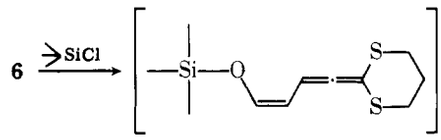
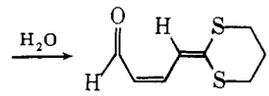
saturated aldehyde, which has a coupling constant of 16 Hz.[7] Nonaqueous workup led to an extremely unstable product. This product exhibited no absorptions indicative of an aldehyde in the IR or NMR. This is consistent with O-silylation rather than C-silylation and suggests the possible intermediacy of allene **8**. Although no direct evidence for **8** can be given, it seems to be most consistent with the results.

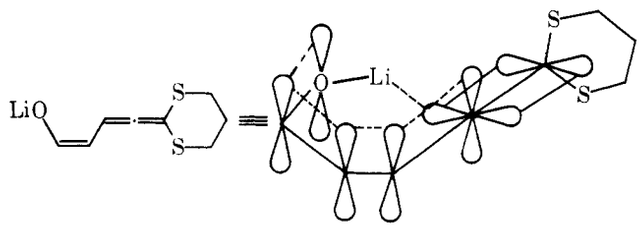


8



9

Reaction of **6** with D_2O led to the quantitative isolation of **9** with incorporation of deuterium in the γ position. In the NMR spectrum of the deuterated sample, a doublet at δ 6.63 in the spectrum of **9** was absent. Formation of the enol-OD followed by a 1,5-suprafacial shift of D would account for the position of the deuterium and the cis configuration about the double bond.[8] Anion **6** might best be depicted as shown below.



Attempts to quench **6** with other electrophiles (CH_3I, PhCOCl, and Ac_2O) led to unidentifiable products.

Experimental Section

All melting points were taken on a Fisher-Johns Mel-Temp apparatus and are uncorrected. IR spectra were obtained on a Beckman IR 4250 spectrometer. NMR spectra were recorded using a Varian A-60 spectrometer. All chemical shifts are reported in δ relative to tetramethylsilane as an internal standard. An AEI-MS902 mass spectrometer was used for mass spectral data. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Visible spectra were recorded on a Cary-14 spectrometer. All organic solutions were dried over sodium sulfate.

2-(2-Furyl)-1,3-dithiane (2). A solution of 50 mmol of 1,3-propanedithiol and 50 mmol of furfural in 50 mL of CH_2Cl_2 was stirred at 0 °C for 30 min under an atmosphere of N_2. Then 5 mmol of BF_3·Et_2O were added and the reaction was slowly warmed to room temperature. The solution was stirred overnight at room temperature. It was then washed with $NaHCO_3$ solution, dried, filtered, and concentrated. The residue was recrystallized from hexane/benzene solution yielding 7.0 g (75%) analytically pure **2** (mp 43 °C): NMR ($CDCl_3$) 2.1 (m, 2 H), 3.0 (m, 4 H), 5.31 (s, 1 H), 6.49 (m, 2 H), 7.5 (m, 1 H).

Anal. Calcd for $C_8H_{10}OS_2$: C, 51.57; H, 5.41. Found C, 51.7; H, 5.62.

Method A: General Procedure for Expected Adducts. A 0.10 M solution of dithiane **2** in THF was cooled to −78 °C. To this was added an equivalent amount of *n*-butyllithium. The reaction was stirred at −78 °C for 10 min. During this time the solution turns deep red. This was followed by addition of a 2 M THF solution of the appropriate electrophile. The reaction was stirred at −78 °C for 15 min. It was then slowly warmed to room temperature. The solution was poured into ether and washed with a buffered (pH 7) NH_4Cl/NH_4OH solution. The organic solution was dried, filtered, and concentrated. The residue was chromatographed on silica gel using ether/hexane.

2-(2-Furyl)-2-(1-hydroxy-2-butenyl)-1,3-dithiane (4): 95% yield; IR (film) 3435 cm^{-1}; NMR ($CDCl_3$) 1.70 (d, J = 4.0 Hz, 3 H), 2.00 (m, 2 H), 2.77 (m, 4 H), 4.37 (d, J = 4.0 Hz, 1 H), 5.55 (m, 2 H), 6.37 (m, 1 H), 6.60 (m, 1 H), 7.50 (m, 1 H). High resolution mass spectrum *m/e* 256.0600 ($C_{12}H_{16}O_2S_2$ requires 256.05918).

2-Formyl-2-(2-furyl)-1,3-dithiane (5). A fourfold excess of ethyl formate was used to quench the anion. The compound after chromatography was recrystallized from hexane/CH_2Cl_2: 60% yield; white crystals (mp 72 °C); IR ($CHCl_3$) 1730, 2705, and 2820 cm^{-1}; NMR ($CDCl_3$) 2.14 (m, 2 H), 3.05 (m, 4 H), 6.60 (m, 2 H), 7.10 (m, 1 H), 9.40 (s, 1 H). High resolution mass spectrum *m/e* 213.9939 ($C_9H_{10}O_2S_2$ requires 214.0122).

Method B: General Procedure for Rearrangement of 2-(2-Furyl)-1,3-dithiane. A solution of 40 mL of anhydrous THF and 10 mmol of dithiane **2** was cooled to −40 °C. To this solution was added 10 mmol of *n*-butyllithium. The reaction was warmed to −20 °C and stirred at this temperature for 2 h. The resulting dark red solution was cooled to −78 °C. This was followed by addition of 10 mmol of the appropriate electrophile. The reaction was slowly warmed to 0 °C, poured into ether, and washed with a buffered (pH 7) NH_4Cl/NH_4OH solution. The organic solution was dried, filtered, and concentrated. The residue was chromatographed on silica gel using ether/hexane.

2-(5-Formyl-6-methyl-2,4-cyclohexadien-1-ylidene)-1,3-dithiane (7): red oil; 15% yield; IR (film) 2800, 2709, 1650 cm^{-1}; NMR ($CDCl_3$) 1.0 (d, J = 4.0 Hz, 3 H), 2.28 (m, 2 H), 3.05 (m, 4 H), 4.20 (q, J = 4.0 Hz, 1 H), 6.14 (dd, J_{32} = 3.0 Hz, J_{34} = 4.8 Hz, 1 H), 6.98 (d, J_{23} = 3.0 Hz, 1 H), 7.19 (d, J_{43} = 4.8 Hz, 1 H), and 9.65 (s, 1 H). High-resolution mass spectrum *m/e* 238.0434 ($C_{12}H_{14}OS_2$ requires 238.0486). Visible spectra (CH_3OH) 441 nm.

2-(3-Formyl-(*Z*)-2-propen-1-ylidene)-1,3-dithiane (9): red oil; 100% yield; IR (film) 2800, 2710, 1655 cm^{-1}; NMR ($CDCl_3$) 2.28 (m, 2 H), 3.10 (m, 4 H), 6.10 (dd, J_{32} = 7.5 Hz, J_{34} = 4.2 Hz, 1 H), 6.63 (d, J_{12} = 6.0 Hz, 1 H), 7.68 (dd, J_{21} = 6.0 Hz, J_{23} = 7.5 Hz, 1 H), and 9.78 (d, J_{43} = 4.2 Hz, 1 H). High-resolution mass spectrum *m/e* 186.0154 ($C_6H_{10}OS_2$ requires 186.0173). Visible spectra (CH_3OH) 365 nm.

2-(4-Hydroxy-(*Z*)-2-buten-1-ylidene)-1,3-dithiane. To a solution of 4 mL of CH_3OH and 2 mmol of **9** was added 0.55 mmol of $NaBH_4$. The reaction was stirred at room temperature for 30 min. It was diluted with 30 mL of Et_2O and washed with saturated NaCl solution. The Et_2O was dried and concentrated: yield 0.30 g (8); IR (film) 3434 cm^{-1}; NMR ($CDCl_3$) 2.20 (m, 2 H), 3.10 (m, 4 H), 4.20 (d, J = 5.0 Hz, 2 H), 5.85 (m, 1 H), 6.50 (m, 2 H).

***n*-Pentyl Alcohol.** A solution of 0.53 mmol of 2-(4-hydroxy-(*Z*)-2-buten-1-ylidene)-1,3-dithiane and 1 g of W-4 Ra-Ni in 25 mL of EtOH was refluxed for 1 h. Analysis by GLC proved the product to be *n*-pentyl alcohol.

Registry No.—**2,** 67421-75-4; **4,** 67421-76-5; **5,** 67421-77-6; **7,** 67421-78-7; **9,** 67421-79-8; 1,3-propanedithiol, 109-80-8; furfural, 98-01-1; 2-(4-hydroxy-(*Z*)-2-buten-1-ylidene)-1,3-dithiane, 67421-80-1; pentanol, 71-41-0; 2-(2-furyl)-2-lithio-1,3-dithiane, 67421-81-2.

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Tri-*tert*-butylmethylsilane

R. J. Wroczynski, Linda D. Iroff, and Kurt Mislow*

Department of Chemistry, Princeton University, Princeton, New Jersey 08540

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In connection with our studies of internal conformational dynamics in systems of the type t-Bu_3MX,[1] it became of interest to prepare tri-*tert*-butylmethylsilane (**1**, t-Bu_3SiCH_3). This compound had resisted a prior attempt at preparation by a copper-catalyzed methylene insertion into tri-*tert*-but-

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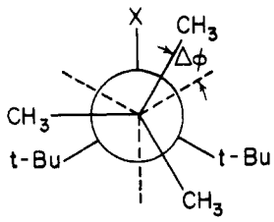
Table I. Calculated Structural Parameters for *t*-Bu_3SiX (X = CH_3 and H)



	X = CH_3 (1)	X = H (2)
$r(Si-C_q{}^a)$, Å	1.925	1.916
$r(Si-X)$, Å	1.878	1.483
$r(C_q-C)$, Å	1.535	1.533
$\theta(C_q-Si-C_q)$, deg	113.5	114.7
$\theta(C-C_q-C)$, deg	106.9	107.8
$\Delta\phi^b$	15.3	14.4

[a] C_q = quaternary carbon atom. [b] $\Delta\phi$ = average angle of twist from the staggered conformation. See structure above.

ylsilane (**2**).[2] We have succeeded in obtaining **1** by *n*-Bu_3SnH reduction of *t*-Bu_3SiCH_2Br (**3**), which was prepared by bromocarbene insertion into **2**.[3]

Full relaxation empirical force field calculations[4] show that **1**, like **2**,[1] has C_3 symmetry in the ground state. Each *tert*-butyl group is twisted ca. 15° from a staggered conformation, thus rendering the three methyls in each group diastereotopic. The silyl methyl group is twisted by 11° in the same sense as the *tert*-butyls. The mutual repulsion of the bulky *tert*-butyl groups is the dominant structural feature of **1** (Table I). This is reflected in the long C_q–Si bonds and in the wide C_q–Si–C_q angles (113.5°). Replacement of the silyl CH_3 by H (**2**) allows the *tert*-butyl groups to move farther apart [θ(C–Si–C) = 114.7°] with a concomitant relaxation of other structural parameters. It is noteworthy that this angle in **2** is essentially the same as the C–Si–C angle calculated for trimesitylsilane (114.9°);[6] in analogous *t*-Bu_3MX and (mesityl)$_3$MX systems, the C–M–C angles[5] are also closely comparable for M = C, X = H (116.0[7] and 115.9°,[8] respectively)[9] and for M = P, X = lone pair (109.9[12] and 109.7°,[13] respectively). Evidently, *tert*-butyl and mesityl groups have similar steric demands in the C_3 ground states of these congested systems.

Hindered rotation about the Si–C bond in tri-*tert*-butylhalosilanes (*t*-Bu_3SiX) has been reported,[2a] with $\Delta G^{\ddagger}$ values of 8.2, 7.8, and 7.6 kcal/mol for X = I, Br, and Cl, respectively.[14] We have observed an analogous process in the variable temperature 100 MHz ^{1}H NMR spectra of **1**. At −117 °C, the *tert*-butyl methyl singlet splits into two peaks in a 2:1 ratio,[15] with $\Delta\nu$ = 16.5 Hz. The calculated value of $\Delta G^{\ddagger}_c$ = 7.9 ± 0.3 kcal/mol lies within the narrow range of barriers for the halosilanes, suggesting that the steric requirements for CH_3, Cl, Br, and I are similar in these systems. The significantly lower barrier for parent compound **2** ($\Delta G^{\ddagger}_{-140}$ = 6.1 kcal/mol[1]) indicates that **2** suffers less intramolecular crowding in the transition state.

Experimental Section

All reactions were carried out under a nitrogen atmosphere. Phenyl(dibromomethyl)mercury[16] and tri-*tert*-butylsilane[17] were prepared using reported procedures. Chlorobenzene was washed with concentrated H_2SO_4 and then aqueous $NaHCO_3$ solution, dried over anhydrous $MgSO_4$, and distilled from P_2O_5 onto type 3Å molecular sieves. Tri-*n*-butyltin hydride was used as purchased from Alfa-Ventron Corp., Danvers, Mass. Melting points were taken on a Thomas-Hoover apparatus and are corrected. Ambient temperature ^{1}H NMR spectra were recorded on a Varian A-60A instrument. All GLC analyses were carried out on a FM Research Chromatograph 810 with a 6 ft × 0.25 in SE-30 (20% on Chromosorb W) column. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y.

DNMR Measurements. All variable temperature ^{1}H NMR spectra were recorded at 100 MHz in the Fourier transform mode on a Varian XL-100. The spectrometer was locked on ^{19}F present in the CF_2Cl_2 solvent. Temperature measurements were made with a copper–constantan thermocouple inserted directly into the 10 mm o.d. sample tube at coil height. Temperatures are considered to be accurate to ±2 °C, although within a given series smaller differences (ca. ±0.5 °C) were considered significant. Activation parameters were obtained by a least-squares fit of the rate data obtained by lineshape analysis using the Saunders program[18] and the Eyring equation.

Preparation of Tri-*tert*-butyl(bromomethyl)silane (3). Compound **2** (9.0 g, 0.045 mol), $PhHgCHBr_2$ (9.3 g, 0.021 mol), and 15 mL of chlorobenzene were placed in a 100-mL two-neck flask equipped with a nitrogen inlet, magnetic stirrer, and condenser. The mixture was then heated at reflux for a period of 96 h. The dark red liquid was cooled to room temperature, and the PhHgBr precipitate was filtered and washed with *n*-pentane. Vacuum distillation of the combined filtrates allowed removal of the remaining solvent and recovery of the excess of unreacted **2**. Consecutive sublimations of the resulting pot residue at 90 °C (0.5 Torr) gave 2.5 g (41%) of **3** as a white waxy solid: mp 189–195 °C; ^{1}H NMR ($CDCl_3$) δ 1.18 (s, CH_3), 2.73 (s, CH_2Br). Anal. Calcd for $C_{13}H_{29}BrSi$: C, 53.22; H, 9.96; Br, 27.24. Found: C, 53.65; H, 9.98; br, 27.04.

Preparation of Tri-*tert*-butylmethylsilane (1). Compound **3** (0.90 g, 0.0031 mol) and 20 mL of heptane were placed in a 25-mL three-neck flask equipped with a condenser, nitrogen inlet, and magnetic stirrer. The reaction vessel was flushed with nitrogen, *n*-Bu_3SnH (0.89 mL, 0.0034 mol) was added by syringe, and the reaction mixture was refluxed for 24 h. The solvent was removed by vacuum distillation. Preparative GLC of the resulting pot residue gave 0.29 g (44%) of **1**: mp (sealed tube) 141–145 °C; ^{1}H NMR ($CDCl_3$) δ −0.06 (s, Si–CH_3), 1.04 (s, CH_3). Anal. Calcd for $C_{13}H_{30}Si$: C, 72.80; H, 14.10; Si, 13.10. Found: C, 72.88; H, 14.10; Si, 12.96.

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Registry No.—**1**, 67382-52-9; **2**, 18159-55-2; **3**, 67382-53-0; $PhHgCHBr_2$, 1124-50-1.

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