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Competitive Acylation of Arylstyrylsilanes: Controlling Silanucleophile Reactivity

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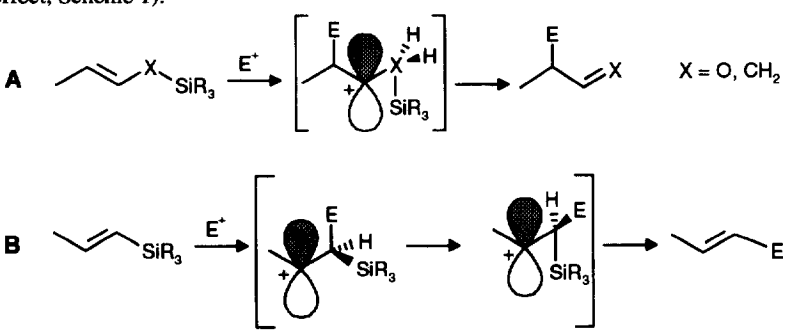
Abstract: Electrophilic substitution reactions occurred cleanly between acyl cations and arylstyrylsilanes **2-4**. With an unsubstituted aryl group, **2** underwent transfer of the styryl group to form styryl ketone **5** as would be predicted from previous kinetic studies. With increasing methyl group substitution of the aryl group, aryl group transfer occurred competitively such that **3** showed a 2:1 preference for destyrylation : dearylation giving **10:11** while **4** underwent exclusive transfer of the mesityl group to give mesityl ketones **6-8**. These results are not consistent with electrophilic aromatic substitution reactions of nonsilylated compounds. With increasing methyl group substitution of the aryl group, its reactivity should increase for electronic reasons but not to the extent that it surpasses that of the styryl group. When the silyl group is flanked by methyl groups, however, cleavage of the silicon-aryl bond is additionally facilitated by the relief of steric congestion such that this process occurs preferentially to transfer of the styryl group.

INTRODUCTION

A variety of silanucleophiles have been used for the preparation of C-C bonds under mild, acidic conditions. These reactions,[2] typically involving vinylsilanes, alkynylsilanes, arylsilanes and allylsilanes, are usually thought to proceed through the intermediacy of a β-silyl carbocation which is stabilized by the presence of silicon (the β-effect, Scheme 1).[3,4]



Scheme 1

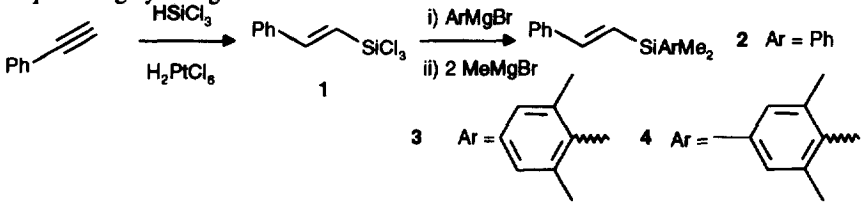
The β-effect is responsible for the regiocontrol observed in the electrophilic substitution reactions with these reagents. It involves the hyperconjugative stabilization of a carbocation by the C-Si σ-bond which, as a

result of geometrical constraints, is optimized when the p-orbital on the carbocation and the σ-bond are coplanar.[3-5] With aryl-, vinyl- and alkynylsilanes,[6,7] this effect can only occur after the addition of the electrophile is nearly complete (Scheme 1B) and the rate enhancement in these reactions is thus less than for allylsilanes and silyl enol ethers (Scheme 1A). Generally, the most important contributing factor to the relative reactivity of the nucleophilic ligand in the former cases is the degree to which the π-bond of the aryl- or vinylsilane is electron rich; this is affected, among other things, by the electronegativity of the spectator groups on silicon.[6]

The magnitude of these effects has been elegantly studied by Mayr[7] and others.[8] Based on these studies, we anticipated when a competitive situation arose with a silane, from which an aryl group could compete with a styryl group for an electrophile, that attack and transfer of the styryl group would occur preferentially. In the following report, we describe conditions under which an arylsilane successfully competes with a styrylsilane for electrophiles and propose reasons for the changeover in relative reactivity of the two π-systems.

RESULTS

The starting materials that were used differed only in the nature of the aryl group. Thus, the basic starting material was trichlorostyrylsilane **1** which was prepared by the hydrosilation of phenylacetylene with $HSiCl_3$.[9,10] Following monoarylation with aryl Grignard reagents, subsequent methylation with MeLi or MeMgBr gave compounds **3-4** (Scheme 2). **2** was made by the hydrosilation of phenylacetylene with Me_2SiClH and subsequent quenching by PhMgBr.

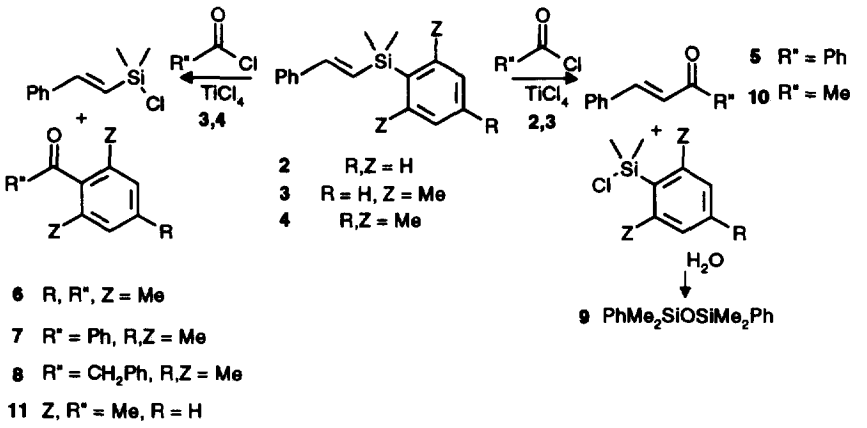


Scheme 2

Acyl cations were chosen as the electrophiles in these reactions for their reactivity[11] and the possibility of modifying the steric and electrophilic demands of the electrophile using electrophilic aromatic substitution. The addition of $BzCl/TiCl_4$ to **2** led to the formation of styrylketone **5** (Scheme 3). In contrast, with three different electrophile systems, the mesitylstyrylsilane **4** underwent exclusive loss of the aryl group to form ketones **6-8**. In these cases, the styryldisiloxane **9** could be isolated after workup. With one less methyl group on the arene ring, dearylation and destyrylation occurred at competitive rates: the reaction of **3** with $AcCl/TiCl_4$ led to a 2:1 mixture of **10** and **11** (Scheme 3). It should be noted in the reaction of **3** that *ipso*-substitution of the arylsilane was occurring. This was shown by independent synthesis of **11** and by comparison with authentic samples of related isomers. We infer that *ipso*-substitution was occurring in the dearylation reactions of **4**.

DISCUSSION

Normally, arylsilanes undergo cleavage of the aryl C-Si bond (*ipso*) via β-effect intermediates. The relative rate of these reactions is determined primarily by the electron density in the aryl π-bond[7,12] which will be affected by the other ring substituents and, additionally, by the electronegativity of the spectator ligands on silicon.[8] Exactly the same considerations are involved in the reactions of vinylsilanes.[7] An important distinction, however, between aryl- and vinylsilanes in their relative reactivity is the effect of aromaticity in the former case. In the parent compound benzene, the energy of the aromatization is approximately 34 kcal/mol.[13] Thus, with similar substitution patterns on silicon, one would expect that an arylsilane would be much less reactive than the vinylsilane, as the loss of aromaticity must be overcome in addition to the other factors present for both arylsilanes and vinylsilanes. In the following paragraphs, we discuss how the various steric and electronic factors play out.



Scheme 3

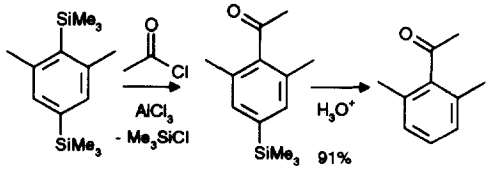
In the system we have examined, a very reactive vinylsilane, a styrylsilane, was used (Table 1). This is an unusual olefin in the sense that electrophilic addition occurs via a β-silyl cation which is also a secondary, benzylic and therefore very stable carbocation.[8] A look at the comparative nucleophilicities of alkenes and arenes towards *p*-methoxy substituted diphenyl carbenium ions shows that styrene is approximately 10^{10} (k_{rel}) more reactive than benzene (Figure 5.1).[7] Thus, the product styrylketone **5** found in the reaction of **2** with benzoyl chloride and indicative of enhanced reactivity of the styryl- over the arylsilane, is consistent with the relative reactivity of the parent molecules styrene and benzene.

Styrene is also 10-10^2 more reactive than mesitylene towards addition of benzylic cations.[7,14] Assuming the relative reactivities of the two π-nucleophiles are the same in the desilylation reactions under consideration, preferential reactivity of the styryl group would still be predicted. However, a reversal in the reactivity rates of the silylstyryl and silylmesityl groups in **4** was observed; the silylmesityl group was found to be more reactive giving **6-8**. Similarly, styrene is 10^4 times more reactive than *m*-xylene[7] which would lead one to expect exclusive reaction of the styryl moiety in the reaction of electrophiles with **3**. In contrast, however, substantial reaction by the 2,6-dimethylphenyl group was seen, implying a rate ratio of only 2:1 based on product ratio **10:11**, under conditions of kinetic control.

In protiodemetallation reactions of arylsilanes, a single *ortho*-Me substituent activates to the same extent as a single *para*-Me substituent so that 1-trimethylsilyl-2-methylbenzene and 1-trimethylsilyl-4-methylbenzene are cleaved at similar rates.[15] Increasing methyl group substitution increases the rate of electrophilic attack at the arene ring provided steric factors do not come into play.[7] In conventional electrophilic aromatic substitution reactions (C-H cleavage), however, it is difficult to effect substitution at a position between two methyl substituents *meta* to each other.[16] In contrast, the electrophilic attack of arylsilanes is *accelerated* by the presence of adjacent groups on the arene ring.[15,17-,18,1920,] For example, 1-trimethylsilyl-3,4-dimethylbenzene is cleaved less rapidly with halogen addition than 1-trimethylsilyl-2,5-dimethylbenzene.[19,21] This enhanced reactivity was attributed by Benkeser and Krysiak to relief in the latter case of steric congestion by the methyl group *ortho* to silicon in the transition state or intermediate.[19] Similarly, 1-trimethylsilyl-2,6-dimethylbenzene and 1-trimethylsilyl-2,4,6-trimethylbenzene react much faster with acid than would be expected based on simple additivity of the electronic effects of the separate *ortho*- and *para*-Me groups.[15,17] Finally, and most relevant for this study, Calas and coworkers found that 1,4-bis (trimethylsilyl)-2,6-dimethylbenzene reacted exclusively at the 1-position when treated with one equivalent of acetyl chloride (Scheme 4).[18] Scheme 5 shows the relative reactivity towards electrophilic aromatic substitution of a series of dialkylphenyltrimethylsilanes.[17]

A look at our substrates, **3** and **4**, suggests that the buttressing of the bulkier $SiMe_2$styryl group (relative to $SiMe_3$) by the adjacent methyl substituents should be even more pronounced, leading to greater steric acceleration of reactions involving these substrates. Thus, the enhanced reactivity of the aryl group over the

styryl group in **3** and **4** may be ascribed to the combination of two effects. With increasing methyl substitution on the arene, the aryl ring becomes a better nucleophile. At the same time, the relief of steric compression provided to the silyl group by the adjacent methyl groups enhances the rate of attack at the aryl ring. The competition can be seen between the two groups in the reaction of **3** and is won by the aryl group by the time 3 methyl groups are present on the ring in **4**.

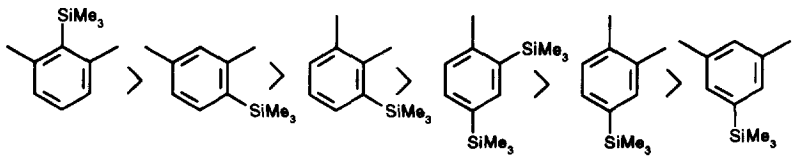


Scheme 4

Table 1: Products of Reactions of Arylstyrylsilanes with Acyl Cations

Starting Material	Electrophile	Ketone Product (Yield %)[a]	Aryl Product (Yield %)[a]
2	PhCOCl	**5** 62%)	**14** (57%)
3	CH_3COCl	**10,11**[b] (2:1)	**15,16**
4	CH_3COCl	**6** (63%)	[c]
4	PhCOCl	**7** (85%)	[c]
4	$PhCH_2COCl$	**8** (60%)	[c]

[a] Based on [arylsilane **2**, **3** or **4**]; [b] GC ratio, recovered **3** 89%; [c] Oligomers of $PhCH{=}CHSiMe_2Cl$.



Scheme 5

CONCLUSION

The normal reactivity of vinylsilanes and arylsilanes favours electrophilic cleavage of the vinyl group. However, the degree of methylation on the aryl group can favour Si-aryl cleavage. In addition to the electronic activation of the ring, certain substitution patterns can lead to synergistic activation through relief of steric stress. This can be seen from the reactivity of **2-4**. Without methyl substitution on the arene ring, selective destyrylation takes place. With three arylmethyl groups, two of which flank the silyl group, dearylation becomes preferable. This observation can be used to control selective, sequential reactions with appropriate difunctional compounds.

ACKNOWLEDGEMENTS

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EXPERIMENTAL SECTION

GENERAL PROCEDURES AND INSTRUMENTATION

The ^{1}H-NMR spectra were recorded on a Varian EM-390 (90-MHz) spectrometer and the Bruker AM-500 (500-MHz) spectrometer, Bruker AC-300 (300 MHz) spectrometer or Bruker AC-200 (200 MHz) spectrometer. ^{13}C and ^{29}Si-NMR were performed on a Bruker AC-200 (at 50.3 MHz for ^{13}C) and Bruker AC-300 (at 59.6 MHz for ^{29}Si), respectively. 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, q = quartet, dd = doublet of doublets, dt = doublet of triplets, 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 ~ 200 °C 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.

Infrared spectra were run on a Perkin Elmer 283 spectrometer or a BIO RAD FTS-40 spectrometer, as a neat film.

The purity of new compounds was confirmed by chromatography on a HP-5890A Gas Chromatograph/TCD detector; glass capillary column, SPB-1, 30 meters long, 0.075 mm inner diameter. GC/MS was carried out at oven temperature 80 °C (initial temperature) to 150 °C (final temperature) with an incremental increase of 10 °C/min. Injection and detector temperatures were set at 250 °C. Injection volume 1.0 μL, sample concentration 100 ng/μL.

All solvents were thoroughly dried before use. Dichloromethane (CH_2Cl_2) was distilled over phosphorus pentoxide (P_2O_5). Diethyl ether, tetrahydrofuran and hexanes were distilled from Na/benzophenone under a nitrogen atmosphere.

SYNTHESIS OF STARTING MATERIALS

(E)-β-(Phenyldimethylsilyl)styrene **2**: Phenylacetylene (20 mL, 182.2 mmol) and chlorodimethylsilane (33 mL, 297.2 mmol) were mixed together and hexachloroplatinic acid (0.5 mL, 0.02 M in ethanol) added to the mixture at -15 °C. The reaction mixture was stirred at this temperature for 4 h. The temperature was raised to 25 °C and the mixture stirred for 2 d. Diethyl ether (200 mL) and phenylmagnesium bromide (60.7 mL, 3.0 M in diethyl ether) were added to the reaction mixture and refluxed overnight. Distillation yielded (*E*)-β-(phenyldimethylsilyl)styrene **2** (28 g, 65%, b.p. 106-108 °C, 0.05 mmHg).

^{1}H NMR ($CDCl_3$, 300 MHz): δ: 0.56 (s, 6H), 6.68-6.74 (d, 1H, J = 19.2 Hz), 7.04-7.10 (d, 1H, J = 19.2 Hz), 7.35-7.71 (m, 10H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ: 145.0, 138.3, 137.9, 133.6, 128.7, 128.2, 127.9, 127.5, 126.8, 126.2, 125.9, -2.8; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ: -11.1; IR (neat): ν: 3067, 3023, 2957, 2899, 1953, 1884, 1819, 1604, 1573, 1493, 1427, 1334, 1251, 1115, 1068, 990, 911, 846, 730, 698, 646 cm^{-1}; MS (EI, m/z): 238 (82), 223 (100), 145 (85),135 (28), 121 (30), 86 (15); HRMS (m/z, M^+): calc. 238.1178; found 238.1188.

(E)-β-[(2,6-Dimethylphenyl)dimethylsilyl]styrene **3**: 2,6-Dimethylphenyl-1-magnesium bromide [prepared by reacting 2,6-dimethyl-1-bromobenzene (6.2 mL, 46.5 mmol) with magnesium (4.7 g, 85 mmol) in tetrahydrofuran, for 4 h at ambient temperature] was added to **1** (10 mL, 42.5 mmol) in 100 mL tetrahydrofuran at 0 °C. The mixture was stirred for 1 h, followed by heating at 50 °C for 3. Methyl magnesium bromide (63 mL, 3.0 M in diethyl ether) was added slowly at ambient temperature and the contents of the reaction flask further heated at 50 °C (16 h). Upon distillation, the reaction yielded (*E*)-β-(trimethylsilyl)styrene (1.6 g, 21%) as the distillate (b.p. 30 °C, 0.1-0.5 mmHg) and (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene **3** as the residue. Following radial chromatography, pure (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl] styrene was obtained (8.9 g, 70%).

^{1}H NMR ($CDCl_3$, 200 MHz): δ: 0.58 (s, 6H), 2.49 (s, 6H), 6.68-7.45 (m, 10H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ: 144.4, 143.0, 138.4, 134.9, 130.4, 129.0, 128.4, 128.1, 127.9, 126.3, 25.1, 2.1; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ: -12.6; IR (neat): ν: 3023, 2957, 1602, 1573, 1493, 1446, 1252, 1130, 1028, 990, 845, 833, 771, 689 cm^{-1}; MS (EI, m/z): 266 (32), 251 (40), 175 (35), 162 (50), 147 (100), 135 (50), 121 (15), 105 (11), 91 (10), 59 (20), 43 (12); HRMS (m/z, M^+): calc. 266.1491; found 266.1497.

(E)-β-(Mesityldimethylsilyl)styrene **4**: Mesityl magnesium bromide (115 mL in diethyl ether, 1.0 M, 1.1 eq) was added slowly to (*E*)-β-(trichlorosilyl)styrene **1** (24.81 g, 104.4 mmol) in tetrahydrofuran (100 mL) at ambient temperature. The mixture was heated at 50 °C (16 h). The removal of diethyl ether (120 mL) by

distillation was followed by the addition of methyl lithium (153 mL, 1.5 M in diethyl ether, 2.2 equiv.) at 22 °C. After stirring at this temperature for 1 h, the reaction mixture was once more heated at 50 °C (16 h). Upon distillation, the reaction yielded (*E*)-β-(trimethylsilyl)styrene (b.p. 52 °C/ 2.0 mmHg, 3.3 g, 18%) and (*E*)-β-(mesityldimethylsilyl)styrene **4** (b.p. 160 °C, 2.0 mmHg, 15 g, 51%).

^{1}H NMR ($CDCl_3$, 200 MHz): δ: 0.52 (s, 6H), 2.24 (s, 3H), 2.42 (s, 6H), 6.62-7.41 (m, 9H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ: 144.6, 142.8, 138.8, 138.5, 131.3, 130.6, 129.1, 128.5, 128.1, 127.9, 126.5, 126.4, 25.0, 20.9, 2.2; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ: -11.8; IR (neat): ν: 3024, 2956, 2732, 1604, 1573, 1493, 1448, 1410, 1252, 1065, 1029, 990, 845, 776, 735, 689 cm^{-1}. MS (EI, m/z): 280 (30), 265 (20), 219 (10), 189 (40), 161 (100) 145 (90), 135 (60), 115 (20), 105 (25), 91 (27), 59 (25); HRMS (m/z, M^+): calc. 280.1667; found 280.1669.

REACTION WITH ACID CHLORIDES

(E)-β-(Phenyldimethylsilyl)styrene 2 With Benzoyl Chloride: Titanium tetrachloride (1.6 mL, 13.4 mmol) was added to benzoyl chloride (0.78 mL, 6.7 mmol) in methylene chloride (20 mL) at -78 °C. (*E*)-β-(Phenyldimethylsilyl)styrene **2** (1.6 g, 6.7 mmol) in methylene chloride (10 mL) was added dropwise and the reaction stirred for 1 h at -78 °C. The reaction mixture was warmed to ambient temperature (22 °C) then quenched with saturated aqueous potassium carbonate (200 mL) and extracted with diethyl ether (2 x 300 mL). Radial chromatography yielded *trans*-chalcone **5** (0.86 g, 62%), and 1,3-diphenyltetramethyldisiloxane **14** (1.1 g, 57%).

5 ^{1}H NMR ($CDCl_3$, 300 MHz): δ: 7.52-7.57 (d, 1H, J = 15.7 Hz), 7.81-7.86 (d, 1H, J = 15.7 Hz), 7.26-8.05 (m, 10H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ: 190.4, 144.7, 138.1, 134.8, 132.7, 130.4, 128.9, 128.5, 128.4, 128.3, 122.0; IR (neat): ν: 3082, 3060, 3028, 1664, 1605, 1576, 1495, 1449, 1336, 1286, 1215, 1178, 1073, 1036, 1017, 980, 860, 787, 747, 689, 566, 526, 485 cm^{-1}; MS (EI, m/z): 208 (100), 179 (20), 165 (12), 131 (30), 105 (25), 77 (31); MS (CI, m/z): M^+ + H 209 (100), 131 (10).

14 ^{1}H NMR ($CDCl_3$, 300 MHz): δ: 0.48 (s, 12H), 7.46-7.71 (m, 10H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ: 139.8, 133.0, 129.2, 127.7, 0.9; ^{29}Si NMR ($CDCl_3$, 59.6 MHz): δ: -1.2; IR (neat): ν: 3136, 3069, 3051, 3012, 2958, 2900, 1591, 1487, 1428, 1255, 1119, 1060, 832, 792, 739, 700, 649 cm^{-1}; MS (EI, m/z): 286 (10), 271 (100), 193 (60), 135 (25).

(E)-β-[(2,6-Dimethylphenyl)dimethylsilyl]styrene 3 With Acetyl Chloride: (*E*)-β-[(2,6-Dimethylphenyl)dimethylsilyl]styrene **3** (0.45 g, 1.69 mmol) was added to a solution of methylene chloride (60 mL), acetyl chloride (0.133 g, 1.69 mmol) and titanium tetrachloride (0.4 mL, 3.40 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 2-4 min, then quenched by adding saturated potassium carbonate (150 mL). GC/MS analysis of the crude organic mixture indicated a 2:1 ratio of *trans*-4-phenyl-3-buten-2-one **10** [MS (EI, m/z): 146 (28), 131 (83), 103 (100), 77 (60), 63 (14), 51 (28)] to 2,6-dimethylacetophenone **11** [MS (EI, m/z): 148 (27), 133 (100), 105 (77), 77 (40), 63 (15), 51 (15)], as well as (*E*)-β-(dimethylhydroxysilyl)styrene **15** [MS (EI, m/z): 178 (22), 163 (60), 145 (100), 137 (22), 115 (10), 103 (15), 91 (10), 77 (34), 61 (26), 51 (15), 45 (37)], and 2,6-(dimethylphenyl)hydroxydimethylsilane **16** [MS (EI, m/z): 180 (26), 165 (100)]. Unreacted (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene **3** (0.40 g, 89%) was recovered after separation by radial chromatography.

2,4-Dimethylacetophenone, purchased from Aldrich, was used as a standard for comparison with 2,6-dimethylacetophenone **11** obtained from the reaction of (*E*)-β-[(2,6-dimethylphenyl)dimethylsilyl]styrene **3** with acetyl chloride. **11**, obtained from the reaction of 2,6-dimethylphenyl-1-magnesium bromide with acetyl chloride, was used as another standard. The retention time obtained from the GC/MS of 2,4-dimethylacetophenone was 16.31 min. Retention times of 14.97 min and 14.95 min were obtained from the GC/MS of 2,6-dimethylacetophenone **11** produced upon reacting acetyl chloride with **3** and 2,6-dimethylphenyl-1-magnesium bromide, respectively. For comparison, the mass spectrum of the commercially obtained 2,4-dimethylacetophenone was recorded under identical conditions used to record the mass spectrum of 2,6-dimethylacetophenone **11**. 2,4-Dimethylacetophenone MS (EI, m/z): 148 (26), 133 (100), 105 (55), 77 (35), 63 (13), 51 (14).

2,6-Dimethylphenyl-1-magnesium Bromide With Acetyl Chloride: The structure of **11** was proved by an independent synthesis and comparison of spectral data, including the retention times described above. 2,6-Dimethylphenyl-1-magnesium bromide (2.96 g, 20.0 mmol) [prepared by reacting 2,6-dimethylphenylbromide (3.0 mL, 20.0 mmol) with magnesium (0.6 g, 24.0 mmol) in 50 mL tetrahydrofuran for 16 h at 55 °C] was added to a solution of tetrahydrofuran (50 mL) and acetyl chloride (2.84 mL, 40.0 mmol) at ambient temperature. The reaction mixture was stirred (22 °C) for 3 d, then quenched by adding saturated potassium carbonate (250 mL), and extracted with diethyl ether (2 x 300 mL). The reaction yielded 2,6-dimethylacetophenone **11** (0.24 g, 8%) after separation by radial chromatography.

^{1}H NMR ($CDCl_3$, 200 MHz): δ: 2.25 (s, 6H), 2.48 (s, 3H), 7.00-7.04 (m, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ: 208.4, 142.5, 132.1, 128.5, 127.7, 32.0, 19.1; IR (neat): ν: 2925, 2859, 1699, 1596, 1460, 1352, 1256, 1057, 773, 700 cm^{-1}; MS (EI, m/z): 148 (25), 133 (100), 105 (75), 77 (37), 63 (14), 51 (14).

(E)-β-(Mesityldimethylsilyl)styrene 4 With Acetyl Chloride: (*E*)-β-(Mesityldimethylsilyl)styrene **4** (0.9 g, 3.15 mmol) was added to a solution of methylene chloride (15 mL) containing acetyl chloride (0.25 g, 3.15 mmol) and titanium tetrachloride (1.5 mL, 12.6 mmol) at -78 °C. The reaction mixture was stirred for 1 h, warmed slowly to -50 °C for 30 min, then the temperature was finally raised to 25 °C for a further 30 min. The reaction mixture was quenched by adding saturated potassium carbonate (150 mL). Extraction with diethyl ether (2 x 100 mL), and radial chromatography yielded 2,4,6-trimethylacetophenone **6** (0.32 g, 63%), and an oligomer of chlorodimethylsilylstyrene.[9]

^{1}H NMR ($CDCl_3$, 300 MHz): δ: 1.98 (s, 6H), 2.04, (s, 3H), 2.20 (s, 3H), 6.60 (s, 2H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ: 207.8, 139.6, 137.8, 131.8, 128.1, 31.7, 20.6, 18.7; IR (neat): ν: 2957, 2921, 1699, 1611, 1453, 1425, 1353, 1252, 1164, 1060, 965, 851, 803, 702, 671, 595, 528 cm^{-1}; MS (EI, m/z): 162 (25), 147 (100), 119 (50), 91 (20), 77 (15); MS (CI, m/z): $M^+ + NH_4$ 180 (8), 163 (100), 147 (20).

(E)-β-(Mesityldimethylsilyl)styrene 4 With Benzoyl Chloride: **4** (0.9 g, 3.15 mmol) was added to a solution of methylene chloride (15 mL) containing benzoyl chloride (0.36 mL, 3.15 mmol) and titanium tetrachloride (1.5 mL, 12.6 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 1 h, warmed slowly to -50 °C for 30 min, then the temperature was finally raised to 25 °C for a further 30 min. The reaction mixture was quenched by adding saturated potassium carbonate (150 mL). Extraction with diethyl ether (2 x 100 mL), and radial chromatography yielded 2,4,6-trimethylbenzophenone **7** (0.60 g, 85%) along with an oligomer of chlorodimethylsilylstyrene.

^{1}H NMR ($CDCl_3$, 300 MHz): δ: 1.88 (s, 6H), 2.10 (s, 3H), 6.68 (s, 2H), 7.14-7.63 (m, 5H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ: 200.0, 138.0, 137.0, 136.6, 133.7, 133.1, 128.9, 128.4, 128.0, 20.7, 19.0; IR (neat): ν: 2953, 2920, 2861, 1672, 1611, 1448, 1379, 1312, 1268, 1170, 1072, 1027, 958, 910, 851, 801, 748, 711, 609 cm^{-1}; MS (EI, m/z): 224 (84), 223 (100), 209 (30), 147 (70) 119 (25), 105 (58), 91 (15), 77 (25).

Isolation of the Disiloxane Product: The reaction procedure described above for **7** was modified so that reactants stirred at -78 °C for 1.0-1.5 h were quenched at this temperature with saturated potassium carbonate. The procedure led to 2,4,6-trimethylbenzophenone **7** (60-70%, 0.42 g -0.49 g) as well as (*E*)-β-distyryltetramethyl disiloxane **9** (0.125 g, 12%) and an oligomer of chlorodimethylsilylstyrene.

^{1}H NMR ($CDCl_3$, 300 MHz): δ: 0.02 (s, 12H), 6.19-6.25 (d, 2H, J = 19.2 Hz), 6.70-6.76 (d, 2H, J = 19.2 Hz), 7.02-7.21 (m, 10H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ: 143.7, 138.0, 127.9, 127.5, 125.9, 0.2; ^{29} Si NMR ($CDCl_3$, 59.6 MHz): δ: -2.2; IR (neat): ν: 3024, 2958, 1605, 1574, 1494, 1447, 1255, 1043, 990, 849, 797, 689, 559, 450 cm^{-1}; MS (EI, m/z): 338(20), 247 (45), 219 (100), 193 (40), 145 (30), 73 (20).

(E)-β-(Mesityldimethylsilyl)styrene 4 With Phenylacetyl Chloride: **4** (1.68 g, 6.0 mmol) was added to a solution of methylene chloride (150 mL) containing phenylacetyl chloride (0.927 g, 6.0 mmol) and titanium tetrachloride 4.6 g, 24 mmol) at -78 °C. The reaction mixture was stirred at -78 °C for 2.5 h, warmed slowly

to -45 °C overnight (16 h), then the temperature was finally raised to 25 °C for a further 30 min. The reaction mixture was quenched by adding saturated potassium carbonate (150 mL). Extraction with diethyl ether (3 x 100 mL), and radial chromatography yielded benzyl mesityl ketone **8** (0.85 g, 60%) along with an oligomer of chlorodimethylsilylstyrene.

^{1}H NMR ($CDCl_3$, 200 MHz): δ: 2.26 (s, 6H), 2.39 (s, 3H), 4.10 (s, 2H), 6.94 (s, 2H), 7.36-7.39 (m, 5H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ: 206.8, 138.8, 138.0, 133.0, 132.3, 129.5, 128.1, 126.6 , 51.3, 20.6, 18.8; IR (neat): ν: 3025, 2961, 2923, 2740, 1701, 1611, 1501, 1450, 1380, 1311, 1250, 1070, 1030, 985, 850, 720, 690 cm^{-1}; MS (EI, m/z): 147 (100), 119 (20), 91 (15); MS (CI, m/z): $M^+ + NH_4$; 256 (15), 239 (20), 147 (100), 119 (5), 91 (10).

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