+ e$^-$ process. We believe that this process is more difficult[6], and thus offers better selectivity. Indeed the high selectivity based on the ratio of **11b**/**11c** (13.5:1) obtained from this experiment compared to that obtained by using lithium (1:3.5) in experiment 5 agrees with our prediction. Comparison of these ratios indicates that the selectivity obtained with calcium is 47 times greater than that obtained with lithium for the reduction of **11a**.

In experiments 6 and 7, although excess of both calcium and lithium were used over a longer reaction time, we found that reduction of the alkyne functionality was significantly less for calcium than for lithium. This indicates that calcium is indeed a milder reducing agent than lithium. Therefore consideration must also be given to the origin of the electrons used in dissolving metal reductions.

In summary, we found that calcium metal in liquid ammonia offers better selectivity than lithium for debenzylation of substrates containing a benzyl ether moiety in conjunction with other functionalities.[12] Our experiments clearly indicate that control of the amount of calcium, in order to utilize the electrons from the $Ca^+ \rightarrow Ca^{2+} + e^-$ process, is critical for obtaining very high selectivity.

Acknowledgment. J.R.H. is grateful to Professor Eugene E. van Tamelen (Stanford University) for suggesting that calcium could prove to be a selective reducing agent. We also thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, the American Heart Association—Maryland Affiliate, Inc., and the Research Corporation for the support of this research.

Registry No. **1a**, 98689-60-2; **1b**, 10229-10-4; **2a**, 70770-06-8; **2b**, 122-97-4; **3a**, 16361-14-1; **3b**, 98-00-0; **4a**, 104948-20-1; **4b**, 515-00-4; **5a**, 104948-21-2; **5b**, 765-42-4; **6a**, 104948-22-3; **6b**, 102229-10-7; **7a**, 104948-23-4; **7b**, 62960-04-7; **7c**, 27415-10-7; **8a**, 104948-24-5; **9a**, 64740-57-4; **10a**, 104948-25-6; **10b**, 59042-34-1; **11a**, 104948-26-7; 11b, 31333-13-8; 11c, 10339-61-4; 12a, 104975-83-9; 12b, 104948-27-8; $PhCH_3$, 108-88-3; PhSSPh, 882-33-7; PhSH, 108-98-5; benzene, 71-43-2.

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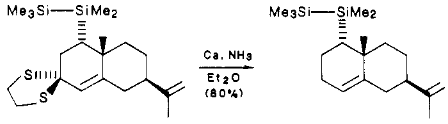
[12] Calcium in liquid ammonia also successfully reduced **12a**, affording **12b** in 80% yield. In contrast, use of sodium in liquid ammonia gave **12b** in only 7% yield with the major product coming from the cleavage of the silicon–silicon bond.



12a 12b

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Stereoselective Synthesis of 2-[(Trimethylsilyl)methyl]-1,3-butadienes†

Summary: Allylborane **3**, readily prepared from 1,2-bis(trimethylsilyl)-2,3-butadiene by hydroboration with 9-borabicyclo[3.3.1]nonane, smoothly condenses with aldehydes and ketones to afford, after basic or acidic workup, a variety of 2-[(trimethylsilyl)methyl]-1,3-butadienes with the dienes derived from aldehydes having high isomeric purity.

Sir: The synthetic applications of 2-[(trimethylsilyl)methyl]-1,3-butadienes are rapidly expanding.[1] The parent diene exhibited extremely high regioselectivity in the Lewis acid catalyzed Diels-Alder reaction.[1c] It has also been utilized to introduce an isoprenyl group to an electrophilic carbon atom.[1d] However, only a few synthetic methods for these dienes have been reported.[1d,2] We describe here a simple and stereoselective route to these compounds.

It was reported that condensations of trimethylsilyl-substituted allylic boranes with aldehydes showed very high diastereoselectivity.[3] In several cases, the resulting β-trimethylsilyl alcohols contained essentially only the *RS*/*SR* pair (>99%). Treatment of these alcohols with potassium hydride provided the (*Z*)-dienes (98% *Z*) after syn elimination of trimethylsilyl oxide. The (*E*)-dienes (99% *E*) were also obtained by using a catalytic amount of concentrated sufuric acid to induce anti elimination. The ability to obtain both isomers from the same intermediate is especially interesting. We envisioned that by properly attaching an additional (trimethylsilyl)methyl group to the allylic borane, 2-[(trimethylsilyl)methyl]-1,3-butadienes could thus be synthesized. A summary of our reaction sequence is outlined in Scheme I.

Hydroboration of 1,2-bis(trimethylsilyl)-2,3-butadiene (**2**), readily prepared from **1** (40% yield) according to the reported procedure,[4] with 9-borabicyclo[3.3.1]nonane[5] afforded the desired allylborane **3**. The geometry of the double bond in **3** has not been determined.[6] Condensations of **3** with aldehydes and cyclohexanone proceeded smoothly and provided 2-[(trimethylsilyl)methyl]-1,3-butadienes after either basic or acidic workup (Table I). The dienes derived from aldehydes had high isomeric purity (≥97%). Apparently, high diastereoselectivity was also achieved during the condensation step to form **4**. In each case, by simply changing the workup condition, either the *E* or the *Z* isomer of the diene was obtained.

The geometry of the double bond in **5a** and **6a** was determined by comparing the ^1H NMR spectra of these two isomers with the reported data.[2c] The chemical shift of the vinylic hydrogen at C(2) of **5a** (δ 6.73) is 0.44 ppm downfield from that of the corresponding hydrogen of **6a** (δ 6.29) and thus allowed easy identification. Such a difference of chemical shifts was also observed for dienes derived from other aldehydes and was utilized to tentatively assign their geometry.[7]

Although cyclohexanone was found to react with **3** at refluxing temperature of THF, 2-pentanone failed to show any significant reactivity even after prolonged heating.

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† Dedicated to Professor George Zweifel on the occasion of his 60th birthday.

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[6] The existence of a rapid allylic rearrangement for allylic borane[5] could allow either the *E* or the *Z* isomer or both to be the reacting species regardless of the geometry of the double bond in **3**.

0022-3263/86/1951-4733$01.50/0

Scheme I

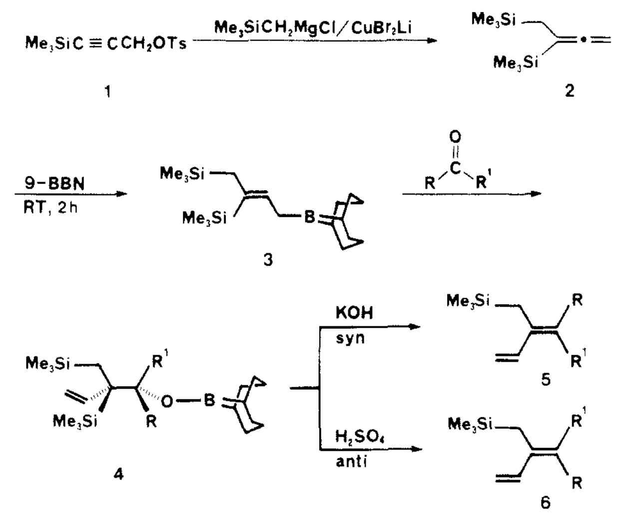


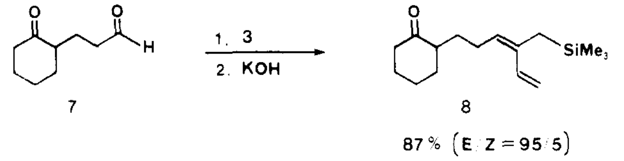
Table I. Stereoselective Synthesis of 2-[(Trimethylsilyl)methyl]-1,3-butadienes

diene	R	R^1	isolated yield,[a] %	5:6[b]
5a	H	CH_3	61	98:2
6a	H	CH_3	50	2:98
5b	H	n-C_5H_{11}	82	97:3
6b	H	n-C_5H_{11}	87	0.5:99.5
5c	H	C_6H_5	88	98:2
6c	H	C_6H_5	83	2:98
5d	H	(E)-$CH_3CH{=}CH$	59	98:2
5e	$-(CH_2)_5-$		58	
5e[c]	$-(CH_2)_5-$		61	
5f[c]	CH_3	n-C_3H_7	68	55:45[d]

[a] The isolated products have been fully characterized by IR, ^1H and ^{13}C NMR (270 MHz in ^1H), and mass spectroscopy. [b] The isomer ratio was determined by integration of ^1H NMR spectrum. [c] The reaction mixture was treated with 5 drops of $BF_3 \cdot OEt_2$ and was stirred for 2 h before workup with alkaline hydrogen peroxide. [d] The stereochemistry was not determined.

However, by simply adding a few drops of $BF_3 \cdot OEt_2$ to the reaction mixtures, condensation with cyclohexanone was essentially complete after only 2 h at room temperature and with 2-pentanone in 2 h at 35 °C. Presumably, the reaction took a different pathway in the presence of $BF_3 \cdot OEt_2$. A cyclic six-membered transition state has been utilized to describe the condensation of allylboranes with carbonyl groups.[3] In the presence of a Lewis acid, an acyclic stepwise mechanism may take place with enhanced reaction rate.[3b]

The lower reactivity of **3** toward the keto group was exploited for selective condensation with the aldehyde group of **7**[8] to **8**.[7]



In conclusion, this procedure offers a simple and stereoselective method for the preparation of 2-[(trimethylsilyl)methyl]-1,3-butadienes for further synthetic elaborations. The ready availability of a variety of trimethylsilyl-substituted allenes[4,9] makes many different types of allylic boranes easily accessible by hydroboration for the synthesis of dienes.

The following procedure for the preparation of **5c** is representative. To a 100-mL reaction flask flushed with dry nitrogen were successively added with syringes 0.468 g of **2** (2.35 mmol), 10 mL of THF, and 4.14 mL of a 0.57 M solution of 9-borabicyclo[3.3.1]nonane (2.36 mmol) in THF. After 2 h of stirring at room temperature, 0.24 mL of benzaldehyde (0.25 g, 2.36 mmol) was introduced. The reaction mixture was stirred for an additional hour[10] and then treated with 5 mL of 3 N NaOH and 5 mL of 30% H_2O_2. The elimination of trimethylsilyl oxide was complete in less than 30 min.[11] The organic layer was then separated, washed with water, and concentrated. The residue was column chromatographed (silica gel/hexane) to afford 0.45 g (88%) of **5c** as a colorless liquid: IR (neat) 1620 (w), 1600 (s), 1585 (m), 1490 (s), 1445 (m), 1420 (m), 1245 (s), 1225 (m), 1200 (m), 1155 (s), 1000 (m), 900 (s), 850 (s), 740 (s), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.34–7.15 (5 H, m), 6.86 (1 H, ddd, J = 17.4, 10.9, and 0.9 Hz), 6.31 (1 H, br s), 5.29 (1 H, dm, J = 17.4 Hz), 5.16 (1 H, dt, J = 11.0 and 1.5 Hz), 1.85 (2 H, d, J = 1 Hz), 0.06 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 138.04, 137.25, 135.17, 129.40, 128.05, 127.74, 126.21, 115.67, 23.54, −0.89; MS, m/e 216 (M^+), 201, 142, 129, 115, 73. Anal. Calcd for $C_{14}H_{20}Si$: C, 77.70; H, 9.32. Found: C, 77.16; H, 9.61.

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Registry No. **2**, 105040-62-8; **5a**, 105040-63-9; **5b**, 105040-64-0; **5c**, 105040-65-1; **5d**, 105040-66-2; **5e**, 105040-67-3; **5f**, 105040-68-4; **6a**, 100580-63-0; **6b**, 105040-69-5; **6c**, 105040-70-8; **6f**, 105040-71-9; **7**, 2568-20-9; (E)-**8**, 105040-72-0; (Z)-**9**, 105040-73-1; 9-BBN, 280-64-8; n-$C_5H_{11}CHO$, 66-25-1; C_6H_5CHO, 100-52-7; (E)-$CH_3CH{=}CHCHO$, 123-73-9; $\overline{(CH_2)_5CO}$, 108-94-1; n-$C_3H_7COCH_3$, 107-87-9; CH_3CHO, 75-07-0.

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[7] Spectral data for **6c** and **8**. **6c**: IR (neat) 1605 (m), 1495 (m), 1445 (m), 1250 (s), 1150 (m), 985 (m), 895 (m), 845 (s), 745 (m), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.31 (4 H, d, J = 4.4 Hz), 7.17 (1 H, m), 6.47 (1 H, ddd, J = 17.4, 10.8, and 0.7 Hz), 6.39 (1 H, br s), 5.21 (1 H, d, J = 17.2 Hz), 5.10 (1 H, d, J = 10.8 Hz), 2.09 (2 H, s), −0.04 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 142.37, 138.85, 135.48, 128.95, 128.90, 128.19, 126.30, 113.03, 16.91, −0.39; MS, m/e 216 (M^+), 201, 142, 129, 115, 73. **8**: IR (neat) 1710 (s), 1630 (w), 1595 (w), 1445 (m), 1245 (s), 840 (s), 690 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.66 (1 H, ddd, J = 17.4, 10.9, and 0.9 Hz), 5.12 (1 H, t, J = 7.2 Hz), 5.08 (1 H, d, J = 17 Hz), 5.02 (1 H, d, J = 11 Hz), 2.4–2.2 (3 H, m), 2.2–2.1 (2 H, m), 2.0 (2 H, br), 1.8 (2 H, m), 1.6 (2 H, br), 1.59 (2 H, s), 1.35 (1 H, m), 1.2 (1 H, m), −0.06 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 213.14, 134.58, 133.49, 128.32, 113.78, 49.86, 42.12, 34.06, 29.81, 28.07, 25.04, 24.94, 22.35, −1.00; MS, m/e 264 (M^+), 183, 166, 92, 79, 73.

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[10] In the case of **5e**, the reaction mixture was heated to reflux for 24 h before workup.

[11] In the cases of **5a** and **5b**, the reaction mixture was treated with 5 mL of 3 N KOH and heated to reflux for 24 h to induce the elimination of trimethylsilyl oxide. In the cases of **6**, 5 drops of concentrated sulfuric acid was introduced and the reaction mixture was stirred at room temperature for 40 min before workup with alkaline hydrogen peroxide.