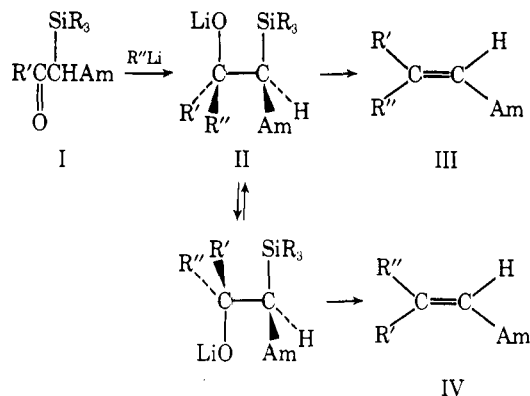


with sodium acetate (-15°C for 30 min and room temperature overnight), the *Z* isomer (IVa) was obtained in 69% overall yield (stereoselectivity 88%).¹⁴ Similar reaction of 5-trimethylsilyl-4-decanone (Ic) with methyllithium gave IIIa in 76% yield (stereoselectivity 91%) by treatment with potassium *tert*-butoxide and IVa in 57% overall yield (stereoselectivity 90%) by treatment with glacial acetic acid saturated with sodium acetate.¹⁵



- a, R = Me; R' = *n*-Pr; R'' = Me
 b, R = Me; R' = Me; R'' = *n*-Pr
 c, R = Et; R' = *n*-Pr; R'' = Me

Further information about the stereoselectivity of this olefin synthesis was obtained from the reaction of 3-trimethylsilyl-2-octanone (Ib) with propyllithium. Treatment of the reaction mixture with potassium *tert*-butoxide gave IVa in 25% yield (stereoselectivity 96%) via IIb.¹⁶

When methylmagnesium bromide, in place of methyllithium, was treated with β -ketosilane Ia, IVa was obtained in 22% (stereoselectivity 77%) after acidic workup (glacial acid saturated with sodium acetate). Reaction of Ia with phenyllithium gave 4-phenyl-4-decene (52% overall yield, 39/61 *E/Z*) after treatment of the reaction mixture with concentrated sulfuric acid.¹⁷

These data show that β -hydroxysilanes are produced from β -ketosilanes and alkylolithium reagents in high stereoselectivity. The potassium salt of the alcohol produces a trisubstituted ethylene by syn-elimination of trimethylsilyl and hydroxy groups whereas treatment with acid in the presence of nucleophile induces anti-elimination of these two groups.^{1-3,6}

Preparation of 4-methyl-4(*E*)-decene (IIIa) and the *Z* isomer (IVa) are representative. A stirred solution of 5-trimethylsilyl-4-decanone (Ia, 0.23 g, 1 mmol) in 5 ml of THF was treated with methyllithium (3 mmol, 3.5 ml of 0.85 M ethereal solution) at -78°C and the reaction mixture was stirred at room temperature overnight. Addition of 1.0 g (9 mmol) of potassium *tert*-butoxide and refluxing of the reaction mixture for 1 h gave IIIa (74% overall yield, 91/9 *E/Z*): NMR (CCl_4) δ 0.6–1.04 (6 H, m), 1.04–1.5 (8 H, m), 1.55 (3 H, br s), 1.70–2.20 (4 H, m), 5.05 (1 H, br t, $J = 7$ Hz). When the reaction mixture from Ia and methyllithium (-78°C for 15 min, then room temperature for 1 h) was treated with 10 ml of glacial acetic acid saturated with sodium acetate under stirring at -15°C for 30 min and at room temperature overnight, workup gave IVa (69%, 12/88 *E/Z*): NMR (CCl_4) δ 0.88 (6 H, t, $J = 6$ Hz), 1.03–1.57 (8 H, m), 1.63 (3 H, br s), 1.70–2.17 (4 H, m), 5.00 (1 H, t, $J = 7$ Hz); MS *m/e* (rel intensity, %), 154 (M^+ , 11), 111 (13), 97 (22), 84 (16), 69 (52), 55 (100).

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- Stereochemistry of olefin-forming reaction from β -hydroxysilanes was studied (ref 1–3).
- 1,1-Disubstituted ethylenes were prepared by analogous procedures: (a) P. F. Hudrik and D. Peterson, *Tetrahedron Lett.*, 1785 (1972); (b) R. A. Ruden and B. L. Gaffney, *Synth. Commun.*, **5**, 15 (1975).
- Prepared from trimethylvinylsilane, butyllithium, and butyraldehyde analogously to the reported procedure (ref 2) for the preparation of β -ketosilanes. This ketosilane was also prepared from trimethylvinylsilane, butyllithium, and butyryl chloride in 45% overall yield: bp 110 – 120°C (23 mm).
- Compound IIa was not isolated. Stereochemistry of IIa as well as its corresponding alcohol could not be determined but estimated from the stereochemistry of olefins prepared by syn- and anti-elimination.
- The structure of IIIa and IVa are based on the NMR. The chemical shift of 7-methyl signal in 3-propyl-7-methyl-2(2),6(*E*)-decadien-1-ol is recorded to be at δ 1.57 ppm, whereas that of the 6(*Z*) isomer is recorded to be at 1.66 (ref 13). The observed chemical shift of vinylic methyl of IIIa appeared at δ 1.55 ppm and that of the *Z* isomer (IVa) at 1.63.
- (a) S. B. Bowlius and J. A. Katzenellenbogen, *J. Org. Chem.*, **38**, 2733 (1973); *Tetrahedron Lett.*, 1277 (1973); (b) M. P. Cooke, Jr., *Tetrahedron Lett.*, 1281 (1973).
- This mixture did not contain other isomers. We could not detect (*Z*- and *E*-)4-methyl-3-decene from the product mixture.
- Further attempts for preparation of olefins: treatment with thioglycolic acid, 61% yield, 46/54 *E/Z*; $\text{BF}_3\cdot\text{OEt}_2$, 82, 37/63. Treatment of the reaction mixture with ammonium chloride gave β -hydroxysilane (IIa', Li = H) which gave IVa: treatment with AcOH saturated with AcONa, 46% yield, 10:90 *E/Z*; AcOH-KF, 72, 12/88; H_2SO_4 -KF, 84, 18/82; H_2SO_4 , 69, 24/76.
- Propyllithium may abstract proton from methyl ketone in Ib. This side reaction may lower the overall yield of IVa.
- Treatment of the reaction mixture with potassium *tert*-butoxide or glacial acetic acid saturated with sodium acetate did not give any olefin. Sulfuric acid produces a benzyl-type cation which gives 4-phenyl-4-decene by the elimination of trimethylsilyl group.

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Stereoselective Synthesis of Vinylsilanes from Alkynylsilanes by Reductive Alkylation via Hydroboration and Carbodemetalation

Summary: Hydroboration of 1-trimethylsilyl-1-alkyne with dicyclohexylborane gave 1-trimethylsilylvinylborane regio- and stereoselectively whose successive treatment with methyllithium, cuprous iodide, and alkyl halides afforded 1,2-dialkylvinylsilane with strict geometry.

Sir: Organosilicon compounds have attracted much attention as versatile reagents for organic synthesis,¹ for example, vinylsilanes have been shown to be useful precursor for ketones, vinyl halides, and olefins of predictable stereochemistry.^{2,3} We wish to describe here a novel stereoselective and generally applicable procedure for the reductive 1,2-dialkylvinylsilanes with fixed configuration, which is based on regioselective hydroboration of 1-alkynylsilane to vinylborane and the following stereoselective transmetalation and carbodemetalation.⁴

Hydroboration of 1-trimethylsilyl-1-octyne (I, R = *n*- C_6H_{13}) with excess dicyclohexylborane gave vinylborane II (R = *n*- C_6H_{13}) regioselectively.^{5,6} Excess borane was quenched with 1-butene and the resulting mixture was treated with

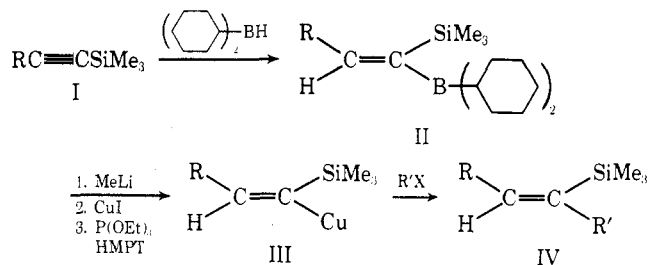
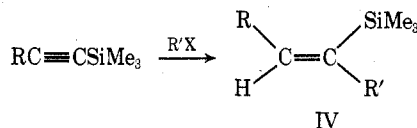


Table I. Stereoselective Synthesis of 1,2-Dialkylvinylsilanes (IV)



| RC≡CSiMe ₃ , R | R'X | Method ^a | Yield, ^b % | Isomer ^c ratio, % Z |
|--|---|---------------------|-----------------------|--------------------------------|
| <i>n</i> -C ₆ H ₁₃ | CH ₃ I | B | 94 (99) ^d | > 99 |
| | CH ₂ =CHCH ₂ Cl | B | 93 | > 99 |
| | CH ₂ =CMeCH ₂ Cl | B | 87 | > 99 |
| | CH ₂ =CClCH ₂ Cl | B | 71 ^e | 99 |
| | CH ₃ CH ₂ I | Cu | 88 | 98 |
| | <i>n</i> -C ₄ H ₉ I | Cu | 81 | 97 |
| | <i>n</i> -C ₆ H ₁₃ I | Cu | 80 | 94 |
| | Me ₂ C=CHCH ₂ CH ₂ I ^f | Cu | (29) ^d | 94 |
| | CH ₃ COCH ₂ CH ₂ O(CH ₂) ₃ I ^k | Cu | 46 | 90 |
| | <i>n</i> -C ₄ H ₉ OTs ^g | Cu | 75 | 97 |
| (CH ₂) ₄ OTHP | CH ₂ =CHCH ₂ Cl | B | 81 | 95 ^h |
| | CH ₃ CH ₂ I | Cu | 85 | 95 ^h |
| | Me ₂ C=CHCH ₂ CH ₂ I ^f | Cu | 31 ⁱ | 94 |
| CH ₂ OCMe ₂ OMe | CH ₃ I | B | 80 | > 99 |
| | CH ₂ =CHCH ₂ Br | B | 59 ^j | > 99 |
| | <i>n</i> -C ₄ H ₉ I | Cu | 41 ⁱ | 85 |

^a Method B means carbodemetalation via borate and method Cu indicates carbodemetalation via vinylcopper. ^b Isolated yield after column chromatography unless otherwise stated. ^c Analysis by GLC (3 m × 3 mm glass column packed with 20% silicon HVSG or 20% PEG 20M on Chromosorb W-AW). ^d Determined by GLC. ^e Isolated by column chromatography followed by distillation. ^f Prepared according to the modified Julia method: J. P. McCormick and D. L. Barton, *J. Chem. Soc., Chem. Commun.*, 303 (1975). ^g Trimethyl phosphite was used in the place of triethyl phosphite. ^h Determined by NMR. ⁱ After isolation of the protected alcohol by column chromatography (silica gel or basic alumina), the alcohol was obtained by methanolysis (5 mM TsOH in MeOH, room temperature, 1 h) followed by distillation (Kugelrohr). ^j After removal of the protecting group, the alcohol was purified by column chromatography (silica gel). ^k 2-Methyl-2-(3-iodopropyl)-1,3-dioxolane.

methylolithium (equimolar to used borane and an additional 1 mol) and cuprous iodide affording α -silylated vinylcopper.⁷ Treatment with a wide variety of alkyl halides afforded stereoselective 1,2-dialkylvinylsilanes IV in excellent yield. The reactivity toward tosylate and homoallyl halide indicated that the above-described α -silylated vinylcopper was more reactive than the simple vinylcopper.⁸ Table I shows the chemical yield and stereoselectivity of the vinylsilanes.

Preparation of 3-trimethylsilyl-3(*Z*)-decene is representative. To a stirred suspension of dicyclohexylborane in THF, prepared from 6 mmol (5.6 ml of 1.08 M solution of BH₃ in THF) of borane and 0.98 g (12 mmol) of cyclohexene in 4.0 ml of THF at 0 °C, was added 0.55 g (3.0 mmol) of 1-trimethylsilyl-1-octyne under argon. After stirring at room temperature for 5 h, the remaining dicyclohexylborane was quenched with 1-butene at 0 °C and transformed into dicyclohexylbutylborane. The reaction mixture was first treated with 9.0 mmol of methylolithium (6.6 ml of 1.36 M ethereal solution), stirred at room temperature for 20 min, and finally treated with cuprous iodide (0.57 g, 3.0 mmol) at -30 °C for 5 min. The resulting dark brown mixture was added with triethyl phosphite (0.60 g, 3.6 mmol) and hexamethylphosphoric triamide (3 ml) then with ethyl iodide (0.70 g, 4.5 mmol) at -30 °C. The reaction mixture was allowed to warm to room temperature overnight and treated with 4 ml of 3 N NaOH and 8 ml of 30% H₂O₂ at 0 °C. After stirring at room temperature for 1 h, the reaction mixture was extracted with ether, washed, dried, and chromatographed on silica gel (hexane), affording 0.56 g (88%) of IV (R = *n*-C₆H₁₃; R' = C₂H₅).

Analogous to the previously reported synthesis of vinylsilane from alanates,⁴ intermediary borates, prepared from 1-trimethylsilyl-1-alkyne, dicyclohexylborane, and methylolithium, could react with methyl iodide and allyl halides in excellent yield.^{9,10}

The above-described procedures, coupled with the facile exchange of trimethylsilyl into hydrogen,^{2b,3} provide highly stereoselective synthesis of olefins from 1-alkyne and are novel additions to the synthetic reactions with organoboron compounds.

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- (5) Hydroboration and successive treatment with acetic acid was reported to produce (*Z*)-vinylsilane from 1-trimethylsilyl-1-alkyne (ref 2c), but regioselectivity of hydroboration has not been described.
- (6) NMR of the crude product showed a single olefinic proton (CCl₄, Me₄Si as internal standard, δ 5.48 ppm, t, *J* = 7 Hz). This observation as well as the yield of carbodemetalation product suggested that 1-trimethylsilylvinylborane II is the sole product.
- (7) The formation of α -silylated vinylcopper upon treatment with cuprous iodide was suggested by the characteristic brown color of the reaction mixture.
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- (9) Under similar reaction conditions, ethyl iodide gave the corresponding ethylated product in 10% yield.
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