7.73, 1 H, $H_{6'}$), 5.07 (dd, J = 4.33 Hz, J = 11.4 Hz, 1 H, H_2), 2.45 (s, 3 H, $H_{2'''}$), ca. 2.4 (m, 1 H, H_3), 2.3 (s, 3 H, $H_{2''}$), ca. 2 (m, 1 H, H_3), ca. 1.5 (m, 1 H, H_4), 0.97 (br t, 6 H, $H_{5,6}$).

N-Trimellitylimido-11-aminoundecanoic acid Prepolymer. IR ($CHCl_3$, cm^{-1}) ν(C=O anhydride) 1805, ν(C=O imide) 1765, ν(C=O stretching vibration) 1710, ν(C-N stretching) 1390, ν(C=O imide) 750; ^1H NMR ($CDCl_3$) δ ca. 8.5 (m, 2 H, $H_{3',5'}$), ca. 8.0 (m, 1 H, $H_{6'}$), 3.72* (m, 2 H, H_{11}), 2.67* (t, J = 7.35 Hz, 2 H, H_2), 2.45* (t, J = 7.35 Hz, 2 H, H_2), 2.4 (s, 3 H, $H_{2'''}$), 2.2 (s, 3 H, $H_{2''}$), 1.7 (m, 4 H, $H_{3,10}$), 1.35 (m, 12 H, H_{4-9}) (* monomer and dimer).

Polymerization. Poly(*N*-trimellitylimidoglycine-*co*-sebacic anhydride). The *N*-trimellitylimidoglycine prepolymer was mixed with sebacic acid prepolymer in a defined ratio (with or without 1-2 mol % of a catalyst) in a Kimax glass tube with a side arm equipped with a capillary nitrogen inlet. The tube was immersed in an oil bath at the selected temperature (100-250 °C). After the prepolymers were melted, high vacuum was applied ($\leq 10^{-1}$ Torr), and the condensation byproduct, acetic anhydride, was collected in a chilled trap. At the end of the reaction the crude polymer was removed from the glass tube and dissolved in anhydrous methylene chloride or chloroform. The solution was filtered and precipitated into excess petroleum ether. The precipitate was collected by filtration, washed with anhydrous ethyl ether, and dried under vacuum at room temperature for 1 h.

All polymers were prepared by using the same synthesis procedure described above. If the polymers were not soluble in methylene chloride, they were purified by stirring in anhydrous ethyl ether for several hours.

The spectral data for poly(*N*-trimellitylimidoglycine-*co*-sebacic anhydride) (22:78) melt polymerized at 150 °C (without any catalyst) are as follows: GPC M_w = 38 783, M_n = 12 277, M_w/M_n = 3.16; ^1H NMR ($CDCl_3$) δ 8.52 (s, $H_{3'}$), 8.48 (d, $H_{5'}$, J = 8 Hz), 8.04 (d, $H_{6'}$, J = 7.8 Hz), 4.59 (s, H_2), 2.67 (t, H_a (SA-TMA), J = 7.3 Hz), 2.53 (t, H_a (SA-Gly), J = 7.3 Hz), 2.44 (t, H_a (SA-SA), J = 7.35 Hz), 1.68 (m, H_b), 1.3 (m, H_c); ^{13}C NMR ($CDCl_3$) δ 169 ($C_{7',8'}$), 168, 165, 162 (C=O, anhydride), 136.3 ($C_{5'}$), 136.1 ($C_{1'}$), 134.9 ($C_{4'}$), 132.4 ($C_{2'}$), 125.1 ($C_{3'}$), 124.1 ($C_{6'}$), 39.8 (C_1), 35.4, 35.2 (C_a), 28.8, 28.7 (C_b), 24 (C_c); IR (KBr, cm^{-1}) 2920, 2850 ν(C-H), 1810 ν(C=O anhydride), 1730 ν(N-C=O imide). Anal. Calcd: C, 63.04; H, 6.95; N, 1.61. Found: C, 62.14; H, 6.71; N, 2.02.

The spectral data for poly(*N*-trimellitylimido-β-alanine-*co*-sebacic anhydride) (16:84) melt polymerized at 120 °C with 2 mol % $Ca(CO_3)_2$ are as follows: GPC M_w = 91 582, M_n = 31 786, M_w/M_n = 2.88; ^1H NMR ($CDCl_3$) δ 8.44 (m, $H_{3',5'}$), 7.98 (d, $H_{6'}$, J = 7.7 Hz), 4.07 (t, H_3, J = 6.88 Hz), 2.93 (t, H_2, J = 6.85 Hz), 2.67 (t, H_a (SA-TMA), J = 7.25 Hz), 2.44 (t, H_a (SA-SA and SA-β-Ala), J = 7.27 Hz), 1.65 (m, H_b), 1.3 (s, H_c); ^{13}C NMR ($CDCl_3$) δ 169.5 ($C_{7',8'}$), 168.7, 168.3, 166.5 (C=O, anhydride), 136.2 ($C_{5'}$), 135.9 ($C_{1'}$), 134.4 ($C_{4'}$), 132.4 ($C_{2'}$), 124.9 ($C_{3'}$), 123.8 ($C_{6'}$), 35.4, 35.1 (C_a), 33.9, 33.5 ($C_{1,2}$), 28.8, 28.6 (C_b), 24 (C_c); IR (KBr, cm^{-1}) 2930, 2860 ν(C-H), 1810 ν(C=O anhydride), 1730 ν(N-C=O imide); mp 65 and 68 °C. Anal. Calcd: C, 63.95; H, 7.53; N, 1.14. Found: C, 62.49; H, 7.28; N, 1.4.

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Supplementary Material Available: Tables of polymerizations performed at various temperatures and with different catalysts, FTIR spectrum of a typical copolymer, and degradation profiles of various copolymers (3 pages). Ordering information is given on any current masthead page.

Stereoselective Synthesis of All Four Geometric Isomers of Internal 1,3-Butadienes by the Condensation Reaction of Aldehydes with the γ-Trimethylsilyl-Substituted Allylboranes

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Abstract: Hydroboration of 2-(trimethylsilyl)-2,3-pentadiene or 4-(trimethylsilyl)-2,3-octadiene with 9-borabicyclo[3.3.1]nonane or dicyclohexylborane produced the corresponding γ-trimethylsilyl-substituted allylborane which condensed smoothly with aldehydes to afford, after elimination of hydroxytrimethylsilane by either basic or acidic workup, a variety of internal 1,3-butadienes. Apparently, high diastereoselectivity was obtained during the condensation step and therefore allowed an easy control of the geometry of one of the two resulting double bonds by simply employing either basic or acidic workup conditions to promote the Peterson olefination reaction. The geometry of the other double bond could also be controlled by selecting either 9-borabicyclo[3.3.1]nonane or dicyclohexylborane as the hydroborating agent. Consequently, all four geometric isomers of several representative internal 1,3-dienes were synthesized with high isomeric purity by utilizing different combinations of the hydroborating agents and the workup conditions. The [1,3] sigmatropic rearrangement of γ-trimethylsilyl-substituted allylboranes was studied by ^1H NMR.

Development of new methodologies for the stereoselective synthesis of 1,3-butadienes has been the focus of attention for many years.[1-3] This interest is due in part to their utilities in the Diels-Alder reaction[4] as well as the discovery of many biologically active natural products having the conjugated diene functionality.[1f] One of the recent advances involves the use of palladium-catalyzed cross-coupling of alkenyl organometallics with alkenyl halides or triflates.[1] However, in order to produce high isomeric purity for the resulting 1,3-dienes, the alkenyl reagents with predetermined geometry must be utilized. It is not always an easy task to prepare certain alkenyl reagents with specific geometry. A different approach utilizes the condensation reaction of aldehydes with

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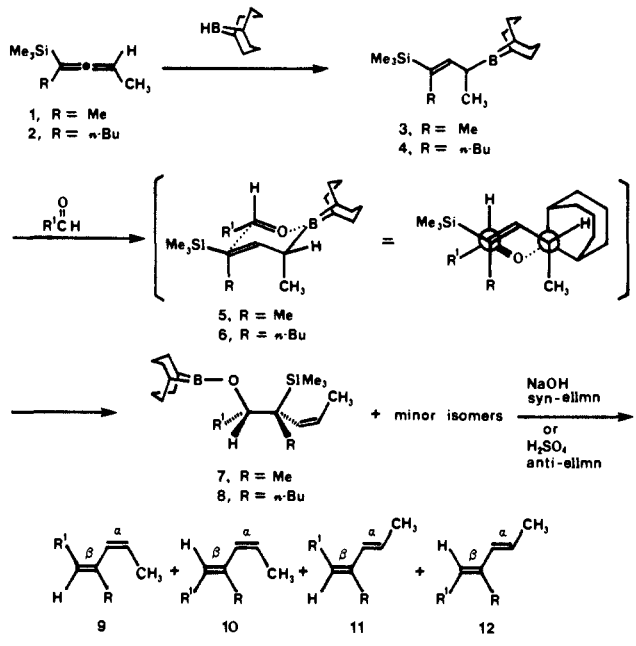
Scheme I



allylic organometallics containing a γ-trimethylsilyl or γ-phosphorus substituent. This methodology constitutes one of the most direct routes to 1,3-dienes, and significant progress in term of controlling the geometrical outcome of the resulting 1,3-dienes has been achieved in recent years.[2]

We recently reported a stereoselective synthesis of terminal 2-[(trimethylsilyl)methyl]-1,3-butadienes by the condensation reaction of aldehydes with the γ-trimethylsilyl-substituted allylborane derived from 1,2-bis(trimethylsilyl)-2,3-butadiene.[2a] We have further extended this methodology to the synthesis of all four geometric isomers of internal 1,3-dienes. Hydroboration of the readily available internal allenes **1** and **2** with 9-borabicyclo-[3.3.1]nonane (9-BBN) produced the corresponding allylboranes **3** and **4**, respectively.[5] Subsequent condensation with aldehyde proceeded smoothly to afford predominantly dienes **9** after basic workup. On the other hand, dienes **10** were obtained as the major product after acidic workup (Scheme I).

Since the understanding of the transition state as well as the stereochemical outcome of the condensation step required the knowledge of the double bond geometry of allylboranes **3** and **4**, attempts were made to determine the geometry of **3** and **4** by converting them to the corresponding allylic alcohols. Oxidation of **3** with alkaline hydrogen peroxide produced 4-(trimethylsilyl)-3-penten-2-ol (geometric isomer ratio = 98:2). The major isomer was found to have the *E* geometry by comparing its ^1H and ^{13}C NMR spectra with those of an authentic sample synthesized from 4-(trimethylsilyl)-3-butyn-2-ol by a reported procedure.[6] Similarly, oxidation of **4** afforded 4-(trimethylsilyl)-3-octen-2-ol (geometric isomer ratio = 94:6). The minor isomer was found to be identical to (*Z*)-4-(trimethylsilyl)-3-octen-2-ol synthesized from 3-octyn-2-ol by a procedure reported previously.[7] These results appear to suggest that hydroboration of allenes **1** and **2** proceeds from the side of the trimethylsilyl group. This is unexpected, because the trimethylsilyl group is sterically bulkier than the methyl or the *n*-butyl group[8] and hydroboration generally occurs from the less hindered side.

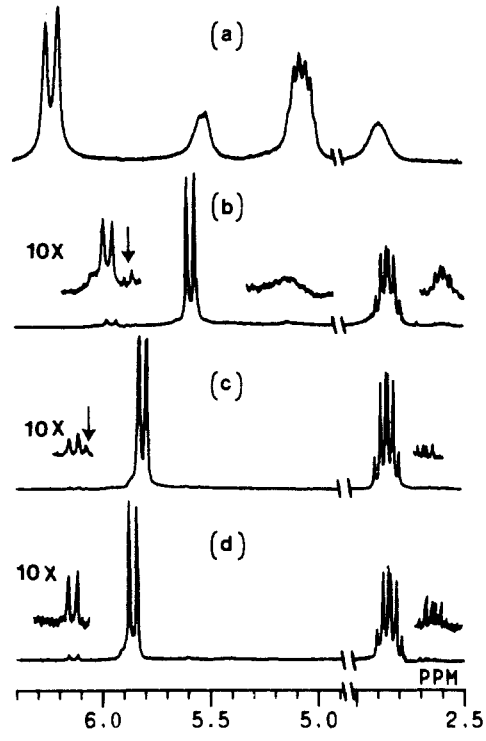
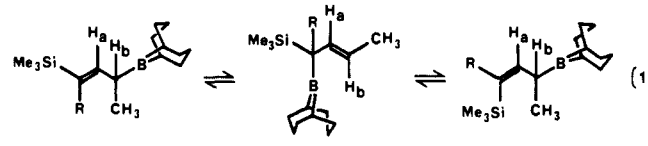


Figure 1. The ^1H NMR spectra of allylboranes (a) **3**, (b) **4**, (c) **17**, and (d) **18**. The small peaks indicated with an arrow are the ^{13}C satellites of the H_a signals of **4a** and **17a**.

It is perhaps possible to explain the unexpected selectivity on the basis of the existence of a rapid equilibration process between the *Z* and *E* isomers through the [1,3] sigmatropic rearrangement (eq 1).[5a] It could allow the initially formed *Z* isomer to isomerize to the corresponding *E* isomer. The existence of such a rapid



(1)

R = Me	3a	3c	3b
n-Bu	4a	4c	4b
i-Pr	13a	13c	13b
t-Bu	14a	14c	14b

equilibration process could also have implications for the subsequent condensation reaction with aldehydes. The *Z* isomer could become an important reacting species if the rate of isomerization is faster than that of the condensation reaction.

In order to determine the rate of the equilibration processes, allenes **1** and **2** and 5-methyl-4-(trimethylsilyl)-2,3-hexadiene were treated with 9-BBN dissolved in tetrahydrofuran-d_8, and the dynamic behaviors of the corresponding allylboranes were studied by ^1H NMR. We were surprised to discover that in the case where R = Me, the ^1H NMR spectrum showed that **3c** was the predominant species (75%), **3a** existed only as the minor isomer (25%), and **3b** was too small to be detected (Figure 1). The signal at δ 6.22 is attributed to H_a of **3c** with a typical trans-coupling constant of 15.4 Hz. The signal at δ 5.06, attributed to H_b of **3c**, is a doublet of quartets with J = 15 and 6 Hz, respectively. The two smaller broad signals at δ 5.52 and 2.89 are assigned to H_a and H_b of **3a**, respectively.

The preference for the boron atom to adopt the more hindered site as observed in **3c** is unprecedented. Whether the well-known ability of carbon–silicon bond in stabilizing an adjacent electron-deficient center through electron-donating hyperconjugation[9] as shown in **15** is also primarily responsible for this unusual observation remains to be investigated. However, it should be

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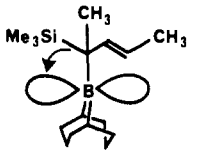

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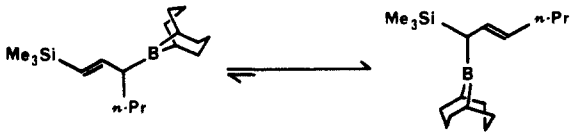
noted that such stabilization could also be utilized to account for the preferential attachment of boron to the carbon bearing the trimethylsilyl group observed previously in a similar allylborane system (eq 2).[10]



(2)

On irradiation of H_a of **3c** at δ 6.22, H_a of **3a** at δ 5.52 disappeared completely, H_b of **3c** at δ 5.06 became a quartet, and H_b of **3a** at δ 2.89 remained unaffected. On the other hand when H_b of **3c** was irradiated, H_b of **3a** disappeared with H_a of **3c** reducing to a singlet and H_a of **3a** showing no change. Similarly, irradiation of H_a and H_b of **3a** resulted in a complete disappearance of the corresponding H_a and H_b of **3c**. These results clearly indicated a relatively rapid equilibration process between **3a** and **3c**, exhibiting magnetization transfer during double resonance experiments. The rate of exchange and therefore the establishment of equilibrium is much faster than the rate of hydroboration of **1** with 9-BBN, which requires 6 h to complete. The measurement of the coalescence temperature was carried out with toluene-d_8 as the solvent. Coalescence between H_a of **3a** at δ 5.58 (22%) and H_a of **3c** at δ 6.24 (78%) occurred at 75 °C, whereas to achieve coalescence between H_b of **3a** at δ 2.89 and H_b of **3c** at δ 5.08 required heating to ca. 105 °C because of a larger difference of chemical shifts. The absence of the ^{1}H NMR signals from **3b** prevented the measurement of the exchange rate between **3b** and **3c**. However, the ^{1}H NMR study of the dynamic behavior of allylborane **4** suggested that exchange between **3b** and **3c** must be facile also. The ^{11}B NMR chemical shift of **3** in both THF-d_8 and toluene-d_8 is at δ 83 relative to external BF_3·OEt, indicating a lack of complexation of THF with various organoborane species.

It is interesting to point out that although **3c** was the predominant species, it was unreactive toward alkaline hydrogen peroxide and aldehydes. Apparently, the steric hinderance around the boron atom in **3c** greatly reduced its reactivity. Instead, **3a** and to a much lesser extent **3b** became the actual reacting species by way of the allylic rearrangement. This was further supported by the observation that introducing 1 equiv of pyridine to **3** in toluene-d_8 resulted in a dramatic redistribution of these organoborane species. The ^{1}H NMR spectrum exhibited a major doublet of quartets (98%) at δ 4.63 (J = 10.4 and 1.7 Hz) attributable to H_a of **3a** coordinated with pyridine and a minor doublet of quartets (2%) at δ 4.90 (J = 11 and 1.5 Hz) attributable to H_a of **3b** also coordinated with pyridine. Signals attributable to the pyridine-complexed **3c** were absent. The assignment of the major signal at δ 4.63 to H_a of the pyridine-complexed **3a** is based on the earlier reports that vinylic hydrogens cis to the trimethylsilyl group consistently exhibited ca. 0.3 ppm upfield shift with respect to the corresponding vinylic hydrogens trans to the trimethylsilyl group.[11] Apparently, selective complexation of pyridine with **3a** and **3b** occurred with the ^{11}B NMR signals now being shifted to δ −1.

Interestingly, the thermodynamic distributions of **4a** (93%), **4b** (5%), and **4c** (2%) were dramatically different. The major signals at δ 5.58 (d, J = 10.1 Hz) and δ 2.85 (dq, J = 10 and 7 Hz) are due to H_a and H_b of **4a**, respectively (Figure 1). The minor peaks at δ 5.96 (d, J = 12 Hz) and δ 2.60 (dq, J = 12 and 7 Hz) belong to H_a and H_b of **4b**. Again, the assignment of the signal at δ 5.58 to H_a of **4a** is based on its upfield chemical shift in comparison with that of H_a of **4b**. Two broad small humps at δ 6.0 and 5.1, attributable to H_a and H_b of **4c**, were also detected. The congestion around the boron atom in **4c** is probably responsible for allowing the slightly more hindered *n*-butyl group to tip the balance in favor of **4a**.

Irradiation of the small hump of H_b of **4c** resulted in a 75% decrease in intensity of H_b of **4a** with H_b of **4b** becoming too small to be detected. Similarly, H_a of **4a** exhibited a 90% decrease in intensity when H_a of both **4b** and **4c** at around δ 6.0 was irradiated. Complete disappearance of H_a of both **4b** and **4c** was observed on irradiation of H_a of **4a**. Coalescence of H_a signals of **4a** (δ 5.67, 92%), **4b** (δ 6.01, 5%), and **4c** (δ 6.02, 3%), measured in toluene-d_8 solvent, occurred at ca. 105 °C. Clearly, **4a**, **4b**, and **4c** are exchanging rapidly. Again, introduction of 1 equiv of pyridine to **4** in toluene-d_8 resulted in the signal of H_a of **4a** being shifted to δ 4.58 (d, J = 10.6 Hz) due to complexation. The ^{11}B NMR signal was also shifted from δ 82 to −1.

The preference for the formation of **3a** and **4a** over **3b** and **4b** is probably due to the large $A^{(1,3)}$ allylic interaction[12] with the sterically bulky trimethylsilyl group[8b] in **3b** and **4b**. This is supported by the observation that increasing the steric requirements of the R group from methyl and *n*-butyl to isopropyl resulted in decreased selectivity (**13a**/**13b** = 83/17). Intermediate **13c** could no longer be detected. The rate of exchange between **13a** (H_a, δ 5.53) and **13b** (H_a, δ 6.01) is still relatively fast as the magnetization transfer could also be observed. Oxidation of **13** with alkaline hydrogen peroxide produced a mixture of (*E*)- and (*Z*)-5-methyl-4-(trimethylsilyl)-3-hexen-2-ol in a 82:18 ratio. Furthermore, a reversal of selectivity was observed when the R group was changed to *tert*-butyl. Oxidation of **14**, derived from hydroboration of 5,5-dimethyl-4-(trimethylsilyl)-2,3-hexadiene with 9-BBN at the reflux temperature of THF for 7 days, afforded a mixture of (*E*)- and (*Z*)-5,5-dimethyl-4-(trimethylsilyl)-3-hexen-2-ol in a 28:72 ratio. However, it should be noted that since the rate of exchange between **14a** and **14b** was not measured and could be very slow, the ratio of the oxidized products might only reflect the kinetic distributions of the hydroboration step instead of the thermodynamic equilibrium of the resulting allylboranes.

The geometries of the dienes in Table I were also carefully determined. The $\alpha Z,\beta Z$ and the $\alpha Z,\beta E$ dienes consistently exhibited a typical cis coupling constant of 11.4–11.5 Hz for the α double bond, whereas the $\alpha E,\beta Z$ and $\alpha E,\beta E$ dienes were identified by a typical trans coupling constant of 15.5–15.8 Hz for the α double bond. The geometry of the β double bond of the $\alpha Z,\beta Z$ dienes was confirmed on the basis of the nuclear

Table I. Stereoselective Synthesis of Internal 1,3-Dienes

borane	workup	diene	R	R^1	isolated yield, %	isomer ratio,[a] 9:10:11:12
9-BBN	NaOH	**9a**	Me	n-C_5H_{11}	77	94:1:4:1
	H_2SO_4	**10a**			80	1:90:3:6
Chx_2BH	NaOH	**11a**			78	0:0:98:2
	H_2SO_4	**12a**			70	0:0:8:92
9-BBN	NaOH	**9b**	Me	C_6H_5	86	92:1:5:2
	H_2SO_4	**10b**			87	1:91:2:6
Chx_2BH	NaOH	**11b**			83	0:0:97:3
	H_2SO_4	**12b**			82	0:0:5:95
9-BBN	NaOH	**9c**	n-Bu	n-C_5H_{11}	68	97:1:2:0
	H_2SO_4	**10c**			65	1:93:2:4
Chx_2BH	NaOH	**11c**			77	0:0:97:3
	H_2SO_4	**12c**			73	0:0:9:91
9-BBN	NaOH	**9d**	n-Bu	C_6H_5	83	92:1:4:2
	H_2SO_4	**10d**			86	1:92:2:5
Chx_2BH	NaOH	**11d**			85	0:0:97:3
	H_2SO_4	**12d**			79	0:0:3:97

[a] The isomer ratios were determined by the integration of the ^{1}H NMR spectra and by gas chromatography. The ratios of the major isomers are accurate to within 3%. The detection level for minor isomers is about 1%.

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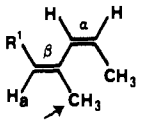
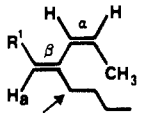
Overhauser effect. On irradiation of the methyl group indicated with an arrow in **9a** and **9b**, H_a showed a 12% and 16% increase in integrated intensity, respectively, strongly indicating a *Z* geometry for the β double bond. Similarly, irradiation of the allylic



9a, $R^1 = n\text{-}C_5H_{11}$
9b, $R^1 = C_6H_5$



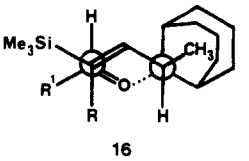
9c, $R^1 = n\text{-}C_5H_{11}$
9d, $R^1 = C_6H_5$

methylene indicated with an arrow in **9c** and **9d** gave a 14% enhancement of the intensity of the H_a signals in both cases. As expected, negligible effect was observed in the cases of the αZ,βE dienes **10c** and **10d**. The overlapping ^1H NMR signals of the αZ,βE dienes **10a** and **10b** prevented the measurement of the nuclear Overhauser effect. It is also worth noting that the ^1H NMR signals of the methyl groups attached to the α double bonds of the αZ,βZ dienes consistently showed a significant upfield shift at δ 1.62–1.42, at least 0.17 ppm upfield from those of the corresponding αZ,βE isomers (δ 1.89–1.75).

The αE,βE dienes were clearly distinguished from the corresponding αE,βZ dienes on the basis of their reactivities toward maleic anhydride. The αE,βE dienes exhibited very high reactivities at 50 °C in $CDCl_3$, whereas the αE,βZ dienes showed virtually no reactivity.

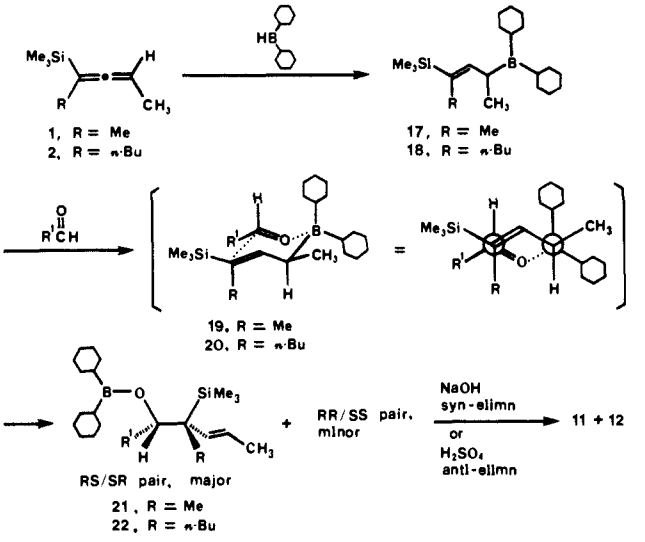
It is interesting to note that high geometrical selectivity was obtained for both double bonds of the resulting dienes in Table I. The observation of high geometrical selectivity for the β double bond strongly implies that the condensation step is highly diastereoselective, producing almost exclusively the *RS*/*SR* pairs of **7** and **8**. Apparently, the R^1 group prefers the equatorial position in the six-membered chair-type transition states **5** and **6**. Since **3a** and **4a** were the predominant reacting species during oxidation with alkaline hydrogen peroxide and complexation with pyridine, we assume that the same preference also occurred during condensation with aldehydes. By selecting sodium hydroxide to induce syn elimination of trimethylsilyl oxide,[13] the *Z* geometry of the β double bond was produced. On the other hand, the *E* geometry was obtained by using concentrated sulfuric acid to induce anti elimination.[13]

The fact that the *Z* geometry was produced predominantly for the α double bond presumably indicates a large preference for the allylic methyl group on the α carbon to adopt the axial position in the transition states **5** and **6**. This is unexpected, since the 1,3-diaxial interaction between the allylic methyl group and the R group would have made the occupation of the axial position very unfavorable. Although the preference for the α substituents to presumably occupy the axial position has been reported previously, in all these cases the 1,3-diaxial interaction is relatively small, involving only a hydrogen atom at the γ-position.[14] It was suggested that the gauche-type steric repulsion between the α-substituents and the ligands on the boron atom was responsible for the observed *Z* preference. Indeed, examination of molecular models shows that the allylic methyl group assuming the equatorial position suffers from a large nonbonded interaction with the rigid bicyclic structure on the boron atom (**16**). Apparently, this



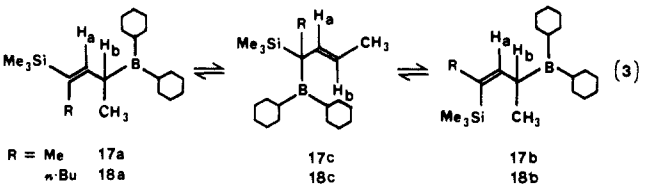
16

Scheme II



repulsion is severe enough to override the 1,3-diaxial interaction even in the present cases. Therefore, it appeared to us that if the nonbonded interaction with the ligands on the boron atom could be reduced, the 1,3-diaxial interaction would become the dominant factor and would force the formation of the *E* geometry for the α double bond.

Dicyclohexylborane (Chx_2BH)[15] was selected as the hydroborating agent because of its ready availability and less rigid nature. Treatment of **1** with Chx_2BH, in sharp contrast with 9-BBN, produced only **17a** and **17b** in a 98:2 ratio (eq 3). In-



termediate **17c** could not be detected (Figure 1), indicating that although the two cyclohexyl ligands on boron are less rigid than the bicyclic structure in the 9-BBN case, they are sterically more demanding. Moreover, decoupling experiments failed to detect significant magnetization transfer using THF-d_8 as the solvent. Oxidation of **17** with alkaline hydrogen peroxide afforded a mixture of (*E*)- and (*Z*)-4-(trimethylsilyl)-3-penten-2-ol in a 98:2 ratio. Similar results were also observed in the case of **18** where the ratio between **18a** and **18b** was 97:3 (Figure 1). Oxidation of **18** produced a mixture of (*E*)- and (*Z*)-4-(trimethylsilyl)-3-octen-2-ol in a 97:3 ratio. The ^{11}B signals of **17** and **18** occurred at δ 82.

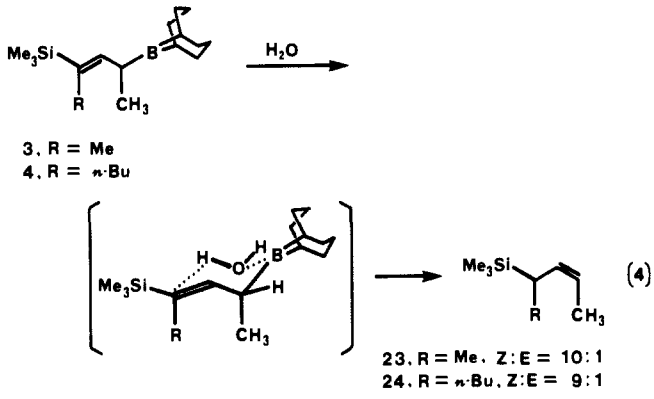
It was gratifying to observe that when allylboranes **17** and **18** were treated with aldehydes, the α double bond of the resulting dienes had exclusively the *E* geometry. The αZ isomers could not be detected (<1%). The preference for the formation of the *E* geometry has also been observed previously.[16] Apparently, the less rigid cyclohexyl ligands could rotate away to avoid excessive nonbonded interaction with the allylic methyl occupying the equatorial position in **19** and **20** as was intended (Scheme II). High diastereoselectivity for the formation of the *RS*/*SR* pairs of **21** and **22** presumably occurred again, allowing easy control of the geometry of the β double bond (Table I).

The preferential formation of the Z geometry of the α double bond from **3** and **4** was also observed when they were simply treated with water. (*Z*)-4-(Trimethylsilyl)-2-pentene (**23**) and

(13) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464–1468.
(14) (a) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 3229–3231. (b) Yamamoto, Y.; Maruyama, K.; Komatsu, T.; Ito, W. *J. Org. Chem.* **1986**, *51*, 886–891. (c) Hoffmann, R. W.; Landmann, B. *Chem. Ber.* **1986**, *119*, 1039–1053. (d) Hoffmann, R. W.; Weidmann, U. *J. Organomet. Chem.* **1980**, *195*, 137–146. (e) Hoffmann, R. W.; Dresely, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 189–190. (f) Moret, E.; Schlosser, M. *Tetrahedron Lett.* **1984**, *25*, 4491–4494. (g) Wuts, P. G. M.; Bigelow, S. S. *J. Org. Chem.* **1982**, *47*, 2498–2500.

(15) Zweifel, G.; Backlund, S. J. *J. Organomet. Chem.* **1978**, *156*, 159–170.
(16) Ditrich, K.; Bube, T.; Stürmer, R.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1028–1030.

(Z)-4-(trimethylsilyl)-2-octene (**24**) were produced predominantly (eq 4). Such preference was also observed previously during

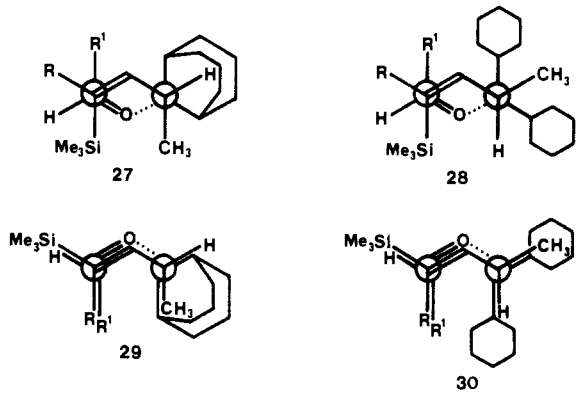


3, R = Me
4, R = *n*-Bu

23, R = Me, Z:E = 10:1
24, R = *n*-Bu, Z:E = 9:1

(4)

protonolysis of *B*-crotyl-9-BBN.[5a] On the other hand, only (*E*)-4-(trimethylsilyl)-2-pentene (**25**) and (*E*)-4-(trimethylsilyl)-2-octene (**26**) were detected from protonolysis of **17** and **18** with water. These results exclude the possible influence of aldehydes as an important factor in controlling the geometrical outcome of the α double bond. Although the use of the chair-type transition states **5**, **6**, **19**, and **20** properly explained the stereochemical outcome of the condensation step, other possibilities need to be considered. It is conceivable that the *Z* isomer of allylboranes could also serve as important reacting species by the way of a fast allylic rearrangement (eqs 1 and 3) prior to condensation with aldehydes, although it was reported that in the case of crotyldiisopinocampheylborane the rate of condensation with aldehydes was faster than that of isomerization.[17] In order to account for the apparent high diastereoselectivity for the *RS*/*SR* pairs, the R^1 group of aldehydes must adopt the axial position of the chair-type transition states **27** and **28**. Condensation through the boat-type transition states **29** and **30** could also produce the observed stereochemistry for the resulting products. However, these



27 **28**

29 **30**

boat-type transition states suffer from additional steric repulsions and offer no apparent advantage over the corresponding chair-type transition states. Furthermore, unlike **5** and **6** the steric interaction in **29** between the bicyclic structure on the boron atom and the allylic methyl on the α carbon is identical from either the axial or the equatorial position. Had the reaction proceeded through the boat-type transition state, one would have predicted a preferential occupation of the equatorial position by the allylic methyl in order to avoid the 1,3-diaxial interaction, forming the αE double bond.

In conclusion, this essentially one-pot procedure provides an efficient and stereoselective route to internal dienes. By simply utilizing different combinations of the hydroborating agents to react with the readily available trimethylsilyl-substituted internal allenes and the workup conditions to induce the Peterson olefination reaction of the condensation adducts with aldehydes, the four possible geometric isomers of several representative internal 1,3-dienes can now be easily synthesized with high isomeric purity.

Experimental Section

General procedures described in Chapter 9 of reference 18 for the manipulation of organoborane and other organometallic reagents were employed. All glassware, syringes, and needles were oven dried at 140 °C for several hours. The glassware were assembled while hot and cooled under a stream of dry nitrogen. ^1H (270 MHz) and ^{13}C (67.9 MHz) NMR spectra were recorded on a JEOL GX-270 NMR spectrometer with $CDCl_3$ as solvent and Me_4Si, $CHCl_3$ (^1H δ 7.26), or $CDCl_3$ (^{13}C δ 77.02) as internal standard. The nuclear Overhauser effect was measured by using the ^1H-homo gated decoupling method. The ^1H NMR spectra had essentially no noise on the baseline, and the ^{13}C NMR spectra had less than 1% noise level. The isomer ratios of dienes were determined by the integration of the ^1H signals of the vinylic and/or allylic hydrogen atoms. They are in good agreement with the results determined by gas chromatography. The GC analyses were performed on a Varian 3700 instrument equipped with a flame-ionization detector, a 10-m narrow-bore (0.20-mm i.d.) fused-silica SE-30 capillary column, and a Hewlett-Packard 3390A integrator. All the isomers were separated by GC with increased retention time from 9 to **12** except dienes **9d**, **10d**, **11d**, and **12d** where **9d** and **10d** exhibited an identical retention time and **11d** and **12d** also overlapped at a longer retention time. IR spectra were taken on a Perkin-Elmer 1310 spectrophotometer. Mass spectra were obtained on a Finnigan 4500 GC/MS instrument at 70 eV. Since the fragmentation patterns are very similar for the diene isomers, only the spectra of the $\alpha Z,\beta Z$ dienes are reported. Elemental analyses were performed by Galbraith Laboratories, Inc. of Knoxville, TN.

Materials. Tetrahydrofuran and diethyl ether were distilled from $LiAlH_4$ and stored under nitrogen. 9-Borabicyclo[3.3.1]nonane[19] and dicyclohexylborane[15] were prepared according to the reported procedures. Solid dicyclohexylborane was isolated by utilizing the procedure described previously.[20] The trimethylsilyl-substituted allenes were synthesized by the method reported previously.[21] Occassionally, the isolated allenes were found to be slightly contaminated with the corresponding trimethylsilyl-substituted acetylenes. We found that these minor isomers could be easily removed by treating with sodium methoxide in ethanol at room temperature for 3 h. Hexanal and benzaldehyde were obtained from Aldrich Chemical Co., Inc. and were distilled prior to use. *n*-Butyllithium in hexane and *tert*-butyllithium in pentane were also purchased from Aldrich and were used after the concentrations were standardized. Lithium aluminum hydride, anhydrous *tert*-butyl hydroperoxide solution in 2,2,4-trimethylpentane, chlorotrimethylsilane, tetrahydrofuran-d_8, and Red-Al were also obtained from Aldrich and were used directly without further purification. Toluene-d_8 was purchased from Aldrich and distilled from CaH_2 prior to use.

1,3-Butadienes. (2*Z*,4*Z*)-4-Methyl-2,4-decadiene (9a). The following procedure for the synthesis of **9a** is representative for the cases using 9-BBN as the hydroborating agent. To a 50-mL round-bottomed flask containing 0.31 g of 2-(trimethylsilyl)-2,3-pentadiene (**1**) (2.2 mmol) in 10 mL of THF was introduced by syringe 5.0 mL of a 0.44 M solution of 9-BBN (2.2 mmol) in THF at room temperature. After 6 h of stirring, 0.26 mL of hexanal (0.22 g, 2.2 mmol) was introduced. After an additional 1 h of stirring, the reaction mixture was treated with 5.0 mL of 3 N NaOH and 5.0 mL of 30% H_2O_2.[22] The elimination of trimethylsilyl oxide was complete after refluxing for 24 h. Hexane (20 mL) was added, and the organic layer was then separated, washed with water, and concentrated. The residue was passed through a short column (silica gel/hexane) and was distilled on a short-path distilling head to afford 0.26 g (77%) of **9a** as a colorless liquid: bp 52 °C (2.5 Torr); IR (neat) 1680 (m), 1630 (w), 1430 (s), 1370 (s), 860 (w), 720 (s) cm^{-1}; ^1H NMR δ 5.87 (1 H, d, J = 11.5 Hz), 5.50 (1 H, dq, J = 11.5 and 7.0 Hz), 5.23 (1 H, t, J = 7 Hz), 1.92 (2 H, q, J = 7 Hz), 1.79 (3 H, s), 1.62 (3 H, dd, J = 7.0 and 1.7 Hz), 1.27 (6 H, br), 0.88 (3 H, t); ^{13}C NMR δ 131.98, 129.30, 128.61, 125.17, 31.68, 29.35, 28.97, 23.88, 22.62, 14.78, 14.08; MS *m*/*e* 152 (M^+, 30), 137 (5), 123 (12), 109 (11), 95 (100), 82 (58), 81 (36).

(17) Brown, H. C.; Bhat, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 293–294.

(18) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.

(19) Soderquist, J.; Brown, H. C. *J. Org. Chem.* **1981**, *46*, 4599–4600.

(20) See reference 18, p 28.

(21) (a) Westmijze, H.; Vermeer, P. *Synthesis* **1979**, 390–392. (b) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935–947.

(22) The acidic workup was carried out by adding 10 drops of concentrated sulfuric acid to the reaction mixture. After 3 h of stirring at room temperature, alkaline hydrogen peroxide was introduced to oxidize the organoborane byproduct at room temperature for 20 min.

(**2Z,4E**)-**4-Methyl-2,4-decadiene** (**10a**): IR (neat) 1680 (w), 1630 (w), 1450 (s), 1370 (s), 870 (w), 720 (s) cm^{-1}; ^1H NMR δ 5.82 (1 H, d, J = 11.7 Hz), 5.38 (1 H, dq, J = 12 and 7 Hz), 5.35 (1 H, t, J = 7 Hz), 2.08 (2 H, q, J = 7 Hz), 1.79 (3 H, dd, J = 7 and 1.7 Hz), 1.77 (3 H, s), 1.31 (6 H, br), 0.89 (3 H, t); ^{13}C NMR δ 134.05, 132.41, 130.96, 123.07, 31.72, 29.44, 28.13, 22.69, 16.72, 14.72, 14.11.

(**2E,4Z**)-**4-Methyl-2,4-decadiene** (**11a**). The following procedure is representative for the cases using dicyclohexylborane, prepared in situ from cyclohexene and BH_3·THF,[15] as the hydroborating agent. To a 50-mL round-bottomed flask containing 2.5 mmol of dicyclohexylborane in 13 mL of THF maintained at 0 °C was introduced by syringe 0.35 g of **1** (2.5 mmol). After 3 h of stirring at 0 °C, 0.30 mL of hexanal (0.25 g, 2.5 mmol) was introduced, and the reaction mixture was stirred for 0.5 h and then was allowed to warm to room temperature. After an additional 0.5 h of stirring, the reaction mixture was treated with 5 mL of 3 N NaOH and 5 mL of 30% H_2O_2.[22] The elimination of trimethylsilyl oxide was complete after refluxing for 24 h. Hexane (20 mL) was added, and the organic layer was then separated, washed with water, and concentrated. The residue was passed through a short column (silica gel/hexane) and distilled on a short-path distilling head to afford 0.30 g (78%) of **11a** as a colorless liquid: bp 59 °C (2.3 Torr); IR (neat) 1440 (s), 1370 (s), 960 (s), 840 (m) cm^{-1}; ^1H NMR δ 6.45 (1 H, dm, J = 15.5 and 1 Hz), 5.68 (1 H, dq, J = 15.5 and 6.6 Hz), 5.23 (1 H, t, J = 7.2 Hz), 2.13 (2 H, q, J = 7.0 Hz), 1.80 (3 H, dd, J = 7 and 1 Hz), 1.785 (3 H, d, J = 1 Hz), 1.30 (6 H, br), 0.89 (3 H, t, J = 7 Hz); ^{13}C NMR δ 131.77, 128.80, 128.68, 124.84, 31.66, 29.77, 27.34, 22.67, 20.65, 18.63, 14.09. Anal. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24. Found: C, 86.64; H, 12.87.

(**2E,4E**)-**4-Methyl-2,4-decadiene** (**12a**): IR (neat) 1620 (w), 1440 (s), 1370 (m), 960 (s), 840 (m) cm^{-1}; ^1H NMR δ 6.07 (1 H, dm, J = 15.6 and 1 Hz), 5.55 (1 H, dq, J = 15.6 and 6.6 Hz), 5.35 (1 H, t, J = 7 Hz), 2.09 (2 H, q, J = 7 Hz), 1.75 (3 H, dd, J = 6.6 and 1 Hz), 1.71 (3 H, s), 1.30 (6 H, br), 0.88 (3 H, t); ^{13}C NMR δ 136.26, 133.45, 130.50, 121.77, 31.66, 29.49, 28.13, 22.67, 18.20, 14.09, 12.41.

(**1Z,3Z**)-**2-Methyl-1-phenyl-1,3-pentadiene** (**9b**): IR (neat) 1630 (w), 1590 (m), 1480 (s), 1430 (s), 1370 (m), 1070 (m), 1000 (m), 910 (m), 840 (m), 740 (s), 690 (s) cm^{-1}; ^1H NMR δ 7.33 (2 H, d, J = 8 Hz), 7.24 (2 H, t, J = 8 Hz), 7.13 (1 H, tt, J = 7 and 2 Hz), 6.31 (1 H, s), 6.12 (1 H, d, J = 11.5 Hz), 5.52 (1 H, dqd, J = 12, 7, and 1 Hz), 2.015 (3 H, d, J = 1 Hz), 1.58 (3 H, dd, J = 7 and 2 Hz); ^{13}C NMR δ 138.30, 135.00, 129.79, 128.72, 128.07, 127.95, 126.57, 126.13, 25.26, 14.95; MS m/e 158 (M^+, 31), 143 (100), 128 (67), 115 (22), 91 (11), 77 (9).

(**1E,3Z**)-**2-Methyl-1-phenyl-1,3-pentadiene** (**10b**): IR (neat) 1630 (w), 1590 (m), 1480 (s), 1430 (s), 1370 (m), 1070 (m), 1020 (m), 1000 (m), 910 (m), 860 (m), 740 (s), 690 (s) cm^{-1}; ^1H NMR δ 7.35–7.25 (4 H, m), 7.18 (1 H, m), 6.41 (1 H, s), 5.99 (1 H, d, J = 11.7 Hz), 5.55 (1 H, dq, J = 11.7 and 7.1 Hz), 2.03 (3 H, d, J = 1 Hz), 1.89 (3 H, dd, J = 7.3 and 2 Hz); ^{13}C NMR δ 138.06, 135.22, 134.37, 129.72, 129.08, 128.08, 126.29, 125.24, 18.65, 14.95. Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.42; H, 8.98.

(**1Z,3E**)-**2-Methyl-1-phenyl-1,3-pentadiene** (**11b**):[23] IR (neat) 1630 (w), 1590 (m), 1480 (s), 1430 (s), 1370 (s), 1070 (m), 1010 (m), 960 (s), 910 (s), 830 (s), 740 (s), 690 (s) cm^{-1}; ^1H NMR δ 7.35–7.15 (5 H, m), 6.60 (1 H, d, J = 15.6 Hz), 6.33 (1 H, s), 5.85 (1 H, dq, J = 15.6 and 6.8 Hz), 1.97 (3 H, d, J = 1 Hz), 1.78 (3 H, dd, J = 6.7 and 1 Hz); ^{13}C NMR δ 137.99, 134.72, 129.64, 129.32, 128.01, 127.50, 127.27, 126.20, 21.25, 18.62.

(**1E,3E**)-**2-Methyl-1-phenyl-1,3-pentadiene** (**12b**):[23] IR (neat) 1590 (m), 1480 (s), 1440 (s), 1380 (m), 1070 (m), 1010 (s), 960 (s), 910 (m), 860 (m), 840 (m), 780 (s), 740 (s), 690 (s) cm^{-1}; ^1H NMR δ 7.35–7.10 (5 H, m), 6.40 (1 H, s), 6.24 (1 H, dq, J = 15.5 and 1 Hz), 5.78 (1 H, dq, J = 15.4 and 6.6 Hz), 1.965 (3 H, d, J = 1 Hz), 1.82 (3 H, dd, J = 6.7 and 1.2 Hz); ^{13}C NMR δ 138.21, 136.54, 135.84, 129.17, 128.98, 128.05, 126.22, 124.76, 18.35, 13.92.

(**2Z,4Z**)-**4-Butyl-2,4-decadiene** (**9c**): IR (neat) 1630 (w), 1450 (s), 1370 (s), 1240 (w), 1100 (w), 930 (w), 840 (m), 720 (s) cm^{-1}; ^1H NMR δ 5.76 (1 H, d, J = 11.4 Hz), 5.54 (1 H, dq, J = 11.4 and 6.7 Hz), 5.22 (1 H, t, J = 7.0 Hz), 2.03 (2 H, t, J = 7 Hz), 1.895 (2 H, q, J = 7 Hz), 1.55 (3 H, dd, J = 6.8 and 1.6 Hz), 1.28 (10 H, br m), 0.88 (3 H, t), 0.87 (3 H, t); ^{13}C NMR δ 136.43, 129.09, 127.32, 125.80, 37.75, 31.75, 30.76, 29.43, 29.15, 22.66, 22.49, 14.82, 14.08, 14.00; MS m/e 194 (M^+, 21) 179 (1), 165 (1), 152 (4), 151 (2), 137 (31), 124 (6), 123 (7), 109 (23), 95 (55), 82 (95), 81 (100). Anal. Calcd for $C_{14}H_{26}$: C, 86.52; H, 13.48. Found: C, 86.15; H, 13.38.

(**2Z,4E**)-**4-Butyl-2,4-decadiene** (**10c**): IR (neat) 1630 (w), 1450 (s), 1370 (s), 1240 (w), 1100 (w), 930 (w), 870 (s), 840 (s), 720 (s) cm^{-1}; ^1H NMR δ 5.78 (1 H, d, J = 11.5 Hz), 5.46 (1 H, dq, J = 11.5 and 7.0 Hz), 5.29 (1 H, t, J = 7.3 Hz), 2.08 (4 H, m), 1.75 (3 H, dd, J = 7.0 and 1.7 Hz), 1.32 (10 H, br m), 0.90 (6 H, t); ^{13}C NMR δ 136.42, 132.98, 129.85, 124.02, 31.74, 31.01, 30.48, 29.73, 27.94, 22.71, 22.66, 14.52, 14.09. Anal. Calcd for $C_{14}H_{26}$: C, 86.52; H, 13.48. Found: C, 86.34; H, 13.37.

(**2E,4Z**)-**4-Butyl-2,4-decadiene** (**11c**): IR (neat) 1450 (s), 1370 (s), 1100 (w), 960 (s), 850 (w) cm^{-1}; ^1H NMR δ 6.33 (1 H, dm, J = 15.6 and 1 Hz), 5.70 (1 H, dq, J = 15.6 and 6.6 Hz), 5.21 (1 H, t, J = 7.2 Hz), 2.13 (4 H, m), 1.795 (3 H, dd, J = 6.6 and 1.5 Hz), 1.30 (10 H, br m), 0.90 (3 H, t), 0.89 (3 H, t); ^{13}C NMR δ 136.20, 128.04, 127.72, 124.29, 34.03, 31.63, 31.36, 29.81, 27.34, 22.76, 22.65, 18.73, 14.09, 14.03.

(**2E,4E**)-**4-Butyl-2,4-decadiene** (**12c**): IR (neat) 1450 (s), 1370 (s), 1240 (w), 1100 (m), 960 (s), 830 (m), 780 (m) cm^{-1}; ^1H NMR δ 5.96 (1 H, d, J = 15.6 Hz), 5.57 (1 H, dq, J = 15.6 and 6.5 Hz), 5.31 (1 H, J = 7.3 Hz), 2.18 (2 H, t, J = 8 Hz), 2.07 (2 H, q, J = 7 Hz), 1.75 (3 H, d, J = 6.6 Hz), 1.33 (10 H, br m), 0.92 (3 H, t), 0.89 (3 H, t); ^{13}C NMR δ 138.30, 135.04, 130.35, 121.45, 31.71, 31.42, 29.60, 28.04, 26.79, 23.10, 22.65, 18.27, 14.06.

(**1Z,3Z**)-**2-Butyl-1-phenyl-1,3-pentadiene** (**9d**): IR (neat) 1630 (w), 1590 (m), 1480 (m), 1440 (s), 1370 (m), 1240 (w), 1070 (m), 1030 (m), 930 (m), 910 (m), 840 (m), 740 (s), 690 (s) cm^{-1}; ^1H NMR δ 7.37 (2 H, d, J = 7.5 Hz), 7.22 (2 H, t, J = 7.4 Hz), 7.11 (1 H, t, J = 7 Hz), 6.29 (1 H, s), 6.02 (1 H, d, J = 11.5 Hz), 5.52 (1 H, dq, J = 11.5 and 7.0 Hz), 2.24 (2 H, t, J = 7 Hz), 1.5–1.25 (4 H, m), 1.42 (3 H, dd, J = 7.0 and 1.6 Hz), 0.92 (3 H, t); ^{13}C NMR δ 139.30, 138.51, 129.12, 128.59, 127.94, 126.95, 126.81, 126.03, 39.00, 30.63, 22.51, 14.78, 14.02; MS m/e 200 (M^+, 26), 157 (12), 143 (100), 129 (37), 128 (26), 115 (16), 91 (28), 77 (6).

(**1E,3Z**)-**2-Butyl-1-phenyl-1,3-pentadiene** (**10d**): IR (neat) 1630 (w), 1590 (w), 1490 (m), 1440 (s), 1360 (m), 1070 (m), 1030 (m), 910 (s), 860 (m), 740 (s), 720 (s), 690 (s) cm^{-1}; ^1H NMR δ 7.35–7.15 (5 H, m), 6.37 (1 H, s), 5.93 (1 H, dm, J = 11.5 and 1 Hz), 5.63 (1 H, dq, J = 11.5 and 7.0 Hz), 2.31 (2 H, t, J = 8 Hz), 1.85 (3 H, dd, J = 7.0 and 1.8 Hz), 1.46 (2 H, m), 1.33 (2 H, m), 0.89 (3 H, t); ^{13}C NMR δ 139.63, 138.12, 133.03, 128.75, 128.50, 128.14, 126.26, 125.95, 31.37, 31.01, 22.79, 14.73, 13.98. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.87; H, 10.03.

(**1Z,3E**)-**2-Butyl-1-phenyl-1,3-pentadiene** (**11d**): IR (neat) 1630 (w), 1590 (m), 1480 (s), 1440 (s), 1370 (s), 1070 (m), 1020 (m), 960 (s), 910 (s), 830 (m), 740 (s), 690 (s) cm^{-1}; ^1H NMR δ 7.35–7.15 (5 H, m), 6.49 (1 H, dm, J = 15.8 and 1 Hz), 6.31 (1 H, s), 5.88 (1 H, dq, J = 15.5 and 6.5 Hz), 2.33 (2 H, t, J = 7.5 Hz), 1.78 (3 H, dd, J = 6.6 and 1 Hz), 1.53 (2 H, m), 1.38 (2 H, m), 0.94 (3 H, t); ^{13}C NMR δ 139.16, 138.17, 129.38, 128.79, 127.98, 126.77, 126.58, 126.13, 34.50, 31.37, 22.77, 18.68, 14.03.

(**1E,3E**)-**2-Butyl-1-phenyl-1,3-pentadiene** (**12d**): IR (neat) 1590 (m), 1490 (s), 1440 (s), 1370 (m), 960 (s), 910 (m), 830 (m), 780 (m), 740 (s), 690 (s) cm^{-1}; ^1H NMR δ 7.35–7.15 (5 H, m), 6.35 (1 H, s), 6.12 (1 H, dm, J = 15.7 and 1 Hz), 5.80 (1 H, dq, J = 15.7 and 6.7 Hz), 2.41 (2 H, t, J = 8 Hz), 1.82 (3 H, dd, J = 6.6 and 1 Hz), 1.53 (2 H, m), 1.38 (2 H, m), 0.92 (3 H, t); ^{13}C NMR δ 140.93, 138.19, 135.43, 128.74, 128.54, 128.16, 126.25, 124.41, 31.52, 27.42, 23.11, 18.46, 13.91.

Oxidation of Allyboranes. Oxidation of allyborane **3** was carried out by transferring **3** (2.2 mmol) in THF via cannula to a flask containing 5 mL of 6 N NaOH and 5 mL of 30% H_2O_2 at room temperature. After 15 h of stirring, the organic layer was then separated and concentrated. The residue was column chromatographed on silica gel by eluting with pure hexane followed by a mixture of hexane–CH_2Cl_2–acetone (75:20:5) solution to afford 0.245 g (79%) of 4-(trimethylsilyl)-3-penten-2-ol (E:Z = 98:2) as a colorless liquid. E isomer: ^1H NMR δ 5.66 (1 H, dq, J = 7.8 and 1.8 Hz), 4.64 (1 H, dq, J = 7.7 and 6.6 Hz), 2.39 (1 H, br, OH), 1.66 (3 H, d, J = 1.8 Hz), 1.17 (3 H, d, J = 6.4 Hz) 0.01 (9 H, s); ^{13}C NMR δ 142.61, 137.19, 64.07, 22.98, 14.43, −2.38. Z isomer: ^1H NMR (partial) δ 5.90 (1 H, dq, J = 9.5 and 1.7 Hz), 4.44 (1 H, dq, J = 9.5 and 6.3 Hz). The isomer ratio was determined by the integration of the vinylic hydrogens and the allylic methine hydrogens of the ^1H NMR spectrum. The ^1H and ^{13}C NMR spectra of the major isomer were found to be identical with those of (*E*)-4-(trimethylsilyl)-3-penten-2-ol independently synthesized from 4-(trimethylsilyl)-3-butyn-2-ol by a reported procedure.[6]

Oxidation of 4. The oxidation procedure was carried out as described for **3**. Purification of the resulting allylic alcohol by column chromatography followed by distillation afforded 0.337 g (77%) of 4-(trimethylsilyl)-3-octen-2-ol (E:Z = 94:6) as a colorless liquid, bp 46 °C (0.03 Torr). E isomer: ^1H NMR δ 5.66 (1 H, d, J = 8.4 Hz), 4.65 (1 H, dq, J = 8.3 and 6.2 Hz), 2.13 (2 H, m), 1.76 (1 H, br, OH), 1.28 (4 H, m), 1.21 (3 H, d, J = 6.2 Hz), 0.88 (3 H, t), 0.05 (9 H, s); ^{13}C NMR δ 142.95, 142.58, 63.94, 30.02, 29.71, 23.44, 23.06, 13.89, −1.30. Anal.

(23) Mitra, R. B.; Natekar, M. V.; Virkar, S. D. *Indian J. Chem.* **1975**, *13*, 251–254.

Calcd for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07. Found: C, 65.85; H, 12.27. The ^1H and ^{13}C NMR spectra of the minor isomer were found to be identical with those of (*Z*)-4-(trimethylsilyl)-3-octen-2-ol independently synthesized from 3-octyn-2-ol by a procedure reported previously:[7] ^1H NMR δ 5.90 (1 H, dt, J = 9.3 and 1.1 Hz), 4.52 (1 H, m), 2.05 (2 H, m), 1.66 (1 H, br, OH), 1.31 (4 H, br m), 1.24 (3 H, d, J = 6.3 Hz), 0.90 (3 H, t), 0.16 (9 H, s); ^{13}C NMR δ 145.32, 142.58, 67.38, 37.72, 32.70, 23.45, 22.49, 13.97, 0.64. The isomer ratio was determined by the integration of the vinylic hydrogens and the allylic methine hydrogens of the ^1H NMR spectrum.

Oxidation of 13. Allylborane **13** was prepared by treating 5-methyl-4-(trimethylsilyl)-2,3-hexadiene (0.59 g, 3.5 mmol) with 9-BBN (3.5 mmol) in THF at room temperature for 48 h. The oxidation procedure was then carried out as described for **3**. After purification by column chromatography and distillation, 0.57 g (88%) of 5-methyl-4-(trimethylsilyl)-3-hexen-2-ol (*E*:*Z* = 82:18) was isolated as a colorless liquid: IR (neat) 3360 (br s), 1460 (m), 1370 (m), 1250 (s), 1060 (s), 865 (s), 840 (s), 760 (s) cm^{-1}. *E* isomer: ^1H NMR δ 5.58 (1 H, d, J = 8.1 Hz), 4.70 (1 H, dq, J = 8.2 and 6.3 Hz), 2.81 (1 H, septet, J = 7.0 Hz), 2.27 (1 H, br, OH), 1.17 (3 H, d, J = 6.2 Hz), 1.02 (3 H, d, J = 7 Hz), 1.00 (3 H, d, J = 7 Hz), 0.07 (9 H, s); ^{13}C NMR δ 148.01, 142.75, 64.07, 30.69, 23.54, 23.19, 23.16, 0.51; MS *m/e* 171, 168, 153, 143, 113, 81, 75, 73. The ^1H and ^{13}C NMR spectra of the minor isomer were found to be identical with those of (*Z*)-5-methyl-4-(trimethylsilyl)-3-hexen-2-ol independently synthesized from 5-methyl-3-hexyn-2-ol by a procedure reported previously.[7] The isomer ratio was determined by the integration of the ^1H NMR spectrum. The following procedure was utilized for the synthesis of (*Z*)-5-methyl-4-(trimethylsilyl)-3-hexen-2-ol. To a solution of Red-Al (3.4 M in toluene, 3.8 mL, 13 mmol) in 10 mL of diethyl ether at 0 °C was added dropwise a solution of 5-methyl-3-hexyn-2-ol (0.72 g, 6.5 mmol) in 5 mL of diethyl ether. The mixture was stirred at 0 °C for 2 h followed by an additional 48 h at room temperature. After the introduction of 1 mL of ethyl acetate, the mixture was cooled to −80 °C and treated dropwise with a solution of iodine (1.8 g, 14 mmol) in THF until the color of iodine persisted. The mixture was warmed to room temperature followed by usual workup to afford a crude product of (*Z*)-4-iodo-5-methyl-3-hexen-2-ol for the subsequent synthetic step without further purification. To the solution of the crude product in 6 mL of 3,4-dihydro-2*H*-pyran at 0 °C was added 60 mg of *p*-toluenesulfonic acid. After 2 h of stirring at room temperature, 5 mL of 3 N NaOH was introduced. Usual workup followed by purification by column chromatography (silica gel/hexane) afforded 1.81 g (87% from 5-methyl-3-hexyn-2-ol) of the corresponding acetal: ^1H NMR (two pairs of diastereomers in 1:1 ratio) δ 5.71 (1 H, dd, J = 7.5 and 0.9 Hz), 5.52 (1 H, dd, J = 7.9 and 0.9 Hz), 4.7–4.4 (4 H, m), 3.87 (2 H, m), 3.47 (2 H, m), 2.24 (2 H, t of septet, J = 0.9 and 6.6 Hz), 1.85–1.45 (12 H, m), 1.24 (3 H, d, J = 6.4 Hz), 1.19 (3 H, d, J = 6.2 Hz), 1.05 (3 H, d, J = 6.6 Hz), 1.03 (6 H, d, J = 6.6 Hz), 1.027 (3 H, d, J = 6.6 Hz); ^{13}C NMR δ 134.77, 134.02, 121.17, 118.29, 97.36, 96.30, 77.57, 75.67, 62.87, 62.78, 41.52, 41.32, 30.95, 30.93, 25.46, 25.37, 23.22, 23.18, 23.14, 22.90, 20.46, 19.96, 19.86, 19.47. To a solution of the isolated acetal (1.66 g, 5.1 mmol) in 20 mL of THF at −80 °C was added dropwise 7 mL of a 1.7 M solution of *tert*-butyllithium (11.9 mmol) in pentane and the resulting mixture was stirred at −80 °C for 0.5 h. Chlorotrimethylsilane (1.1 mL, 8.7 mmol) in 5 mL of THF was then introduced and the reaction mixture was allowed to warm to room temperature. After 48 h of stirring, a crude product was isolated and then dissolved in 10 mL of methanol. A catalytic amount of *p*-toluenesulfonic acid (20 mg) was introduced and the reaction mixture was stirred for 2 h before quenching with saturated aqueous $NaHCO_3$. Usual workup and purification by column chromatography (silica gel–hexane) afforded 0.70 g (64% from 5-methyl-3-hexyn-2-ol) of (*Z*)-5-methyl-4-(trimethylsilyl)-3-hexen-2-ol as a colorless liquid. The product was found to be contaminated by 8% of (*E*)-5-methyl-3-hexen-2-ol: IR (neat) 3340 (br s), 1605 (w), 1450 (m), 1360 (m), 1240 (s), 1040 (s), 830 (s), 750 (s) cm^{-1}; ^1H NMR δ 5.86 (1 H, dd, J = 9.4 and 1.1 Hz), 4.46 (1 H, dq, J = 9.3 and 6.2 Hz), 2.33 (1 H, d of septet, J = 1.1 and 6.8 Hz), 2.11 (1 H, br, OH), 1.14 (3 H, d, J = 6.2 Hz), 0.92 (3 H, d, J = 7 Hz), 0.90 (3 H, d, J = 7 Hz), 0.09 (9 H, s); ^{13}C NMR δ 147.73, 141.56, 67.01, 32.15, 23.36, 23.21, 22.79, 0.76.

Oxidation of 14. Allylborane **14** was prepared by treating 5,5-dimethyl-4-(trimethylsilyl)-2,3-hexadiene (0.53 g, 2.9 mmol) with 9-BBN (2.9 mmol) in THF under reflux for 7 days. The oxidation procedure was then carried out as described for **3**. After purification by column chromatography, 0.23 g (40%) of 5,5-dimethyl-4-(trimethylsilyl)-3-hexen-2-ol (*E*:*Z* = 28:72) was isolated as a colorless liquid and 52% of the starting allene was also recovered. *Z* isomer: IR (neat) 3320 (br s), 1595 (w), 1360 (m), 1250 (s), 1055 (s), 850 (s), 760 (m) cm^{-1}; ^1H NMR δ 5.88 (1 H, d, J = 9.7 Hz), 4.61 (1 H, dq, J = 9.7 and 6.0 Hz), 1.87 (1 H, br, OH), 1.20 (3 H, d, J = 6.0 Hz), 1.05 (9 H, s), 0.23 (9 H, s); ^{13}C NMR δ 150.85, 140.91, 66.61, 37.59, 30.21, 23.32, 3.89; MS *m/e* 185 ($M^+ - CH_3$), 143, 127, 110, 95, 75, 73. The ^1H and ^{13}C NMR spectra of the major isomer were found to be identical with those of (*Z*)-5,5-dimethyl-4-(trimethylsilyl)-3-hexen-2-ol independently synthesized from 5,5-dimethyl-3-hexyn-2-ol by a reported procedure[7] as described for the synthesis of (*Z*)-5-methyl-4-(trimethylsilyl)-3-hexen-2-ol. *E* isomer: ^1H NMR (partial) 5.59 (1 H, d, J = 9.3 Hz), 4.93 (1 H, dq, J = 9.3 and 6.0 Hz), 1.17 (9 H, s), 0.12 (9 H, s); ^{13}C NMR 150.05, 144.53, 65.39, 36.68, 32.60, 23.14, 2.02. The isomer ratio was determined by the integration of the ^1H NMR spectrum.

Oxidation of 17 and 18. Attempts to oxidize **17** and **18** by alkaline hydrogen peroxide resulted in hydrolysis to the corresponding allylsilanes. Pyridine *N*-oxide also failed to oxidize **17** and **18** to the corresponding allylic alcohols.[24] Oxidation was therefore carried out by transferring **17** or **18** (2.2 mmol) to a flask containing 12.9 mmol of lithium *tert*-butyl peroxide at −78 °C. Lithium *tert*-butyl peroxide was prepared by adding dropwise 5.2 mL of a 2.5 M solution of *n*-butyllithium (13.0 mmol) in hexane to a 4.3 mL of a 3.0 M solution of anhydrous *tert*-butyl hydroperoxide in 2,2,4-trimethylpentane at −78 °C.[25] The reaction mixture was then allowed to warm to room temperature and stirred for 12 h before 5 mL of 3 N NaOH was introduced. After an additional 5 h of stirring, the organic layer was separated, washed with water, and concentrated. The residue was column chromatographed on silica gel to afford the corresponding allylic alcohol in about 50% yield.

^1H NMR Studies of the [1,3] Sigmatropic Rearrangement of Allylboranes. Allylboranes were prepared in situ by adding 0.5 mmol of the corresponding trimethylsilyl-substituted allenes dissolved in 0.7 mL of THF-d_8 or toluene-d_8 to 0.5 mmol of solid 9-BBN (0.061 g)[19] or Chx_2BH (0.089 g)[20] at room temperature. The progress of the reactions was monitored by ^1H NMR and was essentially complete within 6 h in the cases of **3** and **4** and within 48 h in the case of **13**. Allylboranes **17** and **18** were completely formed in less than 1 h when THF-d_8 was used as the solvent. The magnetization transfer experiments were performed in both THF-d_8 and toluene-d_8 in the cases of **3**, **4**, and **13** and in THF-d_8 in the cases of **17** and **18**. The coalescence temperatures were obtained by using toluene-d_8 as the solvent. The NMR probe temperature was not calibrated.

In addition to the signals shown in Figure 1, the ^1H NMR spectra of **3**, **4**, and **13** also exhibit two broad multiplets centered about δ 1.85 and 1.70 (the methylene protons of the bicyclic ring) and a broad multiplet centered around δ 1.22 (bridgehead protons). The allylic methyl in **3c** overlaps with the methylene protons of the bicyclic ring and the methyl attached to the carbon bearing the trimethylsilyl group is a broad singlet at δ 1.33. The signal of the methyl groups on the silicon is a singlet at δ 0.03, showing significant line broadening due to the [1,3] sigmatropic rearrangement. The chemical shifts of the diastereotopic allylic methylene protons of **4a** are at δ 2.25 (br m) and 2.1 (br m) and the other two methylenes are at δ 1.33 (br m). A sharp doublet at δ 1.13 (J = 6.8 Hz) is attributed to the α-methyl group. The other terminal methyl is at δ 0.92 (t, J = 6 Hz). A singlet at δ 0.06 is due to Me_3Si group. The ^1H NMR spectrum of **13a** also consists of a doublet at δ 5.53 (H_a, J = 9.9 Hz), a doublet of quartets at δ 2.89 (H_b, J = 9.9 and 6.8 Hz), a septet at δ 2.97 (J = 7 Hz), a doublet at δ 1.13 (α-methyl, J = 6.8 Hz), two doublets at δ 1.08 (J = 7 Hz) and 1.06 (J = 7 Hz) due to the diastereotopic methyl groups, and a singlet at δ 0.11 (Me_3Si). The chemical shifts of H_a and H_b of **13b** are at δ 6.01 (d, J = 11.5 Hz) and 2.63 (dq, J = 11.5 and 7.0 Hz), respectively, with the other methine proton occurs at δ 2.42 (septet, J = 6.8 Hz) and the Me_3Si group occurs at δ 0.17 as a singlet.

The ^1H NMR spectra of **17** and **18** also exhibit broad peaks at δ 1.75, 1.53, and 1.29 due to the two cyclohexyl ligands. The signals of H_a and H_b of **17a** are at δ 5.82 (dq, J = 9.5 and 1.7 Hz) and 2.85 (dq, J = 9.4 and 7.1 H), respectively. The α-methyl is at δ 0.97 (d, J = 7.2 Hz) and the γ-methyl is at δ 1.64 (d, J = 1.7 Hz) with Me_3Si occurs at δ 0.03 as a singlet. The signals of H_a and H_b of **17b** are at δ 6.14 (dq, J = 11.3 and 1.6 Hz) and 2.68 (dq, J = 11.3 and 7.1 Hz), respectively. In the case of **18a**, the signal of H_a occurs at δ 5.87 (d, J = 9.9 Hz) whereas H_b is at δ 2.85 (dq, J = 9.9 and 7.1 Hz). The allylic methylene is a broad multiplet at δ 2.1. The two other methylenes overlap with the cyclohexyl protons at δ 1.3. The α-methyl and the other terminal methyl are at δ 0.95 (d, J = 7.2 Hz) and 0.92 (t, J = 7 Hz), respectively, with Me_3Si occurs at δ 0.05 as a singlet. The signals of H_a and H_b of **18b** are at δ

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6.15 (d, J = 11 Hz) and 2.67 (dq, J = 11 and 7 Hz), respectively. The chemical shifts are reported using internal THF-d_7 (δ 3.58) or internal toluene-d_7 (δ 2.09 or 6.98) as reference.

Hydrolysis of 3. To a reaction flask containing 2.0 mmol of **3** at room temperature was introduced 1.0 mL of water. After 1 h of stirring, the reaction mixture was treated with 5 mL of 3 N NaOH and 5 mL of 30% H_2O_2. After the usual workup and purification by column chromatography (silica gel-pentane) and distillation, 0.23 g (83%) of 4-(trimethylsilyl)-2-pentene (**23**) was isolated as a colorless liquid (Z:E = 10:1): IR (neat) 1640 (w), 1450 (m), 1400 (m), 1250 (s), 850 (s), 725 (s), 690 (s), 670 (s) cm^{-1}. Z isomer: ^{1}H NMR δ 5.30 (1 H, dq, J = 10.8 and 6.4 Hz), 5.18 (1 H, tq, J = 10.8 and 1.5 Hz), 1.83 (1 H, m), 1.54 (3 H, dd, J = 6.4 and 1.5 Hz), 0.99 (3 H, d, J = 7.1 Hz), -0.06 (9 H, s); ^{13}C NMR δ 134.20, 119.84, 21.39, 14.92, 13.12, -3.54; MS m/e 142 (M^+), 127, 99, 85, 73. The isomer ratio was determined by the integration of the ^{1}H NMR spectrum and by gas chromatography.

Hydrolysis of 4. To a reaction flask containing 1.6 mmol of **4** at room temperature was introduced 10 mL of water. After 2 h of stirring, the reaction mixture was treated with 5 mL of 3 N NaOH and 5 mL of 30% H_2O_2. After the usual workup and purification by silica gel chromatography (hexane), 0.235 g of 4-(trimethylsilyl)-2-octene (**24**) (79% yield, Z:E = 9:1) was isolated as a colorless liquid: IR (neat) 1635 (w), 1450 (m), 1390 (m), 1370 (m), 1240 (s), 1120 (w), 1080 (m), 960 (m), 830 (s), 780 (m), 740 (m), 720 (m), 680 (m) cm^{-1}. Z isomer: ^{1}H NMR δ 5.40 (1 H, dqd, J = 10.8, 6.6, and 1 Hz), 5.14 (1 H, tq, J = 10.8 and 1.7 Hz), 1.79 (1 H, tdd, J = 11, 3, and 1 Hz), 1.56 (3 H, dd, J = 6.7 and 1.7 Hz), 1.5-1.1 (6 H, br m), 0.88 (3 H, t), -0.03 (9 H, s); ^{13}C NMR δ 132.92, 121.22, 31.98, 29.41, 28.06, 22.61, 14.12, 13.28, -3.11. Anal. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12. Found: C, 71.09; H, 12.47. The isomer ratio was determined by the integration of the ^{1}H NMR spectrum and by gas chromatography.

Hydrolysis of 17. To a reaction flask containing 1.98 mmol of **17** at 0 °C was introduced 1.0 mL of water. After 1 h of stirring at room temperature, the reaction mixture was treated with 5 mL of 3 N NaOH and 5 mL of 30% H_2O_2. After the usual workup and purification by column chromatography (silica gel-pentane) and distillation, 0.21 g (75%) of (E)-4-(trimethylsilyl)-2-pentene[26] (**25**) was isolated as a colorless liquid: ^{1}H NMR δ 5.45 (1 H, ddq, J = 15.2, 7.8, and 1.5 Hz), 5.23 (1 H, dqd, J = 15.2, 6.2, and 1.1 Hz), 1.67 (3 H, dt, J = 6.2 and 1.5 Hz), 1.51 (1 H, m), 1.04 (3 H, d, J = 7.3 Hz), -0.03 (9 H, s); ^{13}C NMR δ 134.04, 120.62, 26.11, 18.17, 13.79, -3.50; MS m/e 142 (M^+), 127, 99, 85, 73. The Z isomer was not detected by the ^{1}H and ^{13}C NMR spectra and gas chromatography.

Hydrolysis of 18. To a reaction flask containing 1.4 mmol of **18** at 0 °C was introduced 10 mL of water. After 2 h of stirring at room temperature, the reaction mixture was treated with 5 mL of 3 N NaOH and 5 mL of 30% H_2O_2. After the usual workup and purification by silica gel chromatography (hexane), 0.175 g of (E)-4-(trimethylsilyl)-2-octene (**26**) (67% yield) was isolated as a colorless liquid: IR (neat) 1640 (w), 1440 (m), 1370 (m), 1240 (s), 1120 (w), 1080 (m), 960 (s, E geometry), 830 (s), 740 (m), 680 (m) cm^{-1}; ^{1}H NMR δ 5.2 (2 H, m), 1.66 (3 H, d, J = 4.8 Hz), 1.4-1.1 (7 H, br m), 0.88 (3 H, t), -0.05 (9 H, s); ^{13}C NMR δ 132.67, 122.25, 33.09, 31.73, 28.73, 22.65, 18.14, 14.10, -3.11. The Z isomer was not detected by the ^{1}H and ^{13}C NMR spectra and gas chromatography.

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Evidence in Favor of Lithium-Halogen Exchange Being Faster Than Lithium-Acidic Hydrogen (Deuterium) Exchange

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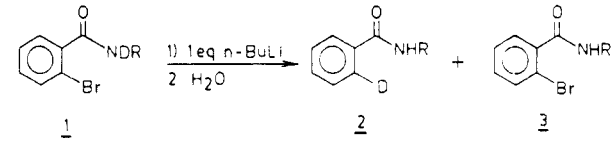
Abstract: Treatment of 2-iodo-3-(deuterioxymethyl)quinoline with 1.5 equiv of n-butyllithium in ether, followed by aqueous work up, furnished 2-deuterio-3-(hydroxymethyl)quinoline in greater than 50% yield, confirming our earlier report,[2] which has been questioned by Beak and co-workers in this journal.[1] A mechanism is proposed, in which the reaction of n-butyllithium is faster with C-I bond than with acidic deuterium. Further experiments are described in which the reaction of n-butyllithium is also faster with the C-I bond than with the ester carbonyl group.

In a recent paper[1] Beak and co-workers report that when N-deuterio-N-isopropyl-2-bromobenzamide (**1**) is treated with 1 equiv of n-butyllithium, N-isopropyl-2-deuteriobenzamide (**2**), and N-isopropyl-2-bromobenzamide (**3**) are formed in 1:1 ratio, each in 33% yield (Scheme I).

They propose a mechanism (Scheme II) which, in particular, is to explain the formation of **2** and **3** in the ratio 1:1.

In the above mechanism, n-butyllithium reacts first with the acidic deuterium of the N-deuterium bond to give the N-lithioamide **4**. Another mole of n-butyllithium then reacts further with the C-Br bond to furnish the dilithiated species **5**. The preference for the n-butyllithium to react with the C-Br of **4** rather than with acidic deuterium of the unreacted **1** is attributed to the local concentration of n-butyllithium in the vicinity of the N-lithiated amide **4** and the fastness of this reaction with respect to mixing of n-butyllithium with the unreacted **1**. Since only 1 equiv of

Scheme I



1 2 3

R = i-Pr

n-butyllithium is used, all the reagent is consumed in its reaction with 50% of **1**. The dilithiated species **5** formed then reacts with the unreacted **1** to give **2** and **3** in the ratio 1:1, the deuterated species **3** itself being formed in no greater than 50% yield.

An alternate pathway for the formation of **3** was considered by the authors. This (Scheme III) is similar to what we had proposed[2] for the lithiation of 2-iodo-3-(hydroxymethyl)quinoline **9**.

(1) Beak, P.; Musick, T. J.; Chen, C.-w. *J. Am. Chem. Soc.* **1988**, *110*, 3538.

(2) Narasimhan, N. S.; Ammanamanchi, R. *J. Chem. Soc., Chem. Commun.* **1985**, 1368.

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