

## Synthesis and reactions of highly sterically hindered organosilicon compounds of the type $(\text{Me}_3\text{Si})_3\text{CSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{X}$

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### Abstract

Reaction of  $\text{TsiLi}$  ( $\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$ ) with  $(p\text{-MeOC}_6\text{H}_4)_2\text{SiF}_2$  gave  $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{F}$ , which was treated with  $\text{LiAlH}_4$  to give  $(\text{Me}_3\text{Si})_3\text{CSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{H}$ . Treatment of the latter with  $\text{ICl}$  in the presence of a large excess of  $\text{Me}_3\text{SiC}_6\text{H}_4\text{OMe-}p$  gave  $(\text{Me}_3\text{Si})_3\text{CSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{Cl}$  rather than the expected  $(\text{Me}_3\text{Si})_3\text{CSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{I}$ . Use of  $\text{Br}_2$  in place of  $\text{ICl}$  gave  $(\text{Me}_3\text{Si})_3\text{CSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{Br}$ . The fluoride  $(\text{Me}_3\text{Si})_3\text{CSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{F}$  was found to react with  $\text{NaOMe}/\text{MeOH}$  and  $\text{NaOEt}/\text{EtOH}$ , to give  $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{OMe}$  and  $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{OEt}$ , respectively, and secondary products formed from them. Only secondary products were observed from the corresponding (prolonged) reactions in  $\text{NaOPr}^i/\text{Pr}^i\text{OH}$ , and  $\text{KOBu}^t/\text{Bu}^t\text{OH}$ . The diol  $(p\text{-MeOC}_6\text{H}_4)_2\text{Si}(\text{OH})_2$  was made by hydrolysis of  $(p\text{-MeOC}_6\text{H}_4)_2\text{SiCl}_2$ . © 1997 Elsevier Science S.A.

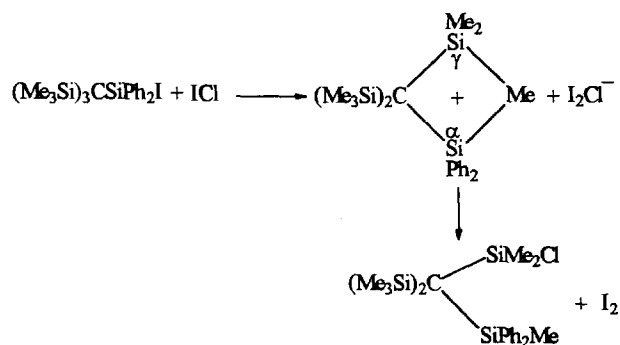
### 1. Introduction

Much novel chemistry has emerged from studies of compounds in which the bulky tris (trimethylsilyl)methyl group,  $(\text{Me}_3\text{Si})_3\text{C}$ , frequently denoted below by the symbol  $\text{Tsi}$ , is attached to a functional silicon centre [1–5]. The novelty in most cases arises from the inhibition of the normally great ease of nucleophilic attack at the functional silicon centre, which allows observation of other mechanisms that are not normally competitive. One example of this is provided by the elimination reaction that occurs when a compound of the type  $\text{TsiSiR}_2\text{X}$ ,  $\text{X} = \text{halogen}$ , is treated with  $\text{NaOMe}$  in  $\text{MeOH}$ , e.g., as shown in Scheme 1 [6]. A second, and perhaps the most striking, example of a novel mechanism is the formation of Me-bridged cations, and possible subsequent 1,3-migration of the Me group, in the reaction of the iodides  $\text{TsiSiR}_2\text{I}$  with electrophiles, such as silver salts,  $\text{ICl}$ , or  $\text{CF}_3\text{CO}_2\text{H}$ , e.g., [7].

The extent of such migration depends largely on the size of the groups  $\text{R}$ , which greatly influences the relative ease of attack of the nucleophile  $\text{Y}^-$  at the  $\alpha$ - and  $\gamma$ - silicon centres; thus there is virtually complete

formation of the rearranged product  $(\text{Me}_3\text{Si})_2(\text{R}_2\text{MeSi})\text{CSiMe}_2\text{Y}$  when  $\text{R} = \text{Ph}$ , but a mixture of rearranged and unrearranged products when  $\text{R} = \text{Et}$  [7].

However, this is not the only factor since, for example, only unrearranged products are obtained when  $\text{X} = \text{OMe}$  [8], and moreover, it has recently been observed that unrearranged products usually dominate in the reactions of the labelled iodide  $\text{TsiSi}(\text{CD}_3)_2\text{I}$ , where there can be only a very small difference between the steric hindrance at the two centres [3]. It thus seemed to us of interest to make the iodide  $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{I}$ , in order to examine the influence of the electron release by



Scheme 1.

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the *p*-anisyl groups on the ease of the formation of the cation and perhaps on the extent of rearrangement. Moreover, the reactions could be expected to yield the rearranged species  $(\text{Me}_3\text{Si})_2[(p\text{-MeOC}_6\text{H}_4)_2\text{MeSi}]\text{CSiMe}_2\text{Y}$ , which would allow study of the effects of the much greater bridging ability of the *p*-anisyl than of the Ph group, on the ease of departure of  $\text{Y}^-$  [9]. Unfortunately, for the reason indicated below, we have so far been unable to obtain this iodide, but we have made some related compounds and examined some of their reactions. For convenience we subsequently denote the *p*-anisyl group by the symbol An.

## 2. Results and discussion

An attempt to make  $\text{TsiSiAn}_2\text{Cl}$  by reaction of  $\text{TsiLi}$  with  $\text{An}_2\text{SiCl}_2$  was unsuccessful, and we thus had to turn to use of the less sterically hindered  $\text{An}_2\text{SiF}_2$ , itself made from the dichloride by treatment with  $\text{KHF}_2$ . The reaction of the difluoride with  $\text{TsiLi}$  gave a satisfactory yield of the fluoride  $\text{TsiSiAn}_2\text{F}$ , 1, and treatment of the latter with  $\text{LiAlH}_4$  in THF gave the hydride  $\text{TsiSiAn}_2\text{H}$ . From this we expected to be able to obtain the iodide  $\text{TsiSiAn}_2\text{I}$  by reaction with  $\text{ICl}$ , by analogy with the corresponding reaction of  $\text{TsiSiPh}_2\text{H}$  [10]. We were aware that the  $\text{HCl}$  or  $\text{HI}$  generated would very readily cleave the  $\text{Si}-\text{An}$  bonds [11], and so carried out the reaction in the presence of a large excess of  $\text{AnSiMe}_3$  to take up the  $\text{HX}$  preferentially. This did ensure survival of the  $\text{Si}-\text{An}$  bonds of the  $\text{TsiSiAn}_2\text{H}$ , but unfortunately the product was the chloride  $\text{TsiSiAn}_2\text{Cl}$ , not the iodide. We can think of no reason why the diphenyl compound should give the iodide and the dianisyl compound the chloride. The possibility that the latter arises from subsequent reaction of initially formed iodide with the excess of  $\text{ICl}$  seems unlikely, since this would, by analogy with the behaviour of the diphenyl iodide [10], be expected to give the rearranged chloride  $(\text{Me}_3\text{Si})_2(\text{An}_2\text{MeSi})\text{CSiMe}_2\text{Cl}$ , partially or exclusively. The bromide  $\text{TsiSiAn}_2\text{Br}$  was obtained when  $\text{Br}_2$  was used in place of  $\text{ICl}$ . Neither  $\text{TsiSiPh}_2\text{H}$  nor  $\text{TsiSiAn}_2\text{H}$  reacts with  $\text{I}_2$ .

The reaction of fluoride 1 with  $\text{NaOMe}$  in  $\text{MeOH}$  was examined in order to see whether it behaved in the same way as  $\text{TsiSiAn}_2\text{F}$  [7], but the reaction time was extended in order to find out what secondary reactions would occur. Reaction with 2.5 M  $\text{NaOMe}$  in refluxing  $\text{MeOH}$  for 58 h followed by aqueous work-up was found to give the expected  $(\text{Me}_3\text{Si})_2\text{CHSiAn}_2\text{OMe}$ , 3, (26%) along with the products of breakdown of the latter, namely  $\text{Me}_3\text{SiCH}_2\text{SiAn}_2\text{OMe}$  (17%) and  $\text{Me}_3\text{SiCH}_2\text{SiAn}_2\text{OH}$ , 4. The formation of 3 can be assumed to occur by the type of mechanism shown for the diphenyl compound in Scheme 1. That of  $\text{Me}_3\text{SiCH}_2\text{SiAn}_2\text{OMe}$  presumably involves attack by

$\text{MeO}^-$  on an  $\text{Me}_3\text{Si}$  group in 3, which is less sterically encumbered than 1, to generate the carbanion,  $(\text{Me}_3\text{Si})(\text{An}_2\text{MeSi})\text{CH}^-$ , which then acquires a proton from the solvent. Some conversion of  $\text{Me}_3\text{SiCH}_2\text{SiAn}_2\text{OMe}$  into  $\text{Me}_3\text{SiCH}_2\text{SiSiAn}_2\text{OH}$  would then be likely to take place during the hydrolytic work-up, but some of the hydroxide products could arise from the addition of adventitious water to the intermediate  $(\text{Me}_3\text{Si})_2\text{C}=\text{SiAn}_2$ , with this followed by the  $\text{Me}_3\text{Si}-\text{C}$  bond cleavage.

We also examined the corresponding reactions of 1 with metal alkoxides in some alcohols that were not used in the case of  $\text{TsiSiPh}_2\text{F}$ . The reactions with 2.5 M  $\text{NaOEt}/\text{EtOH}$ , 2.5 M  $\text{NaOPr}^i/\text{Pr}^i\text{OH}$ , and 1.5 M  $\text{KOBu}^t/\text{Bu}^t\text{OH}$  for 41, 193 and 100 h, respectively, gave products as follows:

From $\text{NaOEt}/\text{EtOH}$	$(\text{Me}_3\text{Si})_2\text{CHSiAn}_2\text{Et}$ , 16%; $\text{Me}_3\text{SiCH}_2\text{SiAn}_2\text{OEt}$ , 21%; 4, 19%
From $\text{NaOPr}^i/\text{Pr}^i\text{OH}$	$\text{Me}_3\text{SiCH}_2\text{SiAn}_2\text{OPr}^i$ , 22%; 4, 6%; recovered 1, 8%
From $\text{KOBu}^t/\text{Bu}^t\text{OH}$	4, 52%

The absence of any of the primary products of the type  $(\text{Me}_3\text{Si})_2\text{CHSiAn}_2\text{OR}$  from the reactions in  $\text{Pr}^i\text{OH}$  and  $\text{Bu}^t\text{OH}$  can be attributed to larger steric hindrance to the initial attack on 1, which necessitates longer reaction times and results in greater opportunity for breakdown of the primary product.

### 2.1. Preparation of the diol $(p\text{-MeOC}_6\text{H}_4)_2\text{Si}(\text{OH})_2$

There is much current interest in the crystal structures of silanediols [12], and particularly in cases in which there is  $\text{SiOH} \pi$  bonding, e.g., to Ph groups [13–15]. The possibility of such bonding would be enhanced in  $\text{An}_2\text{Si}(\text{OH})_2$  because of the strong release of electrons into the aromatic rings by the  $\text{MeO}$  substituents, and so we thought it of interest to make that diol and if possible determine its structure. We obtained the diol satisfactorily by hydrolysis of  $\text{An}_2\text{SiCl}_2$ , but have so far been unable to obtain suitable crystals.

## 3. Experimental

Reactions involving lithium metal, organolithium reagents or  $\text{LiAlH}_4$  were carried out under dry argon. Solvents were dried by standard methods.

### 3.1. Spectra

The  $^1\text{H}$  NMR spectra were recorded on Bruker FT (500 MHz) and FT NMR Bruker (80 MHz) spectrometers for solutions in  $\text{CDCl}_3$ . The IR spectra were

recorded on a Shimadzu IR 408 spectrometer with KBr discs. Mass spectra were obtained with a Finnigan MAT 312 or a Shimadzu Qp 100 × spectrometer at 70 eV. Elemental analyses were carried out with a Heareus CHN-ORAPID instrument. Melting points were determined on a 9100 Electrothermal apparatus.

### 3.2. Preparation of bis(*p*-methoxyphenyl)difluoro silane (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiF<sub>2</sub>

KHF<sub>2</sub> (15.6 g, 0.20 mol) was gradually added with stirring to a solution of (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiCl<sub>2</sub> [16], (31.3 g, 0.10 mol). *n*-heptane (50 cm<sup>3</sup>) was then added and the mixture was stirred at 80°C for 1 h, then filtered hot. The product separated on cooling and was recrystallized from *n*-heptane (87%); m.p. 68°C. IR (KBr, cm<sup>-1</sup>) ν (SiF<sub>2</sub>) 900, 860. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 3.86 (s, 6H, OMe) and 6.96–7.67 ppm (q, 8H, Ar); *m/z* (EI) 280 (100% M<sup>+</sup>), 265 (6, [M-Me]<sup>+</sup>), 250 (12), 219 (7), 199 (12), 171 (9), 77 (6). (Found: C, 60.3; H, 5.1. C<sub>14</sub>H<sub>14</sub>F<sub>2</sub>O<sub>2</sub>Si calculated: C, 59.98; H, 5.03%).

### 3.3. Preparation of trisylbis(*p*-methoxyphenyl)fluoro-silane TsiSi(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>2</sub>F

A solution of (*p*-MeOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SiF<sub>2</sub> (14 g, 50 mmol) in THF (15 cm<sup>3</sup>) was added dropwise with stirring to a solution of TsiLi (50 mmol) in THF (50 cm<sup>3</sup>) that had been made by reaction of TsiH (11.5 g, 50 mmol) with MeLi generated from MeI (8.5 g, 60 mmol) with Li (0.84 g, 120 mmol) [17]. The mixture was refluxed for 210 min, then aqueous NH<sub>4</sub>Cl was added and the organic compounds were extracted with Et<sub>2</sub>O. The extract was dried (MgSO<sub>4</sub>), filtered and evaporated, and the residue recrystallized from EtOH to give TsiSi(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>2</sub>F (62%); m.p. 136°C; IR (KBr, cm<sup>-1</sup>) ν (Tsi) 900–770. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.29 (s, 27H, SiMe<sub>3</sub>), 3.77 (s, 6H, OMe), and 6.86–7.76 ppm (q, 8H, Ar); *m/z* (EI) 492 (19%, M<sup>+</sup>), 477 (14, [M-Me]<sup>+</sup>), 369 (100), 277 (25). (Found: C, 58.1; H, 8.4. C<sub>24</sub>H<sub>41</sub>FO<sub>2</sub>Si<sub>4</sub> calculated: C, 58.5; H, 8.4%).

### 3.4. Preparation of trisylbis(*p*-methoxyphenyl)silane TsiSi(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>2</sub>H

LiAlH<sub>4</sub> (10 g, 0.26 mol) was gradually added with stirring to a solution of TsiSi(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>2</sub>F (5 g, 10.16 mmol) in dried THF (100 cm<sup>3</sup>). The mixture was refluxed for 16 days. (The long reaction time required was probably a consequence of poor quality of the LiAlH<sub>4</sub> available to us). After cooling of the mixture in ice water, aqueous saturated NH<sub>4</sub>Cl was slowly added, the solution was extracted with Et<sub>2</sub>O, then extract was dried (MgSO<sub>4</sub>), filtered and evaporated, and the residue was recrystallized from EtOH to give TsiSi(C<sub>6</sub>H<sub>4</sub>OMe-

*p*)<sub>2</sub>H (94%); m.p. 131°C; IR (KBr, cm<sup>-1</sup>): ν (Si–H) 2100. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.26 (s, 27H, SiMe<sub>3</sub>), 3.78 (s, 6H, OMe), 5.17 (s, 1H, Si–H), and 6.76–7.8 ppm (q, 8H, Ar); *m/z* (EI) 474 (75%, M<sup>+</sup>) 429 (26), 369 (100), 351 (55), 291 (35), 263 (44), 257 (10), 244 (59), 205 (54), 201 (46), 82 (92), 45 (78). (Found: C, 60.2; H, 8.9. C<sub>24</sub>H<sub>42</sub>O<sub>2</sub>Si<sub>4</sub> calculated: C, 60.7; H, 8.9%).

### 3.5. Preparation of trisylbis(*p*-methoxyphenyl)chloro-silane TsiSi(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>2</sub>Cl

A solution of ICl (0.163 g, 1 mmol) in CCl<sub>4</sub> (15 cm<sup>3</sup>) was added dropwise with stirring to a solution of TsiSi(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>2</sub>H (0.47 g, 1 mmol) and *p*-MeOC<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub> in CCl<sub>4</sub> (5 cm<sup>3</sup>). The mixture was stirred for 1 h, the progress of the reaction being monitored by IR spectroscopy. The solvent was removed under reduced pressure and the residue was dissolved in MeOH (10 cm<sup>3</sup>) and aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (10 cm<sup>3</sup>) was added. The solid that separated was extracted with ether (20 cm<sup>3</sup>) and the extract was shaken with water then separated and evaporated. Methanol (15 cm<sup>3</sup>) was added to the residue and the mixture was kept in refrigerator for 1 day, and the product that separated was isolated by decantation, and washed with cold MeOH several times. The resulting product was recrystallized from EtOH to give TsiSi(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>2</sub>Cl (89%); m.p. 143°C. A pure sample for elemental analysis was obtained by TLC (Silicagel, 1:1.8 *n*-heptane–chloroform as eluant). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.31 (s, 27 H, SiMe<sub>3</sub>), 3.82 (s, 6H, OMe) and 6.82–7 ppm (q, 8H, Ar); *m/z* (EI) 508 (32%, M<sup>+</sup>), 457 (31), 443 (49), 400 (59), 389 (85), 313 (47), 279 (92), 201 (78), 165 (100), 150 (13), 145 (33), 135 (62), 121 (32), 93 (39), 73 (54), 59 (77), 45 (65). (Found: C, 56.2; H, 8.0. C<sub>24</sub>H<sub>41</sub>ClO<sub>2</sub>Si<sub>4</sub> calculated: C, 56.4; H, 8.1%).

### 3.6. Preparation of trisylbis(*p*-methoxyphenyl)bromo-silane TsiSi(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>2</sub>Br

A solution of Br<sub>2</sub> (0.160 g, 1 mmol) in CCl<sub>4</sub> (15 cm<sup>3</sup>) was added dropwise with stirring to a solution of TsiSi(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>2</sub>H (0.47 g, 1 mmol) and *p*-MeOC<sub>6</sub>H<sub>4</sub>SiMe<sub>3</sub> (0.5 cm<sup>3</sup>) in CCl<sub>4</sub> (15 cm<sup>3</sup>). The mixture was stirred for 1 h during which progress of the reaction was monitored by IR spectroscopy. Solvent was removed under reduced pressure and the residue recrystallized from EtOH to give TsiSi(C<sub>6</sub>H<sub>4</sub>OMe-*p*)<sub>2</sub>Br (91%); m.p. 136°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) 0.41 (s, 27H, SiMe<sub>3</sub>), 3.86 (s, 6H, OMe) and 6.84–7.97 ppm (s, 8H, Ar); *m/z* (EI) 554 (3%, M<sup>+</sup>), 552 (2), 539 (3), 437 (2), 431 (100), 429 (87), 385 (13), 323 (17), 277 (2), 277 (24), 201 (167), 165 (37), 73 (88), 69 (2), 45 (16). (Found: C, 52.0, H, 7.7. C<sub>24</sub>H<sub>41</sub>BrO<sub>2</sub>Si<sub>4</sub> calculated: C, 52.22; H, 7.46%).

### 3.7. Preparation of $(p\text{-MeOC}_6\text{H}_4)_2\text{Si}(\text{OH})_2$

A solution of  $\text{Cl}_2\text{Si}(\text{C}_6\text{H}_4\text{OMe-}p)_2$  (5.0 g) in ether (20 cm<sup>3</sup>) was added to water containing a little sodium carbonate, and the mixture was stirred at room temperature for 15 min. It was then extracted with ether, and the combined extracts were dried ( $\text{MgSO}_4$ ), and the solvent evaporated off to give  $(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{Si}(\text{OH})_2$  (1.5 g, 34%); m.p. 136°C. Recrystallization from a variety of solvents, including hexane gave only a powder. Recrystallization from benzene gave fluffy crystals but these were unsuitable for an X-ray study.

### 3.8. Reaction of $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{F}$ with $\text{NaOMe}/\text{MeOH}$

A solution of  $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{F}$  (2 g, 4.06 mmol) in 2.5 M  $\text{NaOMe}/\text{MeOH}$  (17 cm<sup>3</sup>) was refluxed for 57.5 h and then added to water. Extraction with hexane followed by washing, drying ( $\text{MgSO}_4$ ) and evaporation of the extract left a liquid, which was subjected to preparative TLC (Silica gel, 4/1 hexane–dichloromethane as eluent) to give the products enumerated below.

(a)  $(\text{Me}_3\text{Si})\text{CH}_2\text{Si}(\text{C}_6\text{H}_4\text{OMe-}p)_2(\text{OH})$  (0.30, 17%) after recrystallization from 80/20 liquid petroleum–hexane; m.p. 71°C; IR (KBr, cm<sup>-1</sup>):  $\nu$  (SiOH) 3420 (Br). <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) –0.025 (s, 9H, SiMe<sub>3</sub>), 0.39 (s, 2H, CH<sub>2</sub>), 3.81 (s, 6H, OMe) and 6.9–7.52 ppm (q, 8H Ar);  $m/z$  (EI) 346 (17%, M<sup>+</sup>), 331 (23, [M-Me]<sup>+</sup>), 259 (59), 223 (100), 193 (93), 165 (25), 131 (40), 121 (17), 91 (101), 73 (5). (Found: C, 61.4; H, 8.7. C<sub>18</sub>H<sub>26</sub>O<sub>3</sub>Si<sub>2</sub> calculated: C, 62.38; H, 7.56%).

(b)  $(\text{Me}_3\text{Si})\text{CH}_2\text{Si}(\text{C}_6\text{H}_4\text{OMe-}p)_2(\text{OMe})$  (0.35 g, 23%) <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) –0.063 (s, 9 H SiMe<sub>3</sub>), 0.037 (s, 2 H, CH<sub>2</sub>), 3.46 (s, 3H, OMe), 3.83 (s, 6H, OMe), and 6.92–7.52 ppm (q, 8H, Ar);  $m/z$  (EI) 360 (15%, M<sup>+</sup>), 345 (92, [M-Me]<sup>+</sup>) 392 (25), 273 (65), 253 (100), 121 37), 73 (15), 59 (27) (Found; C, 62.8; H, 8. C<sub>19</sub>H<sub>28</sub>O<sub>3</sub>Si<sub>2</sub> calculated: C, 62.3; H, 7.78%).

(c)  $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2(\text{OMe})$  (0.46 g, 26%) after recrystallization from EtOH; m.p. 70°C; <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) 0.007 (s, 18H, SiMe<sub>3</sub>), 0.29 (s, 1H, CH), 3.40 (s, 3H, OMe), 3.83 (s, 6H, OMe) and 6.91–7.51 ppm (q, 8H, Ar);  $m/z$  (EI), 417 (53%, [M-Me]<sup>+</sup>), 309 (24), 273 (100), 243 (20), 205 (36), 165 (36), 89 (19), 73 (46). Found: C, 60.4; H, 8.5. C<sub>22</sub>H<sub>36</sub>O<sub>3</sub>Si<sub>3</sub> calculated: C, 61.03; H, 8.38%).

### 3.9. Reaction of $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{F}$ with $\text{NaOEt}/\text{EtOH}$

A solution of  $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{F}$  (2 g, 4.06 mmol) in 2.5 M  $\text{NaOEt}/\text{EtOH}$  (37 cm<sup>3</sup>) was refluxed for 41 h and the mixture worked up as described Section 3.8.

The liquid product mixture was subjected to preparative TLC (Silicagel 4/1 hexane–dichloromethane as eluent) to give the liquid products enumerated below.

(a)  $(\text{Me}_3\text{Si})\text{CH}_2\text{Si}(\text{C}_6\text{H}_4\text{OMe-}p)_2(\text{OH})$  (0.35 g, 19%) with properties identical to those listed in Section 3.8.

(b)  $(\text{Me}_3\text{Si})\text{CH}_2\text{Si}(\text{C}_6\text{H}_4\text{OMe-}p)_2(\text{OEt})$  (0.33 g, 21%); <sup>1</sup>H NMR( $\text{CDCl}_3$ ) –0.052 (s, 9H, SiMe<sub>3</sub>), 0.37 (s, 2H, CH<sub>2</sub>), 1.18 (t, 2H CH<sub>2</sub>), 3.64 (q, 3H, CH<sub>3</sub>), 3.82 (s, 6H, OMe) and 6.91–7.52 ppm (q, 8H, Ar);  $m/z$  (EI) 374 (6%, M<sup>+</sup>), 359 (45 [M-Me]<sup>+</sup>), 287 (11), 267 (100), 223 (13), 165 (10), 135 (40), 91 (9), 73 (20). (Found: C, 63.4; H, 8.1. C<sub>20</sub>H<sub>30</sub>O<sub>3</sub>Si<sub>2</sub> calculated: C, 64.1; H, 8.02%).

(c)  $(\text{Me}_3\text{Si})_2\text{CHSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2(\text{OEt})$  (0.29 g, 16%); <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) –0.01(s, 18H, SiMe<sub>3</sub>), 0.31 (s, 1H, CH), 1.2 (t, 2H, CH<sub>2</sub>), 3.46 (q, 3H, CH<sub>3</sub>), 3.84 (s, 6H, OMe) and 6.90–7.59 ppm (q, 8H, Ar);  $m/z$  (EI) 431 (70%, [M-Me]<sup>+</sup>), 339 (20), 295 (20), 287 (68), 243 (42), 203 (37), 165 (65), 135 (52), 91 (24), 73 (100). (Found: C, 61.4; H, 8.7. C<sub>23</sub>H<sub>38</sub>O<sub>3</sub>Si<sub>3</sub> calculated: C, 61.8; H, 8.52%).

### 3.10. Reaction of $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{F}$ with $\text{NaOPr}^i/\text{Pr}^i\text{OH}$

A solution of  $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{F}$  (4 g, 8.12 mmol) in 2.5 M  $\text{NaOPr}^i/\text{Pr}^i\text{OH}$  was refluxed for 193 h and then worked up as described in Section 3.8. The resulting liquid product mixture was subjected to preparative TLC (Silicagel; 3/1 chloroform–hexane as eluent) to give the following liquid products.

(a)  $(\text{Me}_3\text{Si})\text{CH}_2\text{Si}(\text{C}_6\text{H}_4\text{OMe-}p)_2(\text{OPr}^i)$  (700 mg, 22%); <sup>1</sup>H NMR ( $\text{CDCl}_3$ ) –0.023 (s, 9H, SiMe<sub>3</sub>), 1.82 (d, 6H, CH<sub>3</sub>), 0.33 (s, 2H, CH<sub>2</sub>), 3.82 (s, 6H, OMe), 4.21 (q, 1H, CH) and 6.92–7.6 ppm (q, 8H, Ar);  $m/z$  (EI) 388 (11%, M<sup>+</sup>), 373 (52, [M-Me]<sup>+</sup>), 331 (17), 301 (37), 281 (100), 239 (90), 223 (57), 165 (28), 131 (82), 121 (34), 91 (23), 73 (28), 43 (77).

(b)  $(\text{Me}_3\text{Si})\text{CH}_2\text{Si}(\text{C}_6\text{H}_4\text{OMe-}p)_2(\text{OH})$  (215 mg, 6%) with properties identical to those listed in Section 3.8.

(c) Starting material (320 mg) and unidentified product (190 mg).

### 3.11. Reaction of $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{F}$ with $\text{KOBu}^t/\text{Bu}^t\text{OH}$

A solution of  $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{F}$  (2 g, 4.06 mmol) in 1.5 M  $\text{KOBu}^t/\text{Bu}^t\text{OH}$  (75 cm<sup>3</sup>) was refluxed for 100 h and the mixture then worked up as described in Section 3.8. The residue was subjected to preparative TLC (Silicagel; 4/1 dichloromethane–hexane as eluent) to give only  $(\text{Me}_3\text{Si})\text{CH}_2\text{Si}(\text{C}_6\text{H}_4\text{OMe-}p)_2(\text{OH})$  (0.97 g, 52%) with properties identical to those listed in Section 3.8.

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