equipped with a reflux condenser is charged with diene **1** (7.1 g., 0.050 mole) and *diethyl fumarate* (5.7 g., 0.033 mole) (Note 6). The mixture is stirred under a *nitrogen* atmosphere in an oil bath kept at 130–150° for 24 hours (Note 7). Direct vacuum distillation using a short-path distillation apparatus affords a small amount of lower-boiling material, then 8.02 g. (77%) of *cyclohexene* **2**, b.p. 127–128° (0.5 mm.) (Note 8) and (Note 9).

2. Notes

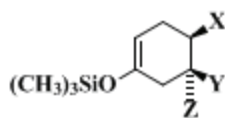
1. The checkers obtained methyl vinyl ketone from Hoffmann-La Roche Company and chlorotrimethylsilane from Aldrich Chemical Company, Inc. Both were distilled from calcium hydride. Triethylamine, obtained from J. T. Baker Chemical Company, was distilled from calcium hydride, and *N,N*-dimethylformamide, from Fisher Scientific Company, was used from a freshly opened bottle.
2. Filtration was conveniently performed through a plug of glass wool directly into the separatory funnel.
3. The hydrogen carbonate extractions must be performed quickly, since the product slowly hydrolyzes in the presence of water. The best yields were obtained when the phases were shaken briskly for 10 seconds and separated as soon as foaming ceased. Foaming also occurred when the pentane extracts were washed with water, but did not prevent the separation of phases.
4. The checkers used a 18-cm. Vigreux column to remove low-boiling material, and then transferred the residue to a 250-ml., round-bottomed flask for fractional distillation under reduced pressure.
5. The distilled diene **1** has been obtained with 99% purity by the submitters. The product has the following spectral properties: ¹H NMR: (CCl₄ with benzene as internal standard). δ (multiplicity, number of protons): 0.4 (s, 9H), 4.4 (broad s, 2H), 5.1 (d of m, 1H), 5.5 (d of d, 1H), 6.3 (d of d, 1H). The impurities were triethylamine and hexamethyldisiloxane. When stored in a serum-capped flask, in a desiccator, and removed *via* syringe, the butadiene is stable for 2 months.
6. The checkers prepared diethyl fumarate by the sulfuric acid-catalyzed esterification of fumaric acid.⁷ Diethyl fumarate obtained from Aldrich Chemical Company, Inc. contained dimethyl fumarate as a contaminant.
7. The submitters allowed the reaction to proceed for 24 hours after monitoring by GC (1.83 m. \times 0.64 cm., 10% SE-30/60–80 mesh Chromosorb W, 150°) indicated that the disappearance of diethyl fumarate was not complete after 5.5 hours. The submitters made no attempt to optimize the reaction time. The checkers found the reaction to be complete after 7 hours at 135–145°.
8. The checkers distilled cyclohexene **2** after 7 hours reaction time using a Büchi Kügelrohr distillation oven to obtain 9.9–10.0 g. (95–96%) of cyclohexene **2**.
9. Cyclohexene **2** has the following spectral properties: IR (liquid film) cm⁻¹: 1730, 1670; ¹H NMR: (CCl₄), δ (multiplicity, coupling constant *J* in Hz., number of protons, assignment): 0.16 [s, 9H, Si(CH₃)₃], 1.17 (t, *J* = 7, 6H, 2OCH₂CH₃), 2.00–3.16 (m, 6H, ring CH), 4.07 (q, *J* = 7, 4H, 2OCH₂CH₃), 4.70 (broad s, 1H, olefinic CH).

3. Discussion

The first reference to 2-trimethylsilyloxy-1,3-butadiene (**1**) was a report² of its reaction with tetracyanoethylene by Cazeau and Frainnet without any mention of experimental details. Later, Conia³ reported its synthesis in 50% yield with only a reference made to the usual House procedure⁴ for silyl enol ethers. The diene **1** has also been prepared using lithium diisopropylamide as base and chlorotrimethylsilane in tetrahydrofuran–ether (1:1) in yields up to 65%, but on a smaller scale.⁵

Butadienes substituted with alkoxy groups in the 2-position, *e.g.*, 2-ethoxy-1,3-butadiene,^{6, 7} have been prepared from methyl vinyl ketone, but required several conversions and a tedious spinning-band distillation to purify the product. This slight modification of the House procedure has been used to conveniently prepare 2-trimethylsilyloxy-1,3-butadiene from the readily available methyl vinyl ketone. This one-step procedure has provided large amounts of a new and reactive diene for Diels–Alder reactions, as illustrated in Table I.

TABLE I
PREPARATION OF
TRIMETHYLSILOXYCYCLOHEXENES



X	Y	Z	Yield(%)
COCH ₃	H	H	 60
CO ₂ CH ₃	H	H	 46
CO ₂ CH ₃	H	CO ₂ CH ₃	 71
CO ₂ C ₂ H ₅	H	CO ₂ C ₂ H ₅	 77
CO ₂ C ₂ H ₅ CO ₂ C ₂ H ₅	H		 39

References and Notes

1. Contribution No. 3759 from the Department of Chemistry, University of California, Los Angeles, California 90024.
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3. C. Girard, P. Amice, J. P. Barnier, and J. M. Conia, *Tetrahedron Lett.*, 3329 (1974).
4. H. O. House, L. J. Czuba, M. Gall, and H. D. Olmstead, *J. Org. Chem.*, **34**, 2324 (1969).
5. M. E. Jung and C. A. McCombs, *Tetrahedron Lett.*, 2935 (1976).
6. H. B. Dykstra, *J. Am. Chem. Soc.*, **57**, 2255 (1935);
7. N. A. Milas, E. Sakel, J. T. Plati, J. T. Rivers, J. K. Gladding, F. X. Grossi, Z. Weiss, M. A. Campbell, and H. F. Wright, *J. Am. Chem. Soc.*, **70**, 1597 (1948).

Appendix

Chemical Abstracts Nomenclature (Collective Index Number);

(Registry Number)

sulfuric acid (7664-93-9)

ether (60-29-7)

sodium hydrogen carbonate (144-55-8)

Cyclohexene (110-83-8)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

Fumaric acid (110-17-8)

diethyl fumarate (623-91-6)

Triethylamine hydrochloride (554-68-7)

Pentane (109-66-0)

Tetrahydrofuran (109-99-9)

N,N-dimethylformamide (68-12-2)

methyl vinyl ketone (78-94-4)

triethylamine (121-44-8)

Tetracyanoethylene (670-54-2)

calcium hydride (7789-78-8)

Dimethyl fumarate (624-49-7)

lithium diisopropylamide (4111-54-0)

CHLOROTRIMETHYLSILANE (75-77-4)

hexamethyldisiloxane (107-46-0)

2-Trimethylsilyloxy-1,3-butadiene (38053-91-7)

2-ethoxy-1,3-butadiene

Diethyl trans-4-trimethylsilyloxy-4-cyclohexene-1,2-dicarboxylate,
4-Cyclohexene-1,2-dicarboxylic acid, 4-trimethylsilyloxy-, diethyl ester, trans- (61692-31-7)