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Electrophilic additions to styrylsilanes: the effect of changing the ligands on silicon†

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Summary – Styrylsilanes readily undergo addition of carbon electrophiles and protons. The products of the reaction depend upon the non-participating substituents on silicon. Thus, while (*E*)-β-(trimethylsilyl)styrene **4** readily reacts with electrophiles, the reaction products did not contain silicon or new C-C bonds; even in the presence of aryl-substituted carbon electrophiles, the favored reaction was protiodesilylation. In contrast, (*E*)-β-(trichlorosilyl)styrene **2** did not participate in the reaction with carbon electrophiles or reasonably strong protic acids. However, with triflic acid, **2** cleanly and diastereoselectively dimerized producing after methylation **25**, as shown by an X-ray crystal structure analysis. The simple change of a methyl for a chloro group **3** under the same conditions produced a different diastereomer **19** along with a trimer **21**. The reasons for the changes in reaction mechanism are discussed.

β-effect / electrophilic addition / styrylsilane / leaving group ability / ligand effect / diastereoselective indane synthesis

Introduction

One of the reasons for the growth in interest in organosilicon chemistry is the relative ease with which new C-C bonds may be formed under mild and controlled conditions [2]. Possibly the most useful class of silyl reagents are the Me_3Si-substituted π-nucleophiles including vinylsilanes, allylsilanes, silyl enol ethers and related compounds. The utility of these species is primarily based on the ability of the C-Si σ-bond to hyperconjugatively stabilize intermediate β-carbenium ions, the β-effect [3].

Styrylsilanes comprise a special subset of vinylsilanes. The presence of a second group (Me_3Si plus phenyl) to stabilize the β-cation intermediates **1** means that addition [4, 5] rather than substitution reactions can occur (fig 1); nucleophilic attack at the carbenium ion is more efficacious than at the silyl group. This unusual situation has been reported by different groups [6-8] and has been used to establish a scale for the β-effect of different silyl groups [9].

The β-effect of a silyl group dramatically changes upon the replacement of electron-rich groups with electron-withdrawing groups. It was of interest to determine if these changes could be exploited synthetically. In particular, as the leaving group ability of halosilanes is lower than that of alkylsilanes, it was hoped that retention of the silyl group during electrophilic addition to styrylsilanes would allow multiple reactions involving the silyl group to be performed. It was also of interest to determine if there are any stereochemical consequences

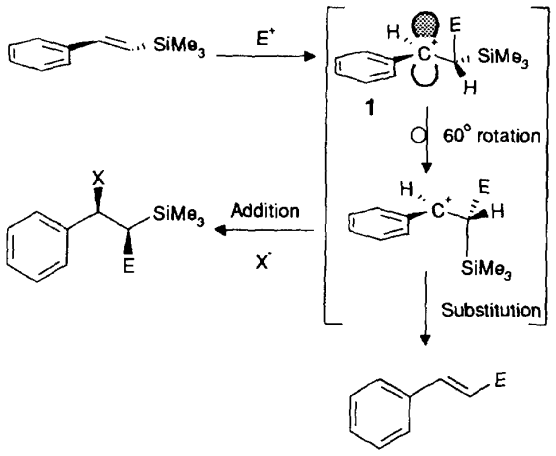

Fig 1

of changing silyl groups. Our report on the electrophilic addition of carbon and proton electrophiles to styrylsilanes with different ligands on silicon is presented below.

Results

Preparation of compounds

(Chloromethylsilyl)styrenes **2** and **3** were prepared by the H_2PtCl_6-catalyzed hydrosilation of phenylacetylene

† It is a pleasure to dedicate this paper to Prof R Calas for his significant contributions to the field of organosilicon chemistry.

* Correspondence and reprints

with $HSiMe_nCl_{3-n}$ (fig 2) [10]. Compound **4** was prepared by reaction of **2** with MeLi or MeMgBr (*Experimental section*).

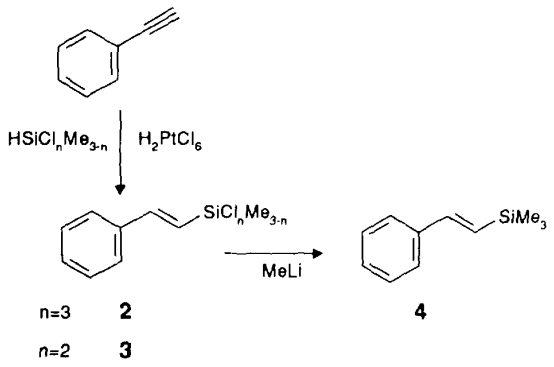

Fig 2

The reaction of acylcations with styrylsilanes

Fleming and Pierce have previously examined the reactivity of styrene and **4** with acetyl chloride and phenylacetyl chloride [11]. They observed that whereas styrene led to a cyclic material **8** with phenylacetyl chloride, the substitution product **7** was the principal product of β-(trimethylsilyl)styrene. The presence of **8** was intriguing as it suggested the possibility of a silicon-containing intermediate **5**. If this intermediate could be captured by external nucleophiles (*eg*, **5** → **6**, **5** → **9**) it could allow subsequent utilization of the silyl group before its cleavage from the molecule (fig 3).

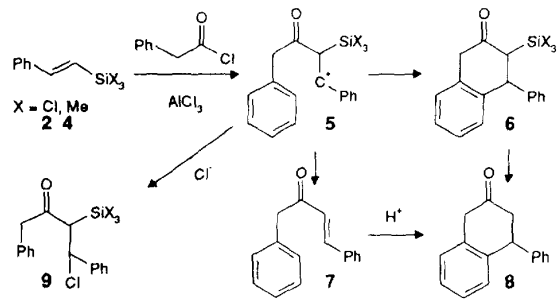

Fig 3

The reaction between **4** and phenylacetyl chloride was repeated but at a lower temperature (−78°C). No compounds containing silyl groups were observed. However, the yield of the cyclized product **8** was 52% (fig 3) at the expense of the product **7**, the yield of which decreased to 18% (from 86% [11]). The reaction between **4** and CH_3COCl led to PhHC=CHCOMe in 72% yield, similar to the yield reported by Fleming (73%).

The fact that a reduction in temperature facilitates the formation of **8** is consistent with the intermediacy of **5** and **6**. Under these conditions, the intramolecular Friedel-Crafts reaction giving **6** could compete with the elimination process giving **7**. The ultimate loss of silicon from **6** could subsequently arise during workup via silyl enolization. These results were sufficiently promising that the corresponding reaction with **2** was attempted.

It was anticipated that the change of starting material from **4** to **2** would result in a different reaction outcome based on the differences in the relative β-effect [9] and leaving group abilities of the silyl groups. Compound **2** was expected to lead to either **6** or other silicon-containing products.

The reaction of **2** and phenylacetyl chloride (or acetyl chloride), with $AlCl_3$ as catalyst, led to a complex reaction mixture which indeed included silicon-containing compounds. Although a variety of workup conditions were attempted, none were successful. A selective Grignard reaction at silicon did not take place, perhaps not surprisingly given the many other electrophilic centers in the vicinity. Although the oxidative cleavage techniques of Fleming [12] and Kumada [13] worked extremely well on related model compounds ($PhCH_2CH_2SiCl_3$ → $PhCH_2CH_2OH$), they led only to more complex reaction mixtures in the case of **2** and phenylacetyl chloride [14]. Oligomers of **2** appeared to be important constituents of the mixture (*vide infra*). Our rationalization of this was that the presence of the adjacent carbonyl group interferes with the reactivity of the $SiCl_3$ group; enolization (1,3-C → O migration) is only one of the possible reaction pathways. To examine this point, the reaction of electrophiles which do not contain Lewis bases (*ie*, C=O) was attempted.

The reaction of simple carbon electrophiles with styrylsilanes

A prototypical carbenium ion is the triphenylmethyl cation (trityl cation) **10**. It was anticipated that the reactivity with the trityl cation would be different for **2** and **4**, respectively. With **2**, no reaction occurred regardless of the counterion or the temperature used for the reaction (−23°C, 0°C, and refluxing CH_2Cl_2). While other counterions were not effective, $Ph_3C^+BF_4^-$ reacted with **4** to give the triphenylindane **11** in very low yield (fig 4, R, R′ = Ph). There was no evidence for silicon-containing products.

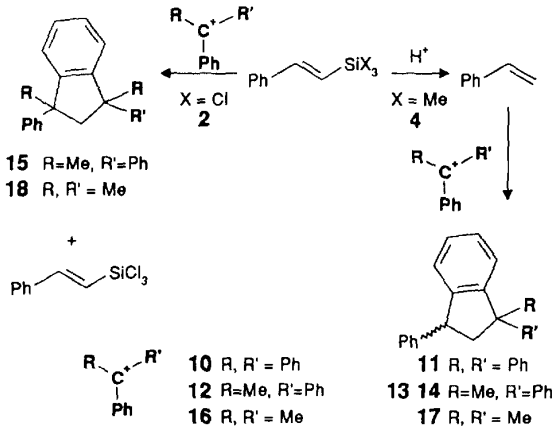

Fig 4

One difficulty with the trityl cation is its size, which will increase the difficulty of approach to the styryl π-bond. Mayr has shown that even less reactive cations, for instance, that derived from α-methoxybenzyl chloride, react readily with vinyl- and allylsilanes whereas the trityl cation does not [15].

In order to address the question of steric encumbrance of the trityl cation, the less hindered diphenylmethyl cation **12** was examined [15]. This can be prepared by a variety of means involving systems which do not have relatively accessible protons ($Ph_2MeCCl/TiCl_4$) and those which do ($Ph_2MeCOH/TiCl_4$). In the former case, we found elimination to $Ph_2C{=}CH_2$ to be very facile and were unable to observe other reaction products. Under the latter conditions in particular, protons can compete as electrophiles.

The reaction between **4** and **12** was quite facile. Unfortunately, the products obtained, the indanes **13**/**14** (fig 4, R′ = Ph, R = Me) did not contain any silyl groups and were accompanied by the formation of polystyrene via protiodesilylation. Styrene can subsequently undergo cationic polymerization or be intercepted by **12** to give diastereomers **13**/**14** (55:45). This structure of **13** was proven by synthesis from styrene and **12**.

There was no reaction between **2** and **12**. However, under these conditions **15**, the dimer of **12**, was produced in good yield; unreacted **2** was recovered (fig 4, R = Me, R′ = Ph).

The analogous reaction was attempted with $PhMe_2C^+$ **16** as the electrophile with similar results. Thus, using $TiCl_4$ as the Lewis acid and $PhCMe_2OH$ as the electrophile source, electrophilic additions to **2** and **4** were attempted. Once again, **4** led to the formation of a non-silylated indane **17** (fig 4, R, R′ = Me); related indanes have been prepared by the protiodesilylation of 3-silyl-1-phenylpropanols [16]. The corresponding Cl_3Si-substituted styrene **2** did not react; the dimer of the electrophile **18** was isolated.

These results point to the vast difference in reactivity of the $SiCl_3$- and $SiMe_3$-substituted styrenes. In order to examine the reactivity of these species under electrophile conditions *in which both species react*, we turned to extremely reactive protons in the form of triflic acid ($HOSO_2CF_3$, HOTf).

The reaction of triflic acid with styrylsilanes

As described by Fleming [11] and Weber *et al* [17], stereoselective protiodesilylation occurs upon the reaction of protic acids with **4**. The stereoselection is a manifestation of the β-effect, the hyperconjugative stabilization of the β-cation by the Si-C σ-bond, which controls the direction of bond rotation and thus the stereochemistry of the elimination of the silyl group (fig 1, E = D). In our hands, the reaction of **4** and TfOH led to a mixture of styrene and polystyrene, as expected.

The identical reaction between HOTf and **3** led to a mixture of desilylated and silylated species; the desilylated species (35%) was a mixture of styrene and polystyrene, the isolated, silylated products (60%) were a mixture of the dimer **19** and trimer **21** (ratio 2:7). The trimer was shown by an X-ray crystal structure (fig 6) of the permethylated derivative **22** ($SiCl_2Me \rightarrow SiMe_3$) to have the relative stereochemistry shown in figure 5 (see table I, II); that of the dimer **19** was established using nuclear Overhauser effect measurements.

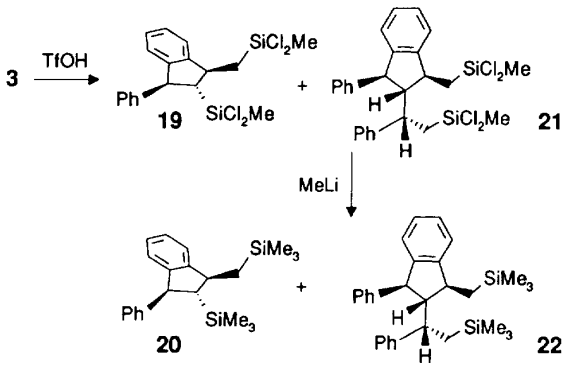

Fig 5

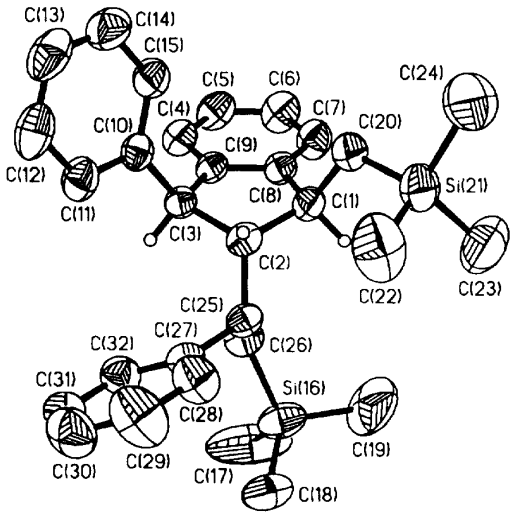

Fig 6. Ortep diagram of **22** from the X-ray crystal structure analysis.

In contrast, when the reaction was performed with TfOH and **2**, the products consisted only of silicon-containing compounds. The bulk of the product (50%), after methylation, was the dimer **25** contaminated with its epimer **20** (**20**/**25** 8:92, fig 7), the structure of which was determined by X-ray analysis (fig 8, table III, IV). The remainder of the material was composed of higher oligomers [10].

Discussion

It is clear that the reactivity of **2** towards electrophiles is much lower than that of **4**. In all the cases described above, in preference to carbenium ions, **4** reacted rapidly with all sources of protons including adventitious protons produced by the interaction of alcohols and $TiCl_4$ or Friedel–Crafts reactions occurring in the mixture. In contrast, only with the exceptionally

Table I. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **22**[a].

	x	y	z	U(eq)
C(1)	4 406(4)	7 884(3)	7 084(3)	45(1)
C(2)	3 888(4)	6 675(3)	7 379(3)	42(1)
C(3)	4 795(4)	6 494(3)	8 563(3)	39(1)
C(4)	6 231(4)	8 094(4)	10 034(3)	51(1)
C(5)	6 781(4)	9 264(4)	10 258(4)	62(1)
C(6)	6 555(5)	10 031(4)	9 434(4)	67(1)
C(7)	5 796(4)	9 660(4)	8 392(4)	59(1)
C(8)	5 247(4)	8 492(3)	8 165(3)	43(1)
C(9)	5 456(3)	7 716(3)	8 982(3)	40(1)
C(10)	5 783(4)	5 505(3)	8 649(3)	42(1)
C(11)	5 370(5)	4 329(4)	8 703(3)	57(1)
C(12)	6 253(6)	3 414(4)	8 777(4)	73(1)
C(13)	7 541(6)	3 661(5)	8 785(4)	74(2)
C(14)	7 972(5)	4 813(5)	8 736(4)	72(1)
C(15)	7 094(5)	5 737(4)	8 660(3)	58(1)
Si(16)	219(1)	8 106(1)	7 436(1)	72(1)
C(17)	−292(5)	8 740(6)	8 579(5)	162(3)
C(18)	−1 009(4)	6 874(4)	6 692(4)	81(1)
C(19)	231(6)	9 271(5)	6 465(5)	142(3)
C(20)	5 214(4)	7 755(4)	6 290(3)	56(1)
Si(21)	4 302(1)	7 498(1)	4 801(1)	65(1)
C(22)	3 319(6)	6 031(4)	4 425(4)	110(2)
C(23)	3 118(6)	8 704(5)	4 339(4)	114(2)
C(24)	5 622(5)	7 574(5)	4 138(4)	112(2)
C(25)	2 355(4)	6 639(3)	7 228(3)	43(1)
C(26)	1 974(4)	7 601(4)	7 962(4)	52(1)
C(27)	1 825(3)	5 380(3)	7 314(3)	45(1)
C(28)	1 480(5)	4 574(4)	6 420(4)	69(1)
C(29)	1 014(6)	3 412(5)	6 454(5)	94(2)
C(30)	871(5)	3 034(5)	7 385(5)	82(2)
C(31)	1 202(4)	3 803(4)	8 287(4)	66(1)
C(32)	1 678(4)	4 972(4)	8 251(3)	56(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

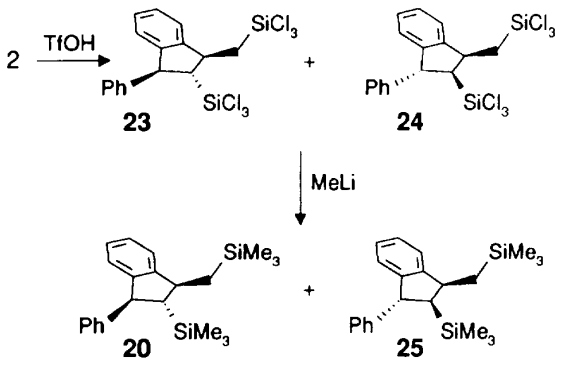

Fig 7

strong acid TfOH did **2** participate in the reaction. This is a consequence of electronic factors.

The π-bond of the styryl group on **4** will be relatively electron rich as a consequence of the electron-donation of the alkyl groups and thus the silyl group. Unlike **4**, the presence of the electron-withdrawing chlorine groups in **2** will lead to a very electron-poor, non-nucleophilic double bond. Thus, only very strong electrophiles were found to react with **2**.

Table II. Selected bond lengths [Å] and angles [°] **22**.

Bond	Bond length	Angle	
C(1)-C(20)	1.538(5)	C(8)-C(1)-C(20)	112.4(3)
		C(8)-C(1)-C(2)	103.9(3)
		C(20)-C(1)-C(2)	114.2(3)
		C(1)-C(2)-C(25)	112.2(3)
C(1)-C(2)	1.545(5)	C(1)-C(2)-C(3)	106.1(3)
C(2)-C(25)	1.545(5)	C(25)-C(2)-C(3)	113.6(3)
		C(9)-C(3)-C(10)	114.4(3)
		C(9)-C(3)-C(2)	104.0(3)
		C(10)-C(3)-C(2)	114.0(3)
C(2)-C(3)	1.560(5)		
C(3)-C(9)	1.496(5)		
C(3)-C(10)	1.525(5)	C(15)-C(10)-C(11)	117.6(4)
		C(15)-C(10)-C(3)	122.3(3)
		C(11)-C(10)-C(3)	120.0(4)
C(12)-C(13)	1.357(7)		
Si(16)-C(26)	1.860(4)	C(18)-Si(16)-C(17)	109.5(2)
		C(18)-Si(16)-C(26)	112.1(2)
		C(17)-Si(16)-C(26)	109.6(2)
		C(18)-Si(16)-C(19)	107.7(3)
		C(17)-Si(16)-C(19)	110.8(3)
		C(26)-Si(16)-C(19)	107.1(3)
C(20)-Si(21)	1.871(4)	C(1)-C(20)-Si(21)	120.1(3)
		C(22)-Si(21)-C(24)	110.0(3)
		C(22)-Si(21)-C(23)	108.3(3)
		C(24)-Si(21)-C(23)	109.6(3)
		C(22)-Si(21)-C(20)	113.1(2)
		C(24)-Si(21)-C(20)	106.1(2)
		C(23)-Si(21)-C(20)	109.7(2)
C(25)-C(27)	1.512(5)	C(27)-C(25)-C(2)	110.9(3)
		C(27)-C(25)-C(26)	113.4(3)
		C(2)-C(25)-C(26)	113.5(3)
C(25)-C(26)	1.550(5)	C(25)-C(26)-Si(16)	115.7(3)

Table III. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for **25**[a].

	x	y	z	U(eq)
C(1)	1 099(3)	2 089(2)	1 248(3)	47(1)
C(2)	436(2)	1 916(2)	2 306(3)	46(1)
C(3)	−1 009(2)	2 379(2)	1 656(3)	49(1)
C(4)	−2 720(3)	1 922(3)	−1 124(3)	66(1)
C(5)	−2 835(4)	1 580(3)	−2 516(4)	79(1)
C(6)	−1 665(3)	1 361(3)	−2 751(3)	73(1)
C(7)	−345(3)	1 502(3)	−1 590(3)	62(1)
C(8)	−210(2)	1 855(2)	−188(3)	49(1)
C(9)	−1 407(2)	2 048(2)	40(3)	50(1)
C(10)	−2 111(2)	1 936(2)	2 103(3)	51(1)
C(11)	−2 499(3)	2 676(3)	3 029(3)	66(1)
C(12)	−3 472(4)	2 263(4)	3 484(4)	83(1)
C(13)	−4 082(4)	1 112(4)	3 013(4)	81(1)
C(14)	−3 728(3)	382(3)	2 090(4)	78(1)
C(15)	−2 749(3)	783(3)	1 635(3)	66(1)
Si(16)	1 559(1)	2 430(1)	4 328(1)	55(1)
C(17)	752(5)	1 637(5)	5 272(5)	89(1)
C(18)	1 692(5)	4 038(3)	4 998(5)	83(1)
C(19)	3 371(4)	2 041(5)	4 823(5)	83(1)
C(20)	1 939(3)	3 323(3)	1 646(3)	58(1)
Si(21)	2 758(1)	3 839(1)	519(1)	63(1)
C(22)	4 199(7)	5 082(5)	1 780(7)	110(2)
C(23)	3 579(5)	2 688(4)	−205(6)	84(1)
C(24)	1 440(6)	4 387(5)	−982(6)	101(1)

[a] U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

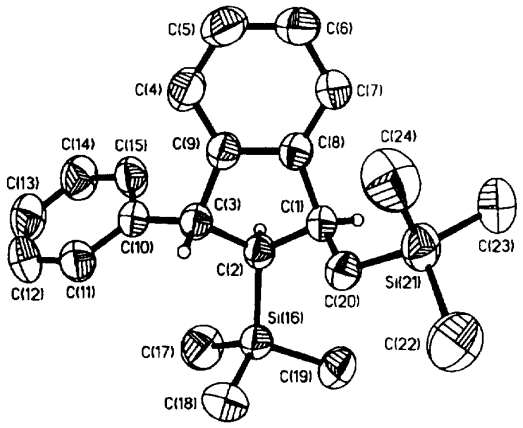

Fig 8. Ortep diagram of **25** from the X-ray crystal structure analysis.

Table IV. Selected bond lengths [Å] and angles [°] for **25**.

Bond	Bond length	Angle	
C(1)-C(8)	1.511(3)	C(8)-C(1)-C(20)	112.2(2)
C(1)-C(20)	1.537(4)	C(20)-C(1)-C(2)	112.9(2)
C(1)-C(2)	1.558(3)	C(8)-C(1)-C(2)	101.5(2)
C(2)-C(3)	1.558(3)	C(3)-C(2)-C(1)	103.3(2)
		C(3)-C(2)-Si(16)	117.0(2)
		C(1)-C(2)-Si(16)	119.4(2)
C(2)-Si(16)	1.885(3)	C(19)-Si(16)-C(17)	106.8(2)
		C(19)-Si(16)-C(18)	109.6(2)
		C(17)-Si(16)-C(18)	108.8(2)
		C(19)-Si(16)-C(2)	110.2(2)
		C(17)-Si(16)-C(2)	108.6(2)
		C(18)-Si(16)-C(2)	112.7(2)
C(3)-C(10)	1.508(3)	C(10)-C(3)-C(9)	115.7(2)
		C(10)-C(3)-C(2)	114.9(2)
C(3)-C(9)	1.518(3)	C(9)-C(3)-C(2)	101.7(2)
C(20)-Si(21)	1.871(3)	C(1)-C(20)-Si(21)	123.4(2)
		C(23)-Si(21)-C(22)	108.3(3)
		C(23)-Si(21)-C(24)	110.5(3)
		C(24)-Si(21)-C(22)	108.9(3)
		C(23)-Si(21)-C(20)	112.2(2)
		C(24)-Si(21)-C(20)	111.2(2)
		C(22)-Si(21)-C(20)	105.6(2)

With TfOH as the electrophile, it was possible to examine the effect of Cl/Me exchange on the reactivity of the styryl groups, which could be done systematically because **2**, **3** and **4** all reacted under these conditions. The differences in leaving group ability of the silyl group, based on the number of electron-withdrawing groups on silicon, is quite apparent. The more electron-rich silyl group in **4** underwent complete protiodesilylation. The same reaction with **3** led to about 50% silicon retention; the trimer form **21** bears only two of the three silyl groups present in the three monomers. Compound **2** underwent no desilylation at all.

These differences can be understood by examining the reaction mechanism necessary for desilylation. In spite of the low electronegativity of silicon, silylium ions have never been isolated although some very interesting cationic complexes have been crystallized [18]. Therefore, an S_N1 reaction (*eg*, loss of SiR_3^+ from **26** (fig 9)) may be discounted. Instead, one must examine an S_N2 reaction at silicon with the styryl residue as the leaving group. It is conceivable that electronically the silicon in **26** should be more receptive to nucleophilic attack than that of **29** which is less electron rich. However, in order for elimination to occur, the carbon ligand must be in the apical position [19]. Generally, the more electron-poor group occupies the apical position. Thus, in the case of the perhalo species **26**, attack at the silicon might occur, but would be transparent to any reaction on the carbon skeleton **27** → **28**. In contrast, with the permethylated species **29**, the carbenium ion ligand should be more electronegative than a methyl group such that it will occupy the apical position **30**. Thus, any nucleophilic attack at silicon will directly lead to protiodesilylation **31** (fig 9) [8].

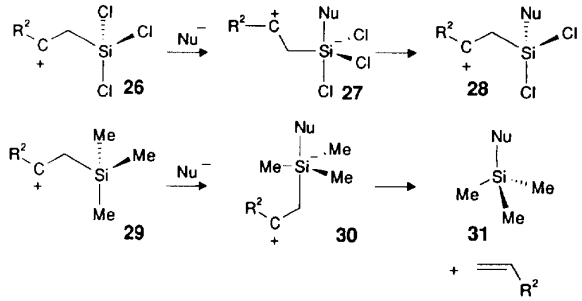

Fig 9

It remains to examine the change in diastereoselectivity which accompanies the change in silyl group from $SiCl_3$ **2** → **24** to $SiCl_2Me$ **3** → **19**. This effect cannot be ascribed to steric effects: Cl and Me are of comparable size. We believe that the difference reflects kinetic control. With the more electron-rich silyl group $SiCl_2Me$, the initial bond formation can be reversible **34** ⇌ **32** ⇌ **33** (fig 10) such that the more stable diastereomer **19** can ultimately result. This suspicion was confirmed by the reaction of **2** with TfOH at room temperature rather than −55°C. In this case, the product ratio was **19**/**21**/**24** 18:15:67, a higher ratio of the more stable isomer (compare with **19**/**24** 8:92 at −55°C, *vide supra*). Furthermore, attempted equilibration of the isomeric dimers **23**/**24** by warming to 25°C and with the addition of more TfOH led to no change in the reaction product ratio.

The electronic effect of the methyl group is also manifested by the increased degree of elimination which is observed in this case. The fact that the trimer **21** is the major product from the reaction of **3** suggests competitive elimination from the dimer cation **33** giving the intermediate **35** which can then further react to give **21** via **36**.

Conclusion

Two profound changes in reactivity accompany the modification of groups on silicon from $SiMe_3$ to $SiCl_3$. First, the electron-withdrawing ability of the chloride serves to reduce the nucleophilicity of the π-bond of the styrylsilane such that it will react only with powerful

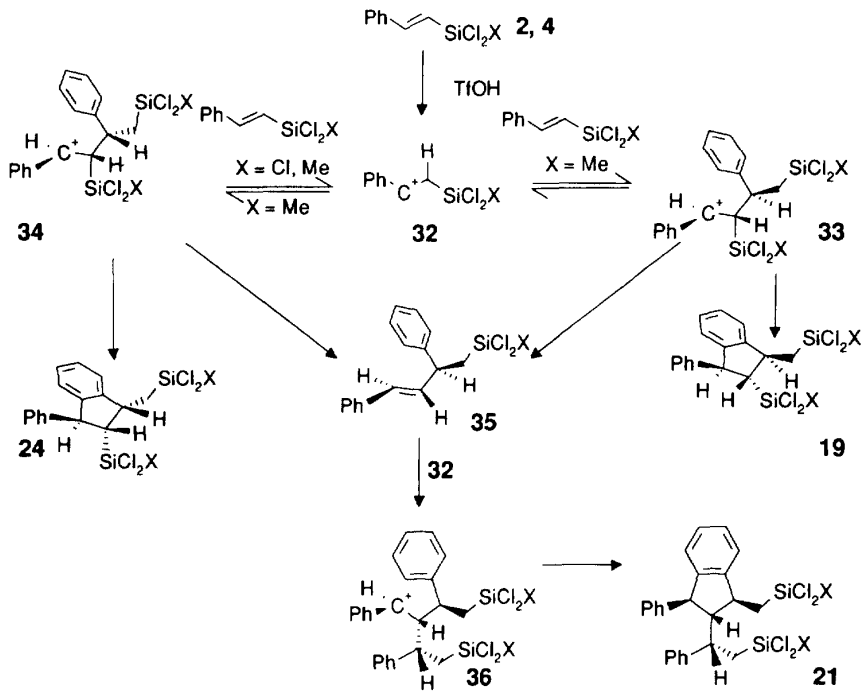

Fig 10

electrophiles. This could be seen from the absence of reactivity of **2** with carbocations derived from acyl groups or aryl-substituted methyl cations. In contrast, **4** reacted readily. Regrettably, the protons present in the reaction media competed with carbenium ions and led to non-silylated indanes and β-tetralone. Second, the leaving group ability of the silyl group is much lower. This property was manifested in the diastereoselective production of **24**; intermediate leaving group ability could be seen from the formation of **19** and **21** from **3**. The difference in the stereochemical outcomes of dimerization of **2** and **3**, giving **19** and **24**, respectively, can be attributed to the difference in the β-effect. This is extremely interesting as it suggests that subtle changes in the substitution pattern of non-reacting ligands on a silyl group could be utilized as stereochemical control elements. The $MeCl_2Si$ group, with the larger β-effect than $SiMe_3$, allows equilibration of the kinetic product **34** to the more stable isomer **33** leading to the less hindered indane **19**. In contrast, the cation derived from **2** reacts irreversibly in the dimerization step.

Experimental section

Apparatus, materials and methods

The continuous wave ^1H NMR spectra were recorded on a Varian EM-390 (90 MHz) spectrometer and the pulsed/Fourier transform spectra on a Bruker AC-300 (at 300 MHz for protons) spectrometer. ^{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.

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 BIORAD FTS-40 spectrometer, as neat films.

X-ray diffraction data for compound **22** was collected at room temperature on a Nicolet R3/m diffractometer with a Mo tube. A variable scan speed was used. Three standards measured at regular intervals indicated that no decay correction was necessary. No absorption correction was applied (μ = 0.14/mm). The data were processed using the texSan PROCESS routine (Molecular Structure Corp, The Woodlands, TX).

X-ray diffraction data for compound **25** was collected at room temperature on a Rigaku AFC6R diffractometer with a Cu anode. A constant scan speed with up to three passes was used. Three standards measured at regular intervals indicated that no decay correction was necessary. No absorption correction was applied (μ = 1.40/mm). The data were processed using the texSan PROCESS routine (Molecular Structure Corp, The Woodlands, TX).

In both cases, the SHELXTL, v5 programs (Siemens Industrial Automation, Inc, Madison, WI) were used for structure solution, refinement, and table and diagram preparation. The nonhydrogen atom positions were determined by direct methods, and refined anisotropically. The hydrogen atoms positions were determined from a Fourier difference map, and refined with isotropic temperature factors. An extinction correction was applied. For **22**, the methyl hydrogens were constrained to maintain the known geometry, and were given temperature factors 150% of that of the attached carbon atom.

Supplementary material data have been deposited with the British Library Document Supply Centre at Boston Spa, Wetherby, West Yorkshire, LS23 7BQ, UK as supplementary publication N° SUP 90386.

Dichloromethane was distilled over P_2O_5. Diethyl ether, THF and hexane were distilled over Na/benzophenone. NEt_3 was distilled from CaH_2. Trifluoromethanesulfonic acid was purchased from Aldrich, stored under N_2 and used without further treatment. Chloroform-*d* ($CDCl_3$, 99.8% *d*, MSD Isotopes) was stored under N_2 over molecular sieves. Phenylacetylene, trichlorosilane, dichloromethylsilane, H_2PtCl_6, acetyl chloride, phenylacetyl chloride, 1-phenyl-1-methylethanol, 1,1-diphenylethanol, 1,1-diphenyl-1-chloroethane, triphenylmethyl carbenium BF_4^- and $SbCl_6^-$ were purchased from Aldrich and used without further purification.

Due to the tendency of halo groups on silicon to hydrolyse easily (CAUTION, hydrolysis leads to production of HCl), all reactions were carried out in dry apparatus under a N_2 atmosphere with the use of septa and syringes for the transfer of reagents.

Preparation of **2-4**

These compounds were prepared as previously described [10, 20].

Preparation of (trichloro-2-phenylethyl)silane)

$HSiCl_3$ (27.00 g, 0.200 mmol) was added dropwise to a solution of styrene (10.4 g, 0.100 mol) at 25°C in THF (35 mL) containing 3 drops of H_2PtCl_6 (0.1 M in isopropanol). After stirring for 2 h, the solution was distilled. The fraction boiling at 72-80°C/0.1-0.7 Torr was collected (23.13 g, 96%).

^{1}H NMR ($CDCl_3$, 90 MHz) δ : 1.78 (t, 2H, J = 9 Hz), 2.95 (t, 2H, J = 9 Hz), 7.3 (s, 5H).

^{29}Si NMR ($CDCl_3$, 49.7 MHz) δ : 11.66.

Acyl cation additions

• *The reaction of* **4** *with* $PhCH_2COCl$

To a cooled solution of CH_2Cl_2 (10 mL) at −77°C was added $AlCl_3$ (0.267 g, 2.0 mmol), and phenylacetyl chloride (0.232 g, 1.5 mmol in 2 mL, CH_2Cl_2) and **4** (0.260 g, 1.5 mmol in 2 mL CH_2Cl_2). Upon the addition of **4** the solution turned orange. The reaction was stirred for 45 min, warmed to rt and the solvents were removed under reduced pressure, followed by drying at high vacuum (0.1 Torr). The material was purified by flash chromatography (Et_2O/petroleum ether 5:95) to give 4-phenyl-3,4-dihydronaphthalen-2(1*H*)-one **8** (52%, 0.173 g) and **7** (18%, 0.060 g).

8 : ^{1}H NMR ($CDCl_3$, 90 MHz) δ : 2.73 (d, 2H, J = 7.7 Hz), 3.40 (s, 2H), 4.23 (t, 1H, J = 7.7 Hz), 6.85-7.34 (m, 4H).

MS : m/z 222 (M^+, 83), 179 (100).

• *The reaction of* **4** *with* CH_3COCl

Reaction as above : $AlCl_3$ (0.267 g, 2.0 mmol), acetyl chloride (0.354 g, 4.5 mmol), **4** (0.260 g, 1.5 mmol), CH_2Cl_2 (10 mL), reaction time 30 min : yield of *trans*-4-phenylbut-3-en-2-one (72%, 0.154 g).

^{1}H NMR ($CDCl_3$, 90 MHz) δ : 2.28 (s, 3H), 6.63 (d, 1H, J = 16.5 Hz), 7.24-7.63 (m, 6H).

MS : m/z 146 (M^+, 70), 131 (100), 103 (93), 77 (53).

• *The reaction of* **2** *with* CH_3COCl

Reaction as above : $AlCl_3$ (0.40 g, 3.0 mmol), acetyl chloride (0.235 g, 1.0 mmol), **2** (0.260 g, 1.5 mmol), CH_2Cl_2 (50 mL), temp −23°C, reaction time 30 min : in addition to starting material **2**, oligomers including **19**, **21**, **24** (see below) and higher oligomeric species were observed; other products were present in the mixture.

■ *Attempted workup with Grignard*

In an attempt to see if other organic moieties had been produced, the reaction mixture was cooled to −78°C and MeMgBr (3.0 M in Et_2O, 2.2 mL, 10 equiv) was added dropwise. After warming and extraction with water, a complex reaction mixture was isolated.

• *The reaction of* **2** *with* $PhCH_2COCl$

To a cooled solution of $CDCl_3$ (1.5 mL) at −77°C was added $AlCl_3$ (0.047 g, 0.35 mmol), and phenylacetyl chloride (0.046 g, 0.30 mmol) and **2** (0.071 g, 0.30 mmol). Upon the addition of **2** the solution turned orange. The reaction was stirred for 45 min, warmed to room temperature and the solvents were removed under reduced pressure, followed by drying at high vacuum (0.1 Torr). The ^{1}H NMR showed a complex mixture.

■ *Oxidation of* $PhCH_2CH_2SiCl_3$ *as model compound*

To a solution of $PhCH_2CH_2SiCl_3$ (0.237 g, 1.00 mmol) in ether (15 mL) and triethylamine (0.418 mL, 3.00 mmol) was added *m*-chloroperbenzoic acid (mcpba, 0.518 g, 3.00 mmol) at −78°C. After 7 h, the reaction was quenched with 5% aqueous $NaHCO_3$. Following extraction with Et_2O, washing with $NaHCO_3$, the combined organic extracts were dried over Na_2SO_4 and the solvents evaporated at reduced pressure to produce the alcohol quantitatively (0.121 g).

^{1}H NMR ($CDCl_3$, 90 MHz) δ : 2.63 (bs, 1H, OH), 2.74 (t, 2H, J = 6.6 Hz), 3.72 (t, 2H, J = 6.6 Hz), 6.81-7.32 (m, 5H).

■ *Attempted workup of the reaction of* **2** *and* $PhCH_2COCl$ *with oxidation*

To a cooled solution of CH_2Cl_2 (50 mL) at −77°C was added $AlCl_3$ (1.47 g, 5 equiv), phenylacetyl chloride (1.71 g, 5 equiv) and **2** (0.500 g, 0.212 mmol). Upon the addition of **2** the solution turned orange. The reaction was stirred for 6 h, triethylamine (0.643, 3 equiv) and mcpba (1.10 g, 3 equiv) were added and the reaction left at −18°C overnight. The solution was diluted with Et_2O, washed with 5% $NaHCO_3$ and 5% Na_2CO_3. The combined organic extracts were dried over Na_2SO_4 and the solvents removed under reduced pressure. A complex mixture of products was present as determine by TLC and ^{1}H NMR.

General procedure for reaction with substituted methyl cations

Unless otherwise noted below, addition reaction of substituted methyl cations were performed as follows. To a solution of the substituted methanol (2.0 mmol) and the silylstyrene (2.0 mmol) in $CDCl_3$ (10 mL) was added $TiCl_4$ (0.22 mL, 2.0 mmol) at −23°C. The solution immediately turned red-orange and was accompanied by the formation of a precipitate. After 1 h, the solution was allowed to warm to room temperature and was quenched by the addition of water (10 mL). The organic layer, diluted in ether, was washed with water, and the combined organic extracts were dried over $MgSO_4$. After removal of solvents under reduced pressure, the mixture was purified using column chromatography to give the adducts.

• *Reactions with* Ph_3C^+

■ *Addition of* $Ph_3C^+BF_4^-$

$Ph_3C^+BF_4^-$ (0.99 g, 3.0 mmol), CH_2Cl_2 (10 mL), **4** (0.53 g, 3.0 mmol), at room temperature. The solution initially turned red and the green color of $Ph_3C^+BF_4^-$ disappeared. After reflux for 30 min, the solution was quenched with Et_2O (10 mL) and 5% $NaHCO_3$ (10 mL). The major constituents of the reaction products were **4** and Ph_3COH. The indane

product **11** comprised < 2% of the product mixture. Similar results were observed with Ph_3CSbCl_6.

^1H NMR ($CDCl_3$, 200 MHz) δ : 2.73 (dd, 1H, J = 9.0, 12.0 Hz), 3.08 (dd, 1H, J = 5.9, 12.0 Hz), 4.04 (dd, 1H, J = 5.9, 9.0 Hz), 6.88-7.40 (m, 19H).

• *Reactions with* Ph_2MeC^+

■ *Addition of 1,1-diphenylethanol to* **4**

1,1-diphenylethanol (0.40 g, 2.0 mmol), **4** (0.36 mL, 2.0 mmol). Column chromatography gave the diastereomeric adducts **13** and **14** (80%, 0.46 g). The relative stereochemistries of **13** and **14** were not established; **13** the major isomer, was assigned the *trans*-1,3-diphenyl geometry on steric grounds.

Major adduct (55%) **13** ^1H NMR ($CDCl_3$, 200 MHz) δ : 1.70 (s, 3H), 2.42 (dd, 1H, J = 8.9, 11.9 Hz), 2.63 (dd, 1H, J = 9.1, 11.9 Hz), 4.53 (dd, 1H, J = 8.9, 9.1 Hz), 6.98-7.65 (m, 14H).

Minor adduct (45%) **14** ^1H NMR ($CDCl_3$, 200 MHz) δ : 1.83 (s, 3H), 2.27 (dd, 1H, J = 12.0, 13.1 Hz), 2.86 (dd, 1H, J = 7.9, 13.1 Hz), 4.14 (dd, 1H, J = 7.9, 12.0 Hz) 6.98-7.65 (m, 14H).

■ *Addition of 1,1-diphenylethanol to styrene*

To 1,1-diphenylethanol (0.3965 g, 2.00 mmol) in $CDCl_3$ (8 mL) was added styrene (0.2083, 2.00 mmol), $TiCl_4$ (2.0 mL, 1 M in CH_2Cl_2, 2.0 mmol) at −23°C under a nitrogen atmosphere. The solution immediately turned yellow-orange. ^1H NMR showed the presence of **13**: **14**/polystyrene/oligomers of 1-diphenylstyrene 1.0:1.75:3.0. for NMR see above.

■ *Addition of 1,1-diphenylethanol to* **2**

1,1-Diphenylethanol (0.40 g, 2.0 mmol), **2** (0.4752 g, 2.0 mmol), $CDCl_3$ (8 mL), $TiCl_4$ (2.0 mL, 1 M in CH_2Cl_2, 2.0 mmol). The solution immediately turned yellow-orange. Following workup, ^1H NMR showed only unreacted **2** and **15**, for NMR see below.

■ *Dimerization of 1,1-diphenylethanol* **15**

1,1-Diphenylethanol (0.3965 g, 2.00 mmol) in $CDCl_3$ (8 mL) was added $TiCl_4$ (2.0 mL, 1 M in CH_2Cl_2, 2.0 mmol) at −23°C under a nitrogen atmosphere. The solution immediately turned yellow-orange. The reaction was allowed to warm to room temperature. ^1H NMR showed quantitative formation of the dimer **15**.

^1H NMR ($CDCl_3$, 90 MHz) δ : 1.51 (s, 3H), 3.11 (d, 1H, J = 13.5 Hz), 3.36 (d, 1H, J = 13.5 Hz), 7.0-7.3 (m, 19H).

• *Reactions with* $PhMe_2C^+$

■ *Addition of 2-methyl-2-phenylethanol to* **4**

2-Methyl-2-phenylethanol (0.2724 g, 2.0 mmol), **4** (0.3527 g, 2.0 mmol), $CDCl_3$ (8 mL), $TiCl_4$ (2.0 mL, 1 M in CH_2Cl_2, 2.0 mmol). The solution immediately turned yellow-orange. Following workup, **17** was isolated (0.4023, 90%).

^1H NMR ($CDCl_3$, 90 MHz) δ : 2.35 (s, 3H), 2.40 (s, 3H), 1.94 (d, 1H, J = 9.9, 11.8 Hz), 2.39 (d, 1H, J = 7.5, 11.8 Hz), 4.40 (d, 1H, J = 7.5, 9.9 Hz), 6.8-7.5 (m, 9H).

■ *Addition of 2-methyl-2-phenylethanol to styrene*

To 2-methyl-2-phenylethanol (0.2724 g, 2.0 mmol) in $CDCl_3$ (8 mL) was added styrene (0.2082, 2.00 mmol), $TiCl_4$ (2.0 mL, 1 M in CH_2Cl_2, 2.0 mmol) at −23°C under a nitrogen atmosphere. The solution immediately turned yellow-orange. ^1H NMR showed the presence of **17** : **18**/polystyrene/oligomers of 1-methylstyrene 3:10:15. for NMR of **17**, see above, of **18** see below.

■ *Addition of 2-methyl-2-phenylethanol to* **2**

2-Methyl-2-phenylethanol (0.2724 g, 2.0 mmol), **2** (0.4752 g, 2.0 mmol), $CDCl_3$ (8 mL), $TiCl_4$ (2.0 mL, 1 M in CH_2Cl_2, 2.0 mmol). The solution immediately turned yellow-orange. Following workup, ^1H NMR showed unreacted **2** and **18**, for NMR see below.

■ *Dimerization of 2-methyl-2-phenylethanol*

To a solution of 2-methyl-2-phenylethanol (0.2724 g, 2.00 mmol) in $CDCl_3$ (8 mL) was added H_2SO_4 (3 drops) at −23°C under a nitrogen atmosphere. The solution was allowed to warm to room temperature. ^1H NMR showed quantitative formation of the dimer **18**.

^1H NMR ($CDCl_3$, 90 MHz) δ : 0.98 (s, 3H), 1.28 (s, 3H), 1.65 (s, 3H), 2.17 (d, 1H, J = 14 Hz), 2.44 (d, 1H, J = 14 Hz), 7.0-7.3 (m, 9H).

• *Reactions with triflic acid*

■ *Preparation of 1-(trichlorosilylmethyl)-2-(trichlorosilyl)-3-phenyl-2,3-dihydro-1H-indene* **25**

To a solution of *β-E*-trichlorosilylstyrene **2** (1.69 g, 7.11 mmol) in $CDCl_3$ (1.0 mL) under a nitrogen atmosphere at −55°C was added triflic acid (F_3CSO_3H, 0.07 mL, 0.79 mmol). After 3 h the sample was allowed to warm to room temperature. ^1H NMR indicated complete consumption of starting materials and that 55% of the product were dimers **23/24** in a ratio of 8:92, the remainder being higher molecular weight oligomers.

As the products were exceptionally unstable towards water, further analysis was performed on the methylated derivatives. These were prepared as follows. The $CDCl_3$ was removed under reduced pressure and the residue was dissolved in Et_2O (5 mL), to which MeMgBr (3.0 M in Et_2O, 20.0 mL, 60.0 mmol), was added at room temperature. The mixture was stirred refluxed for 2 h, quenched with water (15 mL) and acidified with 1 M HCl, extracted with Et_2O (3 × 25 mL) and the combined organic extracts were dried over a mixture of anhydrous $MgSO_4$ and K_2CO_3. The viscous, light yellow liquid was purified using flash chromatography with hexane as the eluent to yield 0.480 g, 38% of the dimeric species (8:92 mixture of **20/25** by ^1H NMR). **20** and **25** were purified by recrystallization from MeOH. The yields in the reaction at −23°C were somewhat higher, but with lower selectivity (isolated **20** 20%, **25** 50%).

25 : mp 75°C.

^1H NMR ($CDCl_3$, 500 MHz) δ : −0.10 (s, 9H), 0.04 (s, 9H), 0.91 (dd, 1H, J = 11.9, 14.2 Hz), 1.02 (dd, 1H, J = 2.9, 14.2 Hz), 1.89 (dd, 1H, J = 6.5, 11.5 Hz), 3.52 (ddd, 1H, J = 2.9, 6.5, 11.9 Hz), 4.39 (d, 1H, J = 11.5 Hz), 6.76-7.30 (m, 9H).

^{13}C NMR ($CDCl_3$, 63.9 MHz) δ : −0.83, −0.27, 21.65, 43.13, 49.08, 51.52, 123.40, 124.59, 125.51, 126.09, 126.39, 128.27, 128.90, 144.73, 148.82, 150.20.

^{29}Si NMR ($CDCl_3$, 49.7 MHz) δ : −0.71, 0.27.

IR (KBr pellet) ν : 3 070, 3 020, 2 950, 2 900, 1 600, 1 490, 1 470, 1 450, 1 410, 1 250, 1 150, 1 025, 990, 935, 850, 750, 690, 640 cm^{-1}.

HRMS (high resolution, EI, m/z) : calc for M^+ ; 353.2043; obs; 352.2030.

Combustion analysis, calc for $C_{22}H_{32}Si_2$ C 74.93, H 9.15, found C 74.83, H 9.27.

■ *Attempted equilibration of isomers* **23/24**

A mixture of **23/24** was prepared as indicated above (10:90 by ^1H NMR). The mixture was warmed to 25°C, ^1H NMR showed no change in the product ratio. Another aliquot of triflic acid added to the mixture but after a further 24 h at 25°C there was still no change observed in the product ratio.

■ *Preparation of 1-[(dichloromethylsilyl)methyl]-2-(dichloromethylsilyl)-3-phenyl-2,3-dihydro-1H-indene* **19** *and 1-[(dichloromethylsilyl)methyl]-2-([2-dichloromethylsilyl)-1-phenyl]ethyl)-3-phenyl-2,3-dihydro-1H-indene* **21** *and the methylated analogues* **20** *and* **22**

These were prepared from β-*E*-dichloromethylsilylstyrene in a manner similar to that described above for **24** with the following exceptions : β-*E*-dichloromethylsilylstyrene **3** (3.60 g, 16.58); $CDCl_3$ (3.0 mL) at −23°C; triflic acid (F_3CSO_3H, 0.2 mL, 2.23 mmol). After 1 and 3 h a further aliquot of triflic acid (0.7 mL, 0.77 mmol) was added as the reaction was shown by ^1H NMR to be incomplete and had stopped progressing. After 4 h, as ^1H NMR indicated complete consumption of starting materials and ca 50% of **19** + **21**, the sample was allowed to warm to room temperature. Methylation : Et_2O (40 mL), MeMgBr (3.0 M in Et_2O, 30.0 mL, 90.0 mmol). Yield **20** 0.200 g, (7%), **22** 0.610 g (24%). Other products of the reaction include polystyrene (from the cationic polymerization of styrene that was produced by protiodesilylation (ca 20%)) and higher silylstyrene oligomers (ca 30%). Increasing the concentration of the reaction or changing the temperature of the reaction did not lead to a significantly greater proportion of the dimeric and trimeric components. The compounds were purified by recrystallization from MeOH.

20 : mp 66°C.

^1H NMR ($CDCl_3$, 500 MHz) δ : −0.02 (s, 9H), 0.04 (s, 9H), 1.13 (dd, 1H, J = 6.6, 15.2 Hz), 1.17 (dd, 1H, J = 5.2, 15.2 Hz), 1.57 (t, 1H, J = 8.5 Hz), 3.35 (dd, 1H, J = 5.2, 6.6 Hz), 4.20 (d, 1H, J = 8.5 Hz), 6.81-7.30 (m, 9H).

^{13}C NMR ($CDCl_3$, 63.9 MHz) δ : −1.82, 0.29, 25.00, 42.57, 44.98, 53.08, 123.47, 124.73, 126.08, 126.22, 126.49, 128.27, 128.54, 146.62, 146.82, 150.01.

^{29}Si NMR ($CDCl_3$, 49.7 MHz) δ : −0.29, 2.64.

IR (KBr pellet) ν : 3 070, 3 030, 2 960, 2 890, 1 600, 1 495, 1 470, 1 450, 1 405, 1 250, 1 165, 1 130, 1 030, 1 010, 875, 865, 830, 750, 700, 685 cm^{-1}.

MS (high resolution, EI, m/z) : calc for M^+ : 353.2043; obs: 352.2039.

Combustion analysis : calc for $C_{22}H_{32}Si_2$ C 74.93, H 9.15, found C 74.83, H 9.27.

22 : mp 61°C.

^1H NMR ($CDCl_3$, 500 MHz) δ : −0.28 (s, 9H), 0.09 (s, 9H), 0.82 (d, 2H, J = 6.7 Hz), 1.04 (dd, 1H, J = 12.1, 14.7 Hz), 1.10 (dd, 1H, J = 3.3, 14.7 Hz), 2.47 (dt, 1H, J = 3.6, 5.3 Hz), 2.88 (ddd, 1H, J = 3.2, 7.1, 11.2 Hz), 3.10 (dt, 1H, J = 5.5, 6.2 Hz), 4.27 (d, 1H, J = 5.3 Hz), 6.90-7.27 (m, 14H).

^{13}C NMR ($CDCl_3$, 63.9 MHz) δ : −1.03, −0.09, 20.50, 25.52, 45.23, 46.45, 54.20, 65.89, 123.90, 125.40, 125.76, 126.22, 126.36, 126.74, 128.19, 128.38, 128.98, 144.95, 146.83, 149.09.

^{29}Si NMR ($CDCl_3$, 49.7 MHz) δ : −0.37, 0.73.

IR (KBr pellet) ν : 3 060, 3 030, 2 950, 2 920, 2 900, 2 860, 1 600, 1 490, 1 450, 1 415, 1 240, 850, 830, 745, 695 cm^{-1}.

HRMS (EI, m/z) : calc for M^+-CH_3 : 441.2434; obs: 441.2389.

Combustion analysis : calc for $C_{30}H_{40}Si_2$ C 78.88, H 8.83, found C 79.28, H 9.03.

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4 Halogens and pseudohalogens usually undergo addition reactions to vinylsilanes. Otherwise regeneration of a double bond by elimination of R_3SiX is usually observed. Some exceptions can be found in reference 4

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