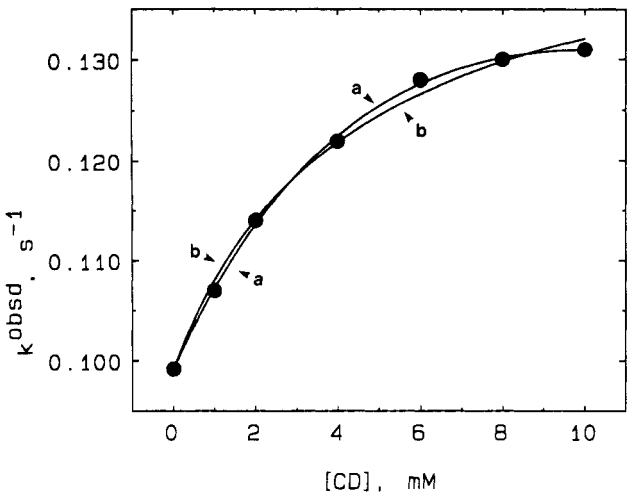

Figure 3. Data for the cleavage of *p*-nitrophenyl propanoate by α-CD. Curve (a) for the model including nonproductive 2:1 binding (eq 12) is clearly superior to that (b) for productive 1:1 binding alone (eq 3). See discussion in the Experimental Section.

0.003 s^{-1} (r = 0.9976, $\chi^2 = 4.39 \times 10^{-6}$).

For the *p*-nitrophenyl esters C2, C4, and C6 there is reasonable agreement with the values of K_S and k_c/k_u obtained earlier,[10] given the differences in reaction conditions (pH 10.4, 1% (v/v) MeCN), the range of [CD] employed (0–5 mM), and the method of analysis (Lineweaver–Burk). The agreement is very good for α-CD but only fair with β-CD. Nevertheless, the discrepancies for β-CD are not large enough to affect any of our conclusions. Our values of k_c/k_u and K_S for the acetates agree well with those of earlier workers.[3,6,7,10]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for an operating grant to O.S.T. and Mr. Bryan Takasaki for initial technical assistance. Professor K. Murakami (Kyushu University) kindly provided a copy of ref 20.

Registry No. **3** (R = Me), 1523-06-4; **3** (R = Me)/α-CD complex, 120040-15-5; **3** (R = Me)/β-CD complex, 74091-81-9; **3** (R = Et), 69844-29-7; **3** (R = Et)/α-CD complex, 126375-48-2; **2** (R = Et)/β-CD complex, 126375-56-2; **3** (R = Pr), 14617-97-1; **3** (R = Pr)/α-CD complex, 126375-49-3; **3** (R = Pr)/β-CD complex, 126375-57-3; **3** (R = Bu), 126375-39-1; **3** (R = Bu)/α-CD complex, 126375-50-6; **3** (R = Bu)/β-CD comp, 126375-58-4; **3** (R = $(CH_2)_4CH_2$), 126375-40-4; **3** (R = (CH_2CH_3)/α-CD complex, 126375-51-7; **3** (R = $(CH_2)_4CH_3$)/β-CD complex, 126421-20-3; **4** (R = Me), 830-03-5; **4** (R = Me)/α-CD complex, 120040-16-6; **4** (R = Me)/β-CD complex, 74069-32-2; **4** (R = Et), 1956-06-5; **4** (R = Et)/α-CD 1:1 complex, 126375-52-8; **4** (R = Et)/α-CD 1:2 complex, 126375-55-1; **4** (R = Et)/β-CD complex, 126421-21-4; **4** (R = Pr), 2635-84-9; **4** (R = Pr)/α-CD complex, 126375-53-9; **4** (R = Pr)/β-CD complex, 126375-59-5; **4** (R = Bu), 1956-07-6; **4** (R = Bu)/α-CD complex, 126375-54-0; **4** (R = Bu)/β-CD complex, 126421-22-5; **4** (R = $(CH_2)_4CH_3$)/α-CD complex, 126421-19-0; **4** (R = $(CH_2)_4CH_3$)/β-CD complex, 126421-23-6; **5** (R = Me), 17336-08-2; **5** (R = Me)/α-CD complex, 126375-60-8; **5** (R = Me)/β-CD complex, 126375-70-0; **5** (R = Et), 126375-41-5; **5** (R = Et)/α-CD complex, 126375-61-9; **5** (R = Et)/β-CD complex, 126375-71-1; **5** (R = Pr), 126375-42-6; **5** (R = Pr)/α-CD complex, 126375-62-0; **5** (R = Pr)/β-CD complex, 126375-72-2; **5** (R = Bu), 126375-43-7; **5** (R = Bu)/α-CD complex, 126375-63-1; **5** (R = Bu)/β-CD complex, 126421-24-7; **5** (R = $(CH_2)_4(CH_3)$, 126375-44-8; **5** (R = $(CH_2)_4CH_3$)/α-CD, 126375-64-2; **5** (R = $(CH_2)_4CH_3$)/β-CD, 126375-73-3; **6** (R = Me), 1734-62-9; **6** (R = Me)/α-CD complex, 126375-65-3; **6** (R = Me)/β-CD complex, 126375-74-4; **6** (R = Et), 1760-88-9; **6** (R = Et)/α-CD complex, 126375-66-4; **6** (R = Et)/β-CD complex, 126375-75-5; **6** (R = Pr), 126375-45-9; **6** (R = Pr)/α-CD complex, 126375-67-5; **6** (R = Pr)/β-CD complex, 126375-76-6; **6** (R = Bu), 126375-46-0; **6** (R = Bu)/α-CD complex, 126375-68-6; **6** (R = Bu)/β-CD complex, 126375-77-7; **6** (R = $(CH_2)_4CH_3$), 126375-47-1; **6** (R = $(CH_2)_4CH_3$)/α-CD complex, 126375-69-7; **6** (R = $(CH_2)_4CH_3$)/β-CD complex, 126375-78-8; α-CD, 10016-20-3; β-CD, 7585-39-9; *m*-nitrophenol, 554-84-7; 4-chlorosalicylic acid, 5106-98-9; 5-chlorosalicylic acid, 321-14-2; acetic anhydride, 108-24-7; propionic anhydride, 123-62-6; butyric anhydride, 106-31-0; pentanoic anhydride, 2082-59-9; hexanoic anhydride, 2051-49-2.

Supplementary Material Available: Tables of first-order rate constants for the cleavage of the esters **3**, **4**, **5**, and **6** as a function of the [α-CD] and [β-CD] (Tables S1–S4) (5 pages). Ordering information is given on any current masthead page.

The β-Effect: Changing the Ligands on Silicon[1]

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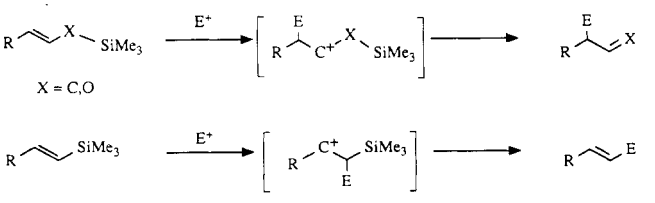
Received December 27, 1989

The ability of a silyl group to stabilize a carbocation β to silicon, the β-effect, is directly related to the electron-withdrawing ability of the groups on silicon. This was shown by using the degree of syn addition of bromine to (*E*)-β-silylstyrenes as a measure of the stabilizing ability. With the exception of alkoxysilanes and phenoxysilanes, a good correlation between the degree of the β-effect and the group electronegativity of the silyl group is observed. The special case of the alkoxysilanes and phenoxysilanes is discussed in the context of the addition mechanism.

The remarkable interest in the use of silicon in organic synthesis and, increasingly, in other fields of chemistry stems from the "unusual" properties[3] that this element conveys to organic molecules. Arguably, the most important of these properties is the β-effect, the ability of silicon to stabilize a carbocation in the β-position. The β-effect has been invoked mechanistically in most of the reactions that involve silicon–carbon bond cleavage (and, usually, carbon–carbon bond formation) under acidic conditions. Such reactions include the Lewis acid cata-

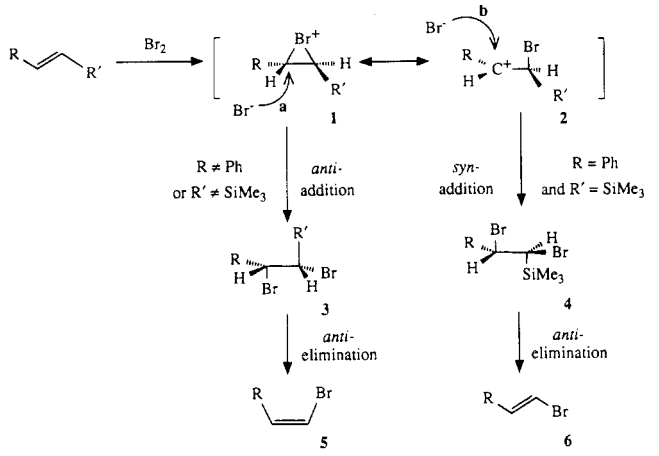
Scheme I



(1) A preliminary account of the work has appeared: Brook, M. A.; Neuy, A.; Hadi, M. A. *J. Chem. Soc., Chem. Commun.* **1989**, 957.
(2) NSERC University Research Fellow, 1985–1990.
(3) The properties are unusual only when carbon-based chemistry is used as a standard against which to measure group IV chemical reactivity.

0022-3263/90/1955-3609$02.50/0

Scheme II



lyzed reactions of allyl-, allenyl-, vinyl-, propargyl-, acetylene-, and arylsilanes. Typically in these reactions, the addition of a Lewis acid activated electrophile to a double bond leads to a β-silyl carbocation (Scheme I), which is stabilized by the presence of the silicon.

Some studies have been done to evaluate the extent of the stabilization. Fleming and co-workers, for example, have demonstrated that the stabilization of a carbocation by a phenyl group is more effective than a β-trimethylsilyl group.[5] Other groups have quantified the effect experimentally and theoretically.[6,7] However, few studies have directly focused on the role played by the ligands or groups on silicon in the stabilization. Notable are the continuing contributions by the groups of Sakurai, Hayashi, Tamao, Kumada, and others in this area who have examined in some detail the differences between methylsilanes, fluorosilanes, and pentafluorosilicates[8-10] and more recently mixed (halo/amino/alkoxy/alkyl)allylsilanes.[11,12] Brook recently compared the reactivity of chloro- and methylstyrylsilanes toward cationic conditions.[13] We therefore decided to embark upon a study of the effects of the ligands and report herein our findings.

β-Effect in an Addition Reaction. The β-effect is commonly invoked mechanistically in the reaction of electrophiles with vinylsilanes. Generally, these reactions involve a stereoselective substitution process in which the silyl group is replaced by the electrophile. The stereoselectivity of the process, retention or inversion of the olefin geometry, depends strongly on the nature of the electrophile, the counterion, the medium,[4] and the ligands on silicon[9] and may also depend on the leaving group ability of the silyl group. In order to compare different silyl groups, we felt it was important to disconnect possible effects of the leaving group ability from the β-effect. Therefore, we chose to study an addition reaction. Although addition reactions to styrylsilanes (not involving the β-effect) have been examined previously, the relative reactivity was not quantified.[14]

The addition of bromine to olefins is generally considered to take place stereoselectively in an anti fashion via S_N2 attack of bromide on bromonium ion **1** (path a in Scheme II).[15]

Vinyltrimethylsilanes react with bromine to give bromotrimethylsilane and an olefin **5** with inverted configuration.[16,17] Mechanistically, this inversion is inferred to arise from an anti addition of bromine to **1** (path a in Scheme II; R′ = $SiMe_3$), giving **3** followed by an anti elimination of bromotrimethylsilane. However, the addition of bromine to (*E*)-β-(trimethylsilyl)styrene leads to the formation of bromostyrene with overall *retention* of configuration.[18,19] Weber and Koenig showed, by isolation of the products, that the reaction takes place in two discrete steps: the addition of the bromine giving **4** and the loss of Me_3SiBr to give the bromostyrene **6** (path b in Scheme II).[20] Both of these steps occur stereoselectively. Thus, the reaction had to involve either a syn addition/anti elimination or an anti addition/syn elimination sequence. Later this question was resolved on an analogous compound, β-(triphenylsilyl)styrene, by Brook and co-workers who demonstrated with an X-ray crystal structure that the addition of bromine takes place in a syn fashion and, therefore, that the elimination takes place in an anti fashion as is the usual case (Scheme IIb).[21,22]

The important feature of the reaction is that, in contrast to vinyltrimethylsilanes or other olefins that undergo preferential anti addition of bromine, the addition of the bromine to (*E*)-β-(trimethylsilyl)styrene occurs syn. In the presence of a strongly stabilizing group, and in this case there are two, the phenyl ring and the silyl group, it is presumed that the bromonium ion **1** can open up to give a carbonium ion **2**—a β-silyl carbocation (Scheme II).[23] Syn addition can result from attack by bromide on **2** simply because of the proximity of the nucleophile[24] to the

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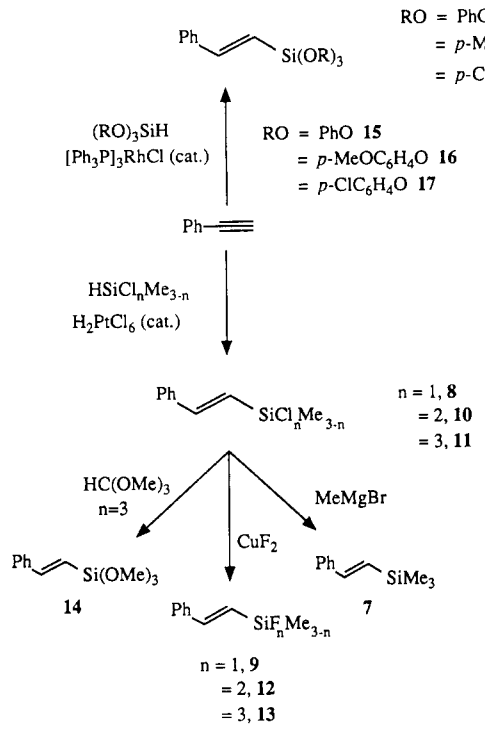
(23) This may be stabilized as well by the presence of the bromine (anchimeric participation) as a pseudo-bromonium ion.[9]

Scheme III



syn face of the molecule (vide infra; path b, Scheme II). As a first approximation, therefore, it is to be expected that anti addition will result from the reaction of bromide with **1** and syn addition from reaction with **2**. Thus, the ratio of isolated products **3** and **4** can be directly related to the ratio of the two carbonium ions. More importantly, this latter ratio directly reflects the stability of the two carbonium ions and, therefore, the stabilizing effects of nearby groups, including the β-effect.

The styrene system is balanced in terms of cation stabilization. With only the phenyl group providing stabilization, methylstyrene brominates to give a 95/5 mixture of the anti and syn products,[26] indicating that the primary route for bromide addition is anti attack on the bromonium ion **1** (path a, Scheme II; R = Ph, R′ = Me). In contrast, with additional stabilization from a strong β-effect, (trimethylsilyl)styrene gives 100% syn addition via reaction of the bromide with the stabilized carbonium ion **2**. Thus, the syn/anti addition ratio of this reaction should be a scale with which to measure the degree of the β-effect for different silyl groups. As a silyl group becomes increasingly electron-withdrawing, the partition between **1** and **2** (R = Ph, R′ = SiXYZ; Scheme II; this may be an equilibrium or a kinetic effect) should increasingly favor **1** and, therefore, formation of the anti product. In all cases the contribution from the phenyl group would be the same. To pursue this thesis, the bromination of a series of (*E*)-β-silylstyrenes was undertaken.

Results

The (*E*)-β-silylstyrenes were synthesized by conventional means (Scheme III). Trichloro- and methylchlorosilanes

Scheme IV

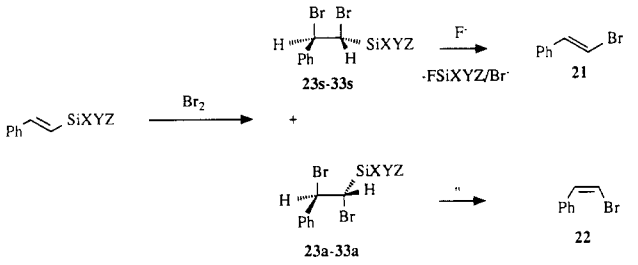


Table I. Comparison of Syn/Anti Addition Ratio to the *E*/*Z* Ratio of Bromostyrene

vinyl compd	ligands on Si	products	syn/anti	21/22
7	Me_3	**23s/23a**	100/0	100/0
8	Me_2Cl	**24s/24a**	73/27	78/22
9	Me_2F	**25s/25a**	50/50	52/48
10	$MeCl_2$	**26s/26a**	88/12	90/10
11	Cl_3	**27s/27a**	79/21	77/23
12	MeF_2	**28s/28a**	80/20	84/16
13	F_3	**29s/29a**		17/83

8, **10**, and **11** were prepared by the hydrosilation of phenylacetylene with Speier's catalyst (H_2PtCl_6).[27] Conversion of chloride to methyl groups was achieved with either MeMgBr or MeLi. Fluoro compounds **9**, **12**, and **13** were synthesized by halide exchange with CuF_2.[28] (Trimethoxysilyl)styrene (**14**) was prepared from the trichloro compound with $HC(OMe)_3$.[29] The phenoxysilanes could not, in our hands, be prepared by the direct reaction of phenols or phenolates with (trichlorosilyl)styrene. Therefore, triphenoxysilanes **15**–**17** were prepared by the addition of the phenol to trichlorosilane. Subsequent hydrosilation of phenylacetylene with the triphenoxysilanes in the presence of Wilkinson's catalyst ($[PPh_3]_3RhCl$) led to the (phenoxysilyl)styrenes **18**–**20**.

Initially, a room-temperature solution of bromine in $CDCl_3$ was added to a cooled (−60 °C) solution of the styrylsilane in $CDCl_3$. The ratio of the two addition products **23s**–**33s** and **23a**–**33a**, resulting from syn and anti addition, respectively, was determined in the crude mixture by integration of the α-Si*CH* proton signals in the ^1H NMR and correlated with the peak intensity of the α-Si*C*H carbon signals in the ^{13}C NMR and of the Si peaks in the ^{29}Si NMR. Relative geometries of **23s**–**33s** and **23a**–**33a** were established conclusively by their conversion with fluoride to the known (*Z*)- and (*E*)-β-bromostyrenes, **21** and **22**, respectively (Scheme IV). The fluoride-induced eliminations were performed in $CDCl_3$ with Bu_4NF (TBAF). The ratio of **21** to **22** was obtained from the ^1H NMR spectra.

The ratio of the two dibromo adducts **23s**–**29s** and **23a**–**29a** correlated directly with the ratio of **21** to **22** as can be seen from Table I. The slight discrepancies that are observed, always in favor of the trans isomer, can be explained by the known propensity of the cis isomer to undergo isomerization to the more stable trans geometry.[20] The reasonable assumption that only the anti elimination mechanism[20,21] is operating for the series of compounds then leads to stereochemical assignment of **23s**–**33s** to the *u* isomer and that of **23a**–**33a** to the *l* isomer as shown in Scheme IV (*unlike* and *like*, respectively[30]).

(24) This assumes the bromide that adds to the carbonium ion comes from the bromine molecule that electrophilically added to the double bond. Far more complex mechanisms may be occurring,[25] but this serves as a useful model with which to explain the observations.
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Table II. Comparison of Syn/Anti Ratio to Group Electronegativity

vinyl compd	ligands on Si	products	syn/anti	group electroneg[32,33]	chem shift[a]
7	Me_3	**23s/23a**	100/0	2.06	6.36
8	Me_2Cl[b]	**24s/24a**	100/0	2.12	6.34
9	Me_2F	**25s/25a**	85/15	2.18	6.29
10	$MeCl_2$	**26s/26a**	75/25	2.19	6.24
11	Cl_3	**27s/27a**	55/45	2.26	6.21
12	MeF_2	**28s/28a**	40/60	2.32	6.11
13	F_3	**29s/29a**	15/85[c]	2.47	5.97

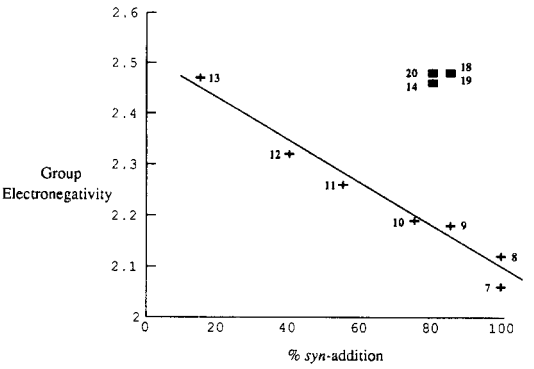
[a] In the ^1H NMR of the α-SiC*H* proton. [b] Approximately one-third of the starting material reacted to form products that were not the usual dibromo derivatives (see the Experimental Section). Of the ca. 65% that did give a dibromo adduct, only the syn addition product was observed. [c] Based on the ratio of bromostyrenes after elimination.

The results presented in Table I show essentially no correlation between the electron-withdrawing ability of the ligands on silicon and the degree of syn addition. In an attempt to ensure that the reaction was taking place under kinetic control, the experiments were repeated with more strict temperature control and at a lower temperature. The product ratios are shown in Table II, and the products result from the addition of a cooled bromine (CS_2) solution (−78 °C) to a cooled solution of the styrene in CS_2 (−78 °C).

Discussion

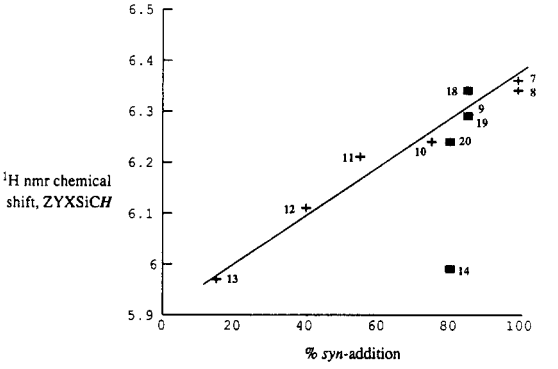
(Halomethylsilyl)styrenes. In a seminal paper, Traylor and co-workers summarized the arguments for $\sigma-\pi$ conjugation (vertical stabilization) and examined in detail the factors that affect the degree of the stabilization.[31] The β-effect, which is the name used to describe this effect when it occurs with elements of low electronegativity such as the transition and main-group elements, is dominated by two of these factors: the polarization and orientation of the stabilizing bond.[4,7] The former of these is probably most important. As a result of its lower electronegativity than carbon, the C–Si bond is polarized $C^{\delta-}$–$Si^{\delta+}$ and the negative charge on the α-carbon can participate in a vertical stabilization of the cation. As electron-withdrawing groups are placed on silicon, this polarization and thus the β-effect will be attenuated. Several parameters could be used to quantify the polarization of the Si–C bond (degree of electron-withdrawing ability of the silyl group). A convenient measure is the group electronegativity scale of Mullay.[32]

As discussed above, the anti addition process is consistent with an S_N2 attack of bromide on the bromonium ion **1** (path a in Scheme II). Assuming that syn addition only results from bromide attack on carbonium ion **2** (path b in Scheme II) and that these two species are the only reactive intermediates present in the reaction mixture, a direct correlation between the group electronegativity and the degree of syn addition should be observed. In the case of the (halomethylsilyl)styrenes, there is a good correlation between the group electronegativity and the degree of syn addition to compounds **7–13** as can be seen from Table II and the plot in Figure 1. Fortuitously, most of the percent syn values fall within the range of the scale chosen. The exceptions, (trimethylsilyl)- and (dimethylchlorosilyl)-styrene have a value at the limit of the scale (100% syn).



PhCH=CHSiXYZ, XYZ=Me_3 **7**; Me_2Cl **8**; Me_2F **9**; Cl_2Me **10**; Cl_3 **11**; MeF_2 **12**; F_3 **13**; $(OMe)_3$ **14**; $(OPh)_3$ **18**; $(p\text{-}OC_6H_4OMe)_3$ **19**; $(p\text{-}OC_6H_4Cl)_3$ **20**.

Figure 1. Plot of group electronegativity versus percent syn addition of bromine.



PhCH=CHSiXYZ, XYZ=Me_3 **7**; Me_2Cl **8**; Me_2F **9**; Cl_2Me **10**; Cl_3 **11**; MeF_2 **12**; F_3 **13**; $(OMe)_3$ **14**; $(OPh)_3$ **18**; $(p\text{-}OC_6H_4OMe)_3$ **19**; $(p\text{-}OC_6H_4Cl)_3$ **20**.

Figure 2. Plot of ^1H NMR chemical shift of the α-SiC*H* proton versus percent syn addition of bromine.

Table III. Comparison of Syn/Anti Addition Ratio for Styrylsiloxanes

vinyl compd	ligands on Si	products	syn/anti	group electroneg[32,33]	chem shift
14	$(OMe)_3$	**30s/30a**	80/20	2.46	5.99
18	$(OPh)_3$	**31s/31a**	85/15	2.48	6.34
19	$(OC_6H_4OMe\text{-}p)_3$	**32s/32a**	85/15	2.48	6.29
20	$(OC_6H_4Cl\text{-}p)_3$	**33s/33a**	80/20	2.48	6.24

[a] In the ^1H NMR of the α-SiC*H* proton.

From the plot of group electronegativity, the "true" percent syn addition can be extrapolated to be about 110% for (trimethylsilyl)styrene and 100% for (dimethylsilyl)-styrene. To determine the relative value directly, a new scale involving a slightly less stabilized carbonium ion **2** would have to be used (e.g., R′ = SiXYZ, R = *p*-nitrophenyl; Scheme II).

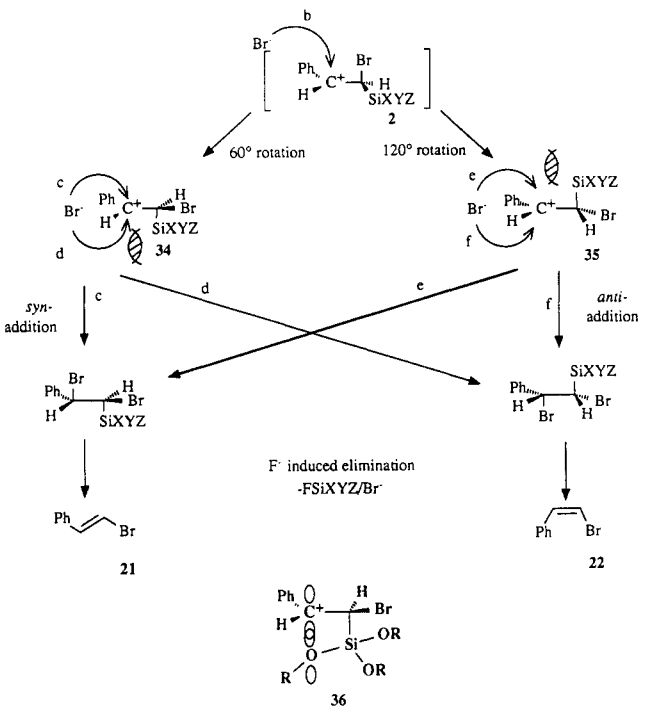
There is also an excellent correlation between the α-SiC*H* ^1H NMR chemical shift in the starting styrylsilanes and the degree of syn addition (Table II, Figure 2). As there are several factors upon which the chemical shift is dependent, the relative importance of which are difficult to establish, this relationship may or may not be of predictive use.[14]

For these compounds then, it can be clearly seen that the β-effect of a silyl group is directly related to the electron-withdrawing abilities of the ligands on silicon as expected.[31]

(Trialkoxy(phenoxy)silyl)styrenes. In the preliminary report of this work,[1] an exception to the electronegativity/syn addition correlation was noted with (trimethoxysilyl)styrene (**14**) (products **30a/s**). To determine

(30) Seebach, D.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 654.
(31) Traylor, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, J. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5717, and references cited therein.
(32) Mullay, J. *J. Am. Chem. Soc.* **1985**, *107*, 7271; **1984**, *106*, 5842.

Scheme V



whether this was an anomalous result, the (triphenoxysilyl)styrenes **18–20** were prepared and reacted under the same conditions. Somewhat surprisingly, the para substituents have little effect on the group electronegativities of the three phenoxy compounds.[33] The results are shown in Table III. It can clearly be seen from both the group electronegativity and chemical shift plots versus syn addition (Figures 1 and 2) that a quite different relationship exists compared to that of the (halomethylsilyl)styrenes.

These are several possible explanations for the observed difference in behavior between the (halomethylsilyl)-styrenes and the (alkoxy/phenoxysilyl)styrenes. The first relates to the nature of the silicon–oxygen bond. This bond is extremely strong and can be described as the sum of an O–Si σ-bond and O[n]–Si[σ*] interaction with π-character[34] (or a p–d π-interaction[35]). The latter interaction in effect pushes electron density toward the α-carbon, reducing the group electronegativity and leading to an enhanced β-effect.[36] Since Mullay's group electronegativity equation does not include a term for this type of back-donation,[33] the calculated electronegativity is too high. Thus, the apparently too high syn addition could just be an artifact of an insufficiently sophisticated model for electron distribution in compounds containing third-row elements.

The previous argument suggests that syn addition of bromide to **2** will be preferred due to electronic effects. However, the steric bulk of the silyl groups might also be expected to play an important role. When the angle between the C–Si bond and the p orbital is constrained to 60°, there is substantial β-stabilization.[37] However, the hyperconjugative stabilization is maximized when the C–Si bond is collinear (**34**, **35**; Scheme V) with the empty p orbital, as has been clearly shown by Lambert, Weber, and co-workers.[37–39] Thus, to maximize hyperconjugative stabilization of the carbonium ion **2** by the silyl group, C–C bond rotation would be expected. A 60° rotation to give **34** should be favored over a 120° rotation giving **35** by the principle of least nuclear motion and by the unfavorable interaction between bromide and the ortho proton on the phenyl ring during a 120° rotation (Scheme V). Irrespective of the degree of rotation, the bromide[24] should still be closest to the syn face of the molecule (paths c and e in Scheme V); the rate of diffusion of the bromide is expected to be slow compared to the rate of internal motions.

A degree of syn addition *higher* than predicted from the group electronegativity would be expected, however, from compounds with a bulky silyl group that preferentially react via **34**; syn bromide attack would be disfavored in paths d and e (Scheme V). A *lower* degree of syn addition would be expected from compounds that have significant β-stabilization, have a sterically demanding silyl group, and preferentially react via **35**. However, reactions taking place through **35** are not expected to be important for the reasons outlined above.

The alkoxy/phenoxysilyl groups have far larger steric bulk than the methyl/halosilyl groups. If as suggested above the attack of bromide preferentially occurs via **34**, then the group electronegativity would predict too *low* a degree of syn addition, an effect that could result in the deviations shown in Figure 1.

Similar deviations from the correlation could result from a through-space interaction of oxygen lone pairs in the alkoxysilanes with the empty p orbital of the carbonium ion. If as expected **34** is the favored rotamer, then the silyl group effectively blocks one face of the molecule (**36**; Scheme V) and bromide would be forced to add to give the syn adduct. Thus, once again, the group electronegativity would underestimate the syn selectivity that would be observed. The intriguing possibility that siloxetanes could be formed in such reactions is currently being examined in our laboratories. These latter two postulates can only be evaluated in light of further experimental results that establish the importance of the rotameric populations.

Conclusion

For silyl groups bearing halogens or methyl groups, the degree of the β-effect has been shown to be directly related to the electron-withdrawing ability of the ligands. The group electronegativity definition provided by Mullay[32] is a useful scale upon which to base relative stabilizing abilities.

In the case of alkoxy and phenoxysilanes, the relationship breaks down. This might simply be due to an insufficiently sophisticated electronegativity model[33] for groups containing atoms that can act as acceptors, such as silicon in the present study, or to other mechanistic

(33) The group electronegativity values presented in Table II are slightly different from those found in the preliminary communication of this work.[1] Dr. Mullay provided these values and the values in Table III for the silyl groups in compounds 14 and **18–20** for which we are very grateful. Several aspects of the Mullay electronegativity model have changed since the work described in ref 31, which will be reported in due course (personal communication).

(34) Reed, A. E.; Schade, C.; Schleyer, P. v. R.; Kamath, P. V.; Chandrasekhar, J. *J. Chem. Soc., Chem. Commun.* **1988**, 67. Oberhammer, H.; Boggs, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 7241.

(35) Voronkov, M. G.; Yuzhelevskii, Yu. A.; Mileshkevich, V. P. *Usp. Khim.* **1975**, *43*, 715. Janes, J.; Oldfield, E. *J. Am. Chem. Soc.* **1986**, *108*, 5743.

(36) Traylor argues that conjugation between the central atom and its substituents should not affect the degree of vertical stabilization provided by the central atom.[31] However, he also provides evidence that silyl groups are an exception to this rule, and therefore, we feel it appropriate to consider this possibility in the absence of more detailed experimental results.

(37) Lambert, J. B.; Wang, G.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.

(38) Koenig, K. E.; Weber, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 3416.

(39) Lambert, J. B.; Finzel, R. B. *J. Am. Chem. Soc.* **1982**, *104*, 2020.

effects that are related to the presence of the oxygen lone pairs and/or the steric bulk of the groups. Attempts to determine the reasons for this deviation by examining a broader range of (alkoxysilyl)styrenes are presently underway.

General Experimental Procedures

Apparatus, Materials, and Methods. Due to the tendency of the halo and alkoxy groups on silicon to hydrolyze easily, all reactions were carried out in dry apparatus under a nitrogen atmosphere with the use of septa and syringes for the transfer of reagents.

The continuous-wave ^1H NMR spectra were recorded on a Varian EM 390 (90-MHz) spectrometer and the Fourier spectra on a Bruker AM 500 (500-MHz) spectrometer. ^{13}C and ^{29}Si NMR were performed on a Bruker WM 250 (at 250 MHz for protons). Unless otherwise specified, the samples were dissolved in chloroform-*d* with tetramethylsilane (TMS) as internal standard. Chemical shifts of the brominated compounds **23a/s–33a/s** are reported with respect to the trimethylsilyl group in **23a** as standard, set to 0 ppm. Coupling constants (*J*) are recorded in hertz (Hz). The abbreviations, s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, and m = multiplet, are used in reporting the spectra. For some of the ^{13}C spectra of minor components (**23–33a/s**), it was not possible to see all the peaks. Such "missing peaks" are indicated by NA.

Electron-impact (EI) and chemical-ionization (NH_3) mass spectra were recorded at 70 eV with a source temperature of ca. 200 °C either on a VG Micromass 7070 F mass spectrometer equipped with a data system comprised of a PDP 8A with VG 2000 software or on a VG analytical ZAB E mass spectrometer equipped with a VG 11-250 data system. High-resolution mass spectral (HRMS) data were obtained with the VG-ZAB-E instrument by the EI method. Due to the thermal and hydrolytic instability of the compounds, combustion data could not be obtained. Therefore, the purity of new compounds **23–33** and **18–20** was confirmed by ^1H NMR that indicated a purity of ≥90% (**24** was an exception, see below).

Infrared spectra were run on a Perkin-Elmer 283 spectrometer in $CHCl_3$ solution, as a $CHCl_3$ film, as a neat film, or as a KBr pellet.

Phenylacetylene was obtained from Fluka, Aldrich, or BDH and distilled prior to use. H_2PtCl_6 and $(PPh_3)_3RhCl$ were obtained from Aldrich. A 0.1 M solution of the unpurified platinum catalyst was prepared in dried isopropyl alcohol (distilled from Mg). CS_2 was obtained from BDH, $CDCl_3$ was from MSD, and they were used without further purification. A 1 M solution of TBAF in $CDCl_3$ was prepared by removing the THF from a 1 M solution of TBAF (Aldrich) under reduced pressure and diluting the crystals with the corresponding volume of $CDCl_3$.

Hydrosilation with Methyl/chlorosilanes: General Procedure.[27] To a solution of phenylacetylene in THF was added a hydrosilane and H_2PtCl_6 (0.1 M in isopropyl alcohol). After the solution was stirred at room temperature overnight, the solvents were removed under reduced pressure and the residue was purified by distillation. *Note: On two occasions this reaction was extremely exothermic, and a rapid buildup of pressure was observed in the reaction vessel.*

(*E*)-β-(Dimethylchlorosilyl)styrene (8): phenylacetylene (11.0 mL, 100 mmol), $HSiMe_2Cl$ (22.2 mL, 200 mmol), THF (10 mL), H_2PtCl_6 (0.12 mL, 0.012 mmol); reaction temperature 80 °C; yield 8.28 g, 42%; bp 120–122 °C (12 Torr) [lit.[40] bp 70 °C (0.1 Torr)]; ^1H NMR (CS_2, 500 MHz) δ 0.51 (s, 6 H), 6.34 (d, 1 H, *J* = 19), 6.98 (d, 1 H, *J* = 19), 7.07–7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ 2.27, 124.86, 127.01, 128.77, 129.03, 137.47, 146.78; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ 18.76; HRMS (M^+) calcd 196.0472, obsd 196.0488; IR (neat) ν 3090, 3072, 3040, 3005, 2975, 1610, 1580, 1498, 1450, 1410–1400, 1335, 1255, 1218, 1198, 1120–1000, 990, 980, 930, 890–750, 740, 725, 685, 670, 658, 580 cm^{-1}.

(*E*)-β-(Dichloromethylsilyl)styrene (10): phenylacetylene (25.0 mL, 228 mmol), $HSiCl_2Me$ (36.4 mL, 350 mmol), THF (10 mL), H_2PtCl_6 (0.24 mL, 0.024 mmol); yield 46.81 g, 94%; bp 65–66 °C (2 Torr) [lit.[40] bp 80 °C (0.1 Torr)]; ^1H NMR (CS_2, 500 MHz) δ 0.77 (s, 3 H), 6.24 (d, 1 H, *J* = 18.9), 7.08 (d, 1 H, *J* = 18.9), 7.18–7.26 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ 5.56, 121.24, 127.22, 128.69, 129.66, 136.16, 149.17; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ 17.43; HRMS (*m/z*, M^+) calcd 215.9927, obsd 215.9939; IR (neat) ν 3085, 3070, 3035, 3010, 2980, 1610, 1580, 1497, 1450, 1405, 1335, 1290, 1263, 1220, 1200, 1190, 1070, 1028, 990, 980, 840, 820, 790, 785, 760, 730, 710, 685, 590 cm^{-1}.

(*E*)-β-(Trichlorosilyl)styrene (11): phenylacetylene (25.0 mL, 228 mmol), $HSiCl_3$ (35.4 mL, 350 mmol), THF (10 mL), H_2PtCl_6 (0.15 mL, 0.015 mmol); yield 43.16 g, 80%; bp 85–87 °C (3 Torr) [lit.[40] bp 78–80 °C (0.1 Torr)]; ^1H NMR (CS_2, 500 MHz) δ 6.21 (d, 1 H, *J* = 18.7), 7.21 (d, 1 H, *J* = 18.7), 7.19–7.25 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ 118.81, 127.64, 128.83, 130.45, 135.30, 151.50; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ −2.51; HRMS (*m/z*, M^+) calcd 235.9382, obsd 235.9404; IR (neat) ν 3090, 3060, 3030, 1670, 1605, 1580, 1495, 1450, 1340, 1335, 1290, 1220, 1195, 1180, 1025, 990, 980, 830, 815, 730, 685, 600 cm^{-1}.

Preparation of (*E*)-β-(Trimethylsilyl)styrene (7). To a solution of **11** (2.6 mL, 14.3 mmol) in THF (20 mL) was added MeLi (Aldrich; 1.4 M in ether; 61.2 mL, 85.8 mmol) at −78 °C. After being stirred for 4 h, the solution was allowed to warm to 25 °C overnight, was then recooled to −78 °C, and was quenched with water (60 mL); the residue was extracted with ether and washed with water; and the combined organic extracts were dried over $MgSO_4$. After removal of the solvents under reduced pressure, the product was distilled under reduced pressure: yield 2.33 g, 92%; bp 30–35 °C (5–7 Torr) [lit.[21] bp 55 °C (30 Torr)]; ^1H NMR (CS_2, 500 MHz) δ 0.15 (s, 9 H), 6.36 (d, 1 H, *J* = 19), 6.79 (d, 1 H, *J* = 19), 7.08–7.29 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ −1.18, 126.38, 127.89, 128.46, 129.37, 138.46, 143.75; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ −6.58; HRMS (*m/z*, M^+) calcd 176.1017, obsd 176.1024; IR (neat) ν 3082, 3066, 3035, 2995, 2962, 1610, 1578, 1496, 1450, 1260, 1250, 1210, 1195, 988, 870–860, 840, 815, 755, 720, 688 cm^{-1}.

Fluorination of (Chlorosilyl)styrenes: General Procedure. To the neat (chloromethylsilyl)styrene was added CuF_2 in the presence of H_2O.[28] After the solution was stirred for 1–1.5 h, the fluoride was distilled from the residue—the progress of the reaction was followed by monitoring the reflux temperature.

(*E*)-β-(Dimethylfluorosilyl)styrene (9): 8 (3.93 mL, 20.0 mmol), CuF_2 (1.01 g, 10.0 mmol), H_2O (0.36 g, 20.0 mmol), Et_2O (7 mL); reaction time 1 h; yield 0.91 g, 25%; bp 55 °C (9 Torr) [lit.[28] bp 102–103 °C (16 Torr)]; ^1H NMR (CS_2, 500 MHz) δ 0.33 (d, 6 H, J_{HF} = 7), 6.29 (dd, 1 H, J_{HH} = 19.3, J_{HF} = 3.3), 6.96 (d, 1 H, *J* = 19.3), 7.17–7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ −0.92 (d, J_{CF} = 15.9), 124.44 (d, J_{CF} = 16.4), 126.94, 128.80, 128.95, 137.76, 146.96 (d, J_{CF} = 2.7); ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ 20.19 (d, J_{SiF} = 274.1); HRMS (*m/z*, M^+) calcd 180.0767, obsd 180.0771; IR (neat) ν 3080, 3060, 3022, 2995, 2960, 2900, 1605, 1575, 1495, 1448, 1395, 1330, 1285, 1260–1250, 1212, 1195, 1175, 1150, 1065, 1020, 990, 930–700, 680, 650, 640 cm^{-1}.

(*E*)-β-(Difluoromethylsilyl)styrene (12): **10** (4.33 mL, 20.0 mmol), CuF_2 (2.02 g, 20.0 mmol), H_2O (0.72 g, 40 mmol), Et_2O (10 mL); reaction time 1.5 h; yield 2.62 g, 71%; bp 49–50 °C (8 Torr) [lit.[28] bp 86 °C (15 Torr)]; ^1H NMR (CS_2, 500 MHz) δ 0.38 (t, 3 H, J_{HF} = 5.9), 6.11 (dt, 1 H, J_{HF} = 2.75, J_{HH} = 19.5), 7.14 (d, 1 H, *J* = 19.5), 7.20–7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ −4.35 (t, J_{CF} = 18), 117.17 (t, J_{CF} = 20), 127.20, 128.90, 129.79, 136.83, 150.84; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ −11.07 (t, J_{SiF} = 286); HRMS (*m/z*, M^+) calcd 184.0517, obsd 184.0530; IR (neat) ν 3080, 3060, 3025, 3000, 2970, 1715, 1608, 1575, 1490, 1445, 1400, 1335, 1285, 1265, 1220, 1200, 1180, 1020, 990, 950–780, 730, 690, 680 cm^{-1}.

(*E*)-β-(Trifluorosilyl)styrene (13): **11** (1.35 mL, 6.7 mmol), CuF_2 (1.01 g, 10.0 mmol), H_2O (0.36 g, 20.0 mmol), Et_2O (5 mL); reaction time 1 h; yield 0.60 g, 47%; bp 56–58 °C (9 Torr) [lit.[28] bp 61–63 °C (15 Torr)]; ^1H NMR (CS_2, 500 MHz) δ 5.97 (dq, 1 H, J_{HF} = 3.0, J_{HH} = 19.6), 7.25–7.42 (m, 6 H); ^{29}Si NMR (CS_2, 49.69 MHz) δ −71.4 (q, *J* = 254.3); HRMS (*m/z*, M^+) calcd 188.0267, obsd 188.0270; IR (neat) ν 3060, 3020, 2950, 2920, 2860, 1650, 1605, 1570, 1490, 1445, 1335, 1285, 1220, 1195, 1180–1030, 1020, 990, 970–780, 765, 720, 675 cm^{-1}.

(40) Brennan, T.; Gilman, H. *J. Organomet. Chem.* **1969**, *16*, 63.

Preparation of (*E*)-β-(Trimethoxysilyl)styrene (14).[29] To a solution of 11 (2.6 mL, 14.3 mmol) in MeOH (1.5 mL) was added $HC(OMe)_3$ (10.0 mL, 90.0 mmol). The solution was stirred overnight at 25 °C and refluxed for 2 h, and the solvents and then the product were distilled from the reaction: yield 2.34 g, 73%; bp 78–80 °C air bath temperature (5 Torr) [lit.[41] bp 110–112 °C (7 Torr)]; ^1H NMR (CS_2, 500 MHz) δ 3.50 (s, 9 H), 5.99 (d, 1 H, J = 19.2), 7.08 (d, 1 H, J = 19.2), 7.17–7.33 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ 50.37, 115.96, 128.40, 128.69, 137.38, 149.56; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ −53.70; HRMS (m/z, M^+) calcd 224.0864, obsd 224.0875; IR (neat) ν 3060, 3030, 3000, 2950, 2850, 1610, 1580, 1500, 1450, 1330, 1290, 1220, 1200–1190, 1150–1030, 995, 850, 830–750, 730, 685, 665 cm^{-1}.

Preparation of Triphenoxysilanes: General Procedure. To the molten phenol (4 equiv) was added trichlorosilane (1 equiv), and the reaction mixture was stirred for 4 h at 50–80 °C depending on the melting point of the phenol. Excess phenol was removed by vacuum distillation and the residue used without purification.

Triphenoxysilane (15): phenol (15.06 g, 0.16 mol), $HSiCl_3$ (4.0 mL, 20 mmol); reaction temperature 50 °C; yield 8.9 g, 96%; ^1H NMR $CDCl_3$, 90 MHz) δ 5.02 (s, 1 H), 6.8–7.4 (m, 15 H); IR (neat) ν 3060, 3020, 2200, 1930, 1700, 1570, 1470, 1445, 1280–1170 (broad), 1150, 1055, 1030–900, 880, 830, 735, 670 cm^{-1}.

Tris(*p*-methoxyphenoxy)silane (16): *p*-methoxyphenol (10.0 g, 80 mol), $HSiCl_3$ (2.0 mL, 20 mmol); reaction temperature 80 °C; yield 5.7 g, 72%; ^1H NMR ($CDCl_3$, 90 MHz) δ 3.66 (s, 9 H), 4.72 (s, 1 H), 6.5–6.8 (m, 12 H); IR (neat) ν 3030, 2980, 2920, 2900, 2820, 2200, 1580, 1485, 1450, 1430, 1300–1180 (broad), 1170, 1090, 1015, 1000, 990–880 (broad), 880–790 (broad), 780, 665 cm^{-1}.

Tris(*p*-chlorophenoxy)silane (17): *p*-chlorophenol (5.15 g, 40 mol), $HSiCl_3$ (1.0 mL, 10 mmol); reaction temperature 65 °C; yield 3.2 g, 78%; ^1H NMR ($CDCl_3$, 90 MHz) δ 4.91 (s, 1 H), 6.83, 7.15 (ABq, 12 H, J = 10 Hz); IR (neat) 3080, 3060, 3030, 2220, 1870, 1575, 1470, 1430, 1390, 1300–1165 (broad), 1150, 1075, 1000–880 (broad), 880–770 (broad), 750, 730 cm^{-1}.

Hydrosilation with Triphenoxysilanes: General Procedure. To a solution of the phenoxysilane derivative in THF at 50 °C was added Wilkinson's catalyst [$(PPh_3)_3RhCl$, 0.005 M in benzene, 0.15 mol %]. Phenylacetylene (150 mol%) was then injected, and the reaction mixture was stirred for 48 h at 50 °C. THF and excess phenylacetylene were removed by vacuum distillation, and the residue was used for further reactions without extra purification.

(*E*)-β-(Triphenoxysilyl)styrene (18): phenylacetylene (5.6 mL, 5.0 mmol), $HSi(OC_6H_5)_3$ (1.0 g, 3.2 mmol), THF (10 mL), $(PPh_3)_3RhCl$ (0.2 mL (0.05 M), 10 μmol); yield 1.1 g, 84%; ^1H NMR (CS_2, 500 MHz) δ 6.19 (d, 1 H, J = 19.2), 6.86–7.33 (m, 21 H); ^{13}C NMR (CS_2, 125.8 MHz) δ 115.13, 120.09, 122.99, 127.43, 129.05, 129.77, 129.92, 137.16, 151.71, 153.31; ^{29}Si NMR (CS_2, 99.4 MH2) δ −69.03; HRMS (m/z, M^+) calcd 410.1332, obsd 410.1336; IR (neat) ν 3040, 3020, 1580, 1570, 1470, 1440, 1300–1170 (broad), 1150, 1060, 1010, 980, 970–850 (broad), 820, 800, 740, 720, 670 cm^{-1}.

(*E*)-β-[Tris(*p*-methoxyphenoxy)silyl]styrene (19): phenylacetylene (0.28 mL, 2.5 mmol), $HSi(OC_6H_4OMe\text{-}p)_3$ (0.40 mL, 1.0 mmol), THF (10 mL), $(PPh_3)_3RhCl$ (0.3 mL (0.005 M), 1.5 μmol); yield 0.28 g, 56%; ^1H NMR (CS_2, 500 MHz) δ 3.60 (s, 9 H), 6.14 (d, 1 H, J = 19.2), 6.49–7.29 (m, 21 H); ^{13}C NMR (CS_2, 125.8 MHz) δ 55.30, 114.83, 114.94, 120.54, 127.33, 128.99, 129.61, 137.24, 147.01, 151.29, 155.12; ^{29}Si NMR (CS_2, 49.7 MHz) δ −68.56; HRMS (m/z, M^+) calcd 500.1647, obsd 500.1648; IR (CS_2) ν 3040, 2980, 2940–2900, 2820, 1590, 1565, 1490, 1450, 1430, 1280–1175 (broad), 1170, 1085, 1020, 1000, 990–870 (broad), 815, 795, 720, 670 cm^{-1}.

(*E*)-β-[Tris(*p*-chlorophenoxy)silyl]styrene (20): phenylacetylene (0.28 mL, 2.5 mmol), $HSi(OC_6H_4Cl\text{-}p)_3$ (0.41 mL, 1.0 mmol), THF (10 mL), $(PPh_3)_3RhCl$ (0.3 mL (.005 M), 1.5 μmol); yield: 0.40 g, 70%; ^1H NMR (CS_2, 500 MHz) δ 6.19 (d, 1 H, J = 19.3), 7.36 (d, 1 H, J = 19.3), 6.68–7.38 (m, 17 H); ^{13}C NMR (CS_2, 125.8 MHz) δ 113.63, 121.25, 127.53, 128.65, 129.19, 130.03, 130.25, 136.76, 151.66, 152.77; ^{29}Si NMR (CS_2, 49.7 MHz) δ −68.23; HRMS (m/z, M^+) calcd 512.0165, obsd 512.0156; IR (neat) ν 3060, 3020, 2940, 2920, 2840, 2120, 1870, 1585, 1560–1400 (broad), 1300–1190 (broad), 1155, 1080, 1000, 990–890 (broad), 820, 760, 720, 675 cm^{-1}.

Bromination and Elimination Procedures for Vinyl Compounds 7–14 (Table I). To ≈0.5 mL of a 0.5 M solution of each styryl compound in $CDCl_3$ (cooled to ≈−60 °C, frozen $CDCl_3$) in an NMR tube was added a 1 M solution of bromine in $CDCl_3$ (room temperature), with constant shaking, until the color of the mixture persisted (ca. 0.3 mL). After the NMR spectrum was recorded, an excess of Bu_4NF (1 M in $CDCl_3$, 1.0 mL, 1.0 mmol) was added in order to produce the elimination products. The relative ratios of (*E*)- and (*Z*)-bromostyrene were determined by ^1H NMR.

Bromination Procedures for Vinyl Compounds 7–14 (Tables II and III). To each vinyl compound (≈1 mL, 0.5 M in CS_2) at −78 °C (acetone/CO_2) was added bromine (1.1 equiv of a 1 M in CS_2) precooled to −78 °C over ≈10 s. The reaction mixture was stirred for 15 min at −78 °C before being allowed to warm to room temperature.

Bromination Procedures for Vinyl Compounds 18–20 (Table III). The preceding procedure was followed except that the bromination was performed at −100 °C (diethyl ether/N_2) and the reaction time, after bromine addition, extended to 30 min at −100 °C before recording the NMR spectrum at room temperature.

***u*-1,2-Dibromo-2-phenyl-1-(trimethylsilyl)ethane (23s).** Syn Br_2 addition product of 7: ^1H NMR (CS_2, 250 MHz) δ 0.00 (s, 9 H), 3.85 (d, 1 H, J = 10), 5.21 (d, 1 H, J = 10), 7.31–7.46 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ 2.14, 49.63, 58.86, 128.42, 128.74, 129.62, 136.14; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ 7.08; HRMS (m/z $M^+ - SiMe_3$) calcd 260.8914, obsd 260.8925; IR (neat) ν 3105, 3080, 3060, 3030, 3006, 2960, 2920, 2900, 1712, 1608, 1570, 1515, 1490, 1450, 1440, 1275, 1250, 1218, 1176, 1135, 1080–1000, 995, 934, 870–800, 750, 725, 690–680, 620, 610, 600, 562 cm^{-1}.

***u*-1-(Chlorodimethylsilyl)-1,2-dibromo-2-phenylethane (24s).** In the bromination of this compound, several undetermined side reactions were observed that led to compounds that did not lead to bromosilane in the reaction with TBAF. Only one of the compounds present (ca. 65% purity by NMR) eliminated $Me_2SiClBr$ to give (*E*)-bromostyrene. It is on this basis that we assign the "100% syn addition". Syn Br_2 addition product of 8: ^1H NMR (CS_2, 250 MHz) δ 0.32 (s, 6 H), 3.88 (d, 1 H, J = 7.3), 5.41 (d, 1 H, J = 7.3), 7.16–7.49 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ 1.80, 2.57, 52.60, 57.09, 128.29, 128.54, 129.04, 139.57; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ −22.28, −21.87, −19.44, 21.70, 22.97; HRMS (m/z, M^+ − Br) calcd 274.9656, obsd 274.9664; IR (neat) ν 2970, 1520, 1495, 1455, 1260, 1120–980, 875–770, 760, 725, 695, 605 cm^{-1}.

***u*/*l*-1,2-Dibromo-1-(fluorodimethylsilyl)-2-phenylethane (25s/25a = 85/15).** Syn Br_2 and anti Br_2 addition product of 9: ^1H NMR ($CDCl_3$, 500 MHz) δ 0.20 (d, 5.10 H, J_{HF} = 7.3, syn), 0.40 (d, 0.90 H, J_{HF} = 7.3, anti), 3.93 (d, 0.85 H, J = 10.0, syn), 4.08 (d, 0.15 H, J = 10.0, anti), 5.23 (d, 0.15 H, J = 10.0, anti), 5.27 (d, 0.85 H, J = 10.0, syn), 7.24–7.46 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) syn δ −2.14 (d, J_{CF} = 53.4), −1.92 (d, J_{CF} = 53.4), 46.11 (d, J_{CF} = 13.4), 58.18, 127.86, 129.04, 129.54, 139.96; ^{13}C NMR anti δ NA, NA, 44.0, 51.92, 128.78, 129.03, NA, NA; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ 21.07 (d, J_{SiF} = 290); HRMS (m/z, M^+ − Br) calcd 258.9951, obsd 258.9953; IR (neat) ν 3060, 3025, 2960, 1490, 1450, 1395, 1280, 1255, 1212, 1175, 1135, 1090, 1070, 1030, 1020, 995, 910–810, 800, 760, 740, 720, 690, 660, 600, 560 cm^{-1}.

***u*/*l*-1,2-Dibromo-1-(dichloromethylsilyl)-2-phenylethane (26s/26a = 75/25).** Syn Br_2 and anti Br_2 addition product of 9: ^1H NMR (CS_2, 500 MHz) δ 0.60 (s, 0.75 H, anti), 0.81 (s, 2.25 H, syn), 3.91 (d, 0.75 H, J = 6.7, syn), 4.11 (d, 0.25 H, J = 7.1, anti), 5.36 (d, 0.75 Hz, J = 6.7, syn), 5.40 (d, 0.25 H, J = 7.1, anti), 7.24–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) syn δ 5.62, 47.46, 55.26, 128.04, 128.68, 129.33, 138.86; ^{13}C NMR anti δ 5.26, 46.17, 50.80, 128.29, 128.43; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ 14.69 anti, 17.66 syn; HRMS (m/z, M^+ − Br) calcd 294.9111, obsd 294.9124; IR (neat) ν 3070, 3040, 1495, 1450, 1400, 1260, 1240, 1220, 1140–1000, 840, 810, 790, 770, 755, 720, 690, 590 cm^{-1}.

***u*/*l*-1,2-Dibromo-2-phenyl-1-(trichlorosilyl)ethane (27s/27a = 55/45).** Syn Br_2 and anti Br_2 addition product of 11: ^1H NMR (CS_2, 500 MHz) δ 4.04 (d, 0.55 H, J = 8.4, syn), 4.23 (d,

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0.45 H, J = 8.4, anti), 5.25 (d, 0.55 H, J = 8.4, syn), 5.29 (d, 0.45 H, J = 8.4, anti), 7.25–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) δ 44.41, 46.18, 49.48, 54.58, 128.13 (double peak), 128.57, 128.90, 129.37, 129.73, 138.24, 138.57; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ −4.78 anti, −2.87 syn; HRMS (m/z, M^+ − Br) calcd 314.8566, obsd 314.8567; IR (neat) ν 3080, 3050, 2950, 1525, 1500, 1460, 1290, 1240, 1220, 1145, 1100, 1080, 1025, 915, 840, 830, 805, 760, 695, 650, 610 cm^{-1}.

***u*/*l*-1,2-Dibromo-1-(difluoromethylsilyl)-2-phenylethane (28s/28a = 40/60).** Syn Br_2 and anti Br_2 addition product of **12**: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.32 (t, 1.2 H, J_{HF} = 6.0, syn), 0.58 (t, 1.8 H, J_{HF} = 5.9, anti), 3.87 (dt, 0.4 H, J_{HH} = 2.2, 9.3, syn), 4.03 (dt, 0.6 H, J_{HH} = 1, 10.6, anti), 5.20 (d, 0.6 H, J = 10.6, anti), 5.27 (d, 0.4 H, J = 9.3, syn), 7.33–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) syn δ −5.40–4.75 (m), 41.26 (t, J_{CF} = 14.9), 55.43, 127.92, 129.13, 129.79, 138.96; ^{13}C NMR anti δ −5.40–4.75 (m), 38.42 (t, J_{CF} = 15.5), 50.03, 127.92, 128.97, 129.43, 139.54; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ −15.90 (t, J_{SiF} = 301) syn, −14.93 (t, J = 297) anti; HRMS (m/z, M^+ − Br) calcd 262.9701, o bsd 262.9721; IR (neat) ν 3080, 3060, 3035, 2930, 1520, 1510, 1495, 1455, 1400, 1300, 1285, 1270, 1235, 1220, 1180, 1140, 1100, 1070, 1030, 1020, 1000, 950–850, 830, 810–800, 760, 690, 670, 620, 605, 590, 560 cm^{-1}.

***u*/*l*-1,2-Dibromo-1-(trifluorosilyl)-2-phenylethane (29s/29a = 15/85).** Syn Br_2 and anti Br_2 addition product of **13** (it was impossible to distinguish the anti and syn products in the ^{1}H NMR): ^{1}H NMR (CS_2, 250 MHz) δ 3.67–4.20 (m, 1 H), 5.02–5.38 (m, 1 H), 7.00–7.51 (m, 5 H); HRMS (m/z, M^+ − Br) calcd 266.9451, obsd 266.9474; IR (neat) ν 3030, 3015, 1600, 1570, 1490, 1445, 1280, 1130–1025, 1020, 985, 960–855, 830, 815, 750, 725, 710, 680 cm^{-1}.

***u*/*l*-1,2-Dibromo-1-(trimethoxysilyl)-2-phenylethane (30s/30a = 80/20).** Syn Br_2 and anti Br_2 addition product of **14**: ^{1}H NMR (CS_2, 250 MHz) δ 3.45 (s, 7.2 H, syn), 3.57 (s, 1.8 H, anti), 3.71 (d, 0.8 H, J = 9.1, syn), 3.87 (d, 0.2 H, J = 8.2, anti), 5.22 (d, 0.8 H, J = 9.1 syn), 5.30 (d, 0.2 H, J = 8.2, anti), 7.28–7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$, 62.90 MHz) syn δ 40.97, 51.61, 58.36, 127.94, 128.34, 128.76, 140.24; ^{13}C NMR anti δ 41.79, 52.32, 57.65, 128.12, 128.62, 129.47, 140.53; ^{29}Si NMR ($CDCl_3$, 49.69 MHz) δ −62.53 syn, −61.51 anti; HRMS (m/z, M^+ − $Si(OMe)_3$) calcd 260.8914, obsd 260.8919; IR (neat) ν 3080, 3050, 3000, 2960, 2860, 1530, 1500, 1460, 1290, 1195, 1170–1050, 1040, 880–785, 770, 700, 670, 610, 570 cm^{-1}.

***u*/*l*-1,2-Dibromo-1-(triphenoxysilyl)-2-phenylethane (31s/31a = 85/15).** Syn Br_2 and anti Br_2 addition product of **18**: ^{1}H NMR (CS_2, 500 MHz) δ 3.98 (d, 0.85 H, J = 9.3, syn), 4.09 (d, 0.15 H, J = 9.0, anti), 5.24 (d, 0.85 H, J = 9.3, syn), 5.31 (d, 0.15 H, J = 9.0, anti), 6.52–7.33 (m, 20 H); ^{13}C NMR (CS_2, 125.8 MHz) δ 40.20, 57.07, 119.88, 123.33, 128.34, 128.71, 129.13, 129.79, 139.82, 152,54; HRMS (m/z, M^+) calcd 567.9700, obsd 567.9692; IR (neat) ν 3060, 3020, 1585, 1530–1450 (broad), 1445, 1290–1190 (broad), 1155, 1060, 1015, 995, 980–930 (broad), 920, 745, 680 cm^{-1}.

***u*/*l*-1,2-Dibromo-1-[tris(*p*-methoxyphenoxy)silyl]-2-phenylethane (32s/32a = 85/15).** Syn Br_2 and anti Br_2 addition product of **19**: ^{1}H NMR (CS_2, 500 MHz) δ 3.65 (s, 7.65 H, syn), 3.73 (s, 1.35 H, anti), 3.91 (d, 0.85 H, J = 9.2, syn), 4.03 (d, 0.15 H, J = 8.8, anti), 5.20 (d, 0.85 H, J = 9.2, syn), 5.28 (d, 0.15 H, J = 8.8, anti), 6.54–7.24 (m, 17 H); ^{13}C NMR (CS_2, 125.8 MHz) δ 55.36, 56.33, 57.27, 114.70, 120.38, 124.98, 128.36, 128.71, 129.02, 146.29, 155.29; HRMS (m/z, M^+) calcd 658.0015, obsd 658.0024; IR (neat) ν 3000, 2940, 2920, 2820, 2280, 2140, 1610–1400 (broad), 1260, 1200, 1175, 1050, 970, 855, 790 cm^{-1}.

***u*/*l*-1,2-Dibromo-1-[tris(*p*-chlorophenoxy)silyl]-2-phenylethane (33s/33a 80/20).** Syn Br_2 and anti Br_2 addition product of **20**: ^{1}H NMR (CS_2, 500 MHz) δ 3.98 (d, 0.8 H, J = 9.0), 4.09 (d, 0.2 H, J = 9.4), 5.23 (d, 0.8 H, J = 9.0), 5.25 (d, 0.2 H, J = 9.4), 6.62–7.34 (m, 17 H); ^{13}C NMR (CS_2, 125.8 MHz) δ 37.66 anti, 39.63 syn, 51.14 anti, 56.28 syn, 120.97 anti, 121.11 syn, 128.11 128.29, 128.85, 129.14, 129.22, 129.36, 129.50, 129.88, 129.96, 139.41 syn, 150.81 syn, 151.00 anti; HRMS (m/z, M^+) calcd 590.9349, obsd 590.9367; IR (neat) ν 2280, 2140, 1570–1435 (broad), 1260, 1230, 1080, 1000, 960, 815 cm^{-1}.

Elimination Reactions. The CS_2 was blown off in a stream of N_2 and replaced by $CDCl_3$. All elimination reactions were performed at room temperature in an NMR tube by addition of an excess of a 1 M solution of TBAF in $CDCl_3$. The ratio of **15** to **16** as shown in Table I was determined by comparing the ^{1}H NMR peaks with those in a commercial sample (Aldrich).

(*Z*)-Bromostyrene (21)/(*E*)-Bromostyrene (22): (250 MHz, $CDCl_3$) δ 6.46 (d, 0.08 H, J = 8.1 Hz, Z), 6.79 (d, 0.92 H, J = 14.1 Hz, E), 7.10 (d, 0.08 H, J = 8.1 Hz, Z), 7.14 (d, 0.92 H, J = 14.1 Hz, E), 7.23–7.43 (m, 5 H).

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Supplementary Material Available: ^{1}H NMR spectra for compounds **18–20** and **23–33** (14 pages). Ordering information is given on any current masthead page.