

SYNTHESIS OF 2-(TRIMETHYLSILYL)-1,3-BUTADIENES

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Abstract: The reactions of trimethylsilyl-substituted α -allenic alcohols with lithium aluminum hydride afforded 2-(trimethylsilyl)-1,3-butadienes.

Diels-Alder reactions of 2-(trialkylsilyl)-1,3-butadienes are receiving increasing attention.¹ The alkenylsilane moiety formed in these reactions masks numerous latent functional groups.² Recently, it was reported that introduction of a bulky trimethylsilyl group at the internal vinyl carbon positions of the dienes greatly enhanced the diastereoselection of the intramolecular Diels-Alder reactions.^{1c} We describe here a simple synthesis of these compounds.

One synthetic route to 1,3-butadienes is the reduction of α -allenic alcohols with lithium aluminum hydride.³ We recently reported a simple method for the preparation of a variety of trimethylsilyl-substituted α -allenic alcohols.⁴ These compounds were thus easily converted to 2-(trimethylsilyl)-1,3-butadienes (Table I).⁵

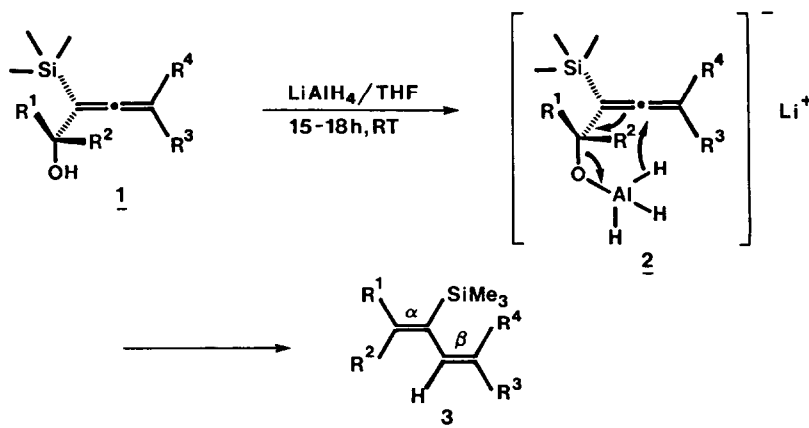
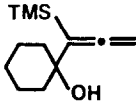
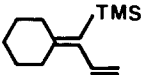
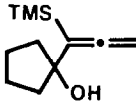
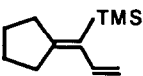
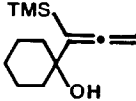
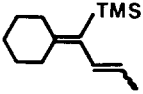
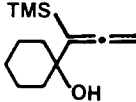
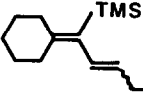
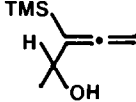
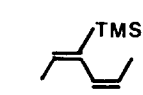
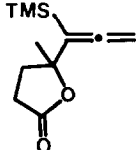
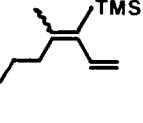
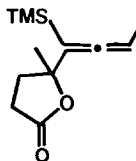
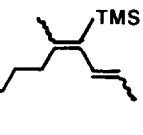


Table I. Synthesis of 2-(Trimethylsilyl)-1,3-butadienes

allene	diene ^a	yield, ^b %	isomer ratio ^c
<u>1a</u> 	<u>3a</u> 	42	-
<u>1b</u> 	<u>3b</u> 	48	-
<u>1c</u> 	<u>3c</u> 	70	E:Z=2:1
<u>1d</u> 	<u>3d</u> 	80	E:Z=4:1
<u>1e</u> 	<u>3e</u> 	48	α :E, β Z ^d , one isomer
<u>1f</u> 	<u>3f</u> 	58 ^e	3:2
<u>1g</u> 	<u>3g</u> 	57 ^e	four isomers

^a The isolated products have been fully characterized by IR and ¹H and ¹³C NMR (Jeol GX-270, 270 MHz in ¹H) spectroscopy and satisfactory elemental composition by combustion analysis (C and H) and/or mass spectroscopy. ^b Isolated yield (10 to 15 mmol reaction) after chromatography on silica gel or distillation. ^c The assignment of the geometry of the β double bond was based on the coupling constants of the E and Z vinyl protons and the isomer ratio was determined by integration. ^d The assignment of the geometry of the α double bond is based on the stereoelectronic consideration and must be regarded as tentative at present. However, it is in agreement with the observation that 3e failed to react with maleic anhydride. ^e Two equiv of LiAlH₄ was utilized.

It is interesting to note that in the reduction of both lc and ld, the hydride attack of the allenyl system is preferentially from the more hindered methyl side to afford the E-isomer predominantly. Such preference has been observed previously for the reduction of simple α -allenyl alcohols.^{3c}

Surprisingly, in the case of le, only one geometric isomer was detected. Moreover, contrary to lc and ld, the hydride attack is from the hydrogen side of the allenyl system to yield the Z-configuration for the β double bond. After examining the molecular model, the reason for such a change becomes apparent. If the carbon-oxygen bond in 2e is lined up parallel to the p-orbitals in order to allow maximum overlap during the formation of the α double bond, the methyl group will prefer to assume the position of R² in 2. Such conformation will reduce the nonbonded interaction with the bulky trimethylsilyl group and will provide the E-configuration for the α double bond. The hydride attack of the allenyl system will have to come from the bottom regardless of whether R³ is hydrogen or methyl group. The fact that only the Z-configuration was produced for the β double bond suggests that R³ is hydrogen and le contains only the SS and RR pair. Indeed, we observed only one set of ¹³C NMR peaks for le. Apparently, high diastereoselectivity was achieved during the formation of le by condensation of acetaldehyde with the propargylic borane derived from 1-(trimethylsilyl)-1-butyne.⁴

In the cases of lf and lg, mixtures of isomers were obtained. Presumably, the steric requirements of R¹ and R² groups in lf and lg are very similar and thus the reductions exhibit low stereoselectivity. The fact that all four isomers were detected in 3g also suggests that lg contains two diastereomeric pairs.

The following procedure for the preparation of 3a is representative. To a 500-mL round-bottomed flask containing a suspension of 0.38 g (10 mmol) of lithium aluminum hydride in 100-mL of tetrahydrofuran at 0°C was slowly introduced by cannula 2.10 g (10 mmol) of 1a⁴ dissolved in 100-mL of tetrahydrofuran. The reaction mixture was allowed to warm to room temperature and stirred for 15-18 hours. The slurry was then slowly poured into a flask containing 200-mL of a saturated aqueous ammonium chloride solution at 0°C. After filtering through celite, the aqueous phase was separated and extracted with hexane, and the combined organic layers were then washed with water, dried over sodium sulfate, and concentrated. Column chromatography on silica gel (elution with petroleum ether) gave 0.82 g (42% yield) of 3a as a colorless liquid: IR (neat) 1615, 1595, 1445, 1245, 980, 900, 870, 830, 750, 680 cm⁻¹; ¹H NMR (CDCl₃) δ 6.23 (dd, 1H, J=10.8 and 17.6 Hz), 4.98 (dd, 1H, J=2.6 and 10.8 Hz), 4.71 (dd, 1H, J=2.6 and 17.6 Hz), 2.26 (br, 4H), 1.55 (br, 6H), 0.11 (s, 9H); ¹³C NMR (CDCl₃) δ 152.68, 139.72, 131.56, 114.37, 35.67, 32.63, 28.95, 28.80, 26.84, 1.01; MS, m/e 194 (M⁺), 179, 139, 120, 73. Anal. Calcd for C₁₂H₂₂Si: C, 74.15; H, 11.41. Found: C, 73.84; H, 11.19.

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5. Spectroscopic data of 3c and 3e.
3c: IR (neat) 1595, 1445, 1245, 960, 875, 835, 755, 685 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.89 (dm, $J \sim 16$ Hz), 5.83 (dm, $J \sim 11$ Hz), 5.40 (dq, $J = 11.0$ and 6.6 Hz), 5.13 (dq, $J = 15.8$ and 6.4 Hz), 2.25 (br), 2.12 (t, $J \sim 6$ Hz), 1.71 (dd, $J = 1.7$ and 6.5 Hz), 1.55 (br), 1.46 (dd, $J = 1.7$ and 6.7 Hz), 0.11 (s, 9H). The peaks at 5.89, 5.13, and 1.71 belong to the E-isomer while the peaks at 5.83, 5.40, and 1.46 are part of the Z-isomer. The isomer ratio was determined by the integration of the well separated peaks at 5.13 and 5.40.; ^{13}C NMR (CDCl_3) δ 152.30, 151.65, 132.65, 132.55, 130.57, 128.82, 125.10, 122.59, 35.65, 35.27, 32.83, 32.57, 28.93, 28.82, 28.76, 27.99, 26.88, 26.87, 18.33, 14.04, 1.10, 0.80; MS, m/e 208 (M^+), 193, 134, 73.
3e: IR (neat) 1610, 1440, 1400, 1365, 1245, 990, 835, 775, 745, 700, 625 cm^{-1} ; ^1H NMR (CDCl_3) δ 5.84 (qm, 1H, $J \sim 6.4$ Hz), 5.81 (dm, 1H, $J \sim 11$ Hz), 5.49 (dq, 1H, $J = 11.6$ and 6.6 Hz), 1.59 (dd, 3H, $J = 1.5$ and 6.4 Hz), 1.44 (dd, 3H, $J = 1.7$ and 6.6 Hz), 0.03 (s, 9H); ^{13}C NMR (CDCl_3) δ 140.62, 134.06, 128.88, 124.10, 16.21, 14.15, -1.82; MS, m/e 154 (M^+), 139, 99, 73.

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