

The Ring Contraction of 1,2-Disilacyclobut-3-ene to the Silacyclopropane System

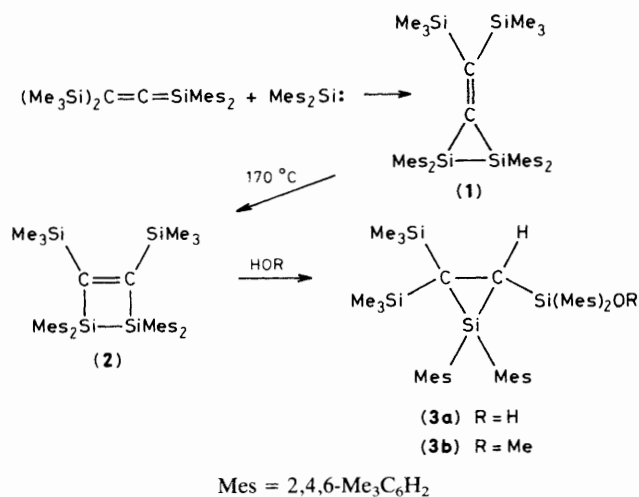
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The reaction of 1,1,2,2-tetramesityl-3,4-bis(trimethylsilyl)-1,2-disilacyclobutene obtained by thermolysis of 1,1,2,2-tetramesityl-3-bis(trimethylsilyl)methylene-1,2-disilacyclopropane with water and methanol afforded the respective silacyclopropanes.

Small-ring compounds involving a silicon-silicon bond in the ring are interesting because of their high strain energy.¹⁻³ Recently, we have found that dimesitylsilanediyne adds to 1,1-dimesityl-3,3-bis(trimethylsilyl)-1-silapropadiene yielding 1,1,2,2-tetramesityl-3-bis(trimethylsilyl)methylene-1,2-disilacyclopropane (1) which is the first example of a stable

disilacyclopropane.² In this paper, we report new chemistry of the silicon-containing small ring system, ring enlargement of compound (1) to 1,1,2,2-tetramesityl-3,4-bis(trimethylsilyl)-1,2-disilacyclobutene (2), and ring contraction of (2) to the silacyclopropane system (3). Thus, heating (1) at 170 °C in a degassed glass tube afforded (2) [m.p. 257.5 °C (decomp.)],



702 (M^+), 400 MHz ^1H n.m.r. δ (CDCl_3) -0.07 (18H, s, Me_3Si), 2.15–2.58 (36H, m, *o*- and *p*-Me), 6.64 (2H, s, ring protons), 6.71 (2H, s, ring protons), 6.79 (2H, s, ring protons), 6.82 (2H, s, ring protons)], as pale yellow crystals in quantitative yield. The fact that the ^{13}C n.m.r. spectrum of **(2)** shows a single resonance at δ 115.1, due to olefinic carbon atoms is consistent with the presence of the 1,2-disilacyclobut-3-ene ring.

Interestingly, when compound **(2)** was refluxed in wet benzene for 2 h, a white crystalline compound, 1,1-dimesityl-3-(dimesitylhydroxysilyl)-2,2-bis(trimethylsilyl)-1-silacyclopropane (**3a**) [m.p. 238–239 °C (decomp.), 720 (M^+), i.r.

3650 cm^{-1} , ^1H n.m.r. δ (CCl_4) -0.02 (9H, s, Me_3Si), 0.07 (3H, s, MeSi), 0.15 (3H, s, MeSi), 0.44 (3H, s, MeSi), 1.42 (1H, s, HO), 1.45 (1H, s, HC), 1.77–2.85 (36H, m, *o*- and *p*-Me), 6.58–6.90 (8H, m, ring protons)] was obtained quantitatively. The structure of **(3a)** was also verified by an X-ray diffraction study which will be reported elsewhere. The reaction of **(2)** with methanol afforded a similar adduct to **(3a)**. Thus, treatment of **(2)** with an excess of dry methanol at 120 °C in a sealed tube for 1 h gave 1,1-dimesityl-3-(dimesitylmethoxysilyl)-2,2-bis(trimethylsilyl)-1-silacyclopropane (**3b**) [m.p. 249–251 °C (decomp.), 734 (M^+), i.r. 1110 cm^{-1} , ^1H n.m.r. δ (CCl_4) -0.07 (9H, s, Me_3Si), 0.18 (6H, br. s, Me_2Si), 0.38 (3H, br. s, MeSi), 1.31 (1H, s, HC), 1.43–2.84 (36H, m, *o*- and *p*-Me), 3.28 (3H, s, MeO), 6.60–6.94 (8H, m, ring protons)] in quantitative yield.

All silacyclopropanes reported to date react readily with water and alcohols to give the corresponding ring opened compounds,⁴ however, both **(3a)** and **(3b)** are unaffected by such reagents, even at high temperature.

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