1- and 2-(Trialkylsilyl)ethanols: New Silyl Reagents from Tin, Lithium, and Boron Chemistry

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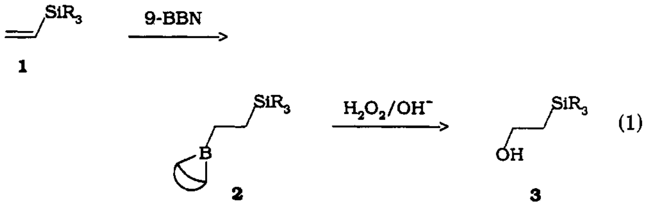
Efficient preparations of isomerically pure 1- and 2-(trialkylsilyl)ethanols from vinylsilanes with borane reagents are described. In the former case, the borane reduction of the appropriate acetylsilane (**12**) gave good yields (82–94%) of the desired 1-R_3Si products (**13**, R = Me, Et, *i*-Pr). The reaction of (α-methoxyvinyl)lithium (**10**) (from Sn/Li exchange) with the appropriate chlorosilanes provided the corresponding (α-methoxyvinyl)silanes (**11**) (89–94%). Hydrolysis of **11** afforded acylsilanes (**12**) in excellent yield (93%). Hydroboration of the vinylsilanes (**1**) with 9-borabicyclo[3.3.1]nonane (9-BBN) gave (β-borylethyl)silanes (**2**), which were oxidized to provide isomerically pure 2-silylethanols (**3**). The formation of Normant's reagent (**4**, vinylmagnesium bromide in THF) and Seyferth's reagent (**7**, unsolvated vinyllithium) were examined in some detail, and several new minor processes were identified. Unlike less hindered chlorosilanes, the triisopropylsilyl compound fails to react cleanly with **4**, but is smoothly converted to **1c** (79%) with **7**. It was demonstrated that **11c** (R = *i*-Pr) afforded **3c** (89%) via a one-pot hydroboration/elimination/hydroboration/oxidation sequence. Complete, assigned ^{13}C NMR data for these silanes are presented and compared to their trimethylsilyl counterparts.

In recent years, 2-(trimethylsilyl)ethanol (**3a**) and its chloromethyl ether have found important applications in the protection of carboxylic acids and alcohols.[3] Several useful routes to **3a** have been reported[4,5] including our hydroboration/oxidation sequence.

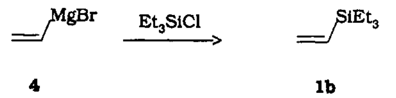


(1)

Unfortunately, there are environmental drawbacks to many of these methods, and, also, due to a lack of available chloromethylsilane precursors, another is limited in scope.[5d] However, because vinylsilanes are readily available from chlorosilanes,[6] the above sequence appeared to be very general, and to demonstrate this, we chose to prepare isotropically bulkier 2-silylethanol derivatives (i.e. **3b**, R = Et; **3c**, R = *i*-Pr). The corresponding isomeric 1-(trialkylsilyl)ethanols were also prepared to extend the scope of our borane reduction of acetylsilanes.[4] In this paper, the results of these investigations are reported.

Results and Discussion

Vinylsilanes are commonly prepared from halosilanes and vinylmagnesium reagents,[7] and this approach gave the pure triethylsilyl derivative, **1b**, in good yield (77%). A multitude of very minor byproducts were chromatographically observed in the reaction mixtures. The two most significant were identified as **5** (3%) and **6** (1%). Thus, in the formation of vinylmagnesium bromide (**4**), these byproducts suggest that acetylene and 1,3-butadiene can also result from minor elimination and reductive coupling processes.[8] These hydrocarbons, in turn, react further, as expected, to give the observed silylated products, **5** and **6**, respectively. While precedented in organomagnesium and/or lithium chemistry,[8] these side reactions apparently have not been previously identified in the formation of Normant's reagent.[9]



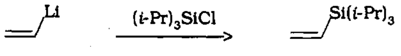
(2)

4 **1b**

$Et_3SiC{\equiv}CSiEt_3$ **5**

$Et_3SiCH_2CH{=}CHCH_2SiEt_3$ **6**

Unfortunately, **4** failed to react signficantly with triisopropylsilyl chloride even at reflux temperature and with long reaction times. However, vinyllithium proved sufficiently reactive to provide **1c** in good yield (79%).



(3)

7 **1c**

In his original study, Seyferth had observed that solid vinyllithium (**7**) could be prepared from tetravinyltin in alkane solvents.[10] Because an equilibrium exists between **7** and the soluble vinyltin compounds, he found that the reagent was best prepared from **8** by limiting the amount of Li(*n*-Bu) to 2–2.5 equiv. We examined this process and,

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[1] Graduate student sponsored by the NSF EPSCoR Program of Puerto Rico.

[2] Graduate student supported by the NIH-MBRS Program (RR08102).

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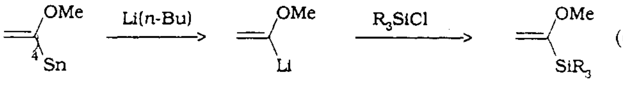
by GC–MS analysis, identified the principal soluble tin-containing compounds as Vi_2SnBu_2 (58%), $ViSnBu_3$ (38%), and $SnBu_4$ (4%).

$$\underset{\mathbf{8}}{SnVi_4} \xrightarrow[C_5H_{12}/C_6H_{14}]{2.5\text{ eq Li}(n\text{-Bu})} \mathbf{7} + Vi_2Sn(n\text{-Bu})_2 + ViSn(n\text{-Bu})_3 + Sn(n\text{-Bu})_4 \qquad (4)$$

While the above butyltin derivatives accounted for ca. 98% of the Li(n-Bu) added, we noted, in the preparation of **1c**, that the reaction mixture contained (n-Bu)Si(i-Pr)$_3$ (<1%), (n-Hx)Si(i-Pr)$_3$ (1.7%), and Sn(Bu)$_4$ (1.3%). Thus, despite several pentane washings, we were unable to completely remove all of the tin products and Li(n-Bu) from the precipitated **7**. To corroborate this reactivity, we carried out the reaction of Li(n-Bu) with both ClSi(i-Pr)$_3$ and **1c** to obtain the expected butyl- and hexylsilane products, respectively.[11]

$$(i\text{-Pr})_3Si(n\text{-Hx}) \xleftarrow[2.\ H_2O]{1.\ \mathbf{1c}} Li(n\text{-Bu}) \xrightarrow{(i\text{-Pr})_3SiCl} (i\text{-Pr})_3Si(n\text{-Bu}) \qquad (5)$$

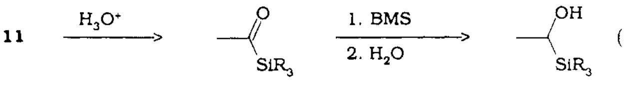
Our previous studies[12] had demonstrated that α-methoxyvinyl derivatives of group 4 metalloids could be efficiently prepared from the corresponding halo compounds and (α-methoxyvinyl)lithium (**10**). Pure, unsolvated **10** is efficiently obtained from tin derivatives such as **9** through a very clean Sn/Li exchange reaction which takes place in alkane solvents.[12d] Unlike the equilibrium situation which limits the efficiency of the **8** to **7** conversion under comparable conditions, 4 equiv of n-butyllithium gives 92% of solid **10** from **9**. The reaction of **10** with chlorosilanes is remarkably clean and the triethyl- and triisopropyl(α-methoxyvinyl)silanes (**11**) were isolated in excellent yields (i.e. 92 and 96%, respectively). Also, we observed neither occluded Li(n-Bu) nor tin-containing impurities in **10** as was the case for **7**.



(6)

9 **10** **11**

The acid-catalyzed hydrolysis of **11** gave the corresponding acylsilanes (**12**) cleanly, in excellent yield (i.e. 93%), as expected from our earlier studies.[12,13] Acylsilanes can easily be reduced with a variety of reagents.[14] However, the borane–methyl sulfide (BMS) procedure[4] afforded the desired 1-(trialkylsilyl)ethanols (**13**) in excellent yields (82–94%). We feel that it is the method of choice for such conversions.



(7)

12 **13**

No systematic study had been reported on the influence of symmetrically increasing the steric bulk of the silyl substituent on the regiochemistry of the hydroboration of vinylsilanes. For the sake of completeness, we carried out a brief investigation of this process employing BMS as the hydroborating agent. Thus, all of the vinylsilanes, **1a–c**, are smoothly hydroborated with BMS (1 h, 25 °C), employing a 1:1 stoichiometry, to give, after oxidation, both **13** and **3** in a 53–55:47–45 ratio. However, the (triisopropylsilyl)alkylborane intermediates could not be quantitatively oxidized to the product alcohols (i.e. 73%). With a 2:1 (1:BMS) stoichiometry, **1b** gave a quantitative 50:50 mixture of **13b** and **3b**. With BMS failing to provide **3**, cleanly, we turned to 9-BBN for a regioselective process.[4a,b]

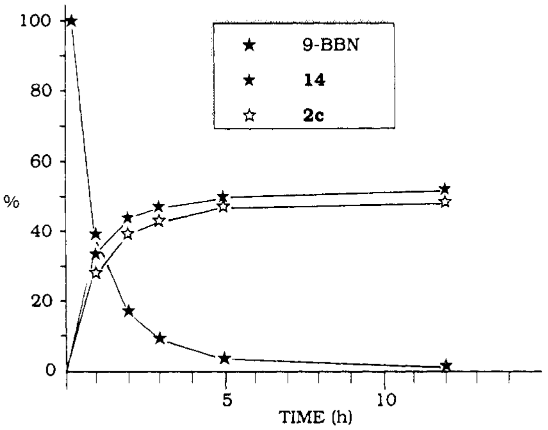


Figure 1. Reaction of **11c** with 2 equiv of 9-BBN at 50 °C.

$$\mathbf{1} \xrightarrow[2.\ H_2O_2/OH^-]{1.\ BMS} \mathbf{13} + \mathbf{3} \qquad (8)$$

For all of the vinylsilanes (**1**), 9-BBN formed **2** cleanly with >99% regioselectivity, and oxidation gave the corresponding 2-(trialkylsilyl)ethanols (**3**), quantitatively. Isolation of the pure alcohol, free of *cis*-1,5-cyclooctanediol, previously accomplished in 74% yield for **3a**,[4a] was somewhat better for **3b** (i.e. 84%). For vinylsilanes that can be prepared from Normant's reagent, this is clearly a highly efficient, useful process. However, the failure of this reagent to give **1c** necessitated the use of **7**. Since both **1c** and **11c** were prepared by similar Sn/Li procedures, we were afforded an opportunity to directly compare these processes. Unlike **7**, solid **10** can be prepared quantitatively from **9** with at least 3 equiv of n-butyllithium. moreover, **10** settles more rapidly than does **7** from the supernatant, thus avoiding the need for centrifugation. By contrast, even with 2 equiv of Li(n-Bu), **8** always produces the solid **7** with the coprecipitation of other species. Consequently, more byproducts were observed in the case of **1c** than for **11c**. This led us to devise a new route to **3c** from the reaction of **11c** and 2 equiv of 9-BBN. We reasoned, based upon Larson's findings for silyl enol ethers,[15] that **11c** should undergo hydroboration with 9-BBN, followed by β-elimination of the *B*-methoxy-9-BBN (**14**), followed by rehydroboration of the resulting **1c** to give, after oxidation, **3c**. This process was accomplished in a simple one-pot procedure, giving the desired alcohol in 89% isolated yield. Because of the factors mentioned above, we find this synthetic route to **3c** to be preferable to the standard 9-BBN/vinylsilane approach. In a general sense, this demonstrates that (α-methoxyvinyl)silanes can function as key intermediates for the preparation of either 1- or 2-(trialkylsilyl)ethanols.

The process was monitored at 50 °C by ^{11}B NMR and integrated values for 9-BBN (δ 28 ppm), **2c** (δ 82 ppm), and **14** (δ 54 ppm) were obtained with time. These data are illustrated in Figure 1. As can be noted, in contrast to the behavior of **1a–c**, in which the hydroboration is

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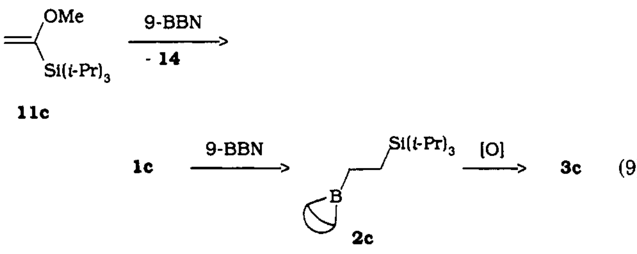


(9).

complete in 2 h at 50 °C, this overall process is much slower. Moreover, from ^{1}H and ^{13}C NMR data, the only significant silylated organoborane observed was **2c**. Also, **1c** is never present in more than trace amounts in these mixtures. Taken together, these findings suggest that after the initial hydroboration of **11a** with 9-BBN monomer, the subsequent steps occur more rapidly, giving **2c** as the final product.[16]

With several series of functionalized organosilanes in hand, it was of interest to examine their ^{13}C NMR data to note any regularities which may be of general value. These data are presented in Table I. For each series, changing from trimethyl- to triethyl- to triisopropylsilyl groups adds three carbons each time to the silylated 2-carbon functionality. These added carbons are γ to the C-1 position, and δ to the C-2 position. We note an upfield γ-gauche effect which occurs for the C-1 carbon with this increasing substitution. It is most noticeable upon changing from trimethyl- to triethylsilyl groups, but can also be observed, in most cases, for the triethyl- to trisopropylsilyl change. Additionally, a small downfield δ-effect can normally be seen for the C-2 carbon. Thus, while perhaps attenuated because of the longer Si–C bonds compared to C–C bonds, organosilanes also exhibit trends and effects which are common in the ^{13}C NMR spectroscopy of all-carbon systems.[17]

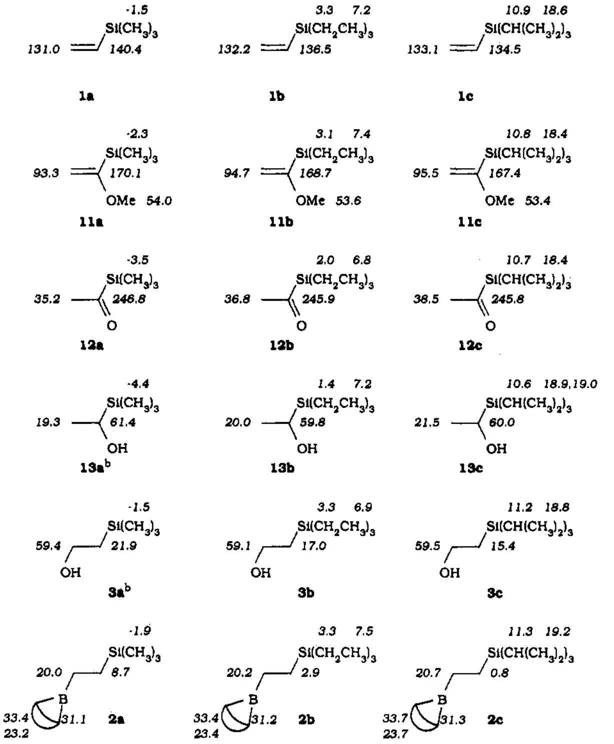
Conclusions

In this study, the preparation of vinylsilanes with vinylmagnesium and -lithium reagents, have been examined in some detail. The triisopropyl substitution dramatically reduces the reactivity of chlorosilanes toward these organometallics, and only **7** gave the desired vinylsilane, **1c**, in good yield. The hydroboration protocol was extended to include two new 2-silylethanols (**3**) from vinylsilanes in a completely regioselective process. The utility of (α-methoxyvinyl)silanes (**11**) as precursors to acetylsilanes (**12**) was further demonstrated, and the borane reduction of **12** was shown to give excellent yields of 1-silylethanols (**13**) even when the silicon contains very bulky alkyl groups. These vinylsilanes, **11**, were also demonstrated, in the case of the triisopropylsilyl compound, **11c**, to provide an efficient entry to **3c** through a one-pot hydroboration/elimination/hydroboration sequence. With a number of related organosilanes, it was possible to note the effects of added carbons on their ^{13}C NMR spectra.

Experimental Section

General Methods. All experiments were carried out in predried (4 h, 150 °C) glassware under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study.[18] THF was distilled from sodium/benzophenone prior to use. Other reagents were obtained from commercial sources or prepared as reported.[4,19] ^{1}H, ^{11}B, ^{13}C, and ^{29}Si NMR data were recorded at 300, 96, 75, and 60 MHz, respectively. Standard APT or DEPT experiments were carried out for the ^{13}C NMR assignments given in Table I and elsewhere.[20] GC analyses were performed using 6 ft × $^1/_8$ in. 20% SE-30 on DCDMS-treated Chrom W packed columns and 30 m × 0.23 mm. i.d. 20% SE-30 vitreous silica open tubular columns. Columns were silylated (MSTFA, Aldrich) prior to analytical runs.

Table I. ^{13}C NMR Assignments for the Organosilanes[a]



[a] Recorded in CDCl$_3$ solution, except **2c** and **11b** (C$_6$D$_6$) (TMS δ = 0.00 ppm). [b] Values taken from ref 4b.

Triethylvinylsilane (1b). A reaction flask surmounted by an addition funnel and a dry-ice condenser was charged with Mg gravel (4.40 g, 181 mg-atoms), and a solution of vinyl bromide (18.0 g, 169 mmol) in THF (90 mL) was added dropwise at a rate sufficient to maintain reflux temperature. After reaching 25 °C over 1 h, chlorotriethylsilane (19.0 g, 126 mmol) was added dropwise, and the mixture was allowed to stir overnight. The mixture was poured onto ice/saturated NH$_4$Cl solution. Pentane (80 mL) was added, and after separation, the organic layer was washed with water (10 × 100 mL) to remove the THF, dried (K$_2$CO$_3$), and distilled at 760 Torr to give 13.0–13.8 g (72–7%) of **1b** (99.7% GC purity): bp 146–7 °C [lit.[21] bp 146.5 °C (750 Torr)]; ^{1}H NMR (CDCl$_3$) δ 0.56 (q, 2 H, J = 7.9 Hz), 0.92 (t, 3 H, J = 7.9 Hz), 5.66 (dd, 1 H, J = 19.2, 5.3 Hz), 5.98 (dd, 1 H, J = 14.8, 5.3 Hz), 6.05 (dd, 1 H, J = 19.2, 14.8 Hz); IR (TF) 1593 (C=C), 1460, 1406, 1237, 971 (SiEt$_3$) cm^{-1}; MS[22] m/z 142 (2), 114 (33), 113 (74), 85 (100), 57 (36). The major byproduct (ca. 3%) was isolated from the residue by preparative GC and identified as **5**: ^{1}H NMR (CDCl$_3$) δ 0.59 (q, 12 H, J = 7.8 Hz), 1.04 (t, 18 H, J = 7.8 Hz); ^{13}C NMR (CDCl$_3$) δ 4.87 (SiCH$_2$CH$_3$), 7.66 (SiCH$_2$CH$_3$), 113.1 (C≡C); MS m/z 254 (2), 226 (26), 225 (100), 197 (44), 169 (32), 141 (43), 113 (27), 111 (16), 85 (13), 83 (13). A second byproduct, **6** (1%), gave the following GC–MS data: m/z 284 (2), 140 (9), 115 (100), 111 (22), 87 (89), 83 (19), 59 (47).

Attempted Preparation of Triisopropylvinylsilane from 4. As for **1b**, **4** (200 mmol) in THF (100 mL) was heated for 12

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[16] Brown, H. C.; Wang, K. K.; Scouten, C. G. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 698. See also: ref 4b.

[17] Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*, 3rd ed.; VCH: New York, 1987.

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[22] For a discussion of some of the aspects which are relevant to the MS fragmentations for this and other silanes, see: Soderquist, J. A.; Hassner, A. *J. Organomet. Chem.* **1981**, *217*, 151.

at reflux temperature with (*i*-Pr)$_3$SiCl (19.3 g, 100 mmol). The NH_4Cl-quenched mixture was dried (K_2CO_3), concentrated, and distilled to give 11.1 g (bp 46–48 °C at 0.2 Torr), which was found, by capillary GC and ^{13}C NMR, to be a ca. 10:67:23 mixture of **1c**, (*i*-Pr)$_3$SiOH, and ((*i*-Pr)$_3$Si)$_2$O, together with other minor products.

Triisopropylvinylsilane (1c). To cooled (0 °C) **8** (3.03 g, 13.4 mmol) was added Li(*n*-Bu) (11.8 mL, 2.5 M, 29.4 mmol) in hexanes dropwise via syringe. After 0.5 h, the mixture was allowed to reach 25 °C, and stirring was continued for an additional 0.25 h. After centrifuging, the supernatant was decanted via a double-ended needle. In a similar manner, the solid **7** was washed (3 × 10 mL) and cooled to −78 °C, and THF (10 mL), followed by (*i*-Pr)$_3$SiCl (5.30 g, 27.5 mmol), was added dropwise. The stirred mixture was allowed to reach 25 °C, and, after 1 h, it was transferred to a separatory funnel and quenched with water (50 mL), and pentane (50 mL) was added. The organic layer was dried (K_2CO_3), concentrated, and distilled to give 4.0 g (79%) of **1c** (bp 52–4 °C (2.3 Torr), >98% GC purity): ^{1}H NMR ($CDCl_3$) δ 1.00–1.15 (m, 21 H), 5.6–6.15 (m, 3 H, abc pattern (calcd): 5.73 (a), 6.05 (b), and 6.09 (c) and *J*'s of 14.8 (ab), 5.0 (ac), and 19.2 (bc) Hz); IR (TF) 1593 (C=C), 1384, 1368, 883 (Si(*i*-Pr)$_3$) cm^{-1}; MS *m/z* 184 (4), 141 (61), 113 (23), 99 (78), 85 (45), 71 (100), 59 (47). Anal. Calcd for $C_{11}H_{24}Si$: C, 71.64; H, 13.15. Found: C, 71.45; H, 13.17. The combined washings were analyzed by GC–MS (^{120}Sn isotope only): Bu_2SnVi_2 *m/z* 231 (M − Bu, 33), 175 (100), 149 (42), 121 (46), 120 (42), 57 (30); Bu_3SnVi *m/z* 261 (M − Bu, 25), 205 (67), 149 (87), 147 (100), 121 (65), 120 (42), 57 (36); $SnBu_4$ *m/z* 291 (M − Bu, 27), 235 (58), 179 (100), 177 (98), 123 (37), 121 (62), 120 (56). Further, to confirm the presence of (*n*-Bu)Si(*i*-Pr)$_3$ in the reaction mixture, ClSi(*i*-Pr)$_3$ was added to Li(*n*-Bu) (1.1 equiv) in hexanes/THF (1:2) at −78 °C. After reaching 25 °C, GC analysis revealed incomplete conversion, even after 24 h. A sample of the product was isolated by preparative GC (^{13}C NMR ($CDCl_3$) δ 9.14, 11.13, 13.67, 18.89, 26.65, 27.31). This material was chromatographically identical with the minor co-product, which gave the following MS data: *m/z* 171 (M − (*i*-Pr), 23), 169 (55), 127 (83), 115 (32), 99 (82), 87 (53), 73 (64), 59 (100). The second byproduct, (*n*-Hx)Si(*i*-Pr)$_3$, was prepared from the addition of Li(*n*-Bu) to 1 equiv of **1c** in THF at −78 °C followed by reaction at −15 °C for 5 h. After the addition of *n*-tridecane as an internal GC standard, quenching with H_2O gave a 94% yield of the desired hexylsilane. A pure sample was isolated by preparative GC (^{13}C NMR ($CDCl_3$) δ 9.43, 11.05, 14.14, 18.89, 22.73, 24.36, 31.57, 34.23), which was chromatographically identical with the second minor byproduct which gave the following MS data: *m/z* 199 (M − (*i*-Pr), 19), 157 (29), 115 (39), 87 (36), 73 (67), 59 (100).

General Procedure for the Preparation of 2 for NMR Analysis. After flushing an NMR tube containing 9-BBN (ca. 1.2 mmol) with dry N_2, $CDCl_3$ (1 mL) was added via syringe followed by **1** (1 equiv). After 2 h at 50 °C, the ^{11}B NMR for each vinylsilane adduct was observed: 86 (**2a**), 82 (**2b**), 82 (**2c**) ppm. The ^{13}C NMR data are presented in Table I. For the hydroboration/oxidation of vinylsilanes with BMS, see ref 4.

2-(Triethylsilyl)ethanol (3b). The basic procedure used for the preparation of **3a**[4a] was modified for **3b**. To 9-BBN (1.23 g, 10.1 mmol) in dry THF (5 mL) was added **1b** (1.27 g, 8.9 mmol) via syringe. after 1 h at reflux temperature, the reaction was cooled to 25 °C and water (10 mL) and NaOH solution (11 mL, 2.67 M, 29 mmol) were added, followed by the dropwise addition of 35% H_2O_2 (9 mL). Following this, the stirred mixture was heated at reflux temperature for 1.5 h to destroy the excess of H_2O_2. After reaching 25 °C, pentane (20 mL) was added and the layers were separated. The aqueous phase was extracted with ether (2 × 25 mL), and the combined organic material was extracted with water (4 × 25 mL), dried over K_2CO_3, concentrated, and distilled at 0.35 Torr to give 1.2 g (84%) of **3b** (bp 64–6 °C, >98% GC purity) [lit.[23] bp 100 °C (14 Torr)]: ^{1}H NMR ($CDCl_3$) δ 0.49 (q, 6 H, *J* = 7.5 Hz), 0.90 (t, 9 H, *J* = 7.5 Hz), 0.96 (m, 2 H), 2.1 (b s, 1 H), 3.69 (m, 2 H); IR (TF) 3350 (OH), 1460, 1420, 1240, 975 ($SiEt_3$) cm^{-1}; MS *m/z* 160 (0), 129 (M − CH_2OH, 3), 103 (68), 75 (100), 47 (28).

2-(Triisopropylsilyl)ethanol (3c). To 9-BBN (15.9 g, 130 mmol) in dry THF (100 mL) was added **11c** (13.6 g, 63.3 mmol) via syringe. After 2 h at reflux temperature, NaOH solution (137 mL 2.33 M, 320 mmol) was added followed by the dropwise addition of 30% H_2O_2 (40 mL). Following this, the stirred mixture was heated at reflux temperature for 1.5 h. The aqueous phase was extracted with ether (3 × 70 mL), and the combined organic material was extracted with water (4 × 60 mL), dried over K_2CO_3, concentrated, and distilled at 0.35 Torr to give 11.4 g (89%) of **3c** (bp 114 °C, >99% GC purity): ^{1}H NMR ($CDCl_3$) δ 0.8–1.1 (m, 23 H), 3.62 (m, 2 H), 4.04 (b s, 1 H); IR (TF) 3360 (OH), 1384, 1367, 883 (Si(*i*-Pr)$_3$) cm^{-1}; MS *m/z* 202 (0), 133 (M − (*i*-Pr) − C_2H_4, 63),[22] 103 (65), 75 (100), 61 (50%). Anal. Calcd for $C_{11}H_{26}OSi$: C, 65.27; H, 12.95. Found: C, 65.02; H, 12.92. In a similar manner, **1c** gave a quantitative (GC) yield of **3c**.

(1-Methoxyvinyl)triethylsilane (11b). To a stirred solution of **9** (3.09 g, 8.9 mmol) in pentane (20 mL) at 0 °C was added Li(*n*-Bu) in hexanes (14.3 mL, 2.1 M, 30 mmol), dropwise. After 0.5 h, the cold bath was removed, and the mixture was stirred for an additional 0.5 h at room temperature. The stirring was ceased, and the supernatant liquid, after **10** had settled, was decanted via cannula, to a second flask. Dry pentane (25 mL) was added to wash the solid with subsequent decantation as above. This process was repeated four more times, pentane (15 mL) was added, the slurry was cooled to −78 °C, and Et_3SiCl (4.14 g, 27.5 mmol) in THF (15 mL) was added dropwise. The mixture was allowed to reach 25 °C. After 1 h, the mixture was carefully poured into a separatory funnel containing ice (20 g) and NH_4Cl (sat.) solution (20 mL). Pentane (40 mL) was added, and after separation, the aqueous phase was washed with ether (3 × 30 mL), and the combined organic portions were dried (K_2CO_3), concentrated under reduced pressure, and distilled to give 4.2 g of pure **11b** (89%) (bp 97–9 °C, 46 Torr): ^{1}H NMR ($CDCl_3$) δ 0.62 (q, 6 H, *J* = 7.8 Hz), 0.95 (t, 9 H), 3.50 (s, 3 H), 4.27 (d, 1 H, *J* = 1.9 Hz), 4.66 (d, 1 H, *J* = 1.9 Hz); IR (TF) 3105, 3005, 2830, 1590, 1385, 1225, 1058, 842 (H_2C=C(OMe)), 1470, 1425, 1225, 985 ($SiEt_3$) cm^{-1}; MS *m/z* 157 (18, M = Me), 117 (58), 115 (41), 89 (100), 87 (32), 61 (51), 59 (63). Anal. Calcd for $C_9H_{20}OSi$: C, 62.72; H, 11.70. Found: C, 63.00; H, 11.76.

(1-Methoxyvinyl)triisopropylsilane (11c). As for **11b**, from **9** (15.9 g, 46 mmol) in pentane (90 mL), *n*-BuLi in hexanes (80 mL 1.73 M, 138 mmol), **10**, was allowed to react with (*i*-Pr)$_3$SiCl (15.8 g, 82 mmol) at 25 °C for 12 h, to afford 16.8 g of **11c** (96% yield, 99.9% GC purity) (bp 64 °C, 0.2 Torr): ^{1}H NMR ($CDCl_3$) δ 1.10 (m, 21 H), 3.52 (s, 3 H), 4.33 (d, 1 H, *J* = 2.1 Hz), 4.76 (d, 1 H, *J* = 2.1 Hz); ^{29}Si NMR δ 1.3; IR (TF) 3080, 2830, 1580, 1384, 1209, 1039, 822 (H_2C=C(OMe)), 1384, 1366, 885 (Si(*i*-Pr)$_3$) cm^{-1}; MS *m/z* 199 (21, M − Me), 145 (76), 117 (60), 89 (82), 75 (99), 59 (100). Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 67.36; H, 12.19.

Acetyltriethylsilane (12b). Compound **11b** (3.70 g, 21.5 mmol) was added to a stirred 4:1 acetone/1.0 M HCl(aq) solution (20 mL) at 25 °C. After 1.5 h, the mixture was poured into a separatory funnel containing water (30 mL) and pentane (30 mL). After separation, the aqueous phase was washed with ether (3 × 30 mL), and the combined organic portions were washed with water (3 × 30 mL), dried ($MgSO_4$), concentrated under reduced pressure, and distilled to give 3.18 g of **12b** (93% yield, 98.1% GC purity) (bp 104–5 °C, 75 Torr) [lit.[24] bp 180 °C (760 Torr)]. ^{1}H NMR ($CDCl_3$) δ 0.93 (q, 6 H, *J* = 7.8 Hz), 1.17 (t, 9 H, *J* = 7.8 Hz), 2.43 (s, 3 H); IR (TF) 1645 (C=O), 1465, 1420, 1240, 980 ($SiEt_3$) cm^{-1}; MS *m/z* 156 (7, M − H_2), 129 (56), 115 (33), 89 (28), 87 (100), 73 (32), 59 (52). Anal. Calcd for $C_8H_{18}OSi$: C, 60.69; H, 11.46. Found: C, 60.50; H, 11.46.

Acetyltriisopropylsilane (12c). As for **12b**, from **11c** (8.42 g, 39.3 mmol) and a 4:1 acetone/1 M HCl(aq) solution (35 mL) was obtained 7.3 g of **12c** (93% yield, 99.7% GC purity) (bp 59 °C, 0.2 Torr): ^{1}H NMR ($CDCl_3$) δ 1.05 (d, 18 H, *J* = 7.5 Hz), 1.25 (sept, 3 H, *J* = 7.5 Hz), 2.22 (s, 3 H); ^{29}Si NMR δ −2.43; IR (TF) 1642 (C=O), 1386, 1368, 883 (Si(*i*-Pr)$_3$) cm^{-1}; MS *m/z* 157 (40, M − Ac), 115 (39), 87 (44), 73 (63), 59 (100). Anal. Cald for $C_{11}H_{24}OSi$: C, 65.93; H, 12.07. Found: C, 65.87; H, 12.03.

1-(Triethylsilyl)ethanol (13b). The basic procedure employed for **13a**[4a] was modified for **13b**. To a stirred solution of BMS (2.00 mL, 10.0 M, 20.0 mmol) in THF (10 mL) was added

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12b (2.82 g, 17.8 mmol), dropwise. After 1 h, the mixture was quenched by the controlled, dropwise addition of aqueous NaOH (10 mL, 3.0 N.) (*Caution! H_2 evolution!*). Pentane (30 mL) and water (30 mL) were added, and after separation, the aqueous layer was extracted with ether (3 × 30 mL). The combined organic layers were dried (K_2CO_3), concentrated, and distilled to give 2.67 g (93%) of pure **13b** (bp 130–2 °C, 95 Torr) [lit.[23] bp 122 °C (11 Torr)]: ^{1}H NMR ($CDCl_3$) δ 0.62 (q, 6 H, J = 7.8 Hz); 1.00 (t, 9 H, J = 7.8 Hz), 1.32 (d, 3 H, J = 7.5 Hz), 1.1–1.5 (b, 1 H), 3.64 (q, 1 H, J = 7.5 Hz); IR (TF) 3360 (OH), 1460, 1420, 1240, 980 ($SiEt_3$) cm^{-1}; MS m/z 131 (24, M − Et), 115 (18), 103 (33), 87 (100), 75 (50), 59 (57), 58 (18), 47 (29). Anal. Calcd for $C_8H_{20}OSi$: C, 59.90; H, 12.59. Found: C, 60.03; H, 12.55.

1-(Triisopropylsilyl)ethanol (13c). As for **13b**, from **12c** (1.94 g, 9.7 mmol) and BMS (1.50 mL, 10.0 M, 15.0 mmol) in THF (10 mL) was obtained 1.60 g (82%) of pure **13c** (bp 82 °C, 0.2 Torr): ^{1}H NMR ($CDCl_3$) δ 1.0–1.4 (m, 22 H), 1.47 (d, 3 H, J = 7.5 Hz), 3.91 (q, 1 H, J = 7.5 Hz); ^{29}Si NMR δ 2.09; IR (TF) 3390 (OH), 1380, 1368, 883 ($Si(i\text{-}Pr)_3$) cm^{-1}, MS m/z 202 (0.6), 159 (24), 157 (16), 131 (40), 129 (16), 115 (48), 103 (40), 101 (21), 89 (17), 87 (43), 75 (83), 73 (61), 61 (90), 59 (100), 47 (17). Anal. Calcd for $C_{11}H_{26}OSi$: C, 65.24; H, 12.96. Found: C, 65.41; H, 12.90.

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Registry No. **1a**, 754-05-2; **1b**, 1112-54-5; **1c**, 121675-48-7; **2a**, 72610-05-0; **2b**, 121675-52-3; **2c**, 121675-53-4; **3b**, 2916-67-8; **3c**, 121675-55-6; **5**, 17947-98-7; **6**, 58458-84-7; **7**, 917-57-7; **8**, 1112-56-7; **9**, 81177-91-5; **10**, 42722-80-5; **11a**, 79678-01-6; **11b**, 121675-49-8; **11c**, 121675-50-1; **12a**, 13411-48-8; **12b**, 30608-91-4; **12c**, 121675-51-2; **13b**, 18825-02-0; **13c**, 121675-54-5; $CH_2{=}CHBr$, 593-60-2; Et_3SiCl, 994-30-9; $(i\text{-}Pr)_3SiCl$, 13154-24-0; $(i\text{-}Pr)_3SiOH$, 17877-23-5; $((i\text{-}Pr)_3Si)_2O$, 121675-56-7; $Vi_2Sn(n\text{-}Bu)_2$, 7330-43-0; $ViSn(n\text{-}Bu)_3$, 7486-35-3; $(n\text{-}Bu)Si(i\text{-}Pr)_3$, 121675-57-8; $(n\text{-}Hx)Si(i\text{-}Pr)_3$, 121675-58-9.

Organocyanocopper–Trifluoroborane Mediated 1,3-Chirality Transfer Reaction of γ-(Mesyloxy)-α-alkyl α,β-Enoates for the Construction of Chiral Quaternary Carbon Centers with High Optical Purity

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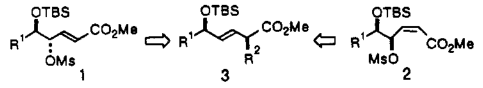
The mesylates of chiral γ-hydroxy-α-methyl (E)-α,β-enoates undergo 1,3-chirality transfer to form chiral α-alkyl-α-methyl (E)-β,γ-enoates with high optical purity using organocyanocopper–trifluoroborane reagents. The degree of asymmetric induction, regiochemistry, and chemoselectivity has been found to be uniformly high. THF or mixed solvents involving THF, a γ-(methylsulfonyl)oxy leaving group, and organocopper–Lewis acid reagents prepared from CuCN, RLi, and $BF_3{\cdot}Et_2O$ were found to be necessary to ensure the success of the preparation of chiral quaternary carbon centers with high optical purity via the 1,3-chirality transfer. The present efficient procedure is compatible with a variety of oxygenated groups such as mesyl, benzyl, *tert*-butyldimethylsilyl, and isopropylidene functions.

As synthetic targets with high biological activities increase in complexity, the requirements for mild and efficient methods for constructing chiral quaternary carbon centers with high optical purity increase.[1] Considerable efforts have been made on the synthesis of chiral quaternary centers and several interesting synthetic procedures have been developed. Except for a few synthetic routes,[2] recently described synthetic methods for construction of chiral quaternary carbon centers have involved the use of the enantio- or diastereoselective α-alkylation of chiral bicyclic lactams,[3] acyclic α-alkyl-α-cyanoacetamides with pyrrolidines as chiral auxiliaries,[4] chiral β-hydroxy esters,[5] and other carbonyl compounds.[6] However, an organocopper–trifluoroborane assisted 1,3-chirality-transfer strategy of γ-oxygenated-α-alkyl α,β-enoates for constructing chiral quaternary carbon centers has no precedent as far as we are aware.

We reported recently that both E and Z chiral γ-mesyloxy α,β-enoates **1** and **2** can be effectively converted to α-alkyl (E)-β,γ-enoates **3** with very high optical purity by treatment with organocyanocopper–trifluoroborane reagents[7] (eq 1).



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