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A REGIO- AND STEREOSELECTIVE SYNTHESIS OF 1,2-DISUBSTITUTED VINYLSILANES *

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Summary

The alkylcopper reagents prepared from RMgBr and CuBr react with trimethylsilylacetylene to give regio- and stereo-selectivity 1-trimethylsilyl-1(*Z*)-alkenylcopper adducts Hydrolysis affords 1-trimethylsilyl-1(*E*)-alkenes exclusively Alkylation, acylation, halogenation, and stannylation proceed stereoselectively to afford synthetically useful intermediates Homopropargylation of alkyl 1-trimethylsilyl-1(*Z*)-alkenylcuprates provided better yield than that of the original vinylcopper reagents

Carbometallation of alkynes with alkylcopper reagents followed by carbodemetallation has provided a novel strategy of stereoselective synthesis of olefins [1] and some acetylenes with hetero substituents on *sp* carbon, RC≡CX where X = SR, SOR, SO_2R, PR_2, POR_2 and PSR_2, can enter the sequence of reactions [2] We studied the application of the procedure to trimethylsilylacetylene and discovered a useful synthesis of vinylsilanes, which have attracted considerable attention as versatile intermediates in organic synthesis [3,4] This paper ** describes the addition of alkylcopper to trimethylsilylacetylene to give 1-trimethylsilyl-1(*Z*)-alkenylcopper compounds (II) ***, which are transformed into the trimethylsilylated olefins (III, IV, V and VI) The advantages of the corresponding alkyl cuprates (VII) for homopropargylation are demonstrated

The reaction of $Me_3SiC{\equiv}CH$ (I) with $n\text{-}C_6H_{13}Cu \cdot MgBr_2$ occurred regio- and stereoselectively in ether at 0°C to give 1-trimethylsilyl-1(*E*)-octene (III) after hydrolytic work up †. (The α-silylated vinylcopper II must have been formed as an intermediate, but it was not isolated.) The yield of III depends on the

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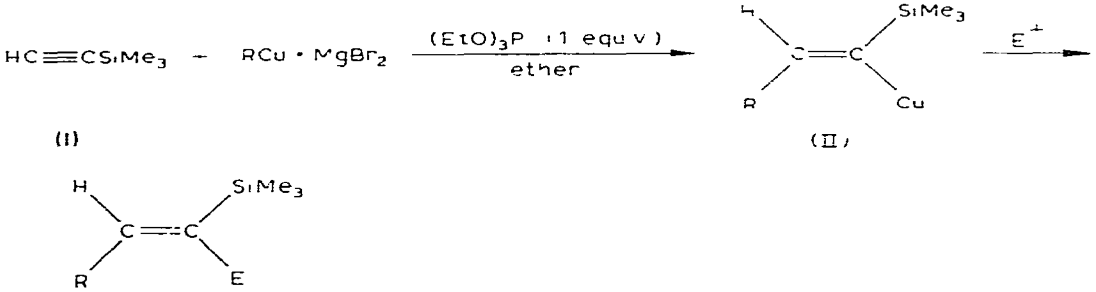
* Dedicated to Professor H Normant on the occasion of his 72nd Birthday on June 25th 1979

** A preliminary report dealing with certain aspects of this work has appeared [5]

*** The reaction has been independently reported [6]

† Vinylsilane III was identical with an authentic sample prepared by the chloroplatinic acid-catalyzed reaction of trichlorosilane and 1-octyne followed by treatment with MeMgI [7]

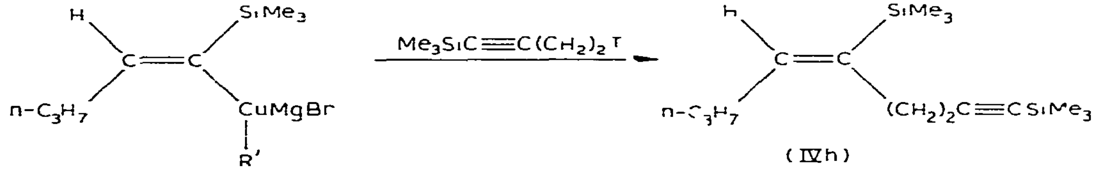
amount of $(EtO)_3P$ added as a ligand, as shown in Table 1 These data indicate that 1 equiv of $(EtO)_3P$ increases the solubility of the alkylcopper to facilitate the addition, and at the same time moderately stabilizes the alkylcopper by preventing its dimerization [8]



(I)

(II)

(III, E = H IV E = Alkyl,
V E = Acyl VI E = I Br Cl
(n-Bu₃Sn))



(VII)

(IVh)

In contrast to I, terminally silylated alkynes in general, 1-trimethylsilyl-1-alkynes, did not react with alkylcopper reagents under the same conditions *, probably because of steric hindrance by the C(2)-alkyl group

The α-silylated vinylcopper products (II) thus prepared are easily converted into 1,2-disubstituted vinylsilanes (IV, V, and VI) with >99% stereoselectivity. Alkylation of II with several kinds of alkyl halides in the presence of $(EtO)_3P$ and HMPT [10] produced (*E*)-1,2-dialkylvinylsilanes, which are important intermediates for stereoselective synthesis of di- and tri-substituted ethylenes [11,12] and of vinyl halides [13] In particular homopropargylation of 1-trimethylsilyl-1(*Z*)-pentenylcopper (II) proceeds in a moderate yield to give 1,5-bis(trimethylsilyl)-5(*E*)-nonen-1-yne (IVh, R = $n\text{-}C_3H_7$, E = $(CH_2)_2C{\equiv}CSiMe_3$), which can easily be transformed into the tetrahomonerol obtained from the codling moth [12c]. This is in contrast with the reaction with vinyllithium or magnesium compounds, in which elimination of HI from homopropargyl iodide predominates. The present procedure is therefore of practical importance **.

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* Recently some examples of carbometallation of 1-trimethylsilyl-1-alkynes have been described [9]

** The reaction of 1-alkenylcopper with homopropargyl chloride gives no coupling product [10]

TABLE 1

CONVERSION OF 1-TRIMETHYLSILYL-1(Z)-ALKENYLCOPPERS (II) INTO 1,2-DISUBSTITUTED VINYLSILANES (III, IV, V AND VI)

R	Electrophile	Product	Yield (%) [a]
n-C_6H_{13}	H_2O	III	76 27 (0) [b,c] 62 (2) [b] 26 (3) [b]
n-C_3H_7	n-$C_5H_{11}I$	IVa	64
n-C_3H_7	n-$C_6H_{13}I$	IVb	69
n-C_5H_{11}	n-C_3H_7I	IVc	71
n-C_6H_{13}	CH_3I	IVd	73
n-C_6H_{13}	n-C_3H_7I	IVe	58
n-C_6H_{13}	n-$C_6H_{13}I$	IVf	72
n-C_6H_{13}	$CH_2{=}CHCH_2Br$	IVg	57
n-C_3H_7	$Me_3SiC{\equiv}C(CH_2)_2I$	IVh	52 76 (R = CH_3) [d] 66 (R = C_2H_5) [d] 72 (R = n-C_3H_7) [d] 62 (R = n-C_3H_7) [e]
C_2H_5	n-C_3H_7COCl	Va	63
n-C_3H_7	n-C_3H_7COCl	Vb	76
n-C_6H_{13}	n-C_3H_7COCl	Vc	80
C_2H_5	I_2	VIa	67
n-C_3H_7	I_2	VIb	71
n-C_6H_{13}	I_2	VIc	79
n-C_6H_{13}	NBS	VId	66
n-C_6H_{13}	NCS	VIe	66
C_2H_5	$(n\text{-}Bu)_3SnCl$	VIf	51
n-C_3H_7	$(n\text{-}Bu)_3SnCl$	VIg	56

[a] Yields are based on RMgBr. [b] The number in parentheses is the amount (equiv.) of $(EtO)_3P$ added. [c] Dodecane was obtained in 33% yield. [d] VII prepared by adding 1 equiv. of R'MgBr was used (route A). [e] VII obtained by the reaction of $HC{\equiv}CSiMe_3$ with $(n\text{-}C_3H_7)_2CuMgBr$ was used (route B).

The yield of IVh is improved by the use of vinylcuprates (VII) instead of the original vinylcopper derivatives (II)*. The cuprates VII can easily be obtained either by adding 1 equiv. of R'MgBr to II (route A) or by reaction of trimethylsilylacetylene (I) with $(n\text{-}C_3H_7)_2CuMgBr$ (route B). In route B, the yield of VII was rather low, which reflects lower yield of IVh in route B** as compared with that in route A.

Further reactions of II with other electrophiles have been examined. Acylation with butyryl chloride provided α-silylated enones (V), which are useful precurors of allenes [15] as well as Michael acceptors [16]. Halogenation [6,17] and stannylation [18] of vinylcoppers II afforded α-halo- and α-stannylvinylsilanes (VI), respectively, which are exceedingly versatile synthetic intermediates in a variety of chemical transformations via α-silylated vinyllithium [19]***.

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* Recently it has been reported that ethyl 1-alkenylcuprate is alkylated by homopropargyl iodide in high yield [14].

** The reaction of I with $(n\text{-}C_6H_{13})_2CuMgBr$ in ether at 0°C for 2 h afforded 1-trimethylsilyl-1(*E*)-octene (III) in 69% yield after hydrolytic work up.

*** Carbodematallation of 1-trimethylsilyl-1(*Z*)-octenylcopper (II) with 3-buten-2-one afforded 5-trimethylsilyl-5(*E*)-dodecen-2-one in 14% yield. In further attempts to prepare 1,2-disubstituted vinylsilanes, treatment of 1-trimethylsilyl-1(*Z*)-octenylcopper (II) with Me_3SiCl or $ClCOOEt$ gave none of the desired products.

Experimental

Gas chromatography was performed on a Shimadzu GC-4BPT chromatograph with 3 mm × 3 m glass columns packed with 20% polyethyleneglycol 20M and and 20% HVSG on Chromosorb W-AW (80-100 mesh). Mass spectra were obtained on Hitachi RMU-6L mass spectrometer at 70 eV. NMR were recorded on Varian EM-360, JEOL JNM-PMX 60, and Varian EM-390 spectrometers with Me_4Si as internal standard. IR spectra were recorded on a Shimadzu IR-27G spectrometer. Elemental microanalyses were performed at the Elemental Analyses Center of Kyoto University. All reactions were carried out under dry argon. Trimethylsilylacetylene (I) was prepared by published methods [20].

(E)-1,2-Dialkylvinylsilanes (IV)

5-Trimethylsilyl-4(E)decene (VIa, R = n-C_3H_7, E = n-C_5H_{11}). To a suspension of propylcopper prepared from n-C_3H_7MgBr (1 mmol, 0.91 ml of 1.10 *M* ethereal solution) and CuBr (0.16 g, 1.1 mmol) at −20°C for 15 min, was added $Me_3SiC{\equiv}CH$ (I, 0.18 ml, 1.4 mmol) and $(EtO)_3P$ (0.23 ml, 1.1 mmol). The mixture was gradually warmed to 0°C and stirring was continued for 2 h. After addition of $(EtO)_3P$ (0.46 ml, 2.2 mmol), HMPT (1 ml), and n-$C_5H_{11}I$ (0.20 ml, 1.5 mmol) at −40 to −45°C the mixture was kept at that temperature for 1 h then overnight at room temperature. After addition of aq. NH_4Cl the ethereal solution was washed (aq. NH_4Cl, sat. NaCl) and dried ($MgSO_4$). Chromatographic separation of the concentrate on silica-gel column (hexane) afforded 0.14 g (64%) of IVa ($E > 99\%$). B.p. 118–122° C/20 mmHg, IR (neat) 1612, 1247, 837, 754, 691 cm^{-1}; mass spectrum *m/e* (rel. %) 212 (M^+, 0.3), 197 (11), 73 (100); NMR (CCl_4) δ (ppm), 0.00 (9 H, s), 0.67–1.08 (6 H, m), 1.08–1.70 (8 H, m), 1.70–2.30 (4 H, m), 5.65 (1 H, br-t, *J* 7 Hz). Anal. Found: C, 73.41, H, 13.53. $C_{13}H_{28}Si$ calcd.: C, 73.50; H, 13.28%.

5-Trimethylsilyl-4(E)-undecene (IVb, R = n-C_3H_7, E = n-C_6H_{13}). Yield, 69%, $E > 99\%$; b.p. 118–122°C/14 mmHg. IR (neat) 1611, 1240, 850, 833, 752, 689 cm^{-1}; mass spectrum: *m/e* (rel. %) 226 (M^+, 0.4), 211 (10), 73 (100). NMR (CCl_4) δ (ppm), 0.00 (9 H, s), 0.67–1.08 (6 H, m), 1.08–1.67 (10 H, m), 1.67–2.33 (4 H, m), 5.63 (1 H, br-t, *J* 7 Hz). Anal. Found: C, 74.08, H, 13.63. $C_{14}H_{30}Si$ calcd.: C, 74.25, H, 13.35%.

4-Trimethylsilyl-4(E)-decene (IVc, R = n-C_5H_{11}, E = n-C_3H_7). Yield, 71%, $E > 99\%$; b.p. 100°C/10 mmHg, IR (neat) 1612, 1243, 832, 751, 689 cm^{-1}, mass spectrum. *m/e* (rel. %) 212 (M^+, 1), 196 (16), 73 (100), NMR (CCl_4) δ (ppm), 0.00 (9 H, s), 0.67–1.05 (6 H, m), 1.05–1.70 (8 H, m), 1.70–2.30 (4 H, m), 5.63 (1 H, br-t, *J* 7 Hz). Anal. Found: C, 73.29, H, 13.43. $C_{13}H_{28}Si$ calcd.: C, 73.50; H, 13.28%.

2-Trimethylsilyl-2(E)-nonene (IVd, R = n-C_6H_{13}, E = n-C_3H_7). Yield, 73%, $E > 99\%$ [4b].

4-Trimethylsilyl-4(E)-undecene (IVe, R = n-C_6H_{13}, E = n-C_3H_7). Yield, 58%, $E > 99\%$, b.p. 118–122°C/14 mmHg, IR (neat) 1612, 1240, 833, 751, 690 cm^{-1}; mass spectrum: *m/e* (rel. %) 226 (M^+, 0.6), 211 (16), 73 (100), NMR (CCl_4) δ (ppm), 0.03 (9 H, s), 0.87 (6 H, t, *J* 6 Hz), 1.10–1.45 (10 H, m), 1.87–2.20 (4 H, m), 5.59 (1 H, t, *J* 7 Hz). Anal. Found: C, 74.53, H, 13.48. $C_{14}H_{30}Si$ calcd.: C, 74.25, H, 13.35%.

7-Trimethylsilyl-7(E)-tetradecene (IVf, $R = E = n\text{-}C_6H_{13}$) Yield, 72%, $E >$ 99% This material was identical with an authentic sample prepared by the chloroplatinic acid-catalyzed reaction of trichlorosilane and 7-tetradecyne and subsequent treatment with MeMgI [7]

4-Trimethylsilyl-1,4(E)-undecadiene (IVg, $R = n\text{-}C_6H_{13}$, $E = CH_2CH{=}CH_2$) Yield, 57%, $E >$ 99% b p 95°C/15 mmHg IR (neat) 3070, 1635, 1612, 1241, 992, 910, 835, 752, 691 cm^{-1}, mass spectrum *m/e* (rel %) 224 (M^+, 1), 209 (1), 73 (100), NMR (CCl_4) δ (ppm), 0 00 (9 H, s), 0 70—1 07 (3 H, m), 1 07—1 67 (8 H, m), 1 67—2 33 (2 H, m), 2 73—2 97 (2 H, br-t, J = 6 Hz), 4 67—5 93 (4 H, m) Anal Found C, 75 02 H, 12 72 $C_{14}H_{28}Si$ calcd C, 74 91, H, 12.57%

1,5-Bis(trimethylsilyl)-5(E)-nonen-1-yne (IVh, $R = n\text{-}C_3H_7$ $E = (CH_2)_2C{\equiv}CSiMe_3$) Yield, 52%, $E >$ 99% b p 115—120°C/6 mmHg, IR (neat) 2200, 1612, 1241, 1025, 840, 760, 691 cm^{-1}, mass spectrum *m/e* rel %) 266 (M^+, 1), 251 (3), 73 (100), NMR (CCl_4) δ (ppm), 0 03 (9 H, s), 0 07 (9 H, s), 0.67—1 10 (3 H, m), 1 10—2 50 (8 H, m), 5 69 (1 H, br-t, J 7 Hz) Anal Found C, 67 69, H, 11 33 $C_{15}H_{30}Si_2$ calcd C, 67 59, H, 11 34%

Homopropargylation of alkyl 1-trimethylsilyl-1(Z)-pentenylcuprates (VII) to IVh

Route A A solution of 1(*Z*)-pentenylcopper (II) was prepared from n-PrMgBr (1 mmol, 0 75 ml of a 1 34 *M* ethereal solution), CuBr (0 16 g, 1 1 mmol), and $Me_3SiC{\equiv}CH$ (0 18 ml, 1 4 mmol) in the presence of $(EtO)_3P$ (0 23 ml, 1 1 mmol) by the procedure described above and treated with MeMgBr (1 mmol, 1 1 ml of 0 9 *M* ethereal solution) at —40 to —45°C for 0 5 h THF (2 ml), HMPT (1 ml), $(EtO)_3P$ (0.46 ml, 2 2 mmol), and $Me_3SiC{\equiv}C(CH_2)_2I$ (0 39 ml, 2 0 mmol) were then added and the mixture was stirred at —40 to —45°C for 1 h and then overnight at room temperature Addition of aq NH_4Cl, was followed by separation, washing (eq NH_4Cl, sat NaCl), and drying ($MgSO_4$) on the ethereal layer. Chromatography of the concentrate on a silica-gel column (hexane) afforded 0.20 g (76%) of IVh ($E >$ 99%) The use of EtMgBr (1 mmol, 1 2 ml of 0.85 *M* ethereal solution) or n-PrMgBr (1 mmol, 0 75 ml of 1 34 *M* ethereal solution) instead of MeMgBr afforded 0 18 g (66%) and 0 19 g (72%) of IVh, respectively

Route B To a suspension of $n\text{-}Pr_2CuMgBr$, prepared from n-PrMgBr (2 mmol, 1.5 ml of 1 34 *M* ethereal solution) and CuBr (0 16 g, 1 1 mmol) at —40°C for 0 5 h, was added $Me_3SiC{\equiv}CH$ (0 18 ml, 1 4 mmol) and $(EtO)_3P$ (0 23 ml, 1 1 mmol). The mixture was gradually warmed to 0°C and stirring was continued for 2 h. Work-up as described above gave 0.16 g (62%) of IVh ($E >$ 99%).

5-Trimethylsilyl-5(E)-alken-4-ones (V)

5-Trimethylsilyl-5(E)-octen-4-one (Va, $R = C_2H_5$, $E = n\text{-}C_3H_7CO$) A suspension of 1-trimethylsilyl-1(*Z*)-butenylcopper (II, 1 mmol scale) prepared as described above was treated with THF (2 ml), HMPT (1 ml), and butyryl chloride (0.11 ml, 1 mmol) at —45 to —50°C. The mixture was stirred overnight at a room-temperature, and worked-up by addition of saturated $NaHCO_3$, followed by separation, washing (sat $NaHCO_3$, sat. NaCl), and drying ($MgSO_4$) of the ethereal layer. Chromatography of the concentrate on a silica-gel column (benzene) gave 0.13 g (63%) of Va ($E > 99\%$). B.p. 91—96°C/26 mmHg. IR (neat) 1686, 1605, 1250, 1160, 1062, 935, 839, 754, 691 cm^{-1}; mass spectrum *m/e* (rel. %) 198 (M^+, 2), 183 (10), 155 (64). NMR (CCl_4) δ (ppm), 0.13 (9 H, s), 0.80—1.13 (6 H, m), 1.60 (2 H, sext, *J* 7 Hz), 2.07 (2 H, quint, *J* 7 Hz), 2.35 (2 H, t, *J* 7 Hz), 5.73 (1 H, t, *J* 7 Hz). Anal. Found: C, 66.90; H, 11.36. $C_{11}H_{22}OSi$ calcd.: C, 66.60; H, 11.18%.

5-Trimethylsilyl-5(E)-nonen-4-one (*Vb*, $R = n\text{-}C_3H_7$, $E = n\text{-}C_3H_7CO$). Yield, 76%, $E > 99\%$, b.p. 80—85°C/4 mmHg. IR (neat) 1680, 1602, 1240, 1150, 1059, 937, 840, 755, 695 cm^{-1}, mass spectrum *m/e* (rel. %) 212 (M^+, 2), 197 (8), 73 (100); NMR (CCl_4) δ (ppm), 0.11 (9 H, s), 0.92 (6 H, t, *J* 7 Hz), 1.20—1.75 (4 H, m), 2.02 (2 H, q, *J* 7 Hz), 2.33 (2 H, t, *J* 7 Hz), 5.73 (1 H, t, $J = 7$ Hz). Anal. Found: C, 68.02; H, 11.60. $C_{12}H_{24}OSi$ calcd.: C, 67.85; H, 11.39%.

5-Trimethylsilyl-5(E)-dodecen-4-one (*Vc*, $R = n\text{-}C_6H_{13}$, $E = n\text{-}C_3H_7CO$). Yield, 80%, $E > 99\%$, b.p. 100—105°C/6 mmHg, IR (neat) 1685, 1603, 1250, 1150, 1067, 930, 838, 754, 691 cm^{-1}. mass spectrum *m/e* (rel. %) 254 (M^+, 4), 239 (8), 73 (100), NMR (CCl_4) δ (ppm), 0.12 (9 H), 0.80—1.10 (6 H, m), 1.10—1.85 (10 H, m), 1.18—2.23 (2 H, m), 2.35 (2 H, t, *J* 7 Hz), 5.75 (1 H, t, *J* 7 Hz). Anal. Found: C, 70.81; H, 11.73. $C_{15}H_{30}OSi$ calcd.: C, 70.79; H, 11.88%.

α-Halogenated vinylsilanes (VIa—VIe)

1-Iodo-1-trimethylsilyl-1(Z)-butene (*VIa*, $R = C_2H_5$, $E = I$). A suspension of 1-trimethylsilyl-1(Z)-butenylcopper (II, 1 mmol scale), prepared as described above, was treated with THF (2 ml), HMPT (1 ml), and 0.30 g of I_2 (1.2 mmol in 5 ml of THF) at —45 to —50°C. The mixture was stirred overnight at a room-temperature, then worked up by addition of sat. $NaHCO_3$, followed by washing (sat. $NaHCO_3$, sat. NaCl), and drying ($MgSO_4$) of the ethereal layer. Chromatography of the concentrate on a silica-gel column (hexane) afforded 0.17 g (67%) of VIa ($Z > 99\%$). B.p. 82—88°C/32 mmHg. IR (neat) 1601, 1250, 883, 837, 750, 695 cm^{-1}; mass spectrum *m/e* (rel. %) 254 (M^+, 16), 73 (100). NMR (CCl_4) δ (ppm), 0.18 (9 H, s), 1.07 (3 H, t, *J* 7 Hz), 2.25 (2 H, quint, *J* 7 Hz), 6.14 (1 H, t, *J* 7 Hz). Anal. Found: 33.34, H, 6.04. $C_8H_{17}ISi$ calcd.: C, 33.08; H, 5.95%.

1-Iodo-1-trimethylsilyl-1(Z)-pentene (*VIb*, $R = n\text{-}C_3H_7$, $E = I$). Yield, 71%, $Z > 99\%$; b.p. 90—95°C/23 mmHg; IR (neat) 1605, 1250, 912, 860, 840, 751 cm^{-1}; mass spectrum *m/e* (rel. %) 268 (M^+, 8), 185 (38), 73 (100), NMR (CCl_4) δ (ppm), 0.16 (9 H, s), 0.93 (3 H, t, *J* 6 Hz), 1.15—1.65 (2 H, m), 2.17 (2 H, q, *J* 6 Hz), 6.10 (1 H, t, *J* 6 Hz). Anal. Found: C, 35.93, H, 6.49. $C_8H_{17}ISi$ calcd.: C, 35.82; H, 6.39%.

1-Iodo-1-trimethylsilyl-1(Z)-octene (*VIc*, $R = n\text{-}C_6H_{13}$, $E = I$). Yield, 79%, $Z > 99\%$; b.p. 120—124°C/9 mmHg; IR (neat) 1610, 1250, 840, 750 cm^{-1}; mass spectrum: *m/e* (rel. %) 310 (M^+, 5), 185 (25), 73 (100), NMR (CCl_4) δ (ppm), 0.19 (9 H, s), 0.75—1.10 (3 H, m), 1.10—1.60 (8 H, m), 2.00—2.35 (2 H, m), 6.15 (1 H, t, *J* 6 Hz). Anal. Found. C, 42.78, H, 7.70. $C_{11}H_{23}ISi$ calcd.: C, 42.58; H, 7.47.

1-Bromo-1-trimethylsilyl-1(Z)-octene, (*VId*, $R = n\text{-}C_6H_{13}$, $E = Br$). A suspension of 1-trimethylsilyl-1(Z)-octenylcopper (II, 2 mmol scale) was prepared as described above, and THF (4 ml), HMPT (2 ml), and 0.36 g of NBS (2 mmol in 5 ml of THF) were added at —45 to —50°C The mixture was stirred overnight at a room-temperature and worked up in the usual way Chromatography of the concentrate on a silica-gel column (hexane) afforded 0 34 g (66%) of VId ($Z > 99\%$) B p 78—83°C/6 mmHg, IR (neat) 1611, 1247, 870, 837, 750, 691 cm^{-1}, mass spectrum *m/e* (rel %) 264 (M^+, 6), 262 (M^+, 6), 139 (80), 137 (78), 73 (100), NMR (CCl_4) δ (ppm), 0 20 (9 H, s), 0 75—1 10 (3 H, m), 1 10—1 60 (8 H, m), 2 10—2 40 (2 H, m), 6 20 (1 H, t, J 7 Hz) Anal Found C, 50 63, H, 8.69 $C_{11}H_{23}BrSi$ calcd C, 50 18, H, 8 80%

1-Chloro-1-trimethylsilyl-1(Z)-octene (VIe, $R = n\text{-}C_6H_{13}$, $E = Cl$) Similar treatment of 1-trimethylsilyl-1(*Z*)-octenylcopper (II, 1 mmol scale) with 0.14 g of *N*-chlorosuccinamide (NCS) (1 mmol in 5 ml of THF) as described above gave 0 15 g (66%) of VIe ($Z > 99\%$) B.p. 124—128°C/32 mmHg, IR (neat) 1615, 1250, 835, 753, 695 cm^{-1} mass spectrum: *m/e* (rel %) 220 (M^+, 1), 218 (M^+, 3), 93 (100), 73 (84), NMR (CCl_4) δ (ppm), 0 19 (9 H, s), 0.75—1 10 (3 H, m), 1.10—1 60 (8 H, m), 2.10—2.45 (2 H, m), 5 97 (1 H, t, J 6 Hz) Anal Found: C, 60 34; H, 10 58 $C_{11}H_{23}ClSi$ calcd C, 60 37, H, 10 59%

α-Stannylated vinylsilanes (VIf, g)

1-Tributylstannyl-1-trimethylsilyl-1(Z)-butene (VIf, $R = C_2H_5$, $E = (n\text{-}Bu)_3Sn$) A suspension of 1-trimethyl-1(*Z*)-butenylcopper (II, 1 mmol scale, prepared as described above) was treated with THF (2 ml), HMPT (1 ml), and $n\text{-}Bu_3SnCl$ (0 40 ml, 1 5 mmol) at —45 to —50°C. The mixture was stirred overnight at room temperature, and worked up as usual Chromatography (silica-gel column, hexane) of the concentrate afforded 0 21 g (51%) of VIf ($Z > 99\%$). Oil, IR (neat 1574, 1248, 904, 879, 831, 748 cm^{-1}, NMR (CCl_4) δ (ppm), 0 00 (9 H, s), 0 40—1 65 (30 H, m), 2 05 (2 H, q, J 6 Hz), 6 60 (1 H, t, J 6 Hz) Anal Found: C, 54 45, H, 10 02 $C_{19}H_{42}SiSn$ calcd C, 54 68, H, 10 14%.

1-Tributylstannyl-1-trimethylsilyl-1(Z)-pentene (VIg, $R = n\text{-}C_3H_7$, $E = (n\text{-}Bu)_3Sn$) Yield, 56%, $Z > 99\%$, IR (neat) 1570, 1250, 920, 905, 837, 750 cm^{-1}; NMR (CCl_4) δ (ppm), 0 00 (9 H, s), 0 35—1 65 (32 H, m), 2 03 (2 H, q, J 6 Hz), 6 62 (1 H, t, J 6 Hz) Anal Found C, 55 66, H, 10 32, $C_{20}H_{44}SiSn$ calcd C, 55 69, H, 10 28%

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