The Regioselectivity of 1,3-Disubstituted Allylmetal Species Towards Electrophiles: 1-(Trimethylsilyl)alk-2-enylpotassium Compounds

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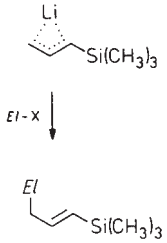
Received 16 October 1997

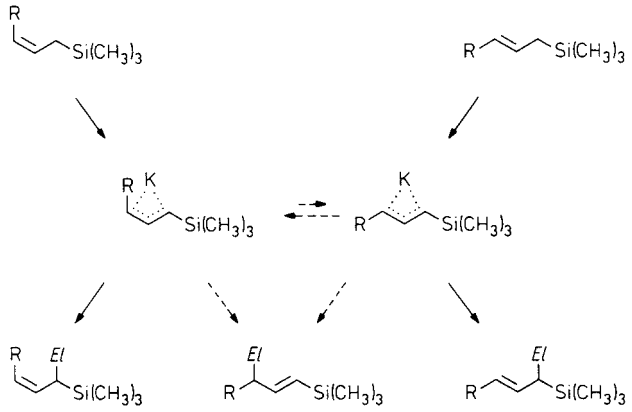
Abstract: 1-(Trimethylsilyl)alk-2-enylpotassium species are readily generated by deprotonation of (alk-2-enyl)trimethylsilanes with the superbasic mixture of butyllithium and potassium *tert*-butoxide. Like the parent compound 1-(trimethylsilyl)allylpotassium, they too react with a variety of electrophiles preferentially, if not exclusively, at the silyl-distant terminus of the allyl moiety, thus producing branched enesilanes. The opposite regioselectivity previously observed with iodomethane hence appears to be an exception.

Key words: 1-(trimethylsilyl)alk-2-enylpotassium species, superbases, regioselectivity, electrophilic reaction

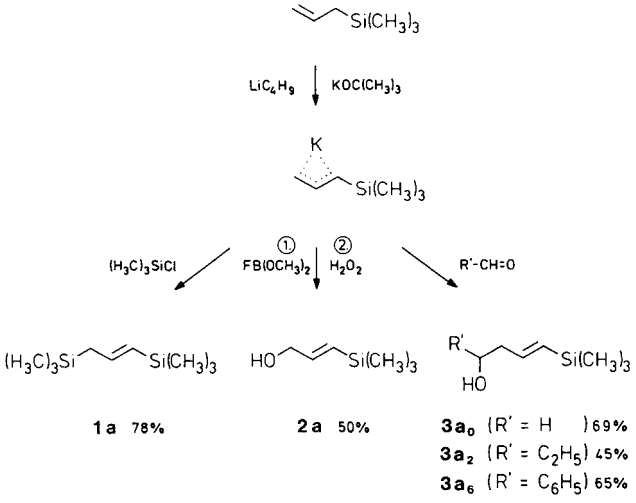
1-(Trimethylsilyl)allyllithium and 1-(triphenylsilyl)allyllithium can be used as versatile building blocks for the construction of organic molecules, as was demonstrated in pioneering work by Corriu,[1] Chan,[2] and Matteson[3] among others. Electrophiles were found to attack mainly, if not exclusively, at the unsubstituted terminus of the allyl moiety. The (*E*) configuration of the resulting enesilanes suggests that the bulky trimethylsilyl moiety occupies the *exo* position in the organolithium intermediate in analogy to the well-documented behavior of the potassium analog.[4]



Later, Taddei, Mordini and co-workers[5] reported on the superbase-promoted deprotonation and subsequent substitution of homologous allylsilanes. When they consecutively treated pure (*Z*) and (*E*) isomers of (but-2-enyl)trimethylsilane or (hex-2-enyl)trimethylsilane with butyllithium in the presence of potassium *tert*-butoxide[6] and with iodomethane, they obtained exclusively the branched allylsilanes having originated from the attachment of the methyl group to the silicon-bearing carbon atom. However, when 1-iodobutane was used as the electrophile, the regioselectivity was lost, with mixtures of the allylsilanes and the isomeric (*E*)-enesilanes in ratios ranging from 1:1 to 4:1 being formed. The stereochemistry of the precursor was completely retained in the allylsilanes as long as metalation times were kept short (30 min at –50 °C). On the other hand, if the intermediate was left for 24 hours at –50 °C before being trapped, torsional equilibrium was established. As expected,[7] the *endo*-alkyl *exo*-trimethylsilyl conformer proved to be the thermodynamically much favored species.

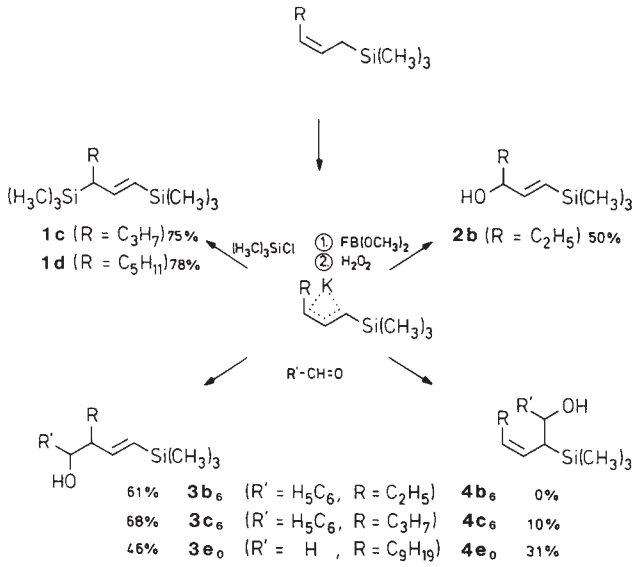


The present work was undertaken in order to extend this investigation and, in particular, to find out how the nature of the electrophile affects the regioselectivity of the interception step. To this purpose, chlorotrimethylsilane, fluorodimethoxyborane, and aldehydes were selected as the principal reagents. The parent member of the series, 1-(trimethylsilyl)allylpotassium, served as the first model compound. It gave the enesilanes **1a** (78%), **2a** (50%), **3a$_0$** (69%), **3a$_2$** (45%) and **3a$_6$** (65%) as the sole identifiable products.



The observed regioselectivity is noteworthy in two respects. It applies not only to bulky, but also to small electrophiles (such as fluorodimethoxyborane and monomeric formaldehyde). Furthermore, benzaldehyde reacts unidirectionally with 1-(trimethylsilyl)allyl*potassium* whereas its *lithium* counterpart has been reported to produce a 83:17 mixture of enesilane- and allylsilane-type regioisomers.[8]

The intriguing question now was how these electrophiles would behave towards medium- and long-chain 1-(trimethylsilyl)alk-2-enylpotassium species. Chlorotrimethylsilane reacted with 1-(trimethylsilyl)hex-2-enylpotassium and 1-(trimethylsilyl)oct-2-enylpotassium again with excellent γ-selectivity affording the bissilanes **1c** (75%) and **1d** (78%), while 1-(trimethylsilyl)pent-2-enylpotassium, after borylation and oxidation, selectively gave the allyl alcohol **2b** (50%). When 1-(trimethylsilyl)pent-2-enylpotassium, 1-(trimethylsilyl)hex-2-enylpotassium and 1-(trimethylsily])dodec-2-enylpotassium were allowed to combine with benzaldehyde or formaldehyde, mixtures of regioisomers were obtained: **3b$_6$** (61 %) and **4b$_6$** (small amounts; not characterized), **3c$_6$** (68%) and **4c$_6$** (10%; isolated as (1*E*,3*Z*)-1-phenylhepta-1,3-diene after chromatography on silica gel[9]) and, respectively, **3e$_0$** (46%) and **4e$_0$** (31% ; isolated as (*Z*)-trideca-1,3-diene after chromatography on silica gel[9]). In other words, enesilanes were no longer the exclusive, though still the predominant, products. Thus, one has to consider the opposite regioselectivity of alkylation, in particular in the reaction with iodomethane,[5] as an exception.



Regarding standard laboratory practice and formalities, see related articles.[10,11] ^{1}H NMR spectra were recorded of samples dissolved in $CDCl_3$ at 250 MHz (or at 400 MHz, if marked by an asterisk). The preparation of (*Z*)-(hex-2-enyl)-, (*Z*)-(hept-2-enyl)-, (*Z*)-(oct-2-enyl)-, (*Z*)-(non-2-enyl)-, (*Z*)-(dec-2-enyl)-, (*Z*)-(undec-2-enyl)-, and (*Z*)-(dodec-2-enyl)trimethylsilane using a similar procedure has been described in another context.[11]

Trapping with Chlorotrimethylsilane:
(*E*)-Prop-1-ene-1,3-diylbis(trimethylsilane)[12] (1a):
At –75 °C, precooled THF (25 mL), allyltrimethylsilane[11] (4.0 mL, 2.8 g, 25 mmol) and *t*-BuOK (3.1 g, 28 mmol) were consecutively added to BuLi (28 mmol) from which the commercial solvent (hexane) had before been stripped off. As soon as the alcoholate had dissolved under gentle shaking, the mixture was allowed to stand for 1 h in a –50 °C cold bath. Upon treatment with chlorotrimethylsilane (3.5 mL, 3.0 g, 28 mmol), its bright red color disappeared immediately. The white suspension was concentrated and the residue distilled. A colorless liquid was collected; bp 48–50 °C/10 Torr; n_D^{20} 1.4332; yield: 3.6 g (78%).
^{1}H NMR: δ = 6.02 (1 H, dt, *J* = 18.2, 7.7 Hz), 5.44 (1 H, dt, *J* = 18.2, 1.3 Hz), 1.63 (2 H, dd, *J* = 7.9, 1.2 Hz), 0.04 (9 H, s), 0.00 (9 H, s).

(*E*)-Hex-1-ene-1,3-diylbis(trimethylsilane) (1c):
The same procedure as used for **1a** was applied to (*Z*)-(hex-2-enyl)trimethylsilane[11] (3.9 g, 25 mmol); bp 95–97 °C/25 Torr; n_D^{20} 1.4430; yield: 4.3 g (75%).
^{1}H NMR: δ = 5.83 (1 H, dd, *J* = 18.8, 8.7 Hz), 5.40 (1 H, dd, *J* = 18.7, 1.2 Hz), 1.6 (1 H, m), 1.4 (3 H, m), 1.2 (1 H, m), 0.87 (3 H, t, *J* = 6.8 Hz), 0.04 (9 H, s), –0.04 (9 H, s).
Anal.: calcd for $C_{12}H_{28}Si_2$ (228.52) C 63.07, H 12.35; found C 63.54, H 12.19.

Oct-1-ene-1,3-diylbis(trimethylsilane) (1d):
The same procedure as used for **1a** was applied to (*Z*)-(oct-2-enyl)trimethylsilane (4.6 g, 25 mmol); bp 65–70 °C/0.7 Torr; n_D^{20} 1.4335; yield: 5.0 g (78%).
^{1}H NMR: δ = 5.82 (1 H, dd, *J* = 18.7, 8.8 Hz), 5.39 (1 H, dd, *J* = l8.7, 1.1 Hz), 1.5 (1 H, m), 1.4 (2 H, m), 1.3 (6 H, m), 0.88 (3 H, t, *J* = 6.8 Hz), 0.04 (9 H, s), –0.05 (9 H, s).
Anal.: calcd for $C_{14}H_{32}Si_2$ (256.58) C 65.54, H 12.57; found C 65.51, H 12.42.

Trapping with Fluorodimethoxyborane Followed by Oxidation:
(*E*)-3-(Trimethylsilyl)prop-2-en-1-ol[13] (2a):
Allyltrimethylsilanel[11] (4.0 mL, 2.8 g, 25 mmol) in THF (25 mL) was treated with BuLi and *t*-BuOK as described for **1a**. At –75 °C, fluorodimethoxyborane–diethyl ether complexl[4] (6.7 mL, 6.0 g, 36 mmol) was added to the red mixture followed, when the white suspension formed had reached 25 °C, by 30% aq H_2O_2 (5.7 mL, 56 mmol). After 12 h of vigorous stirring, sat. aq NH_4Cl (20 mL) was added. Repetitive extraction with Et_2O (3 × 30 mL), washing of the combined organic layers with brine (2 × 20 mL) and distillation afforded a colorless liquid; bp 135–140 °C; n_D^{20} 1.4412; yield: 1.6 g (50%).
^{1}H NMR: δ = 6.17 (1 H, dt, *J* = 18.9, 4.4 Hz), 5.91 (1 H, dt, *J* = 18.9, 1.6 Hz), 4.16 (2 H, dd, *J* = 4.5, 1.5 Hz), 1.9 (1 H, s, broad), 0.07 (9 H, s).

(*E*)-1-(Trimethylsilyl)pent-1-en-3-ol[15] (2b):
The same procedure as used for **2a** was applied to (*Z*)-(pent-2-enyl)trimethylsilane[16] (3.5 g, 25 mmol); a colorless liquid was collected upon distillation; bp 80–85 °C/25 Torr; n_D^{20} 1.4483 ; yield: 2.0 g (50%).
^{1}H NMR: δ = 6.02 (1 H, dd, *J* = 19.0, 5.3 Hz), 5.84 (1 H, dd, *J* = 19.0, 1.1 Hz), 4.02 (1 H, sym. m), 1.55 (3 H, quint, *J* = 6.9 Hz), 0.91 (3 H, t, *J* = 7.0 Hz), 0.07 (9 H, s).

Trapping with Aldehydes:
4-(Trimethylsilyl)but-3-en-1-ol[15] (3a$_0$):
Allyltrimethylsilane[11] (4.0 mL, 2.8 g, 25 mmol) in THF (25 mL) was treated with BuLi and *t*-BuOK as described for **1a**. At –75 °C, 0.8 M monomeric formaldehyde[18] in THF (30 mmol) was added. The red mixture slowly decolorized. After 1 h at 25 °C, the solvent was evaporated under reduced pressure and the residue neutralized with sat. aq NH_4Cl (20 mL). The organic material was extracted with Et_2O (3 × 30 mL), washed with brine (2 × 20 mL) and distilled; bp 50–55 °C/2 Torr; n_D^{20} 1.4587; yield: 2.5 g (69%).
^{1}H NMR*: δ = 6.00 (1 H, dt, *J* = 18.6, 6.3 Hz), 5.78 (1 H, dt, *J* = 18.6, 1.4 Hz), 3.69 (2 H, t, *J* = 6.3 Hz), 2.39 (2 H, qd, *J* = 6.4, 1.4 Hz), 1.5 (1 H, s, broad), 0.06 (9 H, s).

(*E*)-6-(Trimethylsilyl)hex-5-en-3-ol[17] (3a$_2$):
This product was obtained in the same manner as described for **3a$_0$** using propionaldehyde (2.0 mL, 1.6 g, 28 mmol) as the reagent; bp 55–60 °C/0.05 Torr; n_D^{20} 1.4492; yield: 1.9 g (45%).
^{1}H NMR: δ = 6.02 (1 H, ddd, *J* = 18.6, 7.0, 6.6 Hz), 5.76 (1 H, d, *J* =

18.6 Hz), 3.57 (1 H, quint-like m, J ~ 8 Hz), 2.34 (1 H, dddd, J = 14.0, 6.0, 4.3, 1.5 Hz), 2.18 (1 H, dtd, J = 14.0, 7.5, 1.0 Hz), 1.72 (1 H, s, broad), 1.48 (2 H, quint d, J = 7.1, 2.0 Hz), 0.94 (3 H, t, J = 7.5 Hz), 0.05 (9 H, s).

(*E*)-1-Phenyl-4-(trimethylsilyl)but-3-en-1-ol[19] ($3a_0$):
This product was obtained in the same manner as described for $\mathbf{3a_0}$ using benzaldehyde (2.8 mL, 3.0 g, 28 mmol); bp 75–80 °C/0.2 Torr; n_D^{20} 1.4582; yield: 3.5 g (65%).
^{1}H NMR: δ = 7.36 (4 H, d, J = 4.5 Hz), 7.3 (1 H, m), 6.04 (1 H, dt, J = 18.6, 6.5 Hz), 5.81 (1 H, dt, J = 18.6, 1.3 Hz), 4.76 (1 H, dd, J = 7.9, 5.3 Hz), 2.56 (2 H, dd, J = 8.1, 5.4 Hz), 2.1 (1 H, s, broad), 0.07 (9 H, s).

(*E*)-2-Ethyl-1-phenyl-4-(trimethylsilyl)but-3-en-1-ol ($3b_6$):
As described for $\mathbf{3a_0}$, (*Z*)-(pent-2-enyl)trimethylsilane[16] (3.5 g, 25 mmol) was consecutively treated with BuLi in the presence of *t*-BuOK (both 28 mmol) and benzaldehyde (2.8 mL, 3.0 g, 28 mmol). The mixture was neutralized with 2.3 M HCl in Et_2O (ca. 25 mL), absorbed on silica gel (25 mL) and transferred to a column filled with more silica gel (0.15 L). Upon elution (Et_2O/hexane 1:9) a yellow liquid was collected consisting of two diastereoisomers in a 1:1 ratio, which was purified by distillation; bp 85–90 °C/0.1 Torr; yield: 3.8 g (61%).
^{1}H NMR*: δ = 7.3 (5 H, m), 5.9 (0.5 × 2 H, m), 5.66 (0.5 × 1 H, dd, J = 18.5, 7.5 Hz), 5.60 (0.5 × 1 H, d, J = 18.5 Hz), 4.59 (0.5 × 1 H, d, J = 6.0 Hz), 4.41 (0.5 × 1 H, d, J = 7.7 Hz), 2.30 (0.5 × 1 H, sym. m), 2.2 (1 H, m), 1.64 (0.5 × 1 H, dqd, J = 12.0, 6.5, 3.3 Hz), 1.25 (1 H, sym. m), 0.84 (0.5 × 3 H, t, J = 6.6 Hz), 0.72 (0.5 × 3 H, t, J = 6.6 Hz), 0.11 (0.5 × 9 H, s), 0.01 (0.5 × 9 H, s).
Anal.: calcd for $C_{15}H_{24}OSi$ (248.44) C 72.52, H 9.74; found C 72.01, H 9.94.

(*E*)-1-Phenyl-2-propyl-4-(trimethylsilyl)but-3-en-1-ol ($3c_6$) and (*Z*)-1-Phenyl-2-(trimethylsilyl)hept-3-en-1-ol ($4c_6$):
In the same way as for $\mathbf{3b_6}$, reaction between (*Z*)-(hex-2-enyl)trimethylsilane[11] (3.9 g, 25 mmol) and benzaldehyde (2.8 mL, 3.0 g, 28 mmol) was performed. According to the NMR spectrum, the crude mixture contained two regioisomers ($\mathbf{3c_6}$ and $\mathbf{4c_6}$).[20] It was submitted to chromatographic purification as described for $\mathbf{3b_6}$. (1*E*,3*E*)-1-Phenylhepta-1,3-diene[21] (0.4 g; 10% ; from $\mathbf{4c_6}$ by acid-catalyzed elimination of trimethylsilanol) and $\mathbf{3c_6}$ were isolated. According to GC (30 m DB-1, 190 °C; 30 m DB-Wax, 190°C), the latter product was composed of two diastereoisomers in a 1:1 ratio; bp 105–110 °C/0.5 Torr; yield: 4.5 g (68%).
^{1}H NMR: δ = 7.3 (5 H, m), 5.85 (0.5 × 2 H, d-like, sym. m), 5.6 (0.5 × 2 H, m), 4.61 (0.5 × 1 H, d, J = 3.5 Hz), 4.40 (0.5 × 1 H, d, J = 4.5 Hz), 2.3 (1 H, m), 2.20 (0.5 × 1 H, s), 2.09 (0.5 × 1 H, s), 1.4 (1 H, m), 1.2 (2 H, m), 0.87 (0.5 × 3 H, t, J = 7.0 Hz), 0.80 (0.5 × 3 H, t, J = 7.0 Hz), 0.10 (0.5 × 9 H, s).
Anal.: calcd for $C_{16}H_{26}OSi$ (262.42) C 73.22, H 9.98; found C 73.09, H 10.12.

(*E*)-2-Nonyl-4-(trimethylsilyl)but-3-en-1-ol ($3e_0$) and 2-(Trimethylsilyl)tridec-3-en-1-ol ($4e_0$):
In the same way as for $\mathbf{3b_6}$, reaction between (*Z*)-(dodec-2-enyl)trimethylsilane[11] (6.0 g, 25 mmol) and formaldehyde was performed. The crude mixture (consisting of $\mathbf{3e_0}$ and $\mathbf{4e_0}$) was submitted to chromatographic purification, as described for $\mathbf{3b_6}$, to give, besides (*Z*)-trideca-1,3-diene[22] (1.4 g; 31%; from $\mathbf{4e_0}$ by acid-catalyzed elimination of trimethylsilanol), the alcohol $\mathbf{3e_0}$; n_D^{20} 1.4560; yield: 3.1 g (46%).
^{1}H NMR: δ = 5.8 (2 H, m), 3.53 (1 H, dd-like m, J ~ 11, 7 Hz), 3.41 (1 H, t-like m, J ~ 9.5 Hz), 2.23 (1 H, s-like m, broad), 1.4 (1 H, m), 1.26 (16 H, s), 0.88 (3 H, t, J = 7.0 Hz), 0.07 (9 H, s).
Anal.: calcd for $C_{16}H_{34}OSi$ (270.53) C 71.04, H 12.67; found C 71.28, H 12.93.

This work was financially supported by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung, Bern (grants 20-29′838-90 and 20-36′385-92).

(1) Corriu, R. J. P.; Masse, J. P. *J. Organomet. Chem.* **1973**, *57*, C5. Corriu, R. J. P.; Guerin, C.; M'Boula, J. *Tetrahedron Lett.* **1981**, *22*, 2985.
(2) Koumaglo, K.; Chan, T. H. *Tetrahedron Lett.* **1984**, *25*, 717.
(3) Tsai, D. J. S.; Matteson, D. S. *Tetrahedron Lett.* **1981**, *22*, 2751.
(4) Schlosser, M.; Hartmann, J. *J. Am. Chem. Soc.* **1976**, *98*, 4674.
(5) Mordini, A.; Palio, G.; Ricci, A.; Taddei, M. *Tetrahedron Lett.* **1988**, *29*, 4991.
(6) Schlosser, M. *J. Organomet. Chem.* **1967**, *8*, 9. Schlosser, M.; Strunk, S. *Tetrahedron Lett.* **1984**, *25*, 741. Schlosser, M. *Pure Appl. Chem.* **1988**, *60*, 1627.
(7) Schlosser, M.; Desponds, O.; Lehmann, R.; Moret, E.; Rauchschwalbe, G. *Tetrahedron* **1993**, *49*, 10175.
(8) Yamamoto, Y.; Saito, Y.; Maruyama, K. *Tetrahedron Lett.* **1982**, *23*, 4597. See also: Lau, P. W. K.; Chan, T. H. *Tetrahedron Lett.* **1978**, 2383.
(9) Acid-catalyzed *anti* elimination of trimethylsilanol from β-hydroxysilanes: Hudrlik, P. F.; Peterson, D. *Tetrahedron Lett.* **1974**, 1133. Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464. Hudrlik, P. F.; Peterson, D.; Rona, R. J. *J. Org. Chem.* **1975**, *40*, 2263.
(10) Schlosser, M.; Dahan, R.; Cottens, S. *Helv. Chim. Acta* **1984**, *67*, 284.
(11) Desponds, O.; Franzini, L.; Schlosser, M. *Synthesis* **1997**, 150.
(12) Dunoguès, J.; Calas, R.; Ardoin, N.; Biran, C. *J. Organomet. Chem.* **1971**, *32*, C31. Tubul, A.; Santelli, M. *Tetrahedron* **1988**, *44*, 3975.
(13) Stork, G.; Jung, M. E.; Calvin, E.; Noel, Y. *J. Am. Chem. Soc.* **1974**, *96*, 3684. Vedejs, E.; Engler, D. A.; Mullins, M. J. *J. Org. Chem.* **1977**, *42*, 3109.
(14) Rauchschwalbe, G.; Schlosser, M. *Helv. Chim. Acta* **1975**, *58*, 1094. To prepare fluorodimethoxyborane–diethyl ether complex (1.00 mol), one has simply to mix BF_3•Et_2 (42 mL, 47 g, 0.33 mol), trimethyl borate (75 mL, 70 g, 0.67 mol) and Et_2O (70 mL, 50 g, 0.67 mol).
(15) Kishi, N.; Maeda, T.; Mikami, K.; Nakai, T. *Tetrahedron* **1992**, *48*, 4087.
(16) Lappert, M. F.; Nile, T. A.; Takahashi, S. *J. Organomet. Chem.* **1974**, *72*, 425.
(17) Hsiao, C. N.; Shechter, H. *Tetrahedron Lett.* **1983**, *24*, 2371.
(18) Schlosser, M.; Jenny, T.; Guggisberg, Y. *Synlett* **1990**, 704.
(19) Tsai, D. J. S.; Matteson, D. S. *Organometallics* **1983**, *2*, 236.
(20) The regioisomer $\mathbf{4c_6}$, contaminated with small amounts of $\mathbf{3c_6}$, was separately prepared by the addition of dimethyl (*Z*)-hex-2-enylboronate to benzaldehyde: Franzini, L. Ph. D. thesis, University of Lausanne, 1996, pp 29 and 88–89.
(21) Other stereoisomers: Inoue, Y.; Toyofuku, M.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1279. Tsukamoto, M.; Schlosser, M. *Synlett* **1990**, 605.
(22) Ikeda, Y.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 657.