

A STEREOSELECTIVE SYNTHESIS OF (E)-1,2-DISUBSTITUTED VINYLSILANES FROM ETHYNYLTRIMETHYLSILANE AND ALKYL COPPER VIA 1-TRIMETHYLSILYL-1(Z)-ALKENYL COPPER

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The utility of vinylsilanes in organic synthesis is now well recognized.¹ Stereoselective synthesis of 1,2-disubstituted vinylsilanes, however, has been reported in a few cases.² This paper describes a general procedure for the synthesis of (E)-1,2-disubstituted vinylsilanes from ethynyltrimethylsilane via 1-trimethylsilyl-1(Z)-alkenylcopper.

To a suspension of propylcopper³ prepared from propylmagnesium bromide (1 mmol, 1.23 ml of 0.81 M ethereal solution) and cuprous bromide (1.1 mmol, 0.157 g) at -20°C, ethynyltrimethylsilane (0.14 ml) and triethyl phosphite (1.1 mmol, 0.23 ml) was added. The mixture was gradually warmed up to 0°C and stirring was continued for 120 min. The resulting mixture was treated with triethyl phosphite (2.2 mmol, 0.46 ml), hexamethylphosphoric triamide (1 ml) and pentyl iodide (1.5 mmol, 0.20 ml) at -40~-45°C for 60 min and overnight at room temp. The whole was worked up with aq. NH₄Cl and ethereal solution was washed with aq. NH₄Cl and sat. NaCl and dried over MgSO₄. Chromatographic separation of the concentrate on silica gel column (hexane) afforded 5-trimethylsilyl-4(E)-decene [III, R = Me(CH₂)₂, R' = Me(CH₂)₄, yield 58%, E>99%].⁴ Vinylsilanes III prepared by this procedure are summarized in Table I.

Vinylsilanes thus formed can easily be converted to trisubstituted ethylenes via α,β -epoxysilanes.⁵ The α -silylated vinylcopper II would also be a versatile reagent for organic synthesis.

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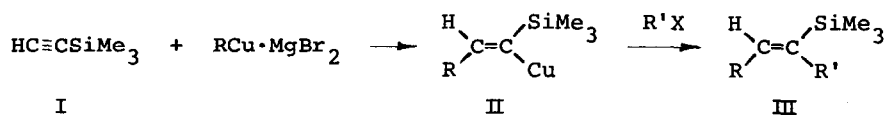


Table I. (E)-1,2-Disubstituted Vinylsilanes (III)

R	R'X	Yield %	Isomeric Purity (E %)
Me(CH ₂) ₂	Me(CH ₂) ₄ I	58	>99
Me(CH ₂) ₂	Me(CH ₂) ₅ I	53	>99
Me(CH ₂) ₂	Me ₃ SiC≡C(CH ₂) ₂ I	39	>99 ^a
Me(CH ₂) ₄	Me(CH ₂) ₂ I	71	>99
Me(CH ₂) ₅	Me(CH ₂) ₂ I	58	>99
Me(CH ₂) ₅	H ₂ C=CHCH ₂ Br	57	>99
Me(CH ₂) ₅	H ₂ O	76	>99

(a) Me₃SiC≡C(CH₂)₂OTs failed to give any expected product.

REFERENCES AND NOTES

- (1) Recent review: I. Fleming, *Chem. Ind. London*, 449 (1975).
- (2) (a) J. J. Eisch and G. A. Damasevitz, *J. Org. Chem.*, **41**, 2214 (1976); (b) K. Uchida, K. Utimoto, and H. Nozaki, *ibid.*, **41**, 2215 (1976); (c) *idem*, *ibid.*, **41**, 2941 (1976); (d) T. H. Chan, W. Michajlowski, B. S. Ong, and D. N. Harpp, *J. Organomet. Chem.*, **107**, C1 (1976); (e) W. Michajlowski and T. H. Chan, *Tetrahedron Lett.*, 4439 (1976).
- (3) Addition of alkylcopper to acetylenes: J. F. Normant, "New Application of Organometallic Reagents in Organic Synthesis", D. Seyferth, Ed., pp 219, Elsevier Scientific Publishing Company, Amsterdam, 1976.
- (4) IR (neat) 1612, 1247, 837, 754, 691 cm⁻¹; nmr (CCl₄) δ ppm, 0.00 (9H, s), 0.67-1.08 (6H, m), 1.08-1.70 (8H, m), 1.70-2.30 (4H, m), 5.65 (1H, broad t, J = 7 Hz); ms m/e (rel. %), 212 (M⁺, 0.3), 197 (11), 169 (3), 155 (2), 138 (15), 127 (6), 113 (7), 101 (4), 99 (9), 95 (7), 82 (10), 74 (10), 73 (100), 59 (29), 45 (12).
- (5) K. Utimoto, M. Obayashi, and H. Nozaki, *J. Org. Chem.*, **41**, 2940 (1976).