15 H), 1.68–2.26 (m + s, 7 H), 4.00 (t, 2 H, J = 6.6 Hz), 5.40 (m, 2 H). ^{13}C NMR: δ 13.8, 20.9, 22.1, 25.7, 28.6, 29.4, 30.8, 31.8, 32.2, 32.4, 64.5, 130.0, 130.5, 170.7. Mass spectrum (chemical ionization): m/e 227 (m + H), 167 (m + H - AcOH).

(*E*)-11-Tetradecen-1-yl acetate (3b) was prepared according to the procedure described for **1b**. 6.03 g (79%) of **3b** (6.03 g, 79%) was obtained by distillation, bp 124–128 °C (0.01 mm), n^{20}_D 1.4475. GC analysis indicated >98% chemical purity. IR (neat): 1740 (C=O), 1240 (CO), 970 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.86 (t, 3 H, J = 7.8 Hz), 1.04–1.66 (m, 16 H), 1.66–2.14 (m + s, 7 H), 3.94 (t, 2 H, J = 7.2 Hz), 5.32 (m, 2 H). ^{13}C NMR: δ 13.9, 20.9, 25.6, 25.9, 28.7, 29.1, 29.2, 29.5, 29.7, 30.8, 32.5, 64.6, 129.3, 131.9, 170.5. Mass spectrum (chemical ionization): m/e 255 (m + H), 195 (m + H - AcOH).

(*E*)-11-Hexadecen-1-yl acetate (4b) was prepared according to the procedure described for **1b**. **4b** (7.05 g, 83%) was obtained by distillation, bp 123–127 °C (0.005 mm), n^{20}_D 1.4494. GC analysis indicated >97% chemical purity. IR (neat): 1741 (C=O), 1238 (CO), 970 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.64–1.72 (m, 23 H), 1.72–2.28 (m + s, 7 H), 3.96 (t, 2 H, J = 6.6 Hz), 5.38 (m, 2 H). ^{13}C NMR: δ 13.8, 20.6, 22.1, 25.9, 28.6, 29.1, 29.2, 29.4, 29.6, 31.8, 32.2, 32.5, 64.3, 130.2, 170.5. Mass spectrum (chemical ionization): m/e 283 (m + H), 223 (m + H - AcOH).

(*E*)-6-Nonen-1-ol (1a). To a mixture of aqueous NaOH (20% solution, 50 mL, 250 mmol) and 95% ethanol (50 mL) in a 250-mL beaker at room temperature was added (*E*)-6-nonen-1-yl acetate (2.7 g, 15 mmol). The mixture was further stirred for 30 min. The mixture was then extracted with pentane, washed with saturated NaCl solution, and dried (K_2CO_3). Removal of solvent under vacuum gave 2.04 g (97%) of **1a**. GC analysis indicated >98% chemical purity. Distillation provided 1.83 g (86%) of pure **1a**, bp 80–84 °C (0.2 mm), n^{20}_D 1.4478. IR (neat): 3300 (OH), 1126 (CO), 965 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.94 (t, 3 H, J = 6.8 Hz), 1.10–1.68 (m, 6 H), 1.68–2.20 (m, 4 H), 2.88 (br, 1 H, OH), 3.36 (t, 2 H, J = 6.6 Hz), 5.40 (m, 2 H). ^{13}C NMR: δ 13.8, 25.3, 25.5, 29.4, 32.4, 62.4, 129.0, 132.0. Mass spectrum (chemical ionization): m/e 143 (m + H), 125 (m + H - H_2O).

(*E*)-11-Tetradecen-1-ol (3a) was prepared according to the procedure described above. **3a** (3.12 g, 98%) was obtained from the extracts. GC analysis indicated >97% chemical purity. Distillation provided 2.70 (85%) of pure **3a**, bp 98–101 °C (0.02 mm), n^{20}_D 1.4558. IR (neat): 3220 (OH), 1070 (CO), 980 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.88 (t, 3 H, J = 7.6 Hz), 1.02–1.68 (m, 16 H), 1.68–2.20 (m, 4 H), 2.82 (br, 1 H, OH), 3.58 (t, 2 H, J = 6.4 Hz), 5.32 (m, 2 H). ^{13}C NMR: δ 13.7, 25.4, 25.9, 29.2, 29.3, 29.6, 32.5, 32.6, 61.7, 129.0, 131.5. Mass spectrum (chemical ionization): m/e 213 (m + H), 195 (m + H - H_2O). Anal. Calcd for C, 79.16; H, 13.28. Found: C, 79.00; H, 13.35.

(*E*)-11-Hexadecen-1-ol (4a) was prepared according to the procedure described for **1a**. **4a** (3.49 g, 97%) was obtained after removing the solvent under vacuum. This product was essentially chemically pure (>98% by GC analysis), n^{20}_D 1.4563. IR (neat): 3300 (OH), 1070 (CO), 980 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.64–1.68 (m, 23 H), 1.68–2.20 (m, 4 H), 2.74 (br, 1 H, OH), 3.60 (t, 2 H, J = 6.2 Hz), 5.38 (m, 2 H). ^{13}C NMR: δ 13.8, 22.1, 25.7, 29.1, 29.5, 30.8, 31.8, 32.2, 32.5, 32.7, 62.8, 131.3. Mass spectrum (chemical ionization): m/e 241 (m + H), 223 (m + H - H_2O).

(*E*)-11-Tetradecen-1-al (5). Method A. The literature procedure[16] was basically followed. A carefully dried 50-mL flask fitted with a septum inlet and a magnetic stirring bar was attached to a mercury bubbler. In the flask was placed oxalyl chloride (0.45 mL, 5 mmol) in CH_2Cl_2 (10 mL). The contents of the flask were cooled to −60 °C. Me_2SO in CH_2Cl_2 (4.5 mL, 1.1 M) was then added dropwise. Stirring was continued for 5 min, followed by the addition of (*E*)-11-tetradecen-1-ol (1 mL, 3.4 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred for 15 min, followed by the addition of triethylamine (1.4 mL, 10 mmol). After 5 min, the cooling bath was removed, and the mixture was further stirred while the temperature was allowed to warm to room temperature in 30 min. Vacuum was applied to remove the solvent and low boiling materials. The residue was again digested with pentane (total 30 mL). Ammonium salt remained undissolved and was filtered off. Pentane was removed by evaporation under vacuum. Oily (*E*)-11-tetradecen-1-al (**5**) (0.69 g, 97%) was collected without further purification. GC analysis indicated >98% chemical purity, n^{20}_D 1.4483. IR (neat): 2700 (C(O)H), 1720 (C=O), 977 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.95 (t, 3 H, J = 7.2 Hz), 1.12–1.68 (m, 14 H), 1.68–2.62 (m, 6 H), 5.40 (m, 2 H), 9.74 (m, 1 H). ^{13}C NMR: δ 14.0, 22.1, 25.6, 29.2, 29.4, 29.7, 30.9, 32.5, 43.9, 129.3, 131.9, 202.3. Mass spectrum (chemical ionization): m/e 211 (m + H), 209 (m - H), 193 (m + H - H_2O).

Method B.[17,18] Chlorine in CH_2Cl_2 (0.4 M, 12.5 mL) cooled to −78 °C in a flask was transferred with a double-ended needle to a solution of dimethyl sulfide in CH_2Cl_2 (0.5 M, 10 mL) also cooled to −78 °C. The mixture was stirred for 5 min followed by the addition of 3.4 mmol of (*E*)-11-tetradecen-1-ol. The mixture was stirred for 15 min, followed by the addition of triethylamine (1.4 mL, 10 mmol). After 5 min, the cooling bath was removed and the mixture was further stirred while the temperature was allowed to warm to room temperature in 30 min. The product was worked up as described above to give 0.69 g (97%) of **5**. GC analysis indicated >98% chemical purity, n^{20}_D 1.4480. Spectral data completely agreed with the above one.

(*E*)-11-Hexadecen-1-al (6) was prepared according to method A described for **5**; 0.75 g (98%) was obtained. GC analysis indicated >98% chemistry purity, n^{20}_D 1.4494. IR (neat): 2705 (C(O)H), 1730 (C=O), 980 cm^{-1} (*trans*-CH=CH—). ^{1}H NMR: δ 0.66–1.70 (m, 21 H), 1.70–2.58 (m, 6 H), 5.38 (m, 2 H), 9.76 (m, 1 H). ^{13}C NMR: δ 13.9, 22.2, 29.1, 30.0, 30.8, 31.9, 32.3, 32.6, 43.9, 130.3, 202.6. Mass spectrum (chemical ionization): m/e 239 (m + H), 237 (m - H), 221 (m + H - H_2).

This compound was also prepared according to method B described for **5**. Similar results were obtained. Yield: 0.75 g (98%), n^{20}_D 1.4501. Other spectral data were completely consistent with those of **6** prepared above.

Acknowledgment. We thank Albany International Chemical Division for support of this work.

Synthesis of (*E*)-(2-Arylethenyl)silanes by Palladium-Catalyzed Arylation of Vinylsilanes in the Presence of Silver Nitrate

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Received July 8, 1986

A series of (*E*)-trimethyl(2-arylethenyl)silanes **1–16** and (*E*)-triethoxy(2-arylethenyl)silanes **17** and **18** has been synthesized by palladium-catalyzed arylation of the corresponding vinylsilanes, in the presence of silver nitrate. Apart from enhancing the rate of the reaction, silver nitrate also completely suppresses the desilylation. In the absence of silver salt, under ordinary Heck arylation conditions, styrene derivatives are formed in good yields. A possible mechanistic rationale for the formation of styrenes is discussed.

Vinylsilanes have become increasingly important intermediates for synthesis.[1-3] We have utilized vinyltrimethylsilane as an ethylene equivalent for the preparation of styrene derivatives from aryl iodides (eq 1).[4] Silver salt

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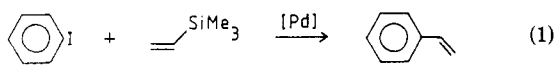
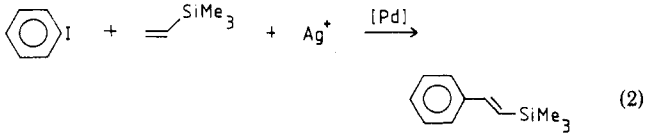


(1)

modification of this palladium-catalyzed reaction suppresses the desilylation and enhances the rate of arylation to form (E)-trimethyl(2-arylethenyl)silanes (eq 2).[5] We



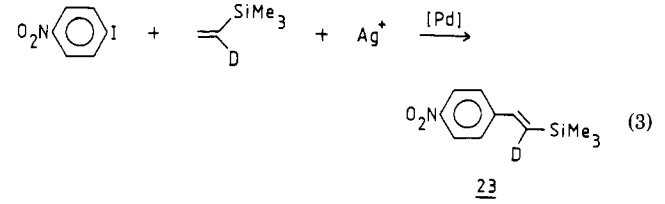
(2)

now report a detailed investigation of this reaction and its utility as a preparative method. Consideration will be given (a) the presumed role of silver ions, (b) desilylation in the absence of silver ions, and (c) stochiometric reactions with arylmercury compounds.

Results and Discussion

(a) Arylation in the Presence of Silver Salts. The preparative results are summarized in Table I. A variety of functional groups may be tolerated, and the reaction proceeds smoothly with both aromatic and heteroaromatic iodides. The rate of conversion was slower in the presence of ortho substituents (entries 8–10), and little coupling was achieved by 2,4,6-trimethyl-1-iodobenzene. The substituents on the silicon atom were also of importance. Thus, arylation of vinyltriethoxysilane required a higher reaction temperature, and the yields of the isolated products were lower (entries 17 and 18). The arylation occurred with high regioselectivity in all of the reactions studied, except for entry 16, and less than 5% of compounds derived from arylation at the internal carbon was formed. A possible mechanistic rationale for the formation of the arylvinylsilanes in Table I is given in Scheme I.

We believe that initially a silver-mediated abstraction of iodide from the arylpalladium iodide[6] takes place, affording the intermediate **20**. The added silver ions presumably also facilitate the oxidative addition of palladium (0) by complexing to the iodo atom and/or by forming an electron donor–acceptor complex with the aromatic ring.[7] The intermediate **20** forms a tight olefin–palladium complex **21**, from which the aryl group is transferred to the terminal position to give **22**, which is not prone to desilylate. The (arylethenyl)silane is eventually formed after an irreversible elimination of a PdH species. This proposal is supported by the results of an experiment using (1-deuteriovinyl)trimethylsilane. No deuterium scrambling occurred in the formation of the (arylethenyl)silane **23**, suggesting that an elimination readdition sequence involving PdH species is probably not involved (eq 3).[8]



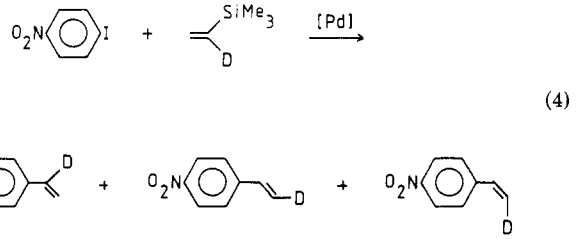
(3)

23

Although silver nitrate was used through this investigation, silver tetrafluoroborate was found to be equally effective. At 100 °C the desilylation was fully suppressed in the presence of silver nitrate or tetrafluoroborate. All reactions were carried out in acetonitrile, but Me_2SO could also be used. A considerably slower reaction took place in acetone. No reaction took place in the presence of $(C_5H_4NCOO^-)_2Ag^{II}$ or $(C_5H_5N)_2Ag^{II}S_2O_8^{2-}$. It is notable that silver acetate in acetic acid has been used as an oxidant of Pd metal to Pd(II).[9] Bromobenzene gave 1 and styrene in approximately equal amounts in the absence of silver salts but did not react at all in the presence of silver nitrate or silver tetrafluoroborate. One explanation could be that silver(I) effectively competes with bromobenzene as oxidant.

(b) Arylation and Desilylation in the Absence of Silver Salts. Palladium(II) compounds are able to cleave Si–C bonds in alkyl- and arylsilanes.[10] Vinylsilanes similarly undergo cleavage. Thus, products derived from ArCH=CHPd intermediates were formed after treatment of $ArCH{=}CHSiMe_3$[11] or $ArCH{=}CHSiF_5^{2-}$[12] with palladium salts. Coupling of two molecules of vinyltrimethylsilane accompanied by a desilylation step afforded allylpalladium complexes.[13] In our hands, the arylation of vinyltrimethylsilane conducted under ordinary Heck arylation conditions[14] furnished styrene derivatives in yields ranging from 50 to 70%.[4]

At least three reasonable explanations can be offered for the formation of styrenes: (i) ordinary Heck arylation at the terminal or internal carbon, followed by elimination–readdition of HPdI and subsequent desilylation; (ii) cross-coupling via alkenyl group transfer from silicon to palladium; (iii) protodesilylation of (arylvinyl)trimethylsilane by $HINEt_3$ formed in the reaction mixture. The last alternative could be excluded, since the ratio of styrene to (phenylethenyl)trimethylsilane proved to be independent of reaction time. In fact, no desilylation of (arylethenyl)silane was found to occur even after treatment with 1 equiv of $HINEt_3$ or $HClNEt_3$ at 120 °C for 16 h. In order to distinguish between (i) and (ii) we carried out an experiment with (1-deuteriovinyl)trimethylsilane (eq 4). On the basis of this experiment, alternative (ii) could



(4)

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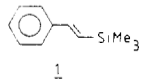
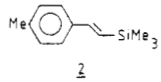
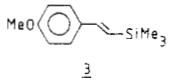
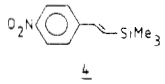
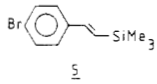
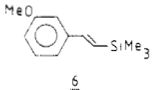
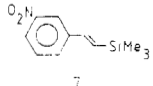
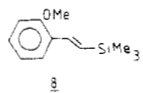
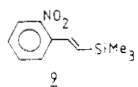
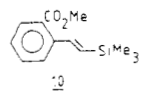
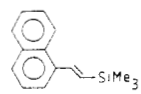
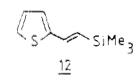
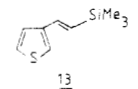
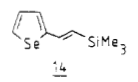
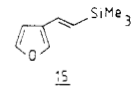
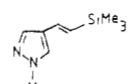
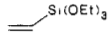
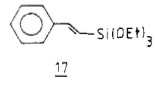
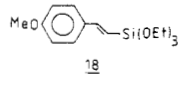
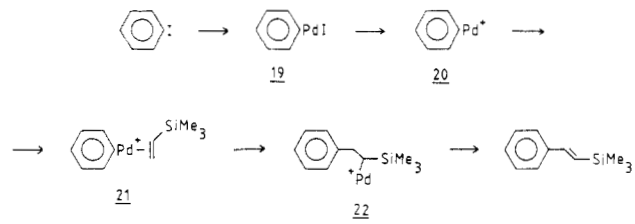
Table I

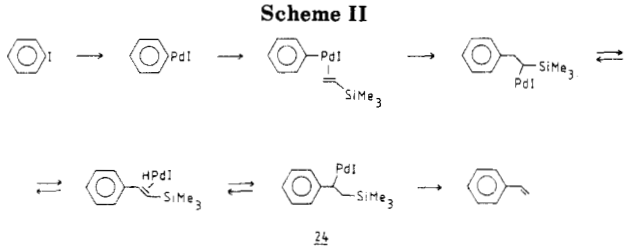
entry	olefin	time, h	temp, °C	isolated yield, %	product
1		5	50	74	 1
2		5	50	67	 2
3		5	50	68	 3
4		5	50	70	 4
5		16	50	84	 5
6		20	50	77	 6
7		19	50	68	 7
8		17	80	79	 8
9		19	100	70	 9
10		19	80	85	 10
11		16	80	93	 11
12		5	50	74	 12
13		20	50	73	 13
14		19	50	79	 14
15		20	50	33	 15
16		19	80	68	 16
17		22	100	47	 17
18		22	100	29	 18

be excluded since we expected only 1-deuterio-1-arylethene to be found in that case. Desilylation via arylation at the internal carbon is less appealing, since Kikukawa's group in recent work[15] showed that phenylpalladium acetate

Scheme I



Scheme II



generated in situ from $PhN(NO)COCH_3$ and $Pd^0(dba)_2$ preferentially arylated 1-(trimethylsilyl)-1-octene in the 2-position, in spite of the alkyl chain attached to that position. Furthermore, we have found that arylation of (*E*)-propenyltrimethylsilane under ordinary Heck arylation conditions[14] predominatly gives 2-phenylpropene. Thus, we believe that the styrene derivatives are derived from an arylation at the terminal position. A possibly mechanistic rationale for the desilylation is given in Scheme II.

The elimination–readdition to the hydridopalladium iodide group accounts for the observed scrambling of deuterium (eq 4). We find it reasonable to assume that the desilylation reaction occurs via an intermediate **24** by an iodide-promoted, intramolecular, irreversible cleavage of the carbon–silicon bond.

(c) Arylation with Phenylmercuric Chloride and Acetate. In an attempt to compare the effect of the addition of silver salts with that of mercury salts, some reactions were conducted in acetonitrile in the presence of a stochiometric amount of $Hg_2(NO_3)_2 \cdot H_2O$, $Hg(CN)_2$, or $HgBr_2$. No conversion of iodobenzene took place. However, when phenylmercuric chloride in the presence of triethylamine and a stochiometric amount of palladium chloride was treated with vinyltrimethylsilane, a mixture of (*E*)-trimethyl(2-phenylethenyl)silane (1) and styrene was formed. Bromobenzene results in 15–20% higher yields of 1 and lower yield of styrene than iodobenzene under palladium-catalyzed Heck arylation conditions. The relatively large amount of 1 formed from phenylmercuric chlorides, 35% and 49% in acetonitrile and Me_2SO, respectively, was therefore expected from an intermediate arylpalladium chloride species (eq 5). Thus, we assume that the presence of mercury salts has no or at most a very small effect on the desilylation reaction. The possibility that styrene could result from cleavage of 1 by palladium(II) chloride[11] seems unlikely, since 1 was intact after treatment with a stoichiometric amount of palladium chloride and amine under reaction conditions similar to those described above. However, in the absence of amine in acetonitrile only styrene and polymeric material were formed, while in Me_2SO 1 was still unaffected. Similarly, arylmercuric chloride, palladium chloride, and vinyltrimethylsilane in the absence of amine in acetonitrile give mainly styrene, while in Me_2SO a product pattern almost identical with that in eq 5 was found. Apparently, in acetonitrile, but not in Me_2SO, the amine has an important

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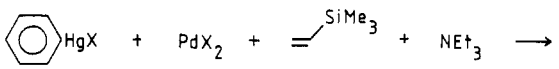
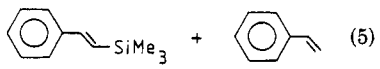


X = Cl, MeCN
X = Cl, Me_2SO
X = OAc, MeCN



(5)

35	40
49	26
94	<1

role for the outcome of the reaction.

The hypothesis that the halide promotes desilylation is supported by an experiment in which the reaction medium was free of halide. Thus, the reaction of arylmercuric acetate with vinyltrimethylsilane in the presence of a stoichiometric amount of palladium acetate afforded 1 in 94% yield according to GLC. Only traces of styrene were detected (eq 5).

Conclusion

Palladium-catalyzed arylation of vinyltrimethylsilane in the presence of added silver ions is apparently a useful method for obtaining (*E*)-(2-arylethenyl)silanes. Due to the simplicity of the experimental procedure and the tolerability of a wide range of substituents in the aryl group, this procedure compares favorably with existing methods.[16] (Arylethenyl)silanes are also obtained from arylmercuric acetate. This approach seems less attractive due to the requirement of a stochiometric amount of organomercury reagent, the difficult of obtaining suitable arylmercury compounds, and the need for stoichiometric amounts of palladium salt for best reaction.

Experimental Section

Materials. Aryl Iodides. Iodobenzene (Fluka), *p*-iodotoluene (Janssen), *p*-iodoanisole (Fluka), *m*-iodoanisole (Janssen), *o*-iodoanisole (Fluka), *p*-iodonitrobenzene (Janssen), *m*-iodonitrobenzene (EGA), *o*-iodonitrobenzene (Aldrich), and *p*-iodobromobenzene (Aldrich) were used as received from the commercial sources indicated. 2-Iodothiophene,[17] 3-iodothiophene,[18] 2-iodoselenophene,[19] 3-iodofuran,[20] and 4-iodo-1-methylpyrazole[21] were generously supplied by Professor Salo Gronowitz. All of the heterocyclic aryl iodides were washed with a saturated sodium thiosulfate solution and destilled before use, with the exception of 4-iodo-1-methylpyrazole, which was used as received. 2-Iodobenzoic acid methyl ester[22] was prepared from 2-iodobenzoic acid (Janssen).

Vinylic Silanes. (1-Deuteriovinyl)trimethylsilane[23] was prepared by treatment of (1-bromovinyl)trimethylsilane (Fluka) with *tert*-butyllithium[24] in ether and subsequent quenching with deuteriated water. Vinyltrimethylsilane (Aldrich) and vinyltriethoxysilane (Aldrich) were used as received. (*E*)-Propenyltrimethylsilane[25] was prepared from (*E*)-propenyl bromide.[26]

Other Reagents. Palladium acetate (Fluka), palladium chloride (Fluka), triphenylphosphine (Fluka), silver nitrate (Merck), triethylamine (Merck), phenylmercuric chloride (Aldrich), acetonitrile (Janssen), and dimethyl sulfoxide (Janssen) were used as received from commercial sources indicated.

General Procedures. ^1H NMR spectra were recorded on Jeol MH 100 and Varian XL 300 spectrometers in $CDCl_3$ with Me_4Si as an internal standard. Mass spectra were obtained on a Finnigan 4021 (Data System Incos 2100) gas chromatogrph/mass spectrometer at 70 eV. Quantitative gas chromatographic analyses were performed on a Varian 1400 instrument equipped with a 2-m glass column of 5% OV17. 2,3-Dimethylnaphthalene was used as an internal standard. Column chromatography was carried out using E. Merck silica gel 60 (230–400 mesh) and pentane (35–38 °C), petroleum ether (60–71 °C), or petroleum ether (60–71 °C)/ether (95:5) as eluent.

General Procedure for the Arylation of Vinyltrimethylsilane and Vinyltriethoxysilane. Each of the reactants was dissolved or dispersed in acetonitrile (totaling 150 mL) and was added to a 250 mL round-bottomed flask in the following order: palladium acetate (67 mg, 0.3 mmol), triphenylphosphine (157 mg, 0.6 mmol), silver nitrate (1.70 g, 10 mmol), aryl iodide (10 mmol), triethylamine 1.21 g, 12 mmol), and vinyltrimethylsilane (2.00 g, 20 mmol) or vinyltriethoxysilane (2.28 g, 12 mmol). The flask was closed, and the contents were magnetically stirred and heated for the appropriate time. When the aryl iodide had been consumed, the mixture was allowed to cool. The contents were filtered and then poured into 100 mL of water. After extraction with ether or petroleum ether (4 × 50 mL), the combined organic phases were washed with 50 mL of water, dried ($MgSO_4$), and evaporated. The crude product obtained was then subjected to column chromatography.

General Procedure for the Reaction of Phenylmercuric Salts with Vinyltrimethylsilane. A mixture consisting of phenylmercuric salt (0.5 mmol), vinyltrimethylsilane (1.0 mmol), triethylamine (0.6 mmol) when present, palladium salt (0.5 mmol), 2,3-dimethylnaphthalene, and 7 mL of the solvent was stirred at 50 °C for 2 h. Samples of 1.0 mL were collected, partitioned between diethyl ether and water, and the organic phase was analyzed by GLC.

Reaction of (*E*)-Trimethyl(2-phenylethenyl)silane with Palladium Chloride. A mixture consisting of (*E*)-trimethyl(2-phenylethenyl)silane (0.5 mmol), triethylamine (0.6 mmol) when present, palladium chloride (0.5 mmol), 2,3-dimethylnaphthalene, and 7 mL of the solvent was stirred at 50 °C for 2 h. Samples of 1.0 mL were collected and partitioned between diethyl ether and water, and the organic phase was analyzed by GLC.

(*E*)-Trimethyl(2-phenylethenyl)silane[27] **(1)**: 74%; colorless oil; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 6.67 (d, 1 H, J = 19.4 Hz), 6.98 (d, 1 H, J = 19.4 Hz), 7.31–7.65 (m, 5 H); mass spectrum, m/e 176 (M^+). The solvent was evaporated at 25 °C.

(*E*)-Trimethyl[2-(4-methylphenyl)ethenyl]silane[16h] **(2)**:

(16) Selected methods for preparation of (*E*)-trimethyl(2-arylethenyl)silanes were from the following. From (phenylethynyl)trimethylsilane and reducing agents: (a) Eisch, J. J.; Foxton, M. W. *J. Org. Chem.* **1971**, *36*, 3520. (b) Zweifel, G.; On, H. P. *Synthesis* **1980**, 803. (c) Duboudin, J. G.; Jousseaume, B. *J. Organomet. Chem.* **1978**, *162*, 209. (d) Green, M.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc. Dalton Trans.* **1977**, 1525. (e) Miller, R. B.; McGarvey, G. *J. Org. Chem.* **1978**, *43*, 4424. (f) Benkeser, R. A.; Burrous, M. L.; Nelson, L. E.; Swisher, J. V. *J. Amer. Chem. Soc.* **1961**, *83*, 4385. From phenylacetylenes and tris(trimethylsilyl)aluminum: (g) Altnau, G.; Rösch, L. *Tetrahedron Lett.* **1980**, 4069. (h) Rösch, L.; Altnau, G. *Chem. Z.* **1982**, *106*, 441. From α-silyl carbanions and aryl aldehydes: (i) Gröbel, B.-T.; Seebach, D. *Angew. Chem.* **1974**, *86*, 102. (j) Gröbel, B.-T.; Seebach, D. *Chem. Ber.* **1977**, *110*, 852. (k) Fleming, I.; Pearce, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2485. (l) Ager, D. J. *J. Org. Chem.* **1984**, *49*, 168. From 2-styryllithium and trimethylsilyl chloride: (m) Seyferth, D.; Vaughan, L. G.; Suzuki, R. *J. Organomet. Chem.* **1964**, *1*, 437. From alkanesulfonyl chloride and (trimethylsilyl)diazomethane: (n) Aoyama, T., Toyama, S.; Tamaki, N.; Shioiri, T. *Chem. Pharm. Bull.* **1983**, *31*, 2957. From vinyltrimethylsilane, arenediazonium tetrafluoroborates, and Pd(O): see ref 8.

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67%; colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 2.32 (s, 3 H), 6.46 (d, 1 H, J = 19.5 Hz), 6.80 (d, 1 H, J = 19.5 Hz), 7.03–7.41 (m, 4 H); mass spectrum, m/e 190 (M^+).

(*E*)-Trimethyl[2-(4-methoxyphenyl)ethenyl]silane[16g] (3): 68%; white crystals; mp 50–52 °C; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9 H), 3.83 (s, 3 H), 6.37 (d, 1 H, J = 19.2 Hz), 6.79 (d, 1 H, J = 19.2 Hz), 6.73–7.47 (m, 4 H); mass spectrum m/e 206 (M^+).

(*E*)-Trimethyl[2-(4-nitrophenyl)ethenyl]silane[16h] (4): 70%; yellow crystals; mp 59–61 °C (lit.[8] mp 61–62 °C); ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9 H), 6.92 (d, 1 H, J = 19.2 Hz), 7.10 (d, 1 H, J = 19.2 Hz), 7.66–8.42 (m, 4 H); mass spectrum, m/e 221 (M^+).

(*E*)-Trimethyl[2-(4-bromophenyl)ethenyl]silane[8] (5): 84%; white crystals; mp 40–42 °C (lit.[8] mp 42–43 °C); ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 6.50 (d, 1 H, J = 19.5 Hz), 6.78 (d, 1 H, J = 19.5 Hz), 7.28–7.47 (m, 4 H); mass spectrum, m/e 254/256 (M^+).

(*E*)-Trimethyl[2-(3-methoxyphenyl)ethenyl]silane (6): 77%; colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.17 (s, 9 H), 3.84 (s, 3 H), 6.51 (d, 1 H, J = 19.0 Hz), 6.82 (d, 1 H, J = 19.0 Hz), 6.80–7.28 (m, 4 H); mass spectrum m/e 206 (M^+). Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 69.80; H, 8.74.

(*E*)-Trimethyl[2-(3-nitrophenyl)ethenyl]silane[16h] (7): 68%; yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 9 H), 6.69 (d, 1 H, J = 19.1 Hz), 6.89 (d, 1 H, J = 19.1 Hz), 7.46–8.32 (m, 4 H); mass spectrum, m/e 221 (M^+).

(*E*)-Trimethyl[2-(2-methoxyphenyl)ethenyl]silane (8): 79%; colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 3.86 (s, 3 H), 6.45 (d, 1 H, J = 19.2 Hz), 7.28 (d, 1 H, J = 19.2 Hz), 6.85–7.55 (m, 4 H); mass spectrum, m/e 206 (M^+). Anal. Calcd for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 69.81; H, 8.69.

(*E*)-Trimethyl[2-(2-nitrophenyl)ethenyl]silane (9): 70%; yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 6.51 (d, 1 H, J = 19.0 Hz), 7.29 (d, 1 H, J = 19.0 Hz), 7.36–7.91 (m, 4 H); mass spectrum, m/e 221 (M^+). Anal. Calcd for $C_{11}H_{15}NO_2Si$: C, 59.69; H, 6.83. Found: C, 59.80; H, 6.87.

(*E*)-Trimethyl[2-(2-carbomethoxyphenyl)ethenyl]silane (10): 85%; colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 3.92 (s, 3 H), 6.40 (d, 1 H, J = 19.0 Hz), 7.61 (d, 1 H, J = 19.0 Hz), 7.26–7.96 (m, 4 H); mass spectrum, m/e 234 (M^+). Anal. Calcd for $C_{13}H_{18}O_2Si$: C, 64.82; H, 8.16. Found: C, 65.01; H, 8.26.

(*E*)-Trimethyl(2-naphth-1-ylethenyl)silane (11): 93%; colorless oil; ^{1}H NMR δ 0.25 (s, 9 H), 6.57 (d, 1 H, J = 19.0 Hz), 7.69 (d, 1 H, J = 19.0 Hz), 7.45–8.20 (m, 7 H); mass spectrum, m/e 226 (M^+). Anal. Calcd for $C_{15}H_{18}Si$: C, 79.58; H, 8.01. Found: C, 79.52; H, 8.07.

(*E*)-Trimethyl(2-thien-2-ylethenyl)silane (12): 74%; yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9 H), 6.22 (d, 1 H, J = 18.8 Hz), 6.95 (d, 1 H, J = 18.8 Hz), 6.92–7.19 (m, 3 H); mass spectrum, m/e 182 (M^+). Anal. Calcd for $C_9H_{14}SiS$: C, 59.28; H, 7.74. Found: C, 59.30; H, 7.69.

(*E*)-Trimethyl(2-thien-3-ylethenyl)silane (13): 73%; yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9 H), 6.24 (d, 1 H, J = 19.0 Hz), 6.83 (d, 1 H, J = 19.0 Hz), 7.20–7.33 (m, 3 H); mass spectrum, m/e 182 (M^+). Anal. Calcd for $C_9H_{14}SiS$: C, 59.28; H, 7.74. Found: C, 59.32; H, 7.68.

(*E*)-Trimethyl(2-selenophene-2-ylethenyl)silane (14): 79%; yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9 H), 6.10 (d, 1 H, J = 18.6 Hz), 6.96 (d, 1 H, J = 18.6 Hz), 7.10–7.86 (m, 3 H); mass spectrum, m/e 230 (M^+). Anal. Calcd for $C_9H_{14}SeSi$: C, 47.15; H, 6.16. Found: C, 47.23; H, 6.24.

(*E*)-Trimethyl(2-furan-3-ylethenyl)silane (15): 33%; colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 9 H), 6.16 (d, 1 H, J = 19.0 Hz), 6.73 (d, 1 H, J = 19.0 Hz), 6.58–7.46 (m, 3 H); mass spectrum, m/e 166 (M^+). Anal. Calcd for $C_9H_{14}OSi$: C, 65.00; H, 8.48. Found: C, 64.98; H, 8.50: Evaporation of the solvent should be carried out carefully at 0 °C. The compound is stored under nitrogen.

(*E*)-Trimethyl[2-(4-*N*-methylpyrazolyl)ethenyl]silane (16): 67%; yellow oil; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9 H), 3.86 (s, 3 H), 6.12 (d, 1 H, J = 19.3 Hz), 6.65 (d, 1 H, J = 19.3 Hz), 7.36 (s, 1 H), 7.57 (s, 1 H); mass spectrum, m/e 180 (M^+). Anal. Calcd for $C_9H_{16}N_2Si$: 59.94; H, 8.98. Found: C, 59.47; H, 8.98. There was 16% (GLC) of trimethyl[1-(4-*N*-methylpyrazolyl)ethenyl]-silane present after column chromatography: ^{1}H NMR ($CDCl_3$) δ 0.18 (s, 9 H), 3.88 (s, 3 H), 5.38 (d, 1 H, J = 2.9 Hz), 5.88 (d, 1 H, J = 2.9 Hz), 7.29 (s, 1 H), 7.49 (s, 1 H); mass spectrum, m/e 180 (M^+).

(*E*)-Triethoxy(2-phenylethenyl)silane[16d] (17): 43%; light yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 9 H), 3.90 (q, 6 H), 6.18 (d, 1 H, J = 19.3 Hz), 7.22 (d, 1 H, J = 19.3 Hz), 7.26–7.50 (m, 5 H); mass spectrum, m/e 266 (M^+).

(*E*)-Triethoxy[2-(4-methoxyphenyl)ethenyl]silane (18): 27%; light yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, 9 H), 3.83 (s, 3 H), 3.88 (q, 6 H), 6.01 (d, 1 H, J = 19.3 Hz), 7.16 (d, 1 H, J = 19.3 Hz), 6.86–7.45 (m, 4 H); mass spectrum, m/e 296 (M^+). Anal. Calcd for $C_{15}H_{24}O_4Si$: C, 60.77; H, 8.16. Found: C, 60.84; H, 7.76.

Acknowledgment. We gratefully acknowledge the support of A.H. through grants from the Swedish Natural Science Research Council.

Registry No. **1**, 19372-00-0; **2**, 73839-45-9; **3**, 76711-42-7; **4**, 85260-63-5; **5**, 94397-78-1; **6**, 105281-53-6; **7**, 88691-43-4; **8**, 105281-54-7; **9**, 101047-40-9; **10**, 101047-41-0; **11**, 105281-55-8; **12**, 105281-56-9; **13**, 105281-57-0; **14**, 105281-58-1; **15**, 105281-59-2; **16**, 105281-60-5; **17**, 65119-09-7; **18**, 105281-61-6; PhHgCl, 100-56-1; PhHgOAc, 62-38-4; $PdCl_2$, 7647-10-1; $Pd(OAc)_2$, 3375-31-3; iodobenzene, 591-50-4; 4-iodotoluene, 624-31-7; 4-iodomethoxybenzene, 696-62-8; 4-iodonitrobenzene, 636-98-6; 4-bromoiodobenzene, 589-87-7; 3-iodomethoxybenzene, 766-85-8; 3-iodonitrobenzene, 645-00-1; 2-iodomethoxybenzene, 529-28-2; 2-iodonitrobenzene, 609-73-4; methyl 2-iodobenzoate, 610-97-9; 1-iodonaphthalene, 90-14-2; 2-iodothiophene, 3437-95-4; 3-iodothiophene, 10486-61-0; 2-iodoselenophene, 37686-36-5; 3-iodofuran, 29172-20-1; 4-iodo-1-methylpyrazole, 39806-90-1; ethenyltrimethylsilane, 754-05-2; ethenyltriethoxysilane, 78-08-0; silver nitrate, 7761-88-8; tetrafluoroborae, 14104-20-2; bromobenzene, 108-86-1; styrene, 100-42-5; (*E*)-propenyltrimethylsilane, 4964-03-8; 2-phenylpropene, 98-83-9.