A Stereoselective Synthesis of 1-Substituted 2-Alkoxy-1,3-butadienes by the Fragmentation of β-Hydroxysilanes

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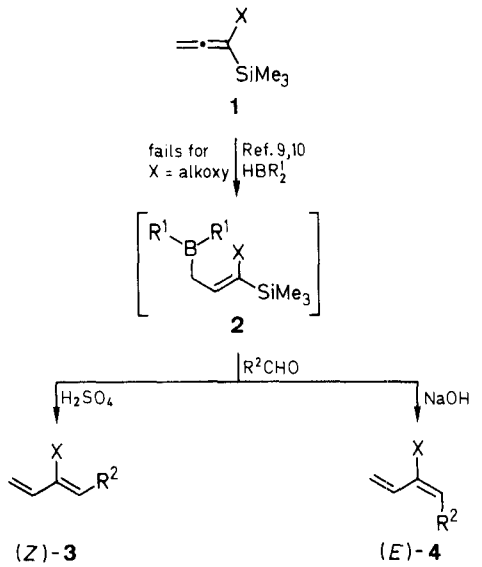
Condensation of 3-(9-borabicyclo[3.3.1]nonan-9-yl)-1-[(diisopropylamino)carbonyloxy]-1-trimethylsilyl-1-propene with aldehydes followed by either acidic or basic workup afforded 1-substituted (*Z*)- or (*E*)-2-[(diisopropylamino)carbonyloxy]-1,3-butadienes, respectively, via fragmentation of an intermediate β-hydroxysilane. A similar process gave an (*E*)-2-(methoxy)methoxy-1,3-butadiene.

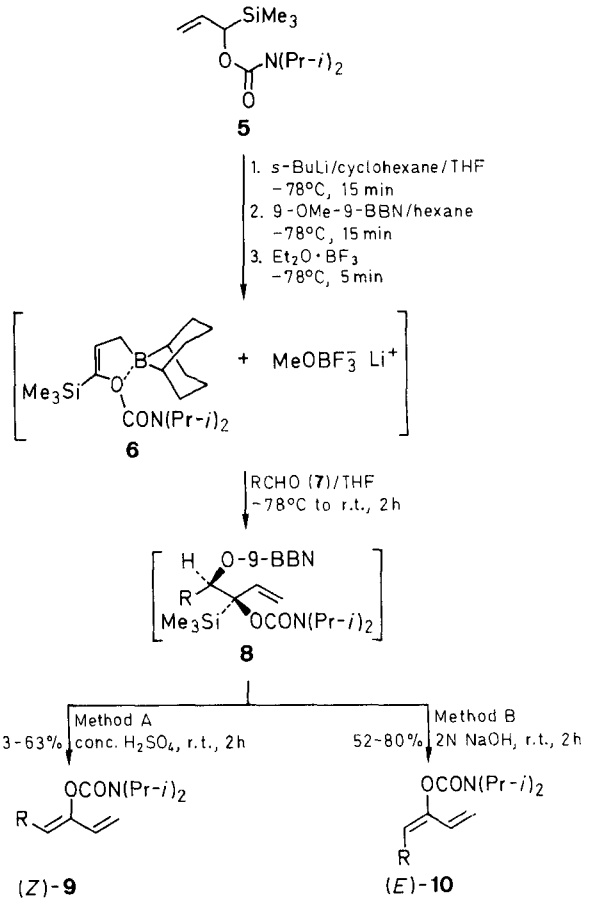
Heterosubstituted 1,3-butadienes are commonly used synthetic intermediates, particularly for Diels–Alder reactions.[1,2] Relatively simple dienes with an oxygen substituent at C-2 have been widely used, but few examples with an alkyl or aryl substituent at C-1 have been reported, particularly in geometrically pure form.[3–7] Access to such dienes was required for our studies on the 1,3-dipolar cycloaddition of azides with 2-heterosubstituted 1,3-butadienes.[8] We wish to report that aldehydes may be converted to 1-substituted 2-alkoxy-1,3-butadienes in a stereoselective fashion.

We have previously shown that 1-substituted 2-(phenylthio)-1,3-butadienes (*Z*)-**3a** and (*E*)-**4a** may be prepared using allylborane chemistry (Scheme **1**).[9,10] Condensation of 3-(9-borabicyclo[3.3.1]nonan-9-yl)-1-(phenylthio)-1-trimethylsilyl-1-propene **(2a)** with aldehydes followed by workup with either sulfuric acid or sodium hydroxide gave the (*Z*)- or (*E*)-dienes, respectively, with good stereoselectivity. The allylborane itself was generated by hydroboration of 1-(phenylthio)-1-(trimethylsilyl)-1,2-propadiene **(1a)** with 9-borabicyclo[3.3.1]nonane (9-BBN). In order to extend this method to the synthesis of 2-alkoxy-1,3-butadienes **3b–d** and **4b–d**, we prepared allenes **1b–d** with the expectation that hydroboration would generate oxygen substituted allylboranes **2b–d**. Unfortunately, all attempts to hydroborate 1-alkoxy-1-(trimethylsilyl)-1,2-propadienes with a variety of reagents failed,[11] presumably due to a combination of inductive deactivation of the double bond and complexation of the borane with the alkoxy substituent, resulting in a sluggish hydroboration.[12] Therefore, we sought other methods to prepare the requisite allylboranes **2**.



1–4	a	b	c	d
X	SPh	OPh	OBn	OMe

Scheme 1



7–10	R	7–10	R
a	CH_2CHMe_2	e	CH=CHPh
b	Me	f	Ph
c	$(CH_2)_4N_3$	g	H
d	$(CH_2)_3N_3$		

Scheme 2

An alternative route to allylboranes involves the reaction of allyl anions with 9-methoxy-9-BBN (9-OMe-9-BBN).[13] We felt that metalation of 1-alkoxy-1-trimethylsilyl-2-propenes followed by reaction with 9-OMe-9-BBN would provide access to the allyl boranes we require for diene synthesis. Our initial studies centered on **5**, which has been metalated by Hoppe.[14] Addition of 9-OMe-9-BBN to this anion generated a solution of the allylborane **6** containing an equivalent of lithium methoxide (Scheme **2**). The direct use of this solution in condensation reactions with aldehydes was unsatisfactory, presumably due to the presence of lithium methoxide. Therefore, an equivalent of diethyl ether–boron trifluoride complex was added to the solution prior to addition of the aldehyde in order to complex the lithium methoxide.[15] Upon addition of aldehydes **7**, smooth reaction with the allylborane afforded intermediate β-boronoxysilanes **8**. This reaction likely proceeds through a chair-like transition state, as is well known for other allylborane condensations.[9,10,16]

The stereospecific loss of trimethylsilanol from β-hydroxysilanes is well known to proceed under acidic conditions by an anti elimination and under basic conditions by a syn elimination.[17] Therefore, treatment of **8** with sulfuric acid afforded (*Z*)-**9** in reasonable yield and with excellent stereoselectivity[18,19] (Table 1). For the generation of the *E*-isomer, aqueous sodium hydroxide was used, producing **10** in good yield and excellent stereoselectivity.[19] Attempted diene formation with cyclohexanone led to low yields.

To demonstrate that this method is not limited to the use of a carbamate group, we carried out a sequence similar to that in Scheme **2**, except with 1-(methoxy)methoxy-1-trimethylsilyl-2-propene (**11**) (Scheme **3**). Isovaleraldehyde (3-methylbutanal) yielded the *E*-diene **12** efficiently. However, the acidic conditions necessary to produce the *Z*-diene led to hydrolysis and formation of the enone.[3] This illustrates the advantage of the carbamate for the generation of the *Z*-isomer, since the product **9** is relatively stable under the acidic conditions necessary for fragmentation of **8**.

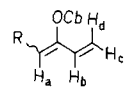
Table 1. 1,3-Dienes **9** and **10** Prepared

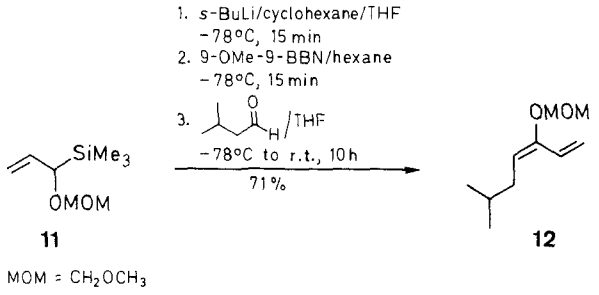
Product	Scale (mmol)	Yield[a] (%)	R_f[b] (% EtOAc in hexane)	Molecular[c] Formula	IR (cm^{-1}) (neat)	^{13}C-NMR (75 MHz, $CDCl_3$/TMS) δ	MS EI (70 eV) m/z (%)
9a	2.01	59	0.23 (2.5)	$C_{15}H_{27}NO_2$ (253.4)	1718, 1610, 1432	20.4, 21.5, 22.4, 28.2, 35.0, 46.0, 46.6, 111.9, 121.6, 132.7, 146.9, 152.8	253 (M^+, 2.8), 128 (58), 86 (100), 43 (82)
9b	1.18	48	0.35 (5.0)	$C_{12}H_{21}NO_2$ (211.3)	1706, 1437	11.3, 20.5, 21.6, 46.0, 46.8, 111.8, 117.2, 132.6, 147.1, 152.5	211 (M^+, 9.2), 128 (56), 86 (100), 43 (86)
9c	3.15	50	0.13 (10.0)	$C_{15}H_{26}N_4O_2$ (294.4)	2094, 1716, 1610, 1435	20.5, 21.5, 23.4, 25.9, 28.5, 46.3, 47.6, 51.2, 112.3, 121.6, 132.4, 146.6, 152.4	295 (M + H, 11),[d] 267 (28), 128 (100), 102 (24), 86 (14)
9d[e]	3.90	63	0.12 (5.0)	$C_{14}H_{24}N_4O_2$ (280.4)	2095, 1716, 1611, 1435	20.4, 21.5, 23.1, 28.0, 46.0, 46.7, 50.9, 112.7, 120.8, 132.8, 147.0, 152.4	281 (M + H, 29),[d] 253 (5), 128 (100), 86 (5)
9e	0.84	43	0.22 (10.0)	$C_{19}H_{25}NO_2$ (299.4)	1703, 1626, 1441	20.4, 21.6, 46.0, 46.9, 113.9, 121.4, 122.1, 126.3, 127.6, 128.5, 132.2, 133.7, 137.2, 146.6, 152.6	299 (M^+, 6.1), 128 (60), 86 (100), 43 (91)
9f[e]	1.39	56	0.09 (5.0)	$C_{17}H_{23}NO_2$ (273.4)	1713, 1611, 1435	20.5, 21.4, 46.3, 46.9, 113.9, 121.0, 127.5, 128.3, 128.8, 133.5, 134.5, 146.2, 151.6	291 (M + NH_4^+, 100),[d] 274 (M + H, 97), 128 (17), 86 (4.0)
9g	see **10g**						
10a	2.00	61	0.25 (2.5)	$C_{15}H_{27}NO_2$ (253.4)	1716, 1598, 1465	20.5, 21.3, 22.2, 28.7, 35.3, 45.9, 46.3, 113.6, 120.9, 127.7, 145.8, 153.7	253 (M^+, 11), 128 (88), 86 (100), 43 (66)
10b[e]	2.74	54	0.10 (2.0)	$C_{12}H_{21}NO_2$ (211.3)	1700, 1600, 1436	11.4, 20.3, 21.2, 45.8, 46.2, 113.5, 116.1, 127.1, 145.7, 153.5	211 (M^+, 1), 128 (10), 86 (32), 43 (100)
10c	1.04	75	0.15 (10.0)	$C_{15}H_{26}N_4O_2$ (294.4)	2095, 1713, 1598, 1434	20.5, 21.2, 25.8, 26.6, 28.3, 46.3, 51.2, 114.2, 120.9, 127.4, 145.6, 153.5	295 (M + H, 5.2),[d] 267 (8.3), 128 (100), 102 (12)
10d	0.80	52	0.11 (7.0)	$C_{14}H_{24}N_4O_2$ (280.4)	2096, 1712, 1599, 1435	20.4, 21.4, 23.3, 28.6, 46.2, 46.6, 50.5, 114.6, 120.0, 127.3, 146.2, 153.6	281 (M + H, 13),[d] 253 (8), 128 (100), 86 (12)
10e[e]	0.90	53	0.13 (5.0)	$C_{19}H_{25}NO_2$ (299.4)	1711, 1636, 1625, 1433	20.5, 21.5, 46.7, 47.0, 115.0, 122.0, 122.3, 126.5, 127.5, 127.7, 128.6, 133.8, 137.4, 146.7, 153.4	299 (M^+, 3.3), 128 (63), 86 (100), 43 (63)
10f[e]	1.51	80	0.11 (5.0)	$C_{17}H_{23}NO_2$ (273.4)	1711, 1643, 1601, 1432	20.3, 21.2, 46.0, 46.4, 115.8, 121.5, 127.0, 128.0, 128.9, 129.1, 134.5, 146.6, 153.2	273 (M^+, 4.2), 145 (22), 128 (71), 86 (100)
10g	3.96	61	0.40 (5.0)	$C_{11}H_{19}NO_2$ (197.3)	1712, 1641, 1596, 1432	20.4, 21.2, 46.2, 105.0, 114.6, 132.0, 152.2, 153.0	197 (M^+, 4), 128 (60), 86 (99), 43 (100)

[a] Yields refer to pure isolated compounds.
[b] Silica.
[c] Correct HRMS data obtained: m/z ±0.0005; purity was >95% as determined by ^{13}C-NMR and ^{1}H-NMR.
[d] Chemical ionization (ammonia).
[e] ^{13}C-NMR taken at 90 MHz.

Table 2. ^{1}H-NMR Spectral Data for 1,3-Dienes **9** and **10** (300 MHz) δ, J (Hz)[a]

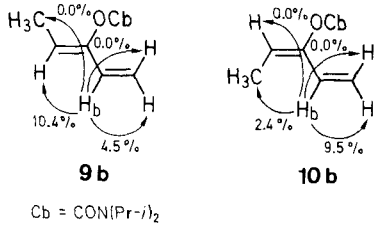
Diene	H_a	H_b	H_c	H_d	R, Cb
9a	5.35 (t, J = 7.6)	6.27 (dd, J = 10.9, 17.2)	5.01 (d, J = 10.9)	5.12 (d, J = 17.2)	0.90 (d, 6H, J = 6.7, CH_3), 1.25 (d, 6H, J = 6.8, CH_3), 1.32 (d, 6H, J = 6.8, CH_3), 1.67 (m, 1H, CH), 1.94 (t, 2H, J = 17.4, CH_2), 3.93 (m, 1H, $NC\underline{H}(CH_3)_2$), 4.08 (m, 1H, $NC\underline{H}(CH_3)_2$)
10a	5.29 (t, J = 8.3)	6.57 (dd, J = 11.0, 17.1)	5.12 (d, J = 11.0)	5.23 (d, J = 17.1)	0.93 (d, 6H, J = 6.6, CH_3), 1.26 (br s, 12H, CH_3), 1.69 (m, 1H, CH), 2.09 (t, 2H, J = 8.2, CH_2), 3.98 (m, 2H, $NC\underline{H}(CH_3)_2$)
9b	5.38 (q, J = 7.0)	6.26 (dd, J = 10.8, 17.2)	4.99 (d, J = 10.8)	5.12 (d, J = 17.2)	1.25 (d, 6H, J = 6.7, CH_3), 1.33 (d, 6H, J = 6.7, CH_3), 1.64 (d, 3H, J = 7.0, CH_3), 3.93 (m, 1H, $NC\underline{H}(CH_3)_2$), 4.1 (m, 1H, $NC\underline{H}(CH_3)_2$)
10b	5.27 (q, J = 7.4)	6.53 (dd, J = 11.0, 17.1)	5.08 (d, J = 11.0)	5.18 (d, J = 17.1)	1.21 (br s, 12H, CH_3), 1.74 (d, 3H, J = 7.4, CH_3), 3.92 (m, 2H, $NC\underline{H}(CH_3)_2$)
9c	5.29 (t, J = 7.5)	6.24 (dd, J = 10.9, 17.2)	5.01 (d, J = 10.9)	5.12 (d, J = 17.2)	1.24 (d, 6H, J = 6.8, CH_3), 1.31 (d, 6H, J = 6.8, CH_3), 1.48 (m, 2H), 1.59 (m, 2H), 2.08 (app. q, 2H, J = 7.4, $CHC\underline{H}_2$), 3.24 (t, 2H, J = 6.6, N_3CH_2), 3.93 (m, 1H, $NC\underline{H}(CH_3)_2$), 4.05 ($NC\underline{H}(CH_3)_2$)
10c	5.16–5.26 (m, 1H, overlaps with H_d)	6.53 (dd, J = 11.0, 17.1)	5.13 (d, J = 11.0)	5.16–5.26 (m, 1H, overlaps with H_a)	1.24 (br s, 12H, CH_3), 1.52 (m, 2H), 1.62 (m, 2H), 2.23 (app. q, 2H, J = 7.6, $CHC\underline{H}_2$), 3.26 (t, 2H, J = 6.6, N_3CH_2), 3.94 (m, 2H, $NC\underline{H}(CH_3)_2$)
9d	5.29 (t, J = 7.5)	6.25 (dd, J = 10.9, 17.2)	5.04 (d, J = 10.9)	5.15 (d, J = 17.2)	1.25 (d, 6H, J = 6.8, CH_3), 1.32 (d, 6H, J = 6.8, CH_3), 1.69 (pent., 2H, J = 7.0, $CH_2C\underline{H}_2CH_2$), 2.14, (app. q, 2H, J = 7.5, $CHC\underline{H}_2$), 3.28 (t, 2H, J = 6.8, N_3CH_2), 3.95 (m, 1H, $NC\underline{H}(CH_3)_2$), 4.06 (m, 1H, $NC\underline{H}(CH_3)_2$)
10d	5.12–5.28 (m, 1H) overlaps with H_c and H_d	6.56 (dd, J = 11.0, 17.0)	5.12–5.28 (m, 1H) overlaps with H_a and H_d	5.12–5.28 (m, 1H) overlaps with H_a and H_c	1.24 (br s, 12H, CH_3), 1.70 (pent., 2H, J = 7.0, $CH_2C\underline{H}_2CH_2$), 2.28 (app. q, 2H, J = 7.3, $CHC\underline{H}_2$), 3.31 (t, 2H, J = 6.6, N_3CH_2), 3.95 (m, 2H, $NC\underline{H}(CH_3)_2$)
9e	6.11 (d, J = 11.0)	6.37 (dd, J = 10.8, 17.1)	5.16 (d, J = 10.8)	5.29 (d, J = 16.9)	1.29 (d, 6H, J = 6.8, CH_3), 1.42 (d, 6H, J = 6.8, CH_3), 4.0 (m, 1H, $NC\underline{H}(CH_3)_2$), 4.17 (m, 1H, $NC\underline{H}(CH_3)_2$), 6.63 (d, 1H, J = 15.7, $ArC\underline{H}$), 6.88 (dd, 1H, J = 11.5, 15.4, $ArCHC\underline{H}$), 7.23–7.44 (m, $5H_{arom}$)
10e	6.09 (d, J = 11.5)	6.87 (dd, J = 10.9, 16.9)	5.26 (d, J = 10.9)	5.36 (d, J = 16.9)	1.31 (br s, 12H, CH_3), 4.04 (m, 2H, $NC\underline{H}(CH_3)_2$), 6.59 (d, 1H, J = 15.4, $ArC\underline{H}$), 7.07 (dd, 1H, J = 11.5, 15.4, $ArCHC\underline{H}$), 7.25–7.42 (m, $5H_{arom}$)
9f	6.22 (s)	6.42 (dd, J = 10.8, 17.2)	5.18 (d, J = 10.8)	5.28 (d, J = 17.2)	1.29 (d, 6H, J = 6.9, CH_3), 1.31 (d, 6H, J = 6.9, CH_3), 3.87 (m, 1H, $NC\underline{H}(CH_3)_2$), 4.26 (m, 1H, $NC\underline{H}(CH_3)_2$), 7.25–7.42 (m, $5H_{arom}$)
10f	6.38 (s)	6.76 (dd, J = 11.0, 17.1)	5.24 (d, J = 11.0)	5.42 (d, J = 17.1)	1.32 (br s, 12H, CH_3), 4.04 (m, 2H, $NC\underline{H}(CH_3)_2$), 7.24–7.34 (m, $5H_{arom}$)
9g	See **10g**				
10g	4.89 (s), 4.96 (s)	6.30 (dd, J = 11.1, 17.7)	5.14 (d, J = 11.1)	5.28 (d, J = 17.7)	1.27 (br s, 12H, CH_3), 3.98 (m, 2H, $NC\underline{H}(CH_3)_2$)

[a] 



Scheme 3

The geometry of the dienes **9b** and **10b** was verified by difference NOE ^{1}H-NMR experiments (Figure). Irradiation of H_b in **9b** and **10b** resulted in the enhancements as shown. The structure of diene **12** was determined similarly.



Figure

In conclusion, the allylborane route to 1-substituted 2-alkoxy-1,3-butadienes proceeds in good yield and allows access to either diene geometry with excellent stereoselectivity.

Reagents were obtained from commercial suppliers, and were used without further purification. Aldehydes were purified by distillation prior to use. THF was distilled from Na/benzophenone ketyl immediately prior to use. All reactions were conducted under an atmosphere of dry N_2. Flash chromatography refers to liquid chromatography on silica gel (230–400 mesh) according to the method of Still.[20] Mass spectroscopy was carried out on a VG-Analytical 70–250 high resolution mass spectrometer. FTIR spectra were obtained using a Perkin-Elmer 1600 spectrophotometer. ^{1}H-NMR spectra were obtained using a Bruker WM-300 or WM-360 spectrometer, using TMS as an internal standard. ^{13}C-NMR were obtained using a Bruker WM-300 (75 MHz) or WM-360 (90 MHz) spectrometer and are reported relative to $CDCl_3$ as an internal standard.

1-Trimethylsilyl-1-[(diisopropylamino)carbonyloxy]-2-propene (5):
This compound has been previously prepared by Hoppe.[14] The following is an improved procedure. A solution of diisopropylcarbamoyl chloride (9.9 g, 61.0 mmol), *N,N*-diisopropylethylamine (7.9 g, 61.0 mmol), and *N,N*-dimethylaminopyridine (.34 g, 3.0 mmol) in toluene (10 mL) is added to a solution of 1-trimethylsilyl-2-propen-1-ol[21] (7.16 g, 55.1 mmol) in toluene (50 mL) at r.t. The solution is then heated at reflux for 24 h, cooled to r.t. and poured into H_2O (100 mL). The organic layer is washed with H_2O (2 × 50 mL) and brine (50 mL), then dried ($MgSO_4$) and concentrated at reduced pressure. Chromatography (5% EtOAc/hexane) gave the title compound as a clear, colorless liquid; yield: 9.48 g (67%); R_f = 0.26. The ^{1}H-NMR spectrum matched that reported by Hoppe.[14]

IR (neat): ν = 1693 cm^{-1} (O–CO–N).

^{1}H-NMR (300 MHz, $CDCl_3$/TMS): δ = 0.08 (s, 9H, $Si(CH_3)_3$), 1.22 (d, 12H, J = 6.1 Hz, $4CH_3$), 3.82 (m, 1H, CH), 4.07 (m, 1H, CH), 4.94 (m, 1H, CH), 5.00 (m, 1H, *trans*-3-CH), 5.10 (m, 1H, *cis*-3-CH), 5.89 (m, 1H, 2-CH).

^{13}C-NMR (75 MHz, $CDCl_3$); δ = −3.7, 21.0, 45.8, 70.7, 110.7, 136.1, 155.6.

MS (CI, CH_3): m/z = 258 (MH^+).

1,3-Dienes 9 and 10; General Procedure:
Method A (for *Z*-Dienes **9**): To a solution of 1-trimethylsilyl-1-[(diisopropylamino)carbonyloxy]-2-propene (**5**) in THF (0.5 M) at −78 °C is added *s*-BuLi (1.05 equiv of a 1.0 M solution in cyclohexane) in a dropwise fashion. After 15 min, 9-OMe-9-BBN (1.1 equiv of a 1.0 M solution in hexane) is added, and the pale yellow solution is stirred for an additional 15 min at −78 °C, followed by the addition of $Et_2O \cdot BF_3$ (1.1 equiv). After 5 min at −78 °C, the aldehyde **7** (1.1 equiv) is added, and the solution is allowed to warm to r.t. where it is stirred for additional 2 h. Conc. H_2SO_4 (10 drops per 1.0 mmol of **5**) is added, and the cloudy solution is stirred for 2 h, then poured into H_2O (25 mL per 1.0 mmol of **5**) and washed with 5% $NaHCO_3$ until the aqueous washes are basic. The aqueous washes are extracted with EtOAc (3 × 25 mL) and the combined organic extracts are washed with H_2O (25 mL) and brine (25 mL), then dried ($MgSO_4$) and concentrated at reduced pressure. Chromatography of the residue (see Table 1 for eluent) gives the dienes **9**.

Method B (for *E*-Dienes **10**): The above procedure is repeated, except that 3N NaOH (5 drops per mmol **5**) is added after the aldehyde **7**, rather than H_2SO_4. After 2 h at r.t., the cloudy mixture is poured into H_2O (25 mL per 1.0 mmol of **5**) and the layers are separated. The aqueous layer is extracted with EtOAc (3 × 25 mL) and the combined organic extracts are washed with H_2O (25 mL) and brine (25 mL), then dried ($MgSO_4$) and concentrated at reduced pressure. Chromatography of the residue (See Table 1 for eluent) gives the dienes **10**. Diene **10g** is purified using 1% Et_2O in petroleum ether.

(*E*)-3-(Methoxy)methoxy-6-methyl-1,3-heptadiene (12):
To 1-trimethylsilyl-1-(methoxy)methoxy-2-propene (**11**;[4] 0.203 g, 1.17 mmol) in THF (1.5 mL) at −78 °C is added *s*-BuLi (1.23 mL of a 1.0 M solution in cyclohexane, 1.23 mmol) in a dropwise fashion. After 15 min, 9-OMe-9-BBN (1.23 mL of a 1.0 M solution in hexanes, 1.23 mmol) is added, and the pale yellow solution is stirred for and additional 15 min at −78 °C. After 5 min at −78 °C, isovaleraldehyde (0.100 g, 1.23 mmol) is added, and the solution is allowed to warm to r.t. where it is stirred for an additional 10 h then poured into H_2O (25 mL) and extracted with EtOAc (3 × 25 mL). The combined organic extracts are washed with H_2O (25 mL) and brine (25 mL), then dried ($MgSO_4$) and concentrated at reduced pressure. Chromatography (1.5% EtOAc/hexane) gave the title compound as a clear, colorless liquid; yield: 0.14 g (71%); R_f = 0.26.

HRMS (EI 70 eV): calc. for $C_{10}H_{18}O_2$: 170.1307, found: 170.1305.

IR (neat): ν = 1647, 1051 cm^{-1}.

^{1}H-NMR ($CDCl_3$/TMS, 300 MHz): δ = 0.86 (d, 6H, J = 6.6 Hz, $(CH_3)_2CH$), 1.63 (m, 1H, $(CH_3)_2CH$), 2.00 (t, 2H, J = 8.3 Hz, CH_2), 3.44 (s, 3H, OCH_3), 4.97 (s, 2H, OCH_2O), 5.04 (t, 1H, J = 8.3 Hz, CH), 5.10 (d, 1H, J = 10.9 Hz, *cis*-CH), 5.56 (d, 1H, J = 17.0 Hz, *trans*-CH), 6.45 (dd, 1H, J = 10.9, 17.0 Hz, CH).

^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 22.3, 29.4, 35.3, 55.9, 94.6, 108.8, 113.9, 128.3, 150.6.

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(1) Petrzilka, M.; Grayson, J.I. *Synthesis* **1981**, 753.
(2) Fringuelli, F.; Taticchi, A. *Dienes in the Diels–Alder Reaction*, J. Wiley, New York, 1990.
(3) Oppolzer, W.; Snowden, R.L.; Simmons, D.P. *Helv. Chim. Acta* **1981**, *64*, 2002.
(4) Murai, A.; Abiko, A.; Shimada, N.; Masamune, T. *Tetrahedron Lett.* **1984**, *25*, 4951.
(5) McDougal, P.G.; Rico, J.G.; VanDerveer, D. *J. Org. Chem.* **1986**, *51*, 4492.
(6) Okazoe, T.; Takai, K.; Oshima, K.; Utimoto, K. *J. Org. Chem.* **1987**, *52*, 4410.
(7) Takai, K.; Kataoka, Y.; Okazoe, T.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 1065.
(8) Pearson, W.H.; Bergmeier, S.C.; Degan, S.; Lin, K.-C.; Schkeryantz, J.M.; Williams, J.P. *J. Org. Chem.* **1990**, *55*, 5719.
(9) Pearson, W.H.; Lin, K.-C.; Poon, Y.-F. *J. Org. Chem.* **1989**, *54*, 5814.
(10) For a related synthesis of 1,3-butadienes with allylborane chemistry which inspired our approach, see: Wang, K.K.; Gu, Y.G.; Liu, C. *J. Am. Chem. Soc.* **1990**, *112*, 4424 and references therein.
(11) For example, 9-BBN, $HBBr_2$, $HBCl_2$ and BH_3 all failed to hydroborate **1b–d** under a variety of conditions. We thank Dr. Ko-Chung Lin for performing some of these reactions.
(12) The hydroboration of an alkoxyallene has been implicated in the hydroboration of propargyl acetals, but a vinylborane resulted. See: Zweifel, G.; Horng, A.; Plamondon, J.E. *J. Am. Chem. Soc.* **1974**, *96*, 316.
(13) Brown, H.C.; Jadhav, K.S.; Bhat, K.S. *J. Am. Chem. Soc.* **1988**, *110*, 1535.
(14) Hoppe, D.; Hanko, R.; Bronneke, A.; Lichtenberg, F.; Hulsen, E.V. *Chem. Ber.* **1985**, *118*, 2822.
(15) Brown, H.C.; Sinclair, J.A. *J. Organomet. Chem.* **1977**, *131*, 163.
(16) Pelter, A.; Smith, K.; Brown, H.C. *Borane Reagents*, Academic Press, New York, 1988.
(17) Hudrlik, P.F.; Peterson, D.J. *J. Am. Chem. Soc.* **1975**, *97*, 1464.
(18) For a recent stereoselective synthesis of 4-substituted 2-[(diethylamino)carbonyloxy]-1,3-butadienes, see: Sengupta, S.; Snieckus, V. *J. Org. Chem.* **1990**, *55*, 5680.
(19) Only one stereoisomer of the diene was detectable in each case by examination of the 300 MHz ^{1}H-NMR spectrum of the crude product from the reaction.
(20) Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(21) Danheiser, R.L.; Fink, D.M.; Okano, K.; Tsai, Y.M.; Szczepanski, S.W. *Org. Syn.* **1987**, *66*, 14.