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REDUCTION AND OXIDATION OF CARBON-CARBON DOUBLE BONDS OF 1,1,4,4-TETRAKIS(TRIMETHYLSILYL)BUTATRIENE

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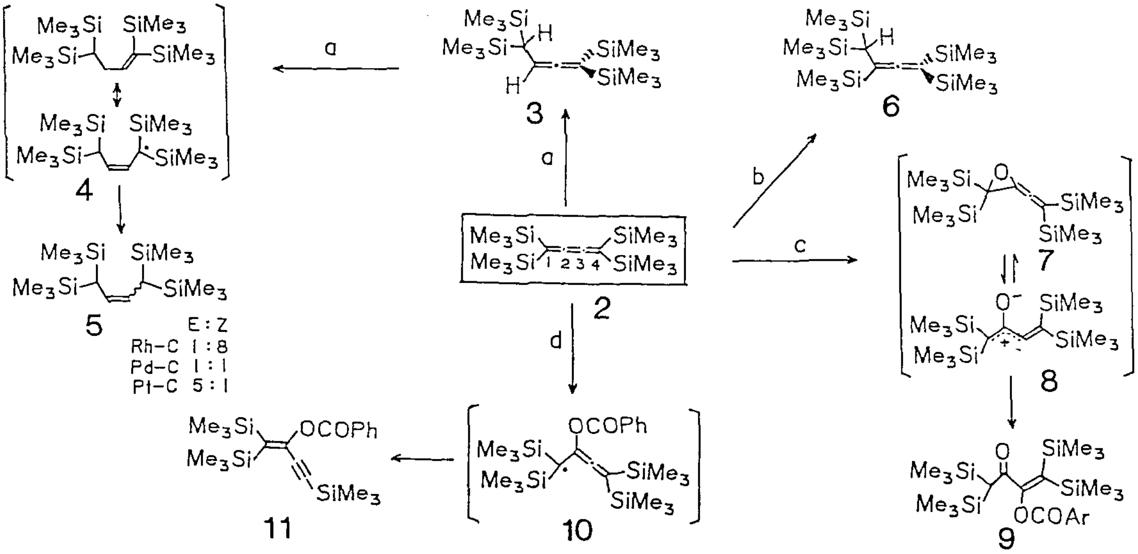
Summary: Hydrogenation, hydrosilylation and oxidation of the title butatriene was found to take place at C(1)=C(2) double bond exclusively.

Although 1,2,3-butatrienes $R_2C=C=C=CR_2$ have been synthesized by various methods, their reactions seems to have remained unexplored.[1-5] Butatrienes have sp-hybridized two central carbon atoms and two terminal sp^2-carbon atoms, and their reactivity is expected to be totally different from allenes or dienes. In the preceding paper, we reported that the double silylation of bis(trimethylsilyl)butadiyne (**1**) opened an easy access to 1,1,4,4-tetrakis-(trimethylsilyl)butatriene (**2**). We studied various addition reactions to the carbon-carbon double bonds of **2**.

The hydrogenation of **2**[6] with Rh-C, Pd-C, or Pt-C catalyst proceeded stepwise to give an allene **3**[7] first, which was further reduced to a 2-butene **5**[8] under atmospheric pressure of hydrogen at room temperature. A regioisomer of **3**, $(Me_3Si)_2C=CH-CH=C(SiMe_3)_2$, was not produced at all, although hydro-



a: H_2, cat. (Rh-C, Pd-C, Pt-C), MeOH-THF, r. t., 70-80%. b: Me_3SiH, $RhCl(PPh_3)_3$, 80 °C, 90%. c: m-CPBA, CH_2Cl_2, r. t., 60%. d: $(PhCO_2)_2$, CH_3CCl_3, 74 °C, 62%.

genation of cis-1,4-diphenylbutatriene occurs at the central C=C bond to give 1,4-diphenyl-1,3-butadiene.[1] The π electron cloud of C(2)=C(3) in **2** is heavily shielded by four bulky trimethylsilyl groups at C(1) and C(4), and probably the coordination of this bond to the catalyst is sterically disfavored. Hydrogenation of the allene **3** with Rh-C catalyst proceeded from less crowded side to give (Z)-**5** mainly. Reduction with Pt-C perhaps proceeded through an intermediary radical **4** to give rise to more stable (E)-**5**. In the same manner, hydrosilylation of **2** using trimethylsilane and Rh catalyst proceeded at C(1)=C(2) to afford **6** in 90 % yield, which remained intact due to remarkable steric hindrance by the silyl groups.

Oxidation of **2**[8] with m-chloroperbenzoic acid (m-CPBA) occurred at room temperature to give **9** in 60 % yield in sharp contrast to the reaction of 1,1,4,4-tetraphenylbutatriene[4] or tetraalkylbutatrienes.[5] Formation of **9** is attributed to an facile isomerization of the initial epoxide **7** to an oxyallyl **8** followed by nucleophilic attack by the accompanying of m-chlorobenzoic acid (m-CBA). The reactivity difference of **2** and 1,1,4,4-tetraalkylbutatrienes[5] may be understood in terms of the β-cation stabilizing effect of the trimethylsilyl groups in the oxyallyl **8**, which is captured by m-CBA before farther isomerization to a cyclopropanone.[5,11] Reaction of **2** with benzoyl peroxide resulted in the elimination of **11**. Initial addition of benzoyloxy radical to C(2) to give **10** followed by elimination of a trimethylsilyl radical should be the reaction course. Oxymetallation of **2** with $Pb(OAc)_4$ or $Mn(OAc)_3$ gave bis(trimethylsilyl)butadiyne (**1**) as the major product along with a small amount of **11**(PhCOO = AcO).

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5) Oxidation of tetraalkylbutatrienes with m-CPBA gives methylene cyclopropanones as reported recently. W. Ando, H. Hayakawa, and N. Tokitoh, Tetrahedron Lett., 27, 6357 (1986).
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7) The allene **3** was isolated as the mixture with **2** and **5**. Following spectra were attributed to **3**. IR (neat) 1910 cm^{-1} (C=C=C); ^1H NMR ($CDCl_3$) δ 0.06 (s, 18 H), 0.12 (s, 18 H), 0.68 (d, J=10.8 Hz, 1 H), 4.30 (d, J=10.8 Hz, 1 H).
8) Structure of **5** and E/Z ratios were determined by ^1H NMR spectra. An authentic sample of (E)-**5** was prepared according to reference 9.
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10) The structure of **6**, **9**, and **11** was determined spectrometrically and analytically. **6**: IR (neat) 1860 cm^{-1} (C=C=C); MS m/z 414 (M^+); ^{13}C NMR ($CDCl_3$) δ -0.15, 1.58, 1.83, 1.85, 14.56 (d), 73.82, 78.76, 20.55; Anal. Calcd for $C_{19}H_{40}Si_5$: C, 54.99; H, 11.17. Found: C, 54.99; H, 11.32. **9**: IR (KBr) 1730 (C=O), 1680 (C=O) cm^{-1}; MS m/z 499 (M^+(Cl*)-Me), 497 (M^+-Me); ^1H NMR ($CDCl_3$) δ 0.07 (s, 18 H), 0.14 (s, 9 H), 2.38 (s, 1 H), 7.2-8.2 (m, 4 H); Anal. Calcd for $C_{23}H_{41}O_3Si_4Cl$: C, 53.81; H, 8.05; Cl, 6.91. Found C, 53.60; H, 8.06; Cl, 6.82. **11**: IR (neat) 2150 (C≡C), 1740 (C=O) cm^{-1}; MS m/z 388 (M^+); ^1H NMR ($CDCl_3$) δ 0.14 (s, 9 H), 0.17 (s, 9 H), 0.34 (s, 9 H), 7.3-7.7 (m, 3 H), 7.9-8.2 (m, 2 H); Anal. Calcd for $C_{20}H_{32}O_2Si_3$: C, 61.80; H, 8.30. Found C, 61.51; H, 8.15.
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