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STEREOCHEMISTRY OF THE WURTZ-FITTIG PREPARATION OF VINYLSILANES

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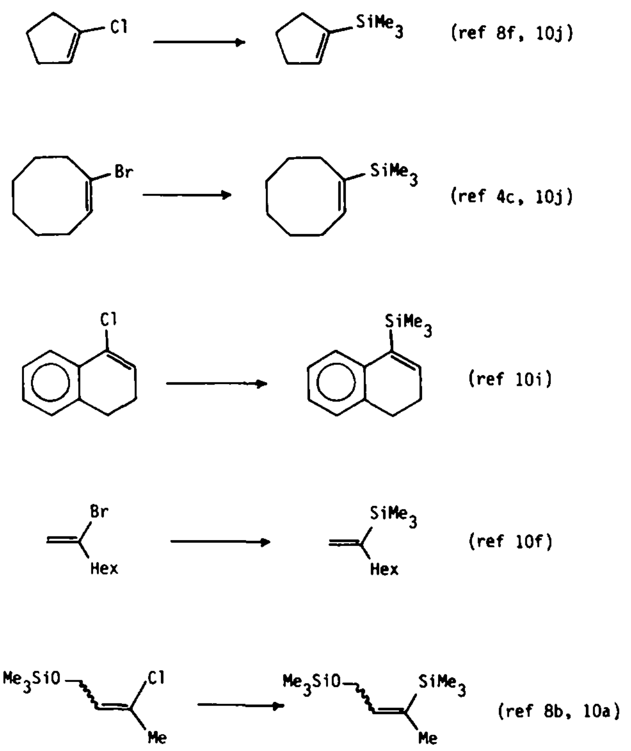
Abstract—The reactions of vinyl chlorides, bromides and iodides with sodium and trimethylsilyl chloride to give vinylsilanes have been shown to be stereospecific, with nearly complete retention of double bond configuration.

Vinylsilanes have become one of the most versatile and useful types of carbon-functional organosilicon compounds available to the synthetic organic chemist.[1,2] They are stable to many reagents (e.g. mild acids, strong bases, most organometallic compounds, hydride reducing agents) and can therefore be carried through a number of steps in a synthetic sequence. With a variety of electrophilic reagents, however, vinylsilanes undergo electrophilic substitution reactions, and retention of double bond geometry has been demonstrated in a number of cases.[1,2]Vinylsilanes thus can serve as vinyl *anion* equivalents for the preparation of a variety of olefinic systems. The derived epoxides (α,β-epoxysilanes) serve as vinyl *cation* equivalents,[3] particularly for the stereospecific preparation of heteroatom-substituted olefins.[4] The epoxides can also be converted to either of two isomeric carbonyl compounds,[5-7] allowing vinylsilanes to serve as latent carbonyl groups in synthesis.

A large number of methods for the synthesis of vinylsilanes have been developed.[1,2] One of the oldest methods is the reaction of a vinyl (alkenyl) halide with a silyl halide (generally Me_3SiCl) in the presence of Na,[8] basically a variation of the Wurtz coupling reaction. This method, sometimes called the Wurtz-Fittig reaction,[9] has been used to prepare a number of simple vinylsilanes.[4c,6a,8,10] Some examples are shown in Scheme 1. A variety of vinyl chlorides and bromides have been employed. The reactions have generally been carried out in ether, although refluxing toluene[10a,b] has also been used. Early workers used a small amount of ethyl acetate to initiate the reaction.[8] Although the first examples of the Wurtz-Fittig reaction were reported in the mid 1950's, only scattered



Scheme 1.

examples have been reported since then,[4c,6a,8e,f,10] and the reaction does not seem to have been generally appreciated in recent years.

In the course of our work, we have used the Wurtz–Fittig reaction on a number of occasions and have been impressed by the potential advantages of this method. The reactions can be run easily on a large scale,[11] the reagents are inexpensive, and the yields are moderately high. Moreover, numerous methods exist for the preparation of vinyl halides of many different structural types, including many that yield vinyl halides in high stereoisomeric purity.[12–23]

The stereochemistry of the Wurtz–Fittig preparation of vinylsilanes has not been investigated, although, as part of a recent study on the preparation of a series of cycloalkenylsilanes, Nagendrappa reported that a 62:38 mixture of stereoisomeric vinyl chlorides and a 58:42 mixture of stereoisomeric vinyl bromides yielded the corresponding vinylsilanes in the same ratios.[10f]

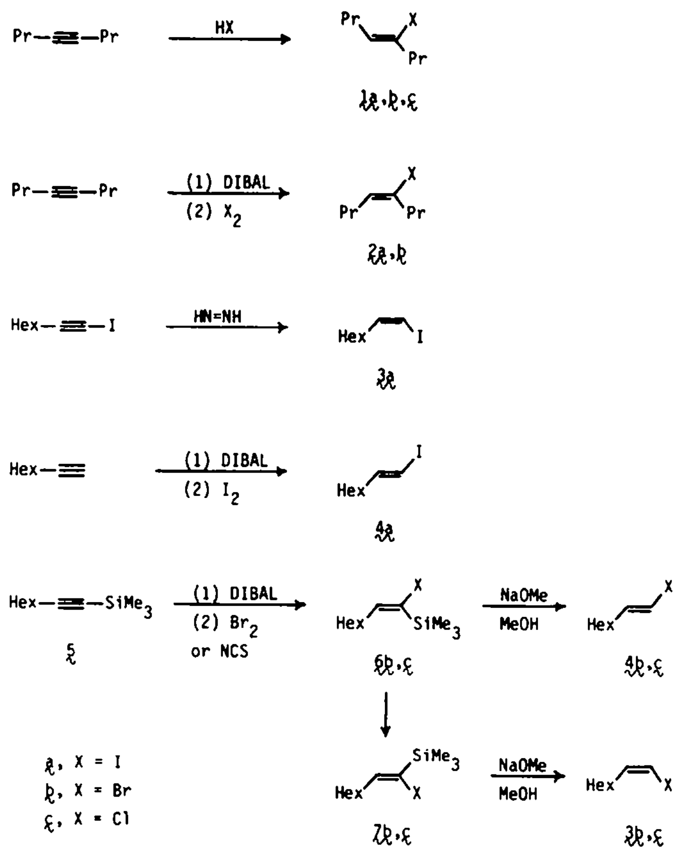
We have examined the stereochemistry of the Wurtz–Fittig preparation of vinylsilanes and have found that the reaction takes place with nearly complete stereospecific retention of double bond configuration.

RESULTS

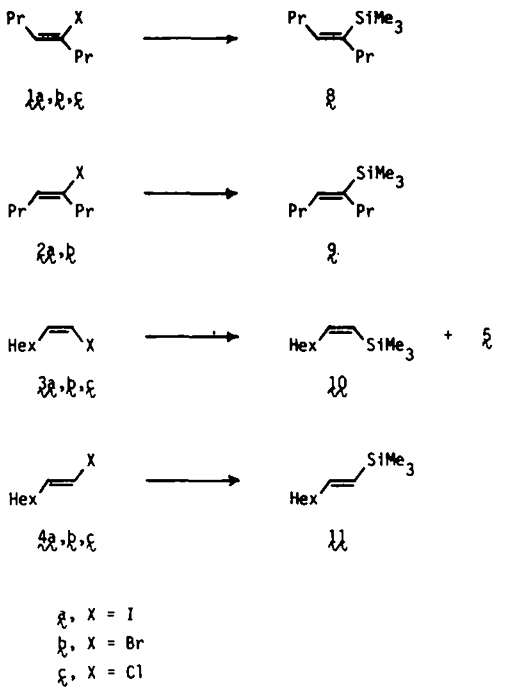
To determine the stereochemistry of the Wurtz–Fittig reaction, vinyl halides **1–4** were prepared by the routes shown in Scheme 2. The Wurtz–Fittig reactions (Scheme 3) were carried out by treating the vinyl halide with 2.5 equivalents of Na wire and 1.5 equivalents of trimethylsilyl chloride in anhydrous ether for 24 hr at room temperature. Isomeric purities of the product vinylsilanes were checked by VPC analysis; the values reported below were determined on the derived epoxides which in some cases were more clearly resolved.

The *Z*-vinyl iodide **1a** was prepared from 4-octyne by treatment with hydriodic acid[15c,d] in yields of 75–92% and stereoisomeric purities of 95–99%. Wurtz–Fittig reactions of **1a** yielded *Z*-vinylsilane **8** (63–77% yields) in nearly the same stereoisomeric purity as that of the starting vinyl iodide. For example, from **1a** having isomeric purity of 98.5% was obtained **8** in 98% isomeric purity. The isomeric *E*-vinyl iodide **2a** was prepared in 71% yield and >99% isomeric purity from 4-octyne by treatment with DIBAL followed by iodine.[19] Wurtz–Fittig reaction yielded *E*-vinylsilane **9** in 68% yield and >99% isomeric purity. Vinylsilane **9** was identical to the product of hydrosilylation of 4-octyne[24] (using $MeCl_2SiH$ followed by treatment of the product with MeMgI), thus confirming the stereochemical assignments. These results indicate that the Wurtz–Fittig reactions of simple internal vinyl iodides take place with nearly complete stereospecificity.

We also carried out a few reactions on internal vinyl bromides and a chloride, and found the reactions appeared to take place in a highly but not completely stereospecific manner. Wurtz–Fittig reactions on *Z*-vinyl bromide **1b** (prepared from 4-octyne by treatment with hydrobromic acid[15d] in 78–82% yields and 98–99% isomeric purity) yielded *Z*-vinylsilane **8** (75–76% yields) in 93–94% isomeric purity. Wurtz–Fittig reaction on the isomeric *E*-vinyl bromide **2b** (prepared from 4-octyne by treatment with



Scheme 2.



Scheme 3.

DIBAL followed by bromine[19] in 38% yield and 91% isomeric purity) yielded *E*-vinylsilane **9** in 63% yield and 89.5% isomeric purity. Wurtz–Fittig reaction on *Z*-vinyl chloride **1c** (prepared in 74–81% yields from 4-octyne by treatment with hydrochloric acid) yielded *Z*-vinylsilane **8** in 65–74% yields and 91–94% isomeric purity. (The isomeric purity of **1c** appeared to be 98% by VPC but the other isomer was not available for comparison.)

The terminal vinyl halides **3** and **4** were prepared by several methods. The *cis*-vinyl iodide **3a** was prepared in >99% isomeric purity by reduction of 1-iodo-1-octyne with diimide (57% yield).[17b,c] [We also prepared **3a** by hydroboration-protonolyis [17a] of 1-iodo-1-octyne, but the product was generally not as pure as that from the diimide reduction.] *trans*-Vinyl iodide **4a** was prepared in 75–81% yields and >99% isomeric purity from 1-octyne by treatment with DIBAL followed by iodine.[19] The *cis*- and *trans*-vinyl bromides (**3b** and **4b**) and chlorides (**3c** and **4c**) were prepared from octynyltrimethylsilane (**5**) by hydroalumination, halogenation and protiodesilylation, as described by Zweifel.[22] On one occasion, the *trans*-vinyl bromide **4b** was obtained in >96% isomeric purity by this method, and on another occasion in only 81% isomeric purity. The *cis*- and *trans*-vinyl chlorides **3c** and **4c** were both obtained in high (98–99%) isomeric purity. On one occasion the *trans*-vinyl chloride **4c** (>99% isomeric purity) was prepared from 1,1-dichlorooctane by prolonged treatment with KOtBu in tBuOH at reflux.

Wurtz–Fittig reactions of the *cis*-vinyl halides **3a–c** yielded the *cis*-vinylsilane **10** contaminated with varying amounts (usually 10–20%) of octynyltrimethylsilane (**5**). Small amounts of *trans*-vinylsilane, generally less than 5%, were also observable.

Wurtz–Fittig reactions of *trans*-vinyl halides **4a–c** yielded *trans*-vinylsilane **11** in high purity. Thus, from *trans*-vinyl iodide **4a** was obtained 63–65% yields of **11** in >99% isomeric purity. From *trans*-vinyl bromide **4b** (>96% isomeric purity) was obtained **11** in 86% yield and >96% isomeric purity. Wurtz–Fittig reaction of *trans*-vinyl chloride **4c** (isomeric purity 98–99%) yielded *trans*-vinylsilane **11** in 67–87% yields and about 93% isomeric purity. On one occasion, the product had an isomeric purity of >99%.

Since many of the early examples of the Wurtz–Fittig preparation of vinylsilanes used small amounts of ethyl acetate as an initiator, we carried out the reaction of vinyl iodide **1a** with Na and trimethylsilyl chloride in either containing 1% ethyl acetate. Under these conditions, the reaction was quite sluggish, and little product was formed.

To determine whether the stereospecificity of the Wurtz–Fittig preparation of vinylsilanes would be maintained on a larger scale, the reaction of vinyl iodide **1a** was carried out on a 10 g scale. From **1a** of 95% isomeric purity was obtained vinylsilane **8** (67% yield) in 94% isomeric purity.

DISCUSSION

These results demonstrate that the Wurtz–Fittig preparation of vinylsilanes takes place with retention of double bond configuration in the cases studied. The stereospecificity appears to be highest with the vinyl iodides. With the terminal *cis*-vinyl halides **3** the products are contaminated with the alkynylsilane **5**.[25] Formation of **5** most likely results from competing (anti) elimination of HX from the vinyl halide to give 1-octyne followed by silylation. In principle, a similar anti elimination of HX could take place during Wurtz–Fittig reaction of the internal vinyl halides (**1**). However, the product (4-octyne) would not be silylated under the reaction conditions, and is sufficiently volatile that it would be removed during workup (rotary evaporator) and distillation.

The mechanism of the Wurtz–Fittig preparation of vinylsilanes has not been studied in detail, but a reasonable pathway would be reaction of the vinyl halide with sodium to generate a vinylsodium reagent, followed by rapid reaction with trimethylsilyl chloride. (Trimethylsilyl chloride reacts only slowly with Na under the conditions used in this work.[26]) It is therefore interesting to compare the stereospecificity observed here with that observed in reactions of vinyl halides with reactive metals to generate vinylmetallic compounds.[27]

Reactions of vinyl halides with Li[14c,28] and Mg[28m,n,29] to generate vinyllithium and Grignard reagents, respectively, are known to take place with stereospecific retention of configuration, although the degree of stereospecificity appears to depend on reaction conditions. For example, the reactions of vinyl halides with Li metal have been reported to take place with anywhere from 75% to 98% retention of configuration.[28] (Vinyllithium reagents have also been prepared from vinyl bromides and iodides by reaction with alkyllithium reagents;[28c,k,30] these reactions appear to be highly stereospecific.) The reactions of vinyl halides with Mg[29] are generally less stereospecific than those with Li.

Reductions of vinyl halides by alkali metals may involve the generation of vinylmetallic intermediates. Reactions of vinyl chlorides[14a] (and iodides[23]) with Na in liquid ammonia are reported to proceed with 95–99% retention of configuration, but reductions with sodium naphthalenide are not stereospecific and are believed to involve radical intermediates.[31] Reductions of vinyl sulfides by Na or Li in ammonia are more than 90% stereospecific; similar reductions with Li in methylamine are nonstereospecific[14c]

Thus, the reductions of vinyl halides with reactive metals to generate vinylmetallic intermediates generally proceed with retention of configuration, but the degree of stereospecificity is variable and depends on substrate and reaction conditions.

Numerous methods for the preparation of vinylsilanes exist.[1,2] Some involve multistep sequences and some are difficult to scale up. Reductions of alkynylsilanes[21a,c] are likely to remain the best method for preparing *cis*-vinylsilanes. Simple internal *E*-vinylsilanes can be prepared very efficiently by hydrosilylation if a symmetrical internal acetylene can be used as a precursor.[2,12a,24] For other types of vinylsilanes, if the starting vinyl halide is available, the Wurtz–Fittig preparation is likely to be the method of choice.

To summarize the advantages of the Wurtz–Fittig preparation of vinylsilanes, the reagents are inexpensive, the reactions are easily carried out on large or small scale, the reactions can take place without external heating or cooling, the yields are moderately high, and as shown in this work, the reactions can be highly stereospecific.

EXPERIMENTAL

General. The verb "concentrated" refers to the evaporation of solvent under reduced pressure (water aspirator) using a rotary evaporator. The term "evaporative distillation" refers to bulb–bulb distillation in a Kugelrohr apparatus under oil pump vacuum; the temperature following in parentheses refers to the oven temp.

In all preparations, IR and NMR spectra were in accord with the structure; values are given only if the compound is previously unreported. IR spectra were obtained using a Beckman IR-33 spectrometer or a Perkin-Elmer Model 1320 spectrometer. NMR spectra were obtained using a Perkin-Elmer Model R-600 FT NMR spectrometer. Chemical shifts are reported in ppm (δ) relative to $CHCl_3$ ($\delta = 7.28$) for compounds containing an Me_3Si group, and to Me_4Si ($\delta = 0.00$) for other compounds. Mass spectra were obtained using a Finnegan Model 3200-E Automated GC-MS instrument. Exact mass determinations were carried out at the University of Nebraska.

In all preparations, the purity of the products was determined by VPC using a Varian Aerograph Model 90-P instrument with helium as the carrier gas. When the complete VPC is given, the retention time is followed by the percentage of total peak area (not corrected for detector response) and the assignment if known; the retention time of a hydrocarbon standard is included.

Tetrahydrofuran (THF) and anhyd. ether were obtained by distillation from Na and benzophenone.

Preparation of vinyl halides

Z-4-*Iodo*-4-*octene* (**1a**) was prepared by heating a mixture of 2 g 4-octyne and 20 mL HI (57%) at 80° for 4 hr.[15c,d] After cooling to room temp, the mixture was extracted with pentane, and the organic extract was washed with water, sat $NaHCO_3$ and water, and was dried ($MgSO_4$), concentrated, and evaporatively distilled (50–55°) giving 3.98 g (92%) of **1a**: IR (film) 2960, 1640, 1460, 1140 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.6 (m, 14 H), 5.48 (t, 1 H); mass spectrum *m/e* (rel. intensity) 238.0207 (M^+, 10) (calc. for $C_8H_{15}I$: 238.0178), 81 (20), 69 (100), 55 (50). VPC analysis[32a] (110°, $C_{12}H_{26}$ = 12.4 min) showed peaks at 7.8 min (> 99%, **1a**) and 8.7 min (< 1%, **2a**).

In a large scale reaction, 10 g of 4-octyne was converted to 17.8 g (82%) of **1a**: b.p. 76–78°C (13 mm). The isomeric purity was determined by VPC analysis as above to be 98.5%.

Z-4-*Bromo*-4-*octene* (**1b**) was prepared by heating a mixture of 1 g 4-octyne and 10 mL HBr (47–49%) at 80° overnight (~ 18 hr). After aqueous workup as described above for **1a**, evaporative distillation (50–55°) yielded 1.36 g (78%) of **1b**.[33] A small peak at 1710 cm^{-1} in the IR spectrum suggested the presence of a small amount of 4-octanone. VPC analysis[32a] (95°, $C_{10}H_{22}$ = 5.0 min) showed peaks at 2.0 min (~ 1.4%, 4-octyne), 4.2 min (~ 1.5%, 4-octanone), 6.0 min (~ 96.1%, **1b**) and 6.8 min (~ 1%, **2b**).

Z-4-*Chloro*-4-*octene* (**1c**) was prepared by heating a mixture of 1 g 4-octyne and 10 mL conc HCl at 80° overnight (~ 18 hr). After aqueous workup as described above for **1a**, evaporative distillation (40–45°) yielded 1.08 g (80.6%) of **1c**.[14b,d,e] A small peak at 1710 cm^{-1} in the IR spectrum suggested the presence of a small amount of 4-octanone. VPC analysis[32a] (95°, $C_{10}H_{22}$ = 5.0 min) showed peaks at 2.0 min (2%, 4-octyne), 4.0 min (96%, **1c**) and 4.2 min (2%, possibly **2c** or 4-octanone).

E-4-*Iodo*-4-*octene* (**2a**) was prepared from 4-octyne by hydroalumination–iodination.[19] Thus 1.1 g (10 mmol) 4-octyne in 5 mL hexane at 0° under a N_2 was treated with 10 mL (1 M soln in hexane, 10 mmol) diisobutylaluminum hydride (DIBAL) (warm to room temp, then 2 hr at 50°). The hexane was removed under reduced pressure, 10 mL THF was added, and the resulting mixture was cooled to − 78°. I_2 (2.54 g, 10 mmol) in 5 mL THF was added dropwise and the mixture was stirred at − 78° for 1 hr and then warmed to room temp overnight. The resulting mixture was cooled in an ice bath and 20% H_2SO_4 was added dropwise until gas evolution ceased. The mixture was then poured into dil H_2SO_4 and ice and the resulting mixture was extracted with pentane. The organic extract was washed with sat $NaHCO_3$, 10% $NaHSO_3$ aq and water, and was dried ($MgSO_4$), concentrated, and evaporatively distilled (50–55°) giving 1.69 g (71%) of **2a**: IR (film) 2960, 1625, 1460, 1135 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.5 (m, 14 H), 6.20 (t, 1 H). VPC analysis[32a] (110°, $C_{12}H_{26}$ = 12.4 min) showed peaks at 8.0 min (< 1%, **1a**) and 9.0 min (> 99%, **2a**).

E-4-*Bromo*-4-*octene* (**2b**) was prepared from 4-octyne by hydroalumination–bromination.[19] Thus 1.1 g (10 mmol) 4-octyne was treated with 10 mmol DIBAL followed by 1.58 g (10 mmol) Br_2 in 5 mL CCl_4, following the procedure for the preparation of **2a** (substituting the Br_2 in CCl_4 for I_2 in THF). Evaporative distillation (50–55°) of the crude product gave 0.662 g (38%) of **2b**.[33] VPC analysis[32a] (95°, $C_{10}H_{22}$ = 6.1 min) showed peaks at 7.4 min (9%, **1b**) and 8.3 min (91%, **2b**).

cis-1-*Iodo*-1-*octene* (**3a**) was prepared from 1-iodo-1-octyne by reduction with diimide following the procedure of Dieck and Heck.[17c] From 4.53 g (19.2 mmol) 1-iodo-1-octyne[34] (prepared from 1-octyne by treatment with BuLi followed by I_2) was obtained 2.61 g (57%) of **3a**.[35] VPC analysis[32a] (110°, $C_{12}H_{26}$ = 7.7 min) showed peaks at 7.1 min (97%, **3a**) and 8.0 min (3%, **4a** or 1-iodo-1-octyne). VPC analysis on a DC-550[32b] column established the smaller peak to be 1-iodo-1-octyne.

trans-1-*Iodo*-1-*octene* (**4a**) was prepared from 1-octyne by hydroalumination–iodination.[19] Thus 1.1 g (10 mmol) 1-octyne was treated with 10 mmol DIBAL followed by 2.54 g (10 mmol) I_2 in 5 mL THF following the procedure for the preparation of **2a**. Evaporative distillation (50–55°) of the crude product gave 1.78 g (75%) of **4a**.[18d,35] VPC analysis[32a] (110°, $C_{12}H_{26}$ = 7.7 min) showed peaks at 7.2 min (< 1%, **3a**), 7.9 min (96%, **4a**) and 8.6 min (4%).

Vinyl halides **3b**,[4a,18a,d,22b] **3c**,[22b] **4b**,[4a,18a] and **4c**[22b] were prepared from **5** as described by Zweifel.[22]

Wurtz–Fittig reactions

The following general procedure was used. To a stirred suspension of 12.5 mmol of freshly drawn Na wire in 15 mL anhydrous ether under N_2 was added 7.5 mmol trimethylsilyl chloride. The resulting mixture was stirred at room temp for 15 min, and then a soln of 5 mmol vinyl halide in 5 mL anhyd ether was added dropwise. (The mixture became warm during the addition.) The resulting mixture, which gradually turned blue (faster for the iodides), was stirred at room temp for 24 hr and then quickly filtered[36] using anhyd ether as a wash. The filtrate was washed with sat $NaHCO_3$ aq followed by water, dried ($MgSO_4$), and concentrated. The product vinylsilanes were purified by evaporative distillation. Vinylsilanes **8** (see below), **9**,[24] **10**[37] and **11**[37] had satisfactory IR and NMR spectra. The purities of the vinylsilanes were checked by VPC analysis using an SE-30[32a] column and sometimes a DC-550[32b] column. Aside from isomeric purities, vinylsilanes **8**, **9** and **11** were generally obtained in 95–99% purity. (As mentioned in the text, vinylsilane **10** was frequently contaminated with considerable amounts of **5**.) The isomeric purities of the vinylsilanes (especially **10** and **11**) could be more accurately established by conversion to the epoxides (1.2 mmol of *m*-chloroperbenzoic acid, 1.3 mmol of Na_2HPO_4, 10 mL CH_2Cl_2, 1 mmol vinylsilane in 1 mL CH_2Cl_2, room temp for 24 hr) and analysis by VPC on the SE-30[32a] column.

In a large scale reaction, from 10 g (42 mmol) **1a** (isomeric purity 95.3%), 8.0 mL (6.9 g, 63 mmol) trimethylsilyl chloride, and 2.42 g (105 mmol) freshly drawn Na wire in 100 mL anhyd ether was obtained 5.19 g (67%) **8**: b.p. 73–75° (18 mm); IR (film) 2950, 1600, 1450, 1240, 825 cm^{-1}; NMR ($CDCl_3$) δ 0.12 (s, 9H), 0.8–1.8 (m, 11 H), 2.03 (m, 4 H), 5.95 (t, 1 H); mass spectrum *m/e* (rel. intensity) 184 (M^+, 3), 169.1397 (M^+–CH_3, 18) (calc. for $C_{10}H_{21}Si$: 169.1412), 73 (100). VPC analysis[32a] (115°, $C_{11}H_{24}$ = 4.3 min) showed peaks at 1.1 min (~ 1.5%), 2.3 min (~ 1.5%), 4.0 min (5.4%, **9**) and 4.4 min (91.6%, **8**).

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[11] We have carried out these reactions on a half-mole scale; some of the examples in the literature were run on an even larger scale.

[12] Some of the more important methods for the stereospecific preparation of vinyl halides are included in Refs. 13–23. For the preparation of vinyl bromides from α,β-epoxysilanes, see Ref. 4*a*. For additional methods for the preparation of vinyl halides from vinyl-boron, -aluminum, -tin, -copper and -zirconium reagents, see [a]P. F. Hudrlik and A. M. Hudrlik, *The Chemistry of the Carbon-Carbon Triple Bond* (Edited by S. Patai), pp. 199–273. Wiley, New York (1978). For other methods and references, see [b]I. T. Harrison and S. Harrison, *Compendium of Organic Synthetic Methods*, Vol. 2, pp. 400–404. Wiley, New York (1974), and later volumes in this series.

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