Regiospecific and Stereospecific Synthesis of *E*- and *Z*-Trisubstituted Alkenes via 2,2-Disubstituted Vinylsilanes

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Treatment of terminal alkynes **1** with the organocopper reagents derived from Grignard reagents, cuprous iodide, and lithium bromide (molar ratio 2:1:2) at low temperature followed by the addition of chlorotrimethylsilane gave the 2,2-disubstituted vinylsilanes **2** with complete regio- and stereospecificity (syn addition). Electrophilic substitution of **2** with ICl, Br_2, and acetyl chloride gave the corresponding vinyl iodides, bromides, and α,β-unsaturated ketones **5** with retention of configuration. Epoxidation of **2** with MCPBA gave the epoxy silanes **6**, which upon treatment with concentrated HX and $BF_3{\cdot}Et_2O$ gave the vinyl halides **7** with net inversion of configuration. If the epoxy silanes **6** were first converted to the β-hydroxy silanes **8** by Gilman's reagents, either *E*- or *Z*-trisubstituted alkenes **9** and **10** could be obtained by treatment with acid or base. Vinyl halides **7** could also be stereoselectively converted to other functionalities via the vinyllithium intermediates.

The stereoselective synthesis of trisubstituted alkenes has been of great interest to organic chemists because of the wide existence of such compounds in natural products.[1] Incorrect stereochemistry of these alkenes may reduce or completely remove their biological activities; thus many new synthetic methodologies have been developed.[2,3] We were interested in using vinylsilanes to synthesize trisubstituted alkenes, since it is well-known that electrophilic substitution reactions of vinylsilanes are highly stereoselective to give substituted alkenes.[4] Although there have been many reports on the synthesis of 1,2-disubstituted vinylsilanes,[5] only a few methods for the synthesis of 2,2-disubstituted vinylsilanes with controlled stereochemistry have appeared.[6] We now report a general method for the synthesis of such vinylsilanes by the addition of organocopper reagents to terminal alkynes.[7] We also describe the stereospecific conversion of these vinylsilanes to both *E*- and *Z*-trisubstituted alkenes.

Table I. Preparation of Vinylsilanes 2 from Terminal Alkynes 1

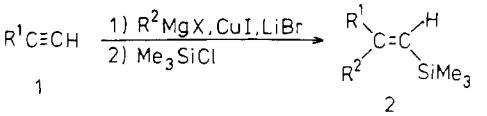
$R^1C{\equiv}CH$	R^2MgBr	vinylsilane **2**	% yield
PhC≡CH	CH_3MgCl	**2a**, R^1 = Ph, R^2 = Me	50
PhC≡CH	EtMgBr	**2b**, R^1 = Ph, R^2 = Et	85
PhC≡CH	*n*-BuMgBr	**2c**, R^1 = Ph, R^2 = *n*-Bu	71
n-BuC≡CH	CH_3MgCl	**2d**, R^1 = *n*-Bu, R^2 = Me	35
n-BuC≡CH	EtMgBr	**2e**, R^1 = *n*-Bu, R^2 = Et	80

Table II. Electrophilic Substitution Reactions of Vinylsilanes 2

vinylsilane **2**	electrophile	product **5**	% yield
2b	ICl	**5a**, X = I	70
2e	ICl	**5b**, X = I	78
2b	Br_2; $NaOCH_3$	**5c**, X = Br	75
2b	$CH_3COCl/AlCl_3$	**5d**, X = CH_3CO	75

Results and Discussion

Terminal alkynes **1** underwent a nucleophilic addition reaction with the organocopper reagents derived from Grignard reagents, cuprous iodide, and lithium bromide (molar ratio 2:1:2) in THF/HMPA (4:1 v/v) at 60 °C. Quenching the reaction intermediate with chlorotrimethylsilane then gave the vinylsilanes **2** (Table I). Lower yields were obtained with methyl Grignard reagents. It was reported by Normant that Grignard reagents and cuprous halide in a 1:1 molar ratio could successfully add to the terminal alkynes, but the resulting vinylcopper intermediates failed to react with chlorotrimethylsilane.[8] If a 2:1 molar ratio of Grignard reagents and cuprous halide was used, only deprotonation of the terminal alkynes occurred.[9] We found that the addition of lithium bromide (2 equiv) completely suppressed such deprotonation.[10] Furthermore, hexamethylphosphoric triamide (HMPA) was essential for the efficient reaction with chlorotrimethylsilane.



1 2

In the above reaction, the organocopper and the silyl groups were found to add to the triple bond from the same side. The structures of vinylsilanes **2** were established by

(1) Nakanishi, K.; Goto, T.; Ito, S.; Natori, S.; Nozoe, S. *Natural Products Chemistry*; Academic Press: New York, 1974; Vols. 1, 2.

(2) For reviews, see: (a) Reucroft, J.; Sammes, P. G. *Q. Rev., Chem. Soc.* **1971**, *25*, 135. (b) Faulkner, J. *Synthesis* **1971**, 175. (c) Normant, J. F.; Alexakis, A. *Synthesis* **1981**, 841.

(3) (a) Bernardi, A.; Cabri, W.; Poli, G.; Prati, L. *J. Chem. Res., Synop.* **1986**, 52. (b) Negishi, E.; Van Horn, D. E.; Yoshida, T. *J. Am. Chem. Soc.* **1985**, *107*, 6639. (c) Ono, N.; Hamamoto, I.; Kaji, A. *J. Chem. Soc., Chem. Commun.* **1984**, 274. (d) Belletire, J. L.; Namie, M. W. *Synth. Commun.* **1983**, *13*, 87. (e) Brown, H. C.; Basavaiah, D. *J. Org. Chem.* **1982**, *47*, 5407. (f) Brown, H. C.; Basavaiah, D.; Kulkarni, S. U. *J. Org. Chem.* **1982**, *47*, 171. (g) Masaki, Y.; Sakuma, K.; Kaji, K. *J. Chem. Soc., Chem. Commun.* **1980**, 434. (h) Takei, H.; Sugimura, H.; Miura, M.; Okamura, H. *Chem. Lett.* **1980**, 1209. (i) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1979**, *44*, 4623. (j) Marfat, A.; McGuirk, P. R.; Helquist, P. *J. Org. Chem.* **1979**, *44*, 3888 and references cited therein.

(4) (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983. (c) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761. (d) Magnus, P. D.; Sarkar, T.; Djuric, S. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxoford, 1982; Vol. 7, pp 515-659.

(5) (a) Eisch, J. J.; Damasevitz, G. A. *J. Org. Chem.* **1976**, *41*, 2214. (b) Uchida, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2215. (c) Uchida, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1977**, *33*, 2987. (d) Zweifel, G.; Lewis, W. *J. Org. Chem.* **1978**, *43*, 2739. (e) Westmijze, H.; Meijer, J.; Vermeer, P. *Tetrahedron Lett.* **1977**, 1823. (f) Obayashi, M.; Utimoto, K.; Nozaki, H. *J. Organomet. Chem.* **1979**, *177*, 145. (g) Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017. (h) Sato, F.; Watanabe, H.; Tanaka, Y.; Yamaji, T.; Sato, M. *Tetrahedron Lett.* **1983**, *24*, 1041.

(6) (a) Snider, B. B.; Karras, M.; Conn, R. S. E. *J. Am. Chem. Soc.* **1978**, *100*, 4624. (b) Snider, B. B.; Karras, M. *J. Organomet. Chem.* **1979**, *179*, C37. (c) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527. (d) Hayama, H.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 4433.

(7) (a) Taken in part from the M.S. Thesis of Kuo, H. L. (b) Preliminary results were presented at the annual meetings of the Chinese Chemical Society, 1982 (Abstract p 159) and 1984 (Abstract p 86).

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(10) Westmijze, H.; Meijer, J.; Bos, H. J. T.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1976**, *95*, 299, 304.

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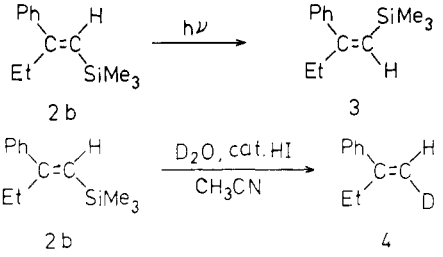
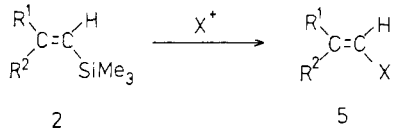
spectroscopic and chemical methods. In the ^1H NMR spectra of vinylsilanes **2a–c**, each vinyl hydrogen appeared as a singlet, consistent with the observation that the cis allylic coupling was greater than the trans coupling in similar systems.[6a] We have also irradiated **2b** in cyclohexane to give the isomerized product **3**.[11] The vinyl proton of **2b** appeared at δ 5.70 as a singlet, whereas the vinyl proton of **3** appeared at δ 5.55 as a triplet (J = 1.5 Hz), also attesting to the greater cis allylic coupling constant. The lower field absorption in **2b** was apparently caused by the deshielding effect of the phenyl group. Furthermore, protodesilylation (which is known to proceed with retention of configuration)[12] of **2b** with a catalytic amount of hydriodic acid in a mixture of D_2O and CH_3CN gave only the (*E*)-1-deuterio-2-phenyl-1-butene (**4**), thus establishing the trans relationship of the silyl group to the phenyl group in **2b**.



Having established a method for the regio- and stereospecific synthesis of 2,2-disubstituted vinylsilanes **2**, we then studied their electrophilic substitution reactions which have heretofore not been reported. Complete retention of configuration was observed, and the results are shown in Table II.



Treatment of **2b** and **2e** with ICl in CCl_4 at 0 °C gave the corresponding vinyl iodides in good yields. The structures of **5a** and **5b** were confirmed by comparing their spectral data with those obtained by a literature method.[13] The reaction of **2b** with bromine at low temperature followed by the treatment with sodium methoxide gave the vinyl bromide **5c**, identical with an authentic sample.[13] It should be pointed out that without sodium methoxide the hydrogen bromide generated from the reaction medium would further add to the vinyl bromide **5c**. Treatment of **2b** with acetyl chloride in the presence of aluminum chloride at 0 °C gave the α,β-unsaturated ketone **5d** in good yield. Compound **5d** had characteristic IR absorptions at 1678 and 1595 cm^{-1} for the C=O and C=C stretchings, respectively. The stereochemistry of **5d** was assigned the *E* configuration similar to a literature report.[14]

It has been generally observed that sterically unhindered (2-alkylvinyl)silanes are converted to the corresponding halides with inversion of configuration involving anti-addition and anti-elimination processes.[15] On the other hand, silylstyrenes give products of retention of alkene geometry, postulated to proceed through syn-addition and anti-elimination processes.[16] But in our case, both phenyl-substituted (**2b**) and alkyl-substituted (**2e**) vinylsilanes gave substitution products with retention of configuration. The following mechanism is proposed (Scheme I). First, the bridging intermediate A is formed with retention of configuration. It can then break one specific C–X bond to give the silyl-bridged carbocation B, which is both tertiary and β to the silyl group. Nucleophile-assisted desilylation (path a) then gives the retention product **5**. It is unlikely that the nucleophile Y^- would undergo an S_N2 reaction at the tertiary carbon to give an anti-addition intermediate C, which would have led to inversion products. Although the direct attack of Y^- at intermediate B to give a syn-addition intermediate D (path b) followed by anti elimination of Me_3SiY cannot be ruled out, we did not obtain any of the addition products D. The key point in the above scheme is that the intermediate B, being a tertiary carbocation irrespective of an alkyl or phenyl substitution, is very stable and is formed readily from intermediate A. Thus, an overall retention of configuration was observed in all our cases.

Scheme I

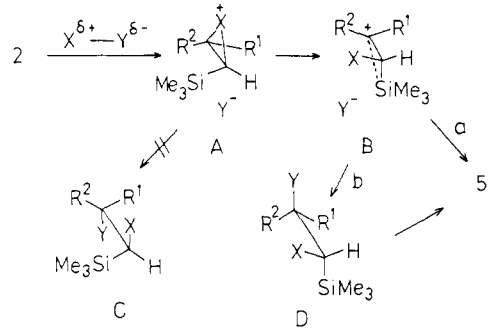
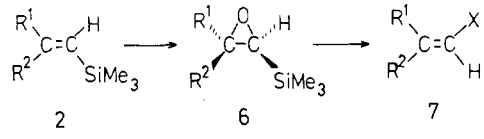


Table III. Conversion of Epoxy Silanes 6 to Vinyl Halides 7

epoxy silane	electrophile	vinyl halide 7	% yield
6a, R^1 = Ph, R^2 = Et	HI	**7a**, X = I	70
	HBr	**7b**, X = Br	60
	HCl	**7c**, X = Cl	50
6b, R^1 = *n*-Bu, R^2 = Et	HI	**7d**, X = I	48

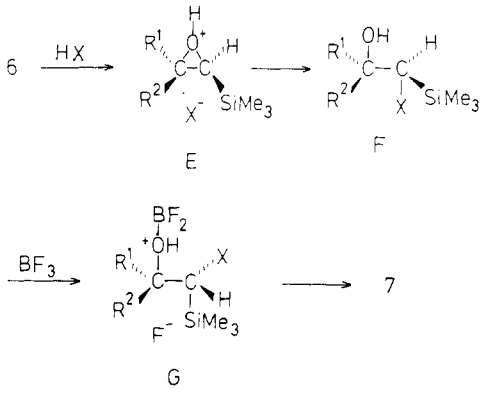
Another important application of vinylsilanes is through the intermediacy of epoxysilanes.[17] Vinylsilanes **2** were oxidized by 1 equiv of MCPBA in CH_2Cl_2 at 10 °C to give the epoxy silanes **6**, which upon sequential treatment with concentrated aqueous HX (X = Cl, Br, I) and $BF_3{\cdot}Et_2O$ afforded the vinyl halides **7** with net inversion of configuration (Table III). The stereochemistry of **7** was opposite to that of **5** obtained from electrophilic substitution reactions of vinylsilanes **2**.



The mechanism for the conversion of **6** to **7** is proposed as follows (Scheme II). Protonation of epoxy silane **6** first gives an intermediate E. Ring-opening by a back-side attack of X^- at the less substituted carbon[18] gives the

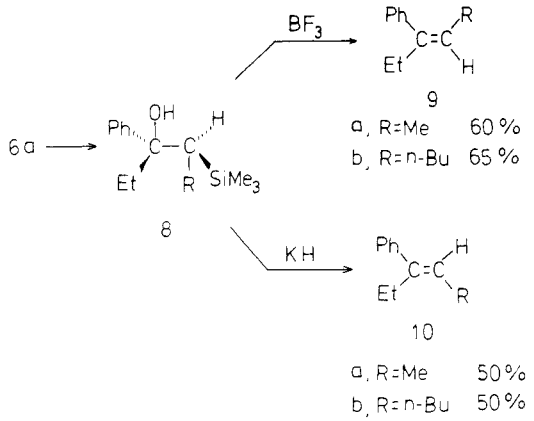
(11) For reviews of photochemical cis–trans isomerization, see: Sonnet, P. E. *Tetrahedron* **1980**, *36*, 557.
(12) (a) Koenig, K. E.; Weber, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 3416. (b) Utimoto, K.; Kitai, M.; Nozaki, H. *Tetrahedron Lett.* **1975**, 2825.
(13) Westmijze, H.; Meijer, J.; Vermeer, P. *Recl. Trav. Chim. Pays-Bas* **1977**, 96, 168.
(14) Yamamoto, K.; Nunokawa, O.; Tsuji, J. *Synthesis* **1977**, 721.
(15) (a) Miller, R. B.; Reichenbach, T. *Tetrahedron Lett.* **1974**, 543. (b) Zweifel, G.; Lewis, W. *J. Org. Chem.* **1978**, *43*, 2739. (c) Miller, R. B.; McGarvey, G. *Synth. Commun.* **1977**, *7*, 475. (d) Tamao, K.; Akita, M.; Maeda, K.; Kumada, M. *J. Org. Chem.* **1987**, *52*, 1100.
(16) (a) Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520. (b) Koenig, K. E.; Weber, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 3416. (c) Koenig, K. E.; Weber, W. P. *Tetrahedron Lett.* **1973**, 2523.
(17) See ref 4a, pp 83–96.

Scheme II

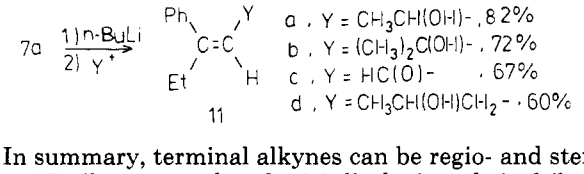


halohydrin F, which in many cases was isolated and characterized, but for synthetic purposes could be directly treated with BF_3-Et_2O. The acid-promoted anti elimination of β-silanols is well precedented.[19]

We have also converted epoxy silanes **6a** to trisubstituted alkenes **9** and **10**. Treatment of **6a** with the organocuprates derived from organolithium reagents and cuprous iodide (2:1 molar ratio) gave the β-hydroxy silanes **8**, which could either undergo acid-promoted anti elimination or base-promoted syn elimination to give the (*Z*)-alkenes **9** or (*E*)-alkenes **10**, respectively.



To further extend the synthetic applications of the above results, we have also converted the heretofore unknown vinyl iodide **7a** to various functionalized trisubstituted alkenes. Treatment of **7a** with *n*-BuLi in Et_2O at 25 °C followed by the addition of acetaldehyde, acetone, *N*,*N*-dimethylformamide, or propylene oxide gave products **11a–d** with retention of configuration.



In summary, terminal alkynes can be regio- and stereospecifically converted to the 2,2-disubstituted vinylsilanes **2**. Direct treatment of **2** with electrophiles gives trisubstituted alkenes **5** with retention of configuration. The vinylsilanes **2** can also be oxidized to the epoxy silanes **6**, which can be converted to vinyl halides **7** with net inversion of configuration. Epoxy silanes **6** can also react with organocopper reagents to give β-hydroxy silanes **8**, which can be further converted to either *E*- or *Z*-trisubstituted alkenes **9** and **10**. We have also demonstrated an efficient transformation of vinyl halides **7** to the other substituted products **11** with retention of configuration. We believe this general approach to the stereospecific synthesis of both *E*- and *Z*-trisubstituted alkenes from terminal alkynes will be useful in organic synthesis.

Experimental Section

Infrared spectra were recorded with a Beckman Acculab TM1 infrared spectrometer. ^1H NMR spectra were taken with a Varian 360L spectrometer, and ^{13}C NMR spectra were recorded on a JEOL HA-100 spectrometer, with tetramethylsilane as the internal standard. Mass spectra were recorded with a JEOL JMS-D-100 spectrometer. Elemental analyses were taken with a Perkin-Elmer 240C analyzer. High-performance liquid chromatography (HPLC) was carried out with a Shimadzu LC-6A chromatograph using LiChrosorb (Merck) as the column. The gas chromatogram was obtained with a Shimadzu GC-3 BT chromatograph using 3% SE 30 or 10% PEG 20M as the column. The silica gel used for flash column chromatography was made by Merck (60 H). Ether and tetrahydrofuran were distilled from lithium aluminum hydride. Cuprous iodide was purified by washing with anhydrous THF in a Soxhlet extractor until colorless. All reactions were run under a positive pressure of dry nitrogen.

General Procedure for the Preparation of Vinylsilanes 2. A solution of lithium bromide (4.18 g, 48 mmol) in THF (40 mL) was added slowly to cuprous iodide (4.56 g, 24 mmol) at −60 °C. After 5 min, a THF solution of Grignard reagent (1.2 M, 40 mL, 48 mmol) was added dropwise. After the addition was completed, the mixture was stirred at −60 °C for 1 h. To this was added a mixture of a terminal alkyne (20 mmol), THF (40 mL) and HMPA (14 mL) at −60 °C. Five minutes later, a mixture of HMPA (5 mL) and chlorotrimethylsilane (6.7 mL, 48 mmol) was added. This was slowly warmed to room temperature and was stirred for another 5 h before it was poured into a saturated ammonium chloride solution containing small amounts of sodium cyanide. The solution was extracted with hexane (40 mL × 4), and the combined organic solution was washed with water (50 mL × 3) and brine (50 mL) and was dried ($MgSO_4$). After the removal of solvent by a rotary evaporator, the residue was passed through a flash column of silica gel (150 g) using hexane as the eluent to give the vinylsilane **2**.

(*E*)-2-Phenyl-1-(trimethylsilyl)-1-propene (2a). The procedure was similar to that described above except that the reaction of methylmagnesium chloride with cuprous iodide and lithium bromide was carried out at −25 °C. After the addition of phenylacetylene at −50 °C, the reaction mixture was warmed to 0 °C for another 30 min at 0 °C. The resulting solution was cooled to −30 °C, and chlorotrimethylsilane together with HMPA was added: IR (neat) 1605, 1255, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (9 H, s), 2.15 (3 H, s), 5.80 (1 H, s), 7.3 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 0.18, 20.44, 125.28, 126.88, 127.23, 127.85, 144.08, 151.35; mass spectrum, *m*/*z* 190 (M^+). Anal. Calcd for $C_{12}H_{18}Si$: C, 75.71; H, 9.53. Found: C, 75.47; H, 9.33.

(*E*)-2-Phenyl-1-(trimethylsilyl)-1-butene (2b). The procedure was the same as that described above: IR (neat) 1600, 1255, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (9 H, s), 0.95 (3 H, t, *J* = 7 Hz), 2.6 (2 H, q, *J* = 7 Hz), 5.7 (1 H, s), 7.3 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 0, 13.76, 27.51, 125.17, 126.13, 126.46, 127.35, 143.25, 157.89; mass spectrum, *m*/*z* 204 (M^+). Anal. Calcd for $C_{13}H_{20}Si$: C, 79.39; H, 9.86. Found: C, 79.63; H, 9.86.

(*E*)-2-Phenyl-1-(trimethylsilyl)-1-hexene (2c). The procedure was similar to that described above except that after phenylacetylene was added, the mixture was warmed to −40 °C in 100 min and then HMPA (10 mL) was added. The reaction mixture was allowed to rise to −30 °C in 30 min, and chlorotrimethylsilane was added. The reaction mixture was warmed to room temperature and was stirred overnight. It was further refluxed for 1 h before it was quenched: IR (neat) 1600, 1255, 860 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0 (9 H, s), 0.7 (3 H, t, *J* = 7 Hz), 1.1 (4 H, m), 2.35 (2 H, t, *J* = 7 Hz), 5.5 (1 H, s) 7.0 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 0.41, 14.06, 22.91, 31.64, 34.80, 125.98, 126.85, 127.62, 127.85, 143.73, 156.61; mass spectrum, *m*/*z* 232 (M^+). Anal. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41. Found: C, 77.38; H, 10.25.

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(19) (a) Hudrlik, P. F.; Peterson, D. *J. Am. Chem. Soc.* **1975**, *97*, 1464. (b) Yamamoto, K.; Tomo, Y.; Suzuki, S. *Tetrahedron Lett.* **1980**, *21*, 2861.

(*E*)-2-Methyl-1-(trimethylsilyl)-1-hexene (2d). The procedure was similar to that for **2a** except that 1-hexyne was added at −25 °C. After slow warming to 10 °C, the temperature was maintained for another 3 h before HMPA was added. The mixture was cooled to 0 °C, chlorotrimethylsilane was added, and the mixture was stirred at room temperature overnight: IR (neat) 1610, 1255, 870 cm^{-1}; ^1H NMR (CCl_4) δ 0 (9 H, s), 0.85 (3 H, t, J = 7 Hz), 1.3 (4 H, m), 1.65 (3 H, s), 1.95 (2 H, t, J = 7 Hz), 5.0 (1 H, s); mass spectrum, m/z 170 (M^+). Anal. Calcd for $C_{10}H_{22}Si$: C, 70.50; H, 13.02. Found: C, 70.43; H, 13.21.

(*E*)-2-Ethyl-1-(trimethylsilyl)-1-hexene (2e). After the addition of 1-hexyne at −50 °C, the mixture was very slowly warmed to 0 °C and stirred at 0 °C for 1 h. It was cooled to −60 °C, and HMPA and TMSCl were added: IR (neat) 1610, 1255, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (9 H, s), 0.7–1.6 (10 H, m), 2.1 (4 H, t, J = 7 Hz), 5.2 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ 0.47, 13.83, 14.12, 22.62, 29.00, 30.47, 38.49, 121.87, 141.42; mass spectrum, m/z 184 (M^+). Anal. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.10. Found: C, 71.66; H, 12.91.

Photolysis of Vinylsilane 2b To Give 3. A solution of vinyl silane **2b** (100 mg) in spectral grade cyclohexane (3.5 mL) was placed in a quartz tube and was bubbled with nitrogen for 1 min. The tube was then capped with a rubber septum and irradiated with mercury lamps of λ 254 nm with air-cooling in a Rayonet reactor for 40 min. The solvent was removed by a rotary evaporator, and the ^1H NMR ($CDCl_3$) spectrum of the product showed two different vinyl protons for the vinylsilane **2b** and its geometrical isomer **3**. The former was a sharp singlet at δ 5.70, and the latter was a small triplet (J = 1.5 Hz) at δ 5.55. The ratio of **2b** to **3** was 1:3.

Conversion of Vinylsilane 2b to (*E*)-1-Deuterio-2-phenyl-1-butene (4). A mixture of concentrated HI (0.25 mL, 2.0 mmol) and D_2O (2.25 mL) was stirred at room temperature for 30 min. A solution of vinylsilane **2b** (0.21 g, 1.03 mmol) in acetonitrile (3.5 mL) was added dropwise. This was then heated at 60 °C for 5 h, cooled to room temperature, and neutralized with saturated aqueous sodium carbonate (5 mL). After extraction with hexane (10 mL × 3), the solvent was removed with a rotary evaporator to give 0.145 g (100% yield) of the product, which comprised **4** and **2b** in a ratio of 9:1. **4**: ^1H NMR ($CDCl_3$) δ 1.1 (3 H, t, J = 7 Hz), 2.5 (2 H, q, J = 7 Hz), 5.2 (1 H, s), 7.3 (5 H, m).

Reaction of Vinylsilane 2 with ICl. A solution of iodine chloride (0.20 g, 1.2 mmol) in CCl_4 (2 mL) was added to a solution of vinylsilane **2b** (0.21 g, 1.0 mmol) in CCl_4 (3 mL) at 0 °C. After stirring at 0 °C for 2 h, the reaction mixture was poured into an aqueous solution of sodium thiosulfate to remove the residual iodine chloride. The organic solution was dried ($MgSO_4$) and evaporated, and the product was then purified by column chromatography (silica gel, hexane) to give (*E*)-1-iodo-2-phenyl-1-butene (**5a**)[13] (0.18 g, 70% yield). Similarly, (*E*)-1-iodo-2-ethyl-1-hexene (**5b**)[13] was prepared from vinylsilane **2e** in 78% yield. **5a**: ^1H NMR ($CDCl_3$) δ 1.0 (3 H, t, J = 7 Hz), 2.7 (2 H, q, J = 7 Hz), 6.37 (1 H, s), 7.3 (5 H, m); mass spectrum, m/z 254 (M^+). **5b**: ^1H NMR ($CDCl_3$) δ 0.8–1.4 (10 H, m), 2.0 (4 H, m), 5.77 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ 11.8, 14.0, 22.4, 30.1, 30.5, 36.5, 73.4, 152.8; mass spectrum, m/z 238 (M^+).

(*E*)-1-Bromo-2-phenyl-1-butene (5c). To a solution of vinylsilane **2b** (0.21 g, 1.0 mmol) in CH_2Cl_2 (1 mL) at −78 °C was added dropwise a solution of bromine in CH_2Cl_2 (2.5 M) until the appearance of a reddish brown color. The mixture was slowly warmed to −35 °C while the solvent was being evaporated under vacuum. To the residue was added a solution of sodium methoxide (0.06 g, 1.5 mmol) in methanol (5 mL), and the reaction mixture was slowly warmed to room temperature. After stirring for another 2 h, the methanol was removed by a rotary evaporator. Dichloromethane (80 mL) was then added to the residue. The organic solution was quenched with water (20 mL × 2) and brine (20 mL) and was dried ($MgSO_4$). After the removal of solvent, the product was purified by column chromatography (silica gel, hexane) to give **5c**[13] (0.16 g, 75% yield): IR (neat) 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 (3 H, t, J = 7 Hz), 2.6 (2 H, q, J = 7 Hz), 6.27 (1 H, s), 7.3 (5 H, m).

(*E*)-4-Phenyl-3-hexen-2-one (5d). A mixture of aluminum chloride (0.27 g, 2 mmol) and acetyl chloride (0.17 g, 2 mmol) in CH_2Cl_2 (10 mL) was stirred at 0 °C for 30 min. A solution of vinylsilane **2b** (0.21 g, 1 mmol) in CH_2Cl_2 (5 mL) was then added. After 30 min, the reaction mixture was neutralized with saturated sodium carbonate solution and was then extracted with ether (50 mL × 3). The extract was evaporated, and the residue was passed through a column of silica gel (20 g) by using ether/hexane (1:5) as the eluent to give **5d** (0.13 g, 75% yield): IR (neat) 1675, 1599 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1 (3 H, t, J = 7 Hz), 2.3 (3 H, s), 3.05 (2 H, q, J = 7 Hz), 5.43 (1 H, s), 7.45 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 13.42, 24.32, 32.05, 123.81, 126.45, 128.20, 128.55, 140.98, 159.90, 197.75; mass spectrum, m/z 174 (M^+). Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.79; H, 8.03.

2-Phenyl-1-(trimethylsilyl)-1-butene Oxide (6a). To a solution of vinylsilane **2b** (1.0 g, 4.9 mmol) in CH_2Cl_2 (20 mL) at 10 °C was added dropwise a solution of MCPBA (1.16 g, 5.4 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred at 10 °C for 4 h, was then washed with cold aqueous sodium thiosulfate (1 M, 25 mL), 5% NaOH (25 mL), water (50 mL), and brine (25 mL), and was dried ($MgSO_4$). After the removal of solvent, the product **6a** (1.18 g, 93% yield) obtained was used without further purification and should be stored in the freezer. Similarly, (*E*)-2-ethyl-1-(trimethylsilyl)-1-hexene oxide (**6b**) was prepared from vinylsilane **2e** in 90% yield. **6a**: IR (neat) 1245, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0 (9 H, s), 0.7 (3 H, t, J = 7 Hz), 1.4 (1 H, m), 1.85 (1 H, s), 2.05 (1 H, m), 7.1 (5 H, m). **6b**: IR (neat) 2970, 1460, 1400, 1250, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (9 H, s), 1.17–1.70 (6 H, m), 1.17–1.83 (8 H, m), 1.97 (1 H, s).

General Procedure for the Preparation of Vinyl Halides 7 from Epoxy Silanes 6. To a solution of epoxy silane **6** (0.9 mmol) in ether (10 mL) at −25 °C was added dropwise concentrated HX (1.35 mmol). After stirring at −25 °C for 30 min, the reaction mixture was poured into ice water and was then extracted with ether (30 mL × 3). The combined organic solution was washed with water (25 mL) and brine (25 mL) and was dried ($MgSO_4$). After the removal of solvent, the halohydrin intermediate obtained was dissolved in CH_2Cl_2 (10 mL) and cooled to 0 °C and boron trifluoride etherate (0.9 mmol) was added. After stirring at 0 °C for 8 h, the reaction mixture was poured into ice water and was extracted with ether (20 mL × 3). The combined organic solution was washed with water (20 mL) and brine (20 mL) and was dried ($MgSO_4$). After the removal of solvent, vinyl halides **7** were obtained. (*Z*)-1-Iodo-2-phenyl-1-butene (**7a**): IR (neat) 3060, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 1.0 (3 H, t, J = 7 Hz), 2.5 (2 H, dq, J = 7, 1.5 Hz), 6.2 (1 H, t, J = 1.5 Hz), 7.2 (5 H, m); mass spectrum, m/z 258 (M^+); HRMS calcd for $C_{10}H_{11}I$ 257.9906, found 257.9918. (*Z*)-1-Bromo-2-phenyl-1-butene (**7b**): IR (neat) 3060, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 0.97 (3 H, t, J = 7 Hz), 2.4 (2 H, dq, J = 7, 1 Hz), 6.08 (1 H, t, J = 1.5 Hz), 7.3 (5 H, m); mass spectrum, m/z 210 (M^+), 212 ($M^+ + 2$); HRMS calcd for $C_{10}H_{11}Br$ 210.0044, found 210.0035. (*Z*)-1-Chloro-2-phenyl-1-butene (**7c**): IR (neat) 3050, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (3 H, t, J = 7 Hz), 2.40 (2 H, dq, J = 7, 1.5 Hz), 6.17 (1 H, t, J = 1.5 Hz), 7.3 (5 H, m); mass spectrum, m/z 166 (M^+), 168 ($M^+ + 2$); HRMS calcd for $C_{10}H_{11}Cl$ 166.0550, found 166.0541. (*Z*)-1-Iodo-2-ethyl-1-hexene (**7d**): IR (neat) 3030, 1640 cm^{-1}; ^1H NMR (CCl_4) δ 0.8–1.6 (10 H, m,), 2.13 (4 H, m), 5.83 (1 H, br s); ^{13}C NMR ($CDCl_3$) δ 12.7, 14.0, 22.7, 29.5, 30.2, 37.1, 73.6, 153.0; mass spectrum, m/z 238 (M^+); HRMS calcd for $C_8H_{15}I$ 238.0215, found 238.0224.

General Procedure for the Preparation of Alkenes 9 from Epoxy Silane 6a. A mixture of the organolithium reagent (2.5 mmol) and cuprous iodide (1.25 mmol) in ether (20 mL) was stirred at −70 °C for 1 h. To this was added dropwise a solution of epoxy silane **6a** (0.5 mmol) in ether (3 mL). After stirring at −70 °C for 1 h, the reaction mixture was allowed to warm to room temperature. This was then poured into saturated ammonium chloride solution, extracted with ether (20 mL × 3), washed with water (20 mL) and brine (20 mL), and dried ($MgSO_4$). The solvent was removed by a rotary evaporator, and the residue was purified by column chromatography (silica gel) using hexane/ethyl acetate (9:1) as eluent. The β-hydroxy silanes **8** obtained were then dissolved in CH_2Cl_2 and treated with boron trifluoride etherate at 0 °C for 1 h. After extraction with CH_2Cl_2, the organic solution was washed with 5% sodium bicarbonate, water, and brine and dried ($MgSO_4$). The alkenes **9** were purified by column chromatography (silica gel) using hexane as eluent. (*Z*)-3-Phenyl-2-pentene (**9a**): IR (neat) 3040, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3

(3 H, t, J = 7 Hz), 2.0 (3 H, d, J = 7 Hz), 2.7 (2 H, q, J = 7 Hz), 5.9 (1 H, q, J = 7 Hz), 7.5 (5 H, m); mass spectrum, m/z 146 (M^+); HRMS calcd for $C_{11}H_{14}$ 146.1092, found 146.1078. (*Z*)-3-Phenyl-3-octene (**9b**): IR (neat) 3040, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 0.93 (6 H, t, J = 7 Hz), 1.27 (4 H, m), 1.80 (2 H, q, J = 7 Hz), 2.27 (2 H, q, J = 7 Hz), 5.40 (1 H, tt, J = 7, 1.5 Hz), 7.23 (5 H, m); mass spectrum, m/z 188 (M^+); HRMS calcd for $C_{14}H_{20}$ 188.1560, found 188.1543.

General Procedure for the Preparation of Alkenes 10. The β-hydroxy silanes **8** obtained above were treated with KH in THF at 0 °C for 1 h. The reaction mixture was poured into a saturated ammonium chloride solution. After extraction with CH_2Cl_2, the solvent was evaporated and the residue was purified by column chromatography (silica gel) using hexane/ethyl acetate (19:1) as eluent. (*E*)-3-Phenyl-2-pentene (**10a**): IR (neat) 3040, 1610 cm^{-1}; ^1H NMR (CCl_4) δ 0.80 (3 H, t, J = 7 Hz), 1.56 (3 H, d, J = 7 Hz), 2.25 (2 H, q, J = 7 Hz), 5.43 (1 H, q, J = 7 Hz), 7.0 (5 H, m); mass spectrum, m/z 146 (M^+); HRMS calcd for $C_{11}H_{14}$ 146.1092, found 146.1075. (*E*)-3-Phenyl-3-octene (**10b**): IR (neat) 3040, 1600 cm^{-1}; ^1H NMR (CCl_4) δ 0.9-1.7 (10 H, m), 2.23 (2 H, m), 2.57 (2 H, q, J = 7 Hz), 5.60 (1 H, t, J = 7 Hz), 7.23 (5 H, m); mass spectrum, m/z 188 (M^+); HRMS calcd for $C_{14}H_{20}$ 188.1560, found 188.1573.

General Procedure for the Preparation of Alkenes 11. To a solution of vinyl iodide **7a** (0.07 g, 0.27 mmol) in ether (5 mL) at -50 °C was added dropwise *n*-butyllithium/hexane (0.33 mmol). The mixture was slowly warmed to -10 °C and then the appropriate electrophile was added (vide supra). After warming to room temperature, the reaction mixture was poured into saturated ammonium chloride solution, extracted with ether, washed with brine, and dried ($MgSO_4$). The solvent was removed by a rotary evaporator, and the residue was purified by column chromatography (silica gel) using hexane/ethyl acetate (9:1) as eluent. (*Z*)-4-Phenyl-3-hexen-2-ol (**11a**): IR (neat) 3350, 1060 cm^{-1}; ^1H NMR (CCl_4) δ 0.97 (3 H, t, J = 7 Hz), 1.2 (3 H, d, J = 6 Hz), 1.63 (1 H, br s), 2.30 (2 H, dq, J = 7, 1 Hz), 4.12 (1 H, dq, J = 9, 7 Hz), 5.37 (1 H, dt, J = 9, 1 Hz), 7.37 (5 H, m); mass spectrum, m/z 176 (M^+); HRMS calcd for $C_{12}H_{16}O$ 176.1197, found 176.1202. (*Z*)-2-Methyl-4-phenyl-3-hexen-2-ol (**11b**): IR (CCl_4) 3400, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (3 H, t, J = 7 Hz), 1.20 (6 H, s), 1.47 (1 H, br s), 2,23 (2 H, q, J = 7 Hz), 5.60 (1 H, t, J = 1 Hz), 7.23 (5 H, m); mass spectrum, m/z 190 (M^+); HRMS calcd for $C_{13}H_{18}O$ 190.1353, found 190.1370. (*Z*)-3-Phenyl-2-pentenal (**11c**): IR (CCl_4) 2850, 2770, 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (3 H, t, J = 7 Hz), 2.58 (2 H, q, J = 7 Hz), 6.20 (1 H, dt, J = 8, 1 Hz), 7.37 (5 H, m), 9.47 (1 H, d, J = 8 Hz); mass spectrum, m/Z 160 (M^+); HRMS calcd for $C_{11}H_{12}O$ 160.0885, found 160.0867. (*Z*)-5-Phenyl-4-hepten-2-ol (**11d**): IR (CCl_4) 3400, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (3 H, t, J = 7 Hz), 1.12 (2 H, q, J = 6 Hz), 1.55 (1 H, br s), 2.07 (2 H, m), 2.37 (2 H, q, J = 7 Hz), 3.77 (1 H, sextet, J = 7 Hz), 5.50 (1 H, tt, J = 7, 1 Hz), 7.23 (5 H, m); mass spectrum, m/z 190 (M^+); HRMS calcd for $C_{13}H_{18}O$ 190.1353, found 190.1358.

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Registry No. 1 (R′ = Ph), 536-74-3; 1 (R′ = *n*-Bu), 693-02-7; **2a**, 68669-68-1; **2b**, 68669-62-5; **2c**, 118226-86-1; **2d**, 94286-32-5; **2e**, 118226-87-2; **3**, 68669-61-4; **4**, 118226-81-6; **5a**, 64245-21-2; **5b**, 57086-65-4; **5c**, 64245-20-1; **5d**, 56422-91-4; **6a**, 118226-82-7; **6b**, 118226-88-3; **7a**, 118226-83-8; **7b**, 78463-05-5; **7c**, 78463-03-3; **7d**, 52812-63-2; **8a**, 118226-84-9; **8b**, 118226-92-9; **9a**, 4165-78-0; **9b**, 118226-89-4; **10a**, 4165-86-0; **10b**, 77161-68-3; **11a**, 118226-85-0; **11b**, 118226-90-7; **11c**, 36872-10-3; **11d**, 118226-91-8; acetaldehyde, 75-07-0; propylene oxide, 75-56-9; methylmagnesium chloride, 676-58-4; ethylmagnesium bromide, 925-90-6; butylmagnesium bromide, 693-03-8.

Synthesis of Organofluorine Building Blocks. 3. An Electrochemical Preparation and Reaction of Dimethyl 2,3-Bis(2,2,2-trifluoroethyl)succinate

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Dimethyl 2,3-bis(2,2,2-trifluoroethyl)succinate (**2**) was prepared in a 50% yield by electrochemical oxidation of trifluoroacetic acid (TFA) and methyl acrylate. Electrolysis was conducted in an MeCN-H_2O (7:1)-NaOH (0.1 equiv to TFA) system by using platinum electrodes under a constant current density (83 mA/cm^2) in an undivided cell. The succinate **2** was a 1:1 mixture of *meso* (**2a**) and *dl* (**2b**) that was separable by fractional crystallization. One of the methoxycarbonyl groups of **2** was transformed to isocyanate, *tert*-butoxy carbamate, or amino groups. Heterocyclic compounds bearing two 2,2,2-trifluoroethyl groups such as γ-lactone (**15**), β-lactam (**16**), succinic anhydride (**17**), succinimide (**18**), acyloin bis(trimethylsilyl ether) (**21**), and pyrimidinedione (**19** and **20**) were prepared from **2**.

Organofluorine compounds have attracted increasing attention for medicinal and agricultural usage and for material science.[1] Among them the trifluoromethylated compounds are promising so that a variety of trifluoromethylated compounds have been prepared. Transformations of the trichloromethyl group with hydrogen fluoride[2] and the carboxyl group with sulfur tetrafluoride[3] to the trifluoromethyl group have been employed for the industrial-scale productions of aromatic trifluoromethylated compounds. On the other hand, preparations of trifluoromethylated aliphatic compounds are not straightforward because of the requirement of the milder reaction conditions. Trifluoromethylation by the use of metal complexes of trifluoromethyl iodide,[4] *N*-(trifluoromethyl)-*N*-nitrosotrifluoromethanesulfonamide,[5] and perfluoroacyl peroxide[6] has been extensively investigated.

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