Pergamon

Tetrahedron Vol. 50, No. 39, pp. 11379-11390, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00703-9

Proton Addition to Silylstyrenes: Overcoming the Predilection for Protiodesilylation

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Abstract: Normally, organosilyl nucleophiles such as vinylsilanes and allylsilanes undergo protiodesilylation reactions with protons. To favour addition reactions under these conditions, the ligands on silicon have been modified such that the leaving group ability and, simultaneously, the β-effect of the silyl group is reduced. In the case of allylsilanes, the use of dichlorosilyl groups does not significantly favour addition over substitution processes at the olefin. However, with vinylsilanes bearing a second π-nucleophile, a dichlorosilyl group can be used to regioselectively direct the formation of two bonds (C-H and C-C) sequentially in a process in which the silicon is not lost from the molecule, but may ultimately be cleaved leading to the formation of diols. Thus, benzyldichlorostyrylsilane **7**, after cyclization to **9** in the presence of triflic acid, is converted into diol **12**. The synthetic utility of this process is restricted by the relatively low reactivity of the styryl π-system and the necessarily reactive electrophiles needed to initiate the process. The effect of changing from electron-donating groups to electronegative groups on silicon on reaction mechanism is discussed.

INTRODUCTION

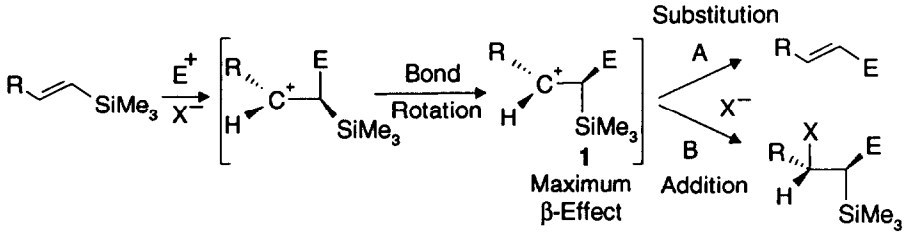
Organosilyl π-nucleophiles (vinylsilanes, allylsilanes, etc.) undergo stereoselective substitution reactions with a wide variety of electrophiles. The regiocontrol of the reaction arises from the β-effect, the hyperconjugatively stabilized intermediate β-silyl cation **1**.[2] Such reactions usually terminate with the loss of silicon (Scheme 1A). A greater synthetic advantage would arise in the circumstance that the silicon remains in the molecule (Scheme 1B) where it could mediate further synthetic elaboration before ultimately being excised from the molecule.[3]

There are several circumstances under which the regioselective reaction results in addition[4,5,6] rather than substitution: i) when the hyperconjugative stabilization cannot be properly realized because of geometrical constraints;[7,8,9] ii) when a primary carbocation would be formed;[10] iii) when nucleophilic attack at silicon is hindered by bulky spectator ligands;[11,12] and, iv) when the leaving group ability of the silyl group is sufficiently low because it bears electron-withdrawing groups.[12,13,14,15,16,17]

The latter two of these strategies for silicon retention appear to be generally applicable. The use of bulky ligands, however, requires a careful choice of groups that will protect the silicon during the first addition step of the reaction but which, for other reasons, may somehow allow the silicon to be subsequently activated to cleavage from the carbon skeleton. We have instead chosen to examine under which conditions electron-poor silyl groups act both as regiochemical directors and surrogates for other functional groups.

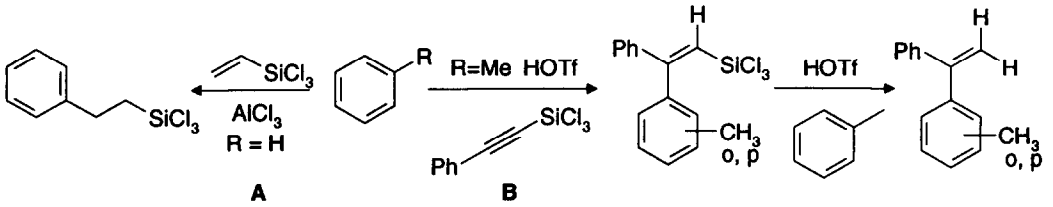
GENERAL CONSIDERATIONS

The β-effect. The ability of silicon to stabilize a β-carbenium ion is directly related to the electronegativity of the ligands bonded to it. Thus, we[18] and others[12,17,19] have shown that the β-effect for trialkylsilyl groups is much higher than that for trihalosilyl species. However, with an increase in the β-effect there is a concurrent increase in the leaving group ability of the silyl group.



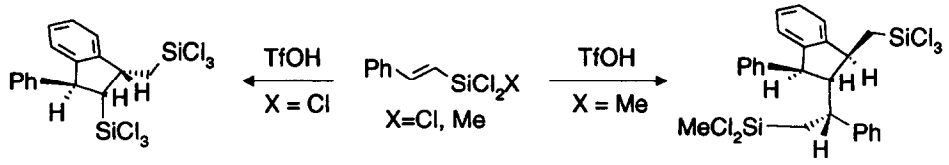
Scheme 1

Leaving group ability. The work of Andrianov[15] and Bailey[16] demonstrated that trichlorosilyl groups can survive electrophilic addition to a vinylsilane (Scheme 2A). Even this group, however, has been shown to be susceptible to elimination (Scheme 2B).[20] How then, to find a silyl group with a sufficiently high β-effect to provide regiochemical control, but a sufficiently low leaving group ability so as to facilitate addition?[21]



Scheme 2

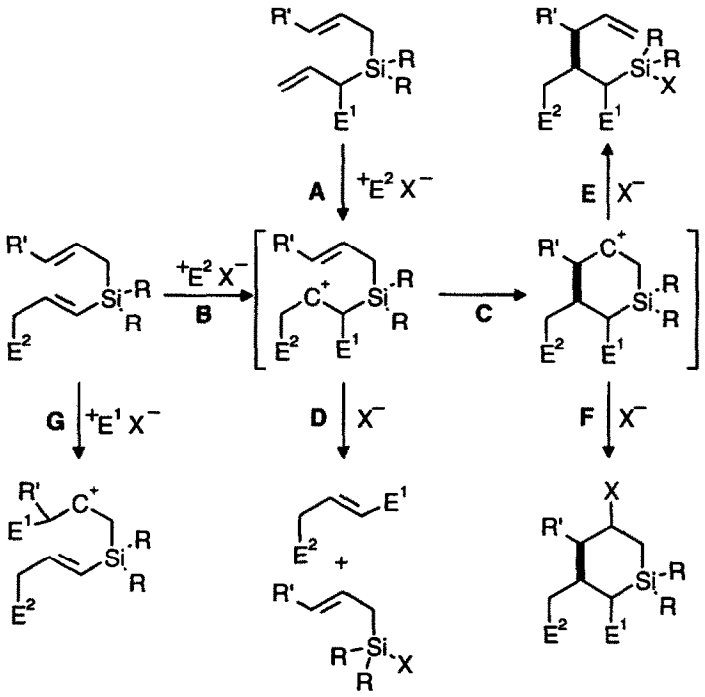
We have previously reported that *E*-β-(trichlorosilyl)styrene undergoes a diastereoselective dimerization reaction with complete retention of the silyl group.[13] The apparently subtle change from trichloro- to *E*-β-(dichloromethylsilyl)styrene led to a diastereoselective trimerization with, importantly, substantial (*ca.* 35%) loss of the silyl group (Scheme 3).[13] The higher β-effect[18] of $SiCl_2Me$ than $SiCl_3$ is accompanied by a better leaving group ability.



Scheme 3

Thus, with an alkyldichlorosilyl group, one is already at the boundary of synthetic utility in an addition reaction; groups with a better β-effect will also undergo elimination more readily (however, *vide infra*). In order to take advantage of this observation, we chose to examine reactions in which the initial electrophilic addition is followed by an intramolecular, dialkyldihalosilyl-mediated rearrangement (Scheme 4). Such a reaction should facilitate the addition process, in that *intra*molecular nucleophilic attack at carbon by a silyl-π-

nucleophile (Scheme 4C) should occur more rapidly than *inter*molecular attack at silicon by a halide counterion (Scheme 4D). Furthermore, the cyclic transition state (Scheme 4C) might lead to the control of relative stereochemistry (Scheme 4, boldface bond).



Scheme 4

We have specifically focused on the use of Cl_2Si groups in the examination of electrophile initiated, cyclization reactions and report the results of our examination below.

RESULTS

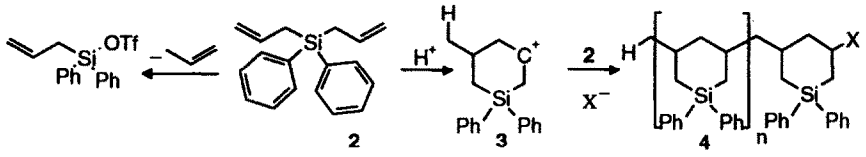
DIALLYL COMPOUNDS

Our first approach was to use diallylsilanes (Scheme 4A). The reaction of diallyldimethylsilane (E^1, R' = H, R = Me) with triflic acid, as expected for a trialkylsilyl leaving group, led to loss of propene and formation of allyldimethylsilyl triflate (Scheme 4D, R = Me, E^1, E^2 = H, X = $^-OSO_2CF_3$).[22]

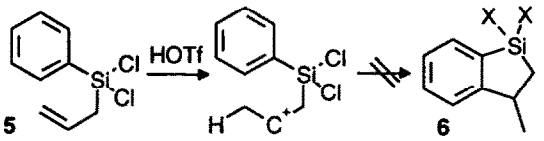
Diallyldichlorosilane and diphenyldiallylsilane **2** were, at first sight, more encouraging in that simple protiodesilylation did not occur. Rather, a mixture of oligomeric products was obtained. Clearly, in addition to protiodesilylation and cyclization, species such as **3** could act as electrophiles in the reaction leading to polymers of type **4** (Scheme 5).[23]

ALLYLVINYL COMPOUNDS

As diallylsilanes were still too reactive with respect to desilylation, we examined allylvinylsilanes. These species should, in principle, be able to form 5-membered rings rather than the 6-membered rings described above (Scheme 4). The reaction of triflic acid with allyldichlorophenylsilane **5** was expected to lead to compound **6**. However, a mixture was formed that included protiodesilylation products and alkylated benzenes but no evidence for **6** (Scheme 6).



Scheme 5



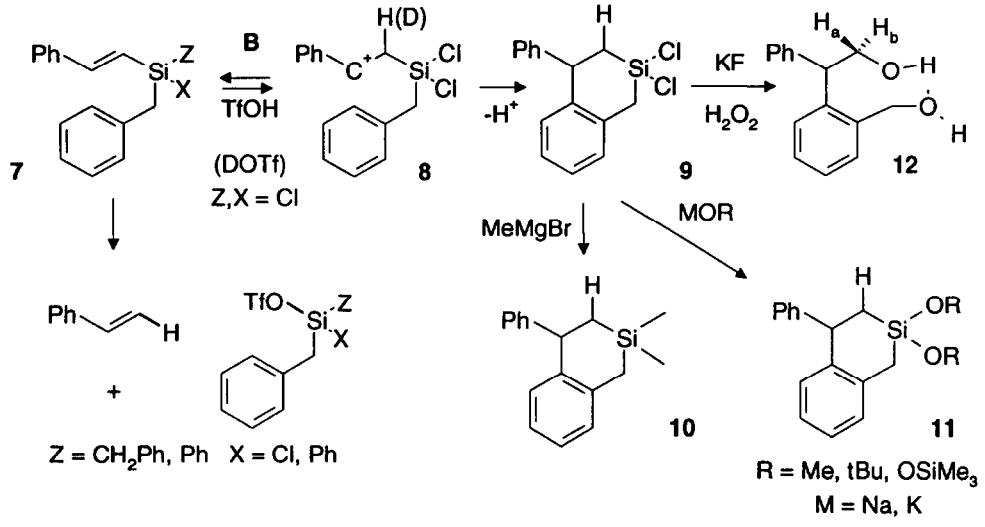
Scheme 6

The cyclization leading to a 5-ring might be hampered[24] by ring strain which arises from the fact that Si-C bonds are much longer than C-C bonds.[25] In order to examine if ring strain was indeed important, we decided to attempt a cyclization involving vinylallylsilanes which involved, in analogy with the diallyl systems, the formation of a 6-membered ring (Scheme 4B). As vinylsilanes are normally much less reactive towards electrophiles than allylsilanes for both steric and electronic reasons (*vide infra*), it was necessary to utilize a special allylsilane in which the reactivity trend is reversed: the desired reaction path leading to a 6-membered ring would not be available if the allyl group were to react first with the electrophile (Scheme 4G). For instance, the addition of triflic acid to allylstyryldichlorosilane led to protiodesilylation of the allyl group and, additionally, oligomeric species reminiscent of those derived from trichlorosilylstyrene;[14] signals from both π-systems disappeared in the ^{1}H NMR.

A benzyl group serves as an allylsilane of lower reactivity than a vinylsilane. The triflic acid initiated reaction of E-β-(benzyldiphenylsilyl)styrene and E-β-(dibenzylchlorosilyl)styrene led simply to protiodesilylation (Scheme 7A). In contrast, the reaction of E-β-(benzyldichlorosilyl)styrene **7** with triflic acid, cleanly gave the cyclization product **9** via the β-silyl cation **8** (Scheme 7B). The NMR suggested quantitative formation of **9**; the isolated yield (65%) was determined after conversion of dichlorosilyl group **9** to the more stable dimethyl derivative **10** and distillation.

9 could alternatively be converted to a series of dialkoxy species **11** leaving the silicon at the same oxidation level. The methoxy and even the more bulky *t*-butoxy derivatives were susceptible to hydrolysis and could not be chromatographed. In contrast, the bis(trimethylsiloxy) derivative **11** (R = $OSiMe_3$), prepared using commercially available Me_3SiOK, could be chromatographically separated on silica gel. In principle, this silicone species could be subsequently reconverted to the chlorosilane by the use of redistribution reactions with $SiCl_4$[26,27] or otherwise functionalized. Thus, this silicone moiety is a convenient protecting group for hydrolytically unstable silane derivatives. Compound **9** could also be oxidized using with H_2O_2 and KF to yield the diol **12**.[28]

In an attempt to probe the reaction mechanism, in particular to examine the stability of the proposed intermediates, we also examined deuteration. The reaction of **7** with DOTf leads to the formation of mono- (38%, 1:1 diastereomeric ratio by ^{1}H NMR and ^{2}H NMR) and dideuterated (16%) **9(*d*)** (Scheme 7). The presence of the dideuterated compound showed that the initial protonation is reversible. At the beginning of the reaction, when the concentration of DOTf is reasonably high, a second deuteration can occur (i.e., **7 (H)** → **8 (DH)** → **7 (D)** → **8 (D_2)** → **9 (D_2)**). The absence of diastereoselectivity in the deuteration process could arise from a loss of stereochemical integrity in the reversible protonation, which may be related to a reduced β-effect (*vide infra*). Alternatively, it could result from both *syn*- and *anti*-additions of the proton/ benzyl group to the styryl double bond.



Scheme 7

DISCUSSION

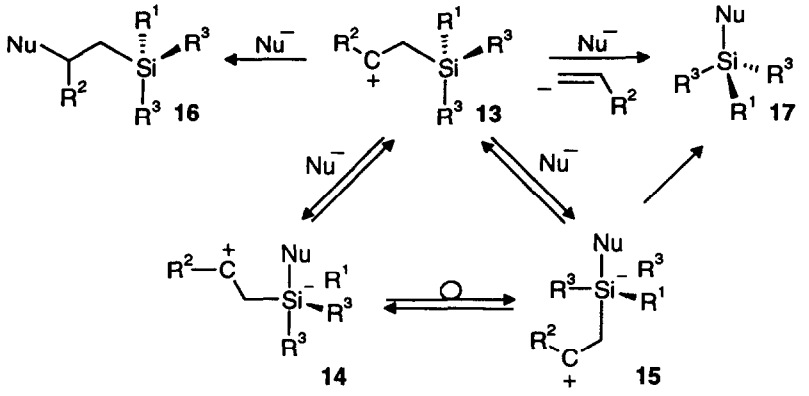
MECHANISTIC IMPLICATIONS

The replacement of the usual electron-donating alkyl groups on silicon with electronegative groups such as chloride dramatically affects the chemical outcome of the reactions of the carbon π-systems bonded to silicon because of changes in reactivity of the silyl nucleophile and leaving group ability of the silyl group.

Electron-withdrawing groups adversely affect the electron density in the carbon π-system. As a result, the desired reactions are only initiated by extremely reactive electrophiles such as triflic acid; our experience shows that a series of less reactive electrophiles including weaker acids and more stable carbon electrophiles such as Ph_3C^+, simply fail to react.[29]

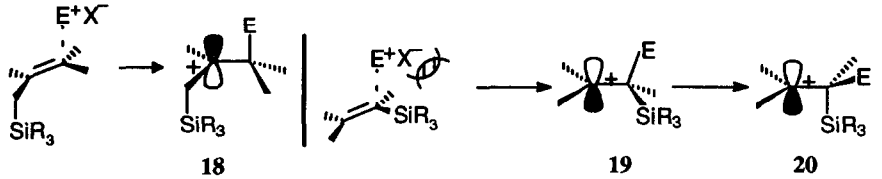
The most important observation for this study was that the leaving group ability of the alkyldichlorosilyl groups was attenuated when compared with trialkylsilyl groups. This could be most clearly seen from the deuteration studies. The production of dideuterated **9** shows that **8** is formed reversibly from **7**; proton (deuteron) loss occurs more efficiently than the formal loss of "$^+SiCl_2CH_2Ph$". This arises from mechanistic features at both silicon and carbon.

Unlike carbenium ions, of which many stable examples exist, silylium ions are extremely rare in condensed phase.[30] Nucleophilic substitution reactions at silicon are normally bimolecular in nature, with attack by the nucleophile the requisite first step. For the silyl group to be cleaved from the carbon backbone (**16** → **20**, Scheme 8), the requisite first step will be nucleophilic attack at silicon. With respect to the mechanism occurring at silicon with chlorosilyl groups, the difference in leaving group ability may result from the relative apicophilicity of chloride and the alkyl carbenium ion. If the chloride has a higher apicophilicity,[31] following addition of the electrophile to give **13**, subsequent nucleophilic attack to give the pentacoordinate species **14** (R^3=Cl) will be favoured over production of **15** (there will also be an energy barrier between the two).[32] Reversion to **13** will be followed by attack of a nucleophile at carbon giving **16**. In contrast, an alkyl group would be expected to be preferentially equatorial **15** (R^3=Me) leading subsequently to the elimination product **17** (Scheme 8).



Scheme 8

With respect to the mechanism at carbon, the coplanar arrangement of the Si-C bond relative to the empty p orbital, required for optimum β-stabilization of the intermediate cation (**18**, **20** from allyl- and vinylsilanes, respectively), is also highly conducive to Si-C bond elimination.[33] Allylsilanes are normally more reactive than vinylsilanes towards electrophiles because there is little or no steric interaction between the incoming electrophile and the silyl group **18**. In contrast, the electrophile must add to the vinylsilane at the carbon bearing the silyl group engendering potentially severe steric interactions **19**; for the β-effect to manifest itself, molecular rotation is required (**19**→**20**, Scheme 9).



Scheme 9

Although alkyldichlorosilyl groups have a lower leaving group ability than trialkylsilyl groups for the reasons cited above, allyl groups were still readily cleaved from these species, suggesting the β-effect was operating. To overcome the general preference in reactivity of allylsilyl over vinylsilyl groups towards both electrophilic addition and elimination, we utilized benzylstyrylsilane **7**, where the benzyl system is a rather special allyl group. In this case, the undesired silyl group elimination was not observed.

To further examine the reasons for retention of the silyl group and to determine the effect of the silyl group in the bond forming processes, we modelled the cyclization reaction of **8** using molecular mechanics to determine the orientational parameters of the reaction. As parameters are not available for the Si-Cl bond, we worked with analogous Si-Me derivatives **21**, **22**. When the distance α between the 2 interacting carbons (Ca-Cb) in **21** was held to 2.5 Å, to mimic the approach in the bond forming process between these two centres, the resultant angle ϕ_1 between the Si-C bond and the empty p orbital in the minimized structure was 84° (Figure 1). This angle implies the β-effect is not facilitating C-C bond formation and, simultaneously, indicates why no elimination occurs; the geometry required for cyclization is not appropriate for facile elimination of the silyl group. It may also help to explain why the initial protonation was reversible. In contrast, following cyclization to, **22** the angle ϕ_2 between the C-Si σ orbital and the pentadienyl cation was found to be 26° and the σ-orbital can, on geometric grounds, provide stabilization of the cation.

That cyclization of **7** occurs, through a geometry similar to **21**, rather than protiodesilylation suggests that the β-effect of the $PhCH_2SiCl_2$ group is rather low, as noted above for other halosilanes. It may not play an important role in the cyclization process of **7**: the all carbon compound similar to **7**, 1,4-diphenyl-1-butene, cyclizes in the presence of electrophiles to tetrahydronaphthalene derivatives.[34] However, if the β-effect were not operating at all, one would not expect the facile protiodesilylation observed for the related $allylSiCl_2CH_2Ph$ species.

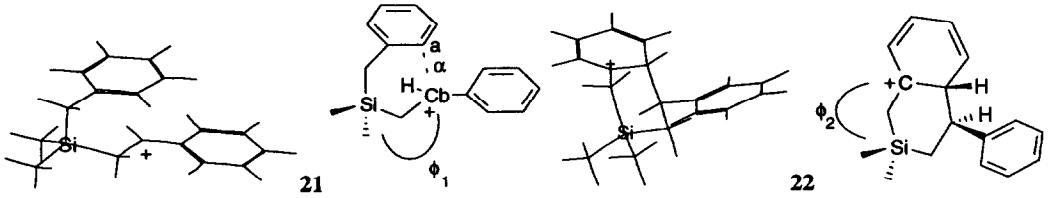


Figure 1: Reaction of **7** with triflic acid: **21**: Intramolecular *syn*-approach, minimized with distance constraint Ca-Cb α = 2.5 Å (resultant ϕ_1 Si-C-C-p orbital = 84 °), **22**: Fully cyclized structure (resultant ϕ_2 Si-C-C-p orbital = 26°).

CONCLUSION

The replacement of trialkylsilyl with dichloroalkyl silyl groups on an olefin reduces the leaving group ability such that, if styryl and benzyl groups are linked to a dichlorosilyl group, a proton initiated cyclization occurs. Sequential CH and C-C bond formation occurs without significant competition from either loss of silicon or oligomerization. The silicon containing 6-membered ring **9** can be oxidatively cleaved leading to diol **12**. Thus, by appropriate combination of the β-effect, alkene reactivity, silyl leaving group ability and geometrical constraint, one can design reactions in which silicon provides a controlling role for more than one bond formation and may be subsequently excised from the molecule in a synthetically useful way.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada and the Canadian International Development Agency (CIDA) for awarding a Graduate Fellowship to *C.H.* We thank Professor Herbert Mayr (Darmstadt) for helpful discussions.

EXPERIMENTAL SECTION

APPARATUS, MATERIALS, AND METHODS

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 or Bruker AC-200 (200 MHz) spectrometer. ^2H, ^{13}C and ^{29}Si-NMR were performed on a Bruker AC-300 (at 300 MHz for protons) and Bruker WM-250 (at 250 MHz for protons). Chemical shifts are reported with respect to tetramethylsilane 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, doublet of quartets, m = multiplet, are used in reporting the spectra.

Electron impact (EI) and chemical ionization (CI, NH_3) mass spectra were recorded at 70 eV with a source temperature of *ca.* 200°C an 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.

Infrared spectra were run on a Perkin Elmer 283 spectrometer and Fourier spectra on a BIO RAD FTS-40 spectrometer, as neat films.

The purity of new compounds was confirmed, after distillation, by HP-5890A Gas Chromatograph; 2-3755 glass capillary column, SPB-1, 30 meters, 1 m, 0.075 mm ID.

All solvents were thoroughly dried before use. Dichloromethane was distilled over P_2O_5. Diethyl ether, THF and hexane were distilled over Na/benzophenone. NEt_3 was dried by refluxing with NaOH and distilling over BaO.

Diallyldimethylsilane, diphenyldichlorosilane and phenylallyldichlorosilane were obtained from Hüls America (Petrarch). Triflic acid-*d* was purchased from Aldrich. Diallyldiphenylsilane[35] was prepared by the reaction in Et_2O of diphenyldichlorosilane with allylmagnesium bromide (Aldrich, 1M in Et_2O). (*E*)-β-(Trichlorosilyl)styrene was prepared by the H_2PtCl_6 catalyzed hydrosilation of phenylacetylene with $HSiCl_3$ in THF.[36]

Due to the tendency of halo groups on silicon to hydrolyze easily (CAUTION, hydrolysis leads to production of HCl), all reactions were carried out in dry apparatus under a nitrogen atmosphere with the use of septa and syringes for the transfer of reagents.

Diallyldichlorosilane. To a solution of tetrachlorosilane (25.9 g, 152.4 mmol) in diethyl ether (240 mL) was slowly added allylmagnesium bromide (305 mL of 1.0 M in Et_2O, 30.5 mmol) at -100 °C. After stirring for 16 h at -100 °C, the reaction mixture was warmed to room temperature. Following filtration and evaporation of solvents, ^{1}H NMR showed diallyldichlorosilane (75%), allyltrichlorosilane (8%), triallylchlorosilane (9.6%) and tetraallylsilane (7.4%). Kugelrohr distillation gave diallyldichlorosilane (26 °C/ 30 torr, 2.2 g, 40%).

Diallyldichlorosilane. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.09-2.11 (m, 2H), 5.07-5.11 (m, 2H), 5.72-5.81 (m, 1H);
^{13}C NMR ($CDCl_3$, 200 MHz) δ 26.6, 117.9, 129.2; ^{29}Si NMR ($CDCl_3$, 250 MHz) δ 23.17; MS (EI, m/z) 180 (16), 165 (8), 152 (12), 139 (100) 117 (25), 103 (22), 63 (65); High resolution MS (m/z, M^+) calc. for $C_6H_{10}Cl_2Si$ 179.9928, found 179.9939; IR (neat) ν 3083, 2978, 2925, 2888, 1633, 1433, 1400, 1169, 1090, 1030, 991, 908, 792, 598, 550, 468 cm^{-1}.

Diallyldiphenylsilane. To a solution of diphenyldichlorosilane (5.0 g, 19.74 mmol) in diethyl ether (100 mL) was slowly added allylmagnesium bromide (43.4 mL, 1.0 M in Et_2O, 43.4 mmol) at ambient temperature. The reaction was followed to completion by TLC. Following filtration and evaporation of solvents, radial chromatography using hexane as eluent gave 4.5 g (90%) diallyldiphenylsilane.
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.12-2.14 (m, 2H), 4.87-4.95 (m, 2H), 5.76-5.84 (m, 1H), 7.24-7.63 (m, $10H_{arom}$); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 19.9, 114.7, 127.7, 129.4, 133.6, 134.9; ^{29}Si NMR ($CDCl_3$, 300 MHz) δ -11.6 MS (EI, m/z) 223 (90, M^+-C_3H_5), 183 (85), 161 (100), 146 (42), 117 (39), 105 (72), 77 (26); IR (neat) ν 3071, 3051, 2973, 2917, 2882, 1630, 1487, 1427, 1391, 1261, 1192, 1155, 1112, 1030, 994, 930, 898, 836, 790, 736, 700, 605, 577, 477 cm^{-1}.

(E)-β-(Allyldichlorosilyl)styrene. To a solution of (*E*)-β-trichlorosilylstyrene (48.0 g, 204 mmol) in diethyl ether (250 mL) was added allylmagnesium bromide (102.0 mL, 1.0 M in Et_2O, 102.0 mmol) at -10 °C. After stirring for 4 d at -10 °C, the reaction mixture was allowed to warm to room temperature and allowed to stir for 1 h. Following filtration and evaporation of solvents, Kugelrohr distillation (100 °C/ 0.4 torr) gave (*E*)-β-(allyldichlorosilyl)styrene (22.5 g, 93%).
^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.27-2.28 (m, 2H), 5.18-5.21 (m, 2H), 5.85-5.93 (m, 1H), 6.46 (d, 1H, J=18.9 Hz), 7.34 (d, 1H, J=18.9 Hz), 7.37-7.54 (m, $5H_{arom}$); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 27.6, 117.8, 119.3, 127.3, 128.7, 129.2, 129.8, 136.2, 150.3; ^{29}Si NMR ($CDCl_3$, 300 MHz) δ 12.90; MS (EI, m/z) 242 (15), 201 (40), 175 (12), 165 (100), 129 (30), 103 (20), 84 (56), 77 (15), 63 (12); High resolution MS (m/z, M^+) calc.

for $C_{11}H_{12}Cl_2Si$ 242.0085, found 242.0088; IR (neat) v 3081, 3062, 3026, 2978, 2888, 1632, 1603, 1574, 1494, 1448, 1417, 1388, 1336, 1219, 1196, 1172, 1032, 988, 911, 834, 816, 733, 688, 609, 552, 474 cm^{-1}.

(E)-β-(Dichlorobenzylsilyl)styrene 7. To a solution of (*E*)-β-(trichlorosilyl) styrene (48.1 g, 204 mmol) was added benzylmagnesium chloride (1M in Et_2O, 102 mL, 102 mmol, 0.5 equiv). After stirring overnight at -50° C, the reaction mixture was allowed to warm to ambient temperature (20 °C) and stirred at that temperature for 1 h. A yield of 28 g (95 %, with reference to BzMgCl) was obtained after removing excess trichlorosilylstyrene at 97 °C / 5 Torr followed by distillation of (*E*)-β-(dichlorobenzylsilyl)styrene at 170 °C / 0.1 Torr; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.63 (s, 2H), 6.19 (d, 1H, J = 18.0 Hz), 7.11 (d, 1H, J = 18.0 Hz), 7.05-7.23 (m, 10H); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 150.4, 136.1, 133.8, 129.7, 128.9, 128.5, 128.3, 127.2, 125.8, 118.7, 30.2; ^{29}Si NMR ($CDCl_3$, 250 MHz) δ 15.67; MS (EI, m/z) 292 (10), 257(12), 201(55), 165(100), 91(38), 77(20), 63(15), 51(10); HRMS (m/z, M^+) calc. 292.0206, found 292.0224; IR (neat) 3027, 2895, 1602, 1493, 1450, 1396, 1210, 1175, 11 00, 1058, 1029, 989,, 908, 833, 803, 764, 733, 697, 591, 500, 459 cm^{-1}.

REACTIONS WITH TRIFLIC ACID: GENERAL PROCEDURE

To a solution of the silane in a methylene chloride was added triflic acid at reduced temperature under a N_2 atmosphere. After a period of time, the solution was allowed to warm to rt. Following ^1H NMR of the crude mixture, workup was performed.

Diallyldimethylsilane. Diallyldimethylsilane (0.2 mL, 1.0 mmol); $CDCl_3$ (4 mL); triflic acid (0.08 mL, 0.95 mmol). After 5 min, the solution was allowed to warm to rt. ^1H NMR indicated about 85% conversion to a new allylsilane, presumably allyldimethylsilyl triflate. This conclusion was reinforced after hydrolysis of the crude mixture led to the formation of diallyltetramethyldisiloxane.[37,38] The remaining 15% was dimethylsilyl ditriflate.[22,39]
Allyldimethylsilyl triflate: ^1H NMR ($CDCl_3$, 200 MHz) δ: 0.49 (s, 6H), 1.92 (d, 2H, J=8.2 Hz), 5.05 (m, 2H) 5.76 (apparent sextet, 1H, J=8.2Hz); Dimethylsilyl ditriflate: ^1H NMR ($CDCl_3$, 200 MHz) δ: 0.87 (s, 6H).

Diallyldichlorosilane, Diallyldiphenylsilane, (E)-β-(Allyldichlorosilyl)styrene. The reactions of each of these compounds with triflic acid led to loss in the ^1H NMR of all vinyl signals and, after workup with MeMgBr (see below for **10** workup A), to the formation of complex reaction mixtures including higher molecular weight oligomers.

3,3-Dimethyl-1-phenyl-3-sila-tetrahydronaphthalene **10.** (*E*)-β-(Dichlorobenzylsilyl)styrene (5.7 g, 19.7 mmol) was added to triflic acid (1.7 mL, 19.7 mmol); CH_2Cl_2 (500 mL); -82°C. The mixture was stirred at -82 °C for 4 d, quenched with NEt_3 (4.1 mL, 29.5 mmol), and warmed to rt. Following removal of CH_2Cl_2 under reduced pressure and replacement with diethyl ether (300 mL), methylation was effected using MeMgBr (3.0 M in Et_2O, 66 mL, 197 mmol).

Workup A; Methylation giving **13.** Methylmagnesium bromide (66 mL, 3.0 M solution in diethyl ether, 197.0 mmol) was added slowly to the reaction vessel, at 0°C and stirred overnight at ambient temperature (20°C). The product was purified by distilling at 150°C/1.0 torr (air temperature, bulb to bulb distillation). Yield 3.2 g, 65%; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.10 (s, 3H), 0.29 (s, 3H), 1.29 (dd, 1H, J = 4.63, -14.21 Hz), 1.34 (dd, 1H, J = 10.40, -14.20 Hz), 2.12 (d, 1H, J = -14.55 Hz), 2.18 (d, 1H, J = -14.5 9 Hz), 4.26 (dd, 1H, J = 4.58, 10.36 Hz), 6.77-7.48 (m, 9H); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 145.1, 144.8, 138.6, 130.4, 129.9,128.9, 127.8, 126.9, 126.8, 125.4, 45.4, 21.8, 18.8, -1.2; ^{29}Si NMR ($CDCl_3$, 250 MHz) δ 0.51; MS (EI, m/z) 252(100), 237(41), 224(7.5), 209(7.5), 191(7.5), 178(41), 161(64), 141(48), 133(40), 121(26), 114 (20), 105(21)), 91(14), 59(21), 43(13); MS (CI, m/z) $M^+ + NH_4$ 270 (100), 252, 237(18), 207(15), 180(40), 152(18), 91(10),

76(15); HRMS (m/z, M^+), calc. 252.1334, found 252.1340; IR (neat) 3002, 2800, 1590, 1470, 1430, 1225, 1190, 1140, 1030, 820, 770, 730, 675 cm^{-1}; Calc. for $C_{17}H_{20}Si$ C 80.97, H 8.00; found: C 80.71, H 8.06.

Workup B; Conversion to silicone **14**. 3,3-Bis(trimethylsiloxy)-1-phenyl-3-sila-tetrahydronaphthalene. To a solution of **9** (0.20 g, 0.68 mmol) in CH_2Cl_2 (50 mL) was slowly added $KOSiMe_3$ (3.0 g, 18 mmol, in CH_2Cl_2 (30 mL)). The reaction was allowed to warm to room temperature and stirred for 16 h. Ammonium chloride (50 mL, satd. soln.) was added to quench the excess Me_3SiOK and the product was extracted with Et_2O, dried over Na_2SO_4 and purified by radial chromatography. Yield 0.23 g, 85%; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.10 (s, 9H), 0.23 (s, 9H), 1.31 (dd, 1H, J = 4.4, -14.5 Hz), 1.32 (dd, 1H, J = 10.40, -14.5 Hz), 2.21 (d, 2H, J = -14.8 Hz), 4.40 (dd, 1H, J = 4.5, 10.4 Hz), 6.77-7.49 (m, 9H); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 144.2, 143.9, 136.9, 130.6, 128.5,128.3, 127.4, 126.4, 126.2, 125.1, 45.0, 22. 9, 18.6, 1.8, 1.6; HRMS (m/z, M^+), calc. 400.1710, found 400.1704.

Workup C; Oxidation: 2(2-Hydroxymethylphenyl)-2-phenylethanol **12**.[28] To a solution of 1-phenyl-3,3-(dichlorosila)tetrahydronaphthalene **9** in CH_2Cl_2 prepared as above at half scale (prior to methylation), NEt_3 (2.0 mL, 14.8 mmol) was added to neutralize the acid present. KF (14 g, 0.25 mol, 25 equiv.) was then added to the reaction mixture at ambient temperature (20°C) and stirred for 2 h. Dimethylformamide (10 mL), water (10 mL), and hydrogen peroxide (27 mL, 236 mmol, 24 equiv., 30% in H_2O) were added and the ensuing solution refluxed for 7 h at 60°C. The reaction was quenched with sodium bisulphite prior to extraction with Et_2O, removal of solvents under reduced pressure and purification by radial chromatography. Yield 0.49 mg, 22% with reference to (*E*)-β-dichlorobenzylsilyl)styrene. ^1H NMR ($CDCl_3$, 500 MHz) δ 2.17 (broad s, 2H, OH), 4.07 (dd, 1H, J = 8.9, 10.4 Hz), 4.15 (dd, 1H, J = 6.2, -10.4 Hz), 4.48 (d, 1H, J = -12.4 Hz), 4.77 (d, 1H, J = -12.33 Hz), 7.12-7.29 (m, 9H); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 141.5, 140.5, 139.2, 129.6, 128.7, 128.1, 127.7, 126.9, 126.8, 66.2, 63.4, 47.8; MS [EI, m/z, M^+-H_2O 210(15)], 192(30), 179(100), 165(23), 152(8), 119(32), 91(50), 77 (10), 65(8); [CI, m/z, $M^+ + NH_4$ 246(95)], 228(100), 209(20), 193(38), 180(20), 11 9(10), 91(5); HRMS (m/z, M^+-H_2O) calc. 210.1041, found 210.1045; IR (neat) 3359, 3082, 3026, 2897, 1600, 1493, 1451, 1400, 1261, 1070, 909, 759, 699 cm^{-1}.

Deuteration of **7**. (*E*)-β-Dichlorobenzylsilylstyrene (1.0 g, 3.4 mmol) was added dropwise to deuterated triflic acid (0.3 mL, 3.4 mmol) in $CDCl_3$ (35 mL) at -50 °C. The mixture was allowed, immediately after the addition, to warm to -2 °C over 3.5 h and was then quenched by the addition of NEt_3 (5.0 mL, 34 mmol, 10 equiv.). The solvents were removed under reduced pressure and MeMgBr (3.0 M in Et_2O, 33 mL) was added to effect methylation. ^1H NMR and ^2H NMR indicated mono- and di-deuteration at the position adjacent to silicon. The monodeuteration occurred at both diastereotopic positions (Scheme 7) in equal proportions. ^2H NMR ($CDCl_3$) δ 0.975, 1.047.

Analysis of the mass spectrum[40] indicated 44.18% of the undeuterated, 39.44% monodeuterated, and 16.38% dideuterated species. MS [EI, m/z, M^+]: 251 (9), 252 (88), 253 (100), 254 (58), 255(17); Compare with the natural abundance distribution MS [EI, m/z, M^+]: 251 (12), 252 (100), 253 (28), 254 (8), 255(1).

MOLECULAR MODELLING

Molecular modelling was done with PC-Model (Serena Software, Bloomington, Indiana) using the supplied MMX force constants. As appropriate force constants are not available for Cl-Si bonds, the intermediates **21** and **22** were modelled with Si-Me groups instead. In compound **21**, the Ca-Cb distance was constrained to 2.5 Å in order to mimic the transition state for bond formation between these two centres. The Si-C-C-p orbital angle in the minimized structures of **21** and **22** were found to be 84° and 26°, respectively.

REFERENCES AND NOTES

1. Natural Sciences and Engineering Research Council of Canada University Research Fellow 1985-1995.
2. Colvin, E. W. *Silicon in Organic Synthesis*, Butterworths, London, 1981; Weber, W. P. *Silicon Reagents for Organic Synthesis*, Springer, Berlin, 1983; Fleming, I. in *Comprehensive Organic Chemistry*, Vol. 3, Jones, D. N., ed., Pergamon, Oxford, 1979, Ch. 13.
3. Increasingly, silicon-containing bioactive organic compounds are becoming synthetic targets in their own right; e.g., Tacke, R.; Becker, B.; Berg, D.; Brandes, W.; Dutzmann, S., Schaller, K.; *J. Organomet. Chem.* **1992**, *438*, 45.
4. Halogens and pseudohalogens usually undergo addition reactions to vinyl silanes. However, with the exceptions of styrene derivatives[5] which may be isolated, or molecules that undergo rapid intramolecular trapping of the β-silyl cation,[6] regeneration of a double bond by elimination of R_3SiX is usually observed.
5. Brook, A. G.; Duff, J. M.; Reynolds, W. F. *J. Organomet. Chem.* **1976**, *121*, 293; Brook, A. G.; Duff, J. M.; Hitchcock, P; Mason, R. J. *ibid.* **1976**, *113*, C11; Koenig, K. E.; Weber, W. P. *J. Am. Chem. Soc.* **1973**, *95*, 3416; Koenig, K. E.; Weber, W. P. *Tetrahedron Lett.* **1974**, 2533.
6. Karpf, M. *Tetrahedron Lett.*, **1982**, *23*, 4923; Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.*, **1981**, *103*, 1604; Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron*, **1983**, *39*, 935; Danheiser, R. L.; Carini, D. J.; Kwasogroch, C. A. *J. Org. Chem.* **1986**, *51*, 3870; Yamazaki, S.; Katoh, S; Yamabe, S. *J. Org. Chem.* **1992**, *57*, 4.
7. Lambert, among others, has clearly demonstrated that the β-effect is maximized when the p orbital to be stabilized and Si-C σ-bond are coplanar. As the angle between the two orbitals approaches 90° from 180°, the β-effect is attenuated. Lambert, J. B.; Wang, G.-T.; Teramura, D. H. *J. Org. Chem.* **1988**, *53*, 5422 and references cited therein; Lambert, J. B.; Wang, G.-T. *Tetrahedron Lett.* **1988**, 2551; Kresge, A. J.; Tobin, J. B. *J. Phys. Org. Chem.* **1991**, *4*, 587.
8. Reetz, M. T.; Hois, P. *J. Chem. Soc, Chem. Commun.*, **1989**, 1081.
9. Examples of reactions of allyl and vinylsilanes with electrophiles that has resulted in silicon retention for varying reasons: Tamao, K.; Yoshida, J.; Mori, M.; Nozaki, H. *J. Org. Chem.* **1983**, *48*, 912; Naruta, Y.; Uno, H.; Maruyama, K. *Tetrahedron Lett.* **1981**, *22*, 5221; Oda, H.; Morizawa, Y.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 3221; Boeckman, Jr., R. K. *J. Am. Chem. Soc.* **1973**, *95*, 6867; Snider, B. B.; Karras, M. *J. Org. Chem.* **1982**, *47*, 4588.
10. Overman, L. E.; Castenada, A.; Blumenkopf, T. A. *J. Am. Chem. Soc.* **1983**, *108*, 1303; Fleming, I.; Pearce, A *J. Chem. Soc. Perkin Trans. 1*, **1980**, 2485.
11. For reviews on the reaction of vinyl- and allylsilane with various electrophiles see: a) Bumenkoff, T. A.; Overman, L. E. *Chem. Rev.* **1986**, *86*, 857; b) Fleming, I.; Dunoguès, J.; Smithers, R. *Organic Reactions*, **1989**, *37*, 57.
12. Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954.
13. Brook, M. A.; Sebastian, T.; Jueschke, R.; Dallaire, C. *J. Org. Chem.* **1991**, *56*, 2274.
14. Brook, M. A.; Hülser, P.; Sebastian, T. *Macromolecules*, **1989**, *22*, 3816; Brook, M. A.; Modi, P.; Dickson, J. M. *Macromolecules*, **1993**, *26*, 2624.
15. Andrianov, K.A.; Zhdanov, A.A.; Odinets, V.A. *J. Gen. Chem. USSR* **1961**, *31*, 3764; Zhdanov, A.A.; Odinets, V.A. *J. Gen. Chem. USSR* **1961**, *32*, 1102.
16. Bailey, D. L; Pines, A. N.; Dunham, M. L.; McIntire, D. B. *Ind. Eng. Chem.* **1953**, *45*, 367.
17. Panek, J.S.; Prock, A.; Eriks, K.; Giering, W.P. *Organometallics*, **1990**, *9*, 2175.
18. Brook, M. A.; Hadi; M. A. Neuy, A. *J. Chem. Soc., Chem. Commun.* **1989**, 957; Brook, M. A.; Neuy, A. *J. Org. Chem.* **1990**, *55*, 3609.

19. Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.*, **1991**, *113*, 7710; Mayr, H.; Hagen, G. *J. Chem. Soc. ,Chem. Commun.*, **1989**, 91; Mayr, H.; Pock, R. *Tetrahedron*, **1986**, *42*, 4211.
20. R. Jüschke and M. A. Brook, unpublished results.
21. Brook, M.A.; Henry, C.; Jueschke, R.; Modi, P. *Synlett* **1993**, *2*, 97.
22. This compound, simultaneously a Lewis acid and silyl nucleophile, will self-catalyze addition of the allyl residue to aromatic aldehydes: Brook, M. A.; Hiemstra, H.; Crowe, G. D. *Can. J. Chem.*, **1994**, *72*, 264.
23. Noll, W. *Chemistry and Technology of Silicones* Academic Press, New York, 1968, p. 141.
24. One possibility that does exist is that indeed the cyclization took place, but was followed by protiodesilylation at the propyl group from the silicon. We have, however, no evidence to support this conclusion.
25. Wilt, J. W. *Tetrahedron* **1985**, *41*, 3979.
26. These processes are often used industrially to prepare functionalized silanes/silicones.
27. Eaborn, C. *Organosilicon Compounds*, Butterworths, London, 1960, Chap. 8.
28. Tamao, K.; Hayashi, T.; Ito, Y. in *Frontiers of Organosilicon Chemistry*, Bassindale, A. R.; Gaspar, P. P. eds., Royal Society of Chemistry, **1989**, 197; Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc, Chem. Commun.* **1984**, 29.
29. For results with a series of more reactive carbon electrophiles see Brook, M.A.; Henry, C. *Inorg. Chim. Acta*, **1994**, *220*, 145.
30. See, however, recent reports of silylium ion formation: Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics*, **1994**, *13*, 2430;Lambert, J. B.; Zhang, S.; Stern, C. L.; Huffman, J. C. *Science*, **1993**, 1917; Lambert, J. B.; Zhang, S. *J. Chem. Soc., Chem. Commun.*, **1993**, 383; Reed, C. A.; Xie, Z.; Bau, R.; Benesi, A. *Science*, *262*, 1993, 402.
31. Corriu, R. J. P. *J. Organomet. Chem.*, **1990**, *400*, 81.
32. Bassindale, A. R.; Taylor, P.G. in *The Chemistry of Organic Silicon Chemistry*, Patai, S.; Rappoport, Z.; eds., Wiley-Interscience, Chichester, **1989**, Chap. 13.
33. In β-functionalized silanes, this effect is sufficiently strong that even in the ground state it manifests itself in the lengthening of the β-C-leaving group bond. White, J. M.; Robertson, G. B. *J. Org. Chem.*, **1992**, *57*, 4638.
34. Schonk, R. M.; Bakker, B. H.; Cerfontain, H. *Recl. Trav. Chim. Pays-Bas* **1992**, *111*, 389; Barluenga, J.; Gonzalez, J. M.; Campos, P. J.; Asensio, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *100*, 1604.
35. Cragg, R. H.; Jones, R. G.; Swain, A. C.; *Eur. Polym. J.* **1991**, *27*, 785.
36. Tamao, K.; Yoshida, J.; Yamamoto, H.; Kakui, T.; Matsumoto, H.; Takahashi, M.; Kurita, A.; Murata, M.; Kumada, M. *Organometallics*, **1982**, *1*, 355 and references cited therein.
37. The ^{1}H NMR spectra of the disiloxane was identical to that reported in the literature[39] or the product of hydrolysis of the commercially available product $ClMe_2SiCH_2CH{=}CH_2$ obtained from Aldrich.
38. Forbes, M. D. E.; Patton, J. T.; Myers, T. L.; Maynard, H. D.; Smith, D. W., Jr.; Schulz, G. R.; Wagener, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 10978.
39. Brook, M. A.; Jiang, J.; Bassindale, *Heteroatom Chem.* in press
40. Werstiuk, N. H.; Banerjee, S. *J. Org. Chem.*, **1981**, *46*, 470.

(*Received in USA* 21 *June* 1994; *revised* 28 *July* 1994; *accepted* 1 *August* 1994)