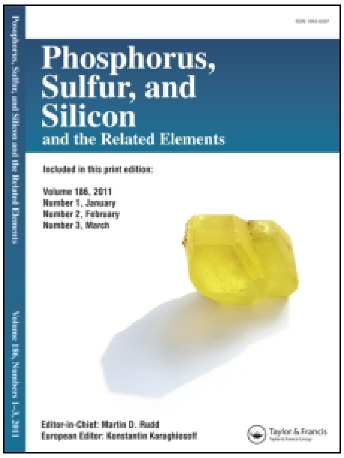

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS OF HIGHLY STERICALLY HINDERED ORGANOSILICON COMPOUNDS AND REACTIONS OF THEM WITH ALCOHOLIC SODIUM ALKOXIDES

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To cite this Article Safa, Kazem D. , Koushki, Ali R. and Asadi, Mohammad G.(2000) 'SYNTHESIS OF HIGHLY STERICALLY HINDERED ORGANOSILICON COMPOUNDS AND REACTIONS OF THEM WITH ALCOHOLIC SODIUM ALKOXIDES', Phosphorus, Sulfur, and Silicon and the Related Elements, 158: 1, 97 — 105

To link to this Article: DOI: 10.1080/10426500008042077

URL: http://dx.doi.org/10.1080/10426500008042077

Phosphorus, Sulfur, and Silicon, 2000, Vol. 158, pp. 97-105
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SYNTHESIS OF HIGHLY STERICALLY HINDERED ORGANOSILICON COMPOUNDS AND REACTIONS OF THEM WITH ALCOHOLIC SODIUM ALKOXIDES

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(Received April 26, 1999,; In final form May 18, 1999)

The Compounds TsiSiXX′X″ [Tsi=$(Me_3Si)_3C$; X=X′=X″=Br; X=$(C_6H_4OMe$-*p*), X′=X″=Cl; X=Bu, X′=X″=Cl; X′=Me, X″=F) synthesised and reacted with boiling NaOR/ROH (R=Me, Et, ^{i}Pr) have been shown to give the products of type $(Me_3Si)_2CHSiYZOR$(Y=OR, X; Z=OR, X′). It is suggested that the reaction proceeds through an elimination, analogous to E2 elimination of alkyl halides, involving cynchronous attack of RO^- at an $SiMe_3$ group, libration of X^-, and formation of $(Me_3Si)_2C{=}SiYZ$. The compound $TsiSiBr_3$ reacts with 0.1 M NaOR/ROH to give the substitution and elimination products, $TsiSiBr_2(OR)$, $TsiSiBr(OR)_2$, and $(Me_3Si)_2CHSi(OR)_3$. The compounds $TsiSi(C_6H_4OMe$-*p*$)Cl_2$, $TsiSiBuCl_2$. and $TsiSi(C_6H_4OMe$-*p*$)MeF$ react analogouly to give $(Me_3Si)_2CHSi$-$(C_6H_4OMe$-*p*$)(OR)_2$. $(Me_3Si)_2CHSi(C_6H_4OMe$-*p*$)OH(OR)$, $(Me_3Si)_2CHSi\ Bu(OR)_2$, $(Me_3Si)CH_2SiBu(OR)_2$ and $(Me_3Si)_2CHSi(C_6H_4OMe$-*p*$)MeOR$

Keywords: alkoxide: organosilicon; trisyl: fragmentation

1. INTRODUCTION

We have shown that the presence of the tris(trimethylsilyl)methyl ("trisyl") group, $(Me_3Si)_3C$-(denoted Tsi), in compounds of the type TsiSiXX′X′ causes very large steric hindrance toward nucleophilic displacement of X [1,2].

Because the normal reaction path is forbidden, such compounds display unusual reactions[3,4,5] and this is the cases in the reactions with sodium alkoxides, which we describe below.

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2. RESULTS AND DISCUSSION

Treatment of TsiLi with $SiCl_4$ gave $TsiSiCl_3$ which was reacted with $LiAlH_4$ to give $TsiSiH_3$[6]. Reaction of the latter with Br_2 in the presence of aluminium powder produced $TsiSiBr_3$.

We next prepared $TsiSiBuCl_2$ by reaction of TsiLi with $BuSiCl_3$. An Attempt to make $TsiSi(C_6H_4OMe\text{-}p)MeCl$ by reaction of TsiLi with $(C_6H_4OMe\text{-}p)MeSiCl_2$ was unsuccessful and thus we had to turn to the less sterically hindered $(C_6H_4OMe\text{-}p)MeSiF_2$, itself made from the dichloride by treatment with KHF_2. The reaction of difluoride with TsiLi gave a satisfactory yield of the fluoride $TsiSi(C_6H_4OMe\text{-}p)MeF$. The dichloride derivative of anisole namely $TsiSi(C_6H_4OMe\text{-}p)Cl_2$ was also prepared by the reaction of TsiLi with $(C_6H_4OMe\text{-}p)SiCl_3$.

The reaction of the tribromide, $TsiSiBr_3$ with NaOMe in MeOH was examined in order to see whether it behaved in the same way as $TsiSiCl_3$ [3, 4]. Reaction with 0. 1 M NaOMe in refluxing MeOH for 2 h followed by aqueous work up was found to give the fragmentation product, $(Me_3Si)_2CHSi(OMe)_3$ and substitution products, $(Me_3Si)_3CSiBr_2OMe$, $(Me_3Si)_3CSiBr(OMe)_2$. The formation of $(Me_3Si)_2CH(OMe)_3$ can be assumed to occur by the type of mechanism shown for the diphenyl compound in scheme 1 to give $(Me_3Si)_2CHSi(OMe)_3$[7, 8]. We also examined the corresponding reactions of $TsiSiBr_3$ with metal alkoxides in EtOH and Pr^iOH.

$$RO^- + Me_3SiC(Me_3Si)_2SiX\,X'X'' \rightarrow RO{-}Me_3Si{-}C(SiMe_3)_2{-}Si\,X'X''{-}X \rightarrow$$

$$ROSiMe_3 + (SiMe_3)_2C{=}SiX'X'' + X^-$$

$$(Me_3Si)_2C{=}Si\,X'X'' + ROH \rightarrow (Me_3Si)_2CHSi\,X'X''(OR)$$

SCHEME 1

The reaction with 0.1 M NaOEt/EtOH for 2.5 h gave $(Me_3Si)_2CHSi(OEt)_3$ and substitution products, $(Me_3Si)_3CSiBr_2OEt$, $(Me_3Si)_3CSiBr(OEt)_2$. The reaction with 0.1 M $NaOPr^i/Pr^iOH$ for 3.5 h gave $(Me_3Si)_2CHSi(OPr^i)_3$ and the substitution product, $(Me_3Si)_3CSiBr_2(OPr^i)$.

We noticed that with increasing of bulkinees of the alkoxide groups direct nucleophilic displacement was difficult and elimination-additon reactions were favoured. As for sodium methoxide and sodium ethoxide two displacement products, while for isopropyloxide only one displacement product were obtained

In the next work the corresponding reactions of $TsiSiBuCl_2$, $TsiSi(C_6H_4OMe\text{-}p)MeF$ and $TsiSi(C_6H_4OMe\text{-}p)Cl_2$ in NaOMe/MeOH and NaOEt/EtOH were examined and gave products as follows (Table I):

TABLE I Reactions of TsiSiXYZ with sodium alkoxide in alcohols

XYZ	*sodium alkoxide (M)*	*time (h)*	*products*
$(C_6H_4OMe\text{-}p)Cl_2$	NaOMe/MeOH 2.0	4	$(Me_3Si)_2CHSi(C_6H_4OMe\text{-}p)(OMe)(OH)$, $(Me_3Si)_2CHSi(C_6H_4OMe\text{-}p)(OMe)_2$
$(C_6H_4OMe\text{-}p)Cl_2$	NaOEt/EtOH 2.0	4	$(Me_3Si)_2CHSi(C_6H_4OMe\text{-}p)(OEt)_2$
$BuCl_2$	NaOMe/MeOH 2.0	4	$(Me_3Si)_2CHSiBu(OMe)_2$, $(Me_3Si)CH_2SiBu(OMe)_2$
$BuCl_2$	NaOEt/EtOH 2.0	4	$(Me_3Si)_2CHSiBu(OEt)_2$, $(Me_3Si)CH_2SiBu(OEt)_2$
$(C_6H_4OMe\text{-}p)MeF$	NaOMe/MeOH 1.5	10	$(Me_3Si)_2CHSi(C_6H_4OMe\text{-}p)(OMe)(Me)$

3. EXPERIMENTAL

3.1. Solvents and reagents

Reaction involving lithium metal, organolithium reagents, alkoxide or $LiAlH_4$, were carried out under dry argon. Solvents were dried by standard methods.

3.2. Spectra

Melting points were taken on a electrothermal 9100 digital-melting-point apparatus. The ^{1}HNMR spectra were recorded on a JEOl NM. PM 60 NMR (90 MHz) or a Bruker FT-80 spectrometers. The mass Spectra were run on a Shimadzu QP-100X spectrometer at 70 eV.

3.3. Preparation of TsiSi(C_6H_4OMe-*p*)Cl_2

(C_6H_4OMe-*p*)$SiCl_3$ (12. g, 50 mmol) was added dropwise with stirring to a solution of TsiLi (50 mmol) in THF (50 ml) 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)[9]. The mixture was refluxed for 30 min. Then aqueous NH_4Cl was added, the organic compounds were extracted with Et_2O. The extract was dried ($MgSO_4$), filtered and evaporated. The residue recrystallized from MeOH. The product was distilled in a sublimation apparatus at 0.01 mmHg/100 °C to yield pure TsiSi(C_6H_4OMe-*p*)Cl_2 (60%) mp 165 °C. FT-IR(KBr, cm^{-1}), (Si-C) 1253. FT-^1H NMR ($CDCl_3$) 0.3 (s, 27H, Tsi), 3.8 (s, 3H, OMe-*p*) 7–7.8 ppm (m, 4H, aryl). *m/z* (EI): 436(1%, $[M]^+$), 406(1.5), 401(13), 385(35), 330(20, 313(17), 221(19), 205(12), 165(130, 135(60, 93(11), 73(100), 45(38). (Found: C, 46.5; H, 7.8. $C_{17}H_{34}Cl_2OSi_4$ calculated: C, 46.65; H, 7.83%).

3.4. Reaction of TsiSi(C_6H_4OMe-*p*)Cl_2 with NaOMe/MeOH

A solution of TsiSi(C_6H_4OMe-*p*)Cl_2 (3 g, 6.85 mmol) in 2 M NaOMe/MeOH (100 ml) was refluxed for 4 h. *n*-Hexane (70 ml) was added, the organic layer washed several times with water dried ($MgSO_4$), filtered, and evaporated. The resulting liquid product mixture was subjected to preparative TLC (Silicagel, 1:1 *n*-hexane : dichloromethane as eluent) to give the following products:

i) $(Me_3Si)_2CHSi(C_6H_4OMe$-*p*)OH(OMe) FT-IR(KBr, cm^{-1}) (Si-OH) 3750; (Si-C), 1250. FT-^1H NMR($CDCl_3$) –0.3 (s, 1H, CH), 0.06 (d, 18H, $SiMe_3$), 2.5 (s, b, 1H, SiOH), 3.4 (s, 3H, SiOMe), 3.8 (s, 3H, OMe-aryl), 7–7.5 ppm (m, 4H, aryl). *m/z* (EI): 342(2%, $[M]^+$), 327(1), 295(5), 281(7), 221(9), 207(4), 147(10), 128(5), 86(3), 73(22), 45(100). (Found: C, 51.8. H, 8.5. $C_{15}H_{30}O_3Si_3$ calculated: C, 52.52; H, 8.82%).

ii) $(Me_3Si)_2CHSi(C_6H_4OMe$-*p*)$(OMe)_2$ FT-IR(KBr, cm^{-1}), (Si-C) 1250. FT-^1H NMR ($CDCl_3$) –0.4 (s, 1H, CH), 0.03 (s, 18H, $SiMe_3$), 3.5 (s, 3H, Si-OMe), 3.8 (s, 3H, OMe-aryl), 6.8–7.5 ppm (m, 4H, aryl). *m/z* (EI): 356(0.5%, $[M^+)$, 341(12), 309(4), 221(2), 147(1), 86(20), 84(31), 73(3.3), 49(100). (Found: C, 53.8; H, 8.8. $C_{16}H_{32}O_3Si_3$ calculated: C, 53.87; H, 9.04%).

3.5. Reaction of TsiSi(C_6H_4OMe-*p*)Cl_2 with NaOEt/EtOH

A solution of TsiSi(C_6H_4OMe-*p*)Cl_2 (3 g, 6.85 mmol) in 2 M NaOEt/EtOH (100 ml) was refluxed for 4 h. *n*-hexane was added, the organic layer washed several times with water, dried ($MgSO_4$), filtered, and evaporated. The resulting liquid product mixture was subjected to preparative TLC (Silicagel, 1:1, *n*-hexane : dichloromethane as eluent) to give $(Me_3Si)_2CHSi(C_6H_4OMe$-*p*$)(OEt)_2$ (53.1%). FT-IR(KBr, cm^{-1}), (Si-C) 1250. FT-^1H NMR ($CDCl_3$) –0.4 (s, 1H, CH), 0.07 (s. 18H. $SiMe_3$), 1.2 (t. 3H, CH_3), 3.7 (q, 2H, OCH_2). *m/z* (EI): 369(10%, $[M\text{-}Me]^+$), 323(1), 341(1), 325(3), 205(2), 189(2), 86(21), 84(33), 73(2), 49(100). (Found: C, 55.3; H, 9.3. $C_{18}H_{36}O_3Si_3$ calculated: C, 56.1; H, 9.43%).

3.6. Preparation of TsiSiBuCl_2

$BuSiCl_3$ (9.575 g, 50 mmol) was added dropwise with stirring to a solution of TsiLi (50 mmol) in THF (50 ml). The mixture was refluxed for 30 min. Then aqueous NH_4Cl was added and the organic compounds were extracted with Et_2O. The extract was dried ($MgSO_4$), filtered, evaporated, and the residue recrystallized from EtOH. The product was subjected to preparative TLC (Silicagel, *n*-hexane as eluent), to give TsiSiBuCl_2 (48%), mp 119°C. FT-IR(KBr, cm^{-1}) (C-H aliphatic) 2911, (C-Si) 1250, (C-Si) 850, (Si-Cl) 675. FT-^1H NMR ($CDCl_3$) 0.35 (s, 27H, Tsi), 0.4–1.5 ppm (m, 9H, Bu). *m/z* (EI): 386(2%, $[M]^+$), 371(80), 315(70), 246(8), 221(65), 129(40), 73(100), 45(30). (Found: C, 42.6; H, 9.3. $C_{14}H_{36}Cl_2Si_4$ calculated: C, 41.3; H, 9.3%).

3.7. Reaction of TsiSiBuCl_2 with NaOMe-MeOH

A solution of TsiSiBuCl_2 (3 g, 7.75 mmol) in 2 M NaOMe/MeOH (70 ml) was refluxed for 4 h. Then worked up with a solution of water and *n*-hexane. The organic layer separated, washed several times with water, dried ($MgSO_4$), filtered and evaporated. The resulting liquid product mixture was subjected to preparative TLC(Silcagel, 4:1 *n*-hexane:dichloromethane as eluent) to give the following products:

i) $(Me_3Si)_2CHSiBu(OMe)_2$ FT-IR (KBr, cm^{-1}), (Si-O-C) 1034. FT-^1H NMR ($CDCl_3$) –0.6 (s, 1H, CH), 0.1 (d, 18H, $SiMe_3$), 0.5–1.5 (m, 9H, Bu), 3.5 ppm (s, 6H, OMe). *m/z* (EI): 306(1%, $[M]^+$), 259(15), 231(23), 199(100), 175(17), 157(30), 143(80), 101(37H, Bu),), 73(28), 57(12). (Found: C, 50.8; H, 11.3. $C_{13}H_{34}O_2Si_3$ calculated: C, 50.9; H, 11.1%).

ii) $(Me_3Si)CH_2SiBu(OMe)_2$ FT-IR(KBr. cm^{-1}), (Si-O-C) 1034, (Si-C) 1245. FT-^{1}H NMR ($CDCl_3$) -0.55 (d. 2H, CH_2), 0.1 (s, 9H. $SiMe_3$), 0.5–1.5 (m. 9H, Bu), 3.5 ppm (s, 6H, OMe). *m/z* (EI): 234(2%, $[M]^+$), 219(20), 203(40), 189(50), 175(18), 145(21), 129(100), 115(23), 73(23), 59(17).

3.8. Reaction of $TsiSiBuCl_2$ with NaOEt-EtOH

A solution of $TsiSiBuCl_2$ (3 g, 7.75 mmol) in 2 M NaOEt/EtOH (70 ml) was refluxed for 4 h. Then worked up with a solution of water and *n*-hexane. The organic layer separated, washed several times with water, dried ($MgSO_4$) filtered and evaporated. The resulting liquid product mixture was subjected to preparative TLC (Silicagel, 9:1, *n*-hexane : dichloromethane as eluent) to give the following products:

i) $(Me_3Si)_2CHSiBu(OEt)_2$ FT-IR(KBr, cm^{-1}) (C-O-Si) 1034, (C-Si)1245. FT-^{1}H NMR ($CDCl_3$) -0.6 (s, 1H, CH), 0.1 (s, 18H, $SiMe_3$), 0.5–1.5 (m, 9H, Bu), 1–1.5 (m, 6H, Me-C), 3.7 ppm (q, 4H, OCH_2). *m/z* (EI): 334(1%, $[M]^+$), 321(40), 227(22), 263(20), 219(11), 203(30), 189(80), 133(12), 129(55), 115(10), 73(100).

ii) $(Me_3Si)CH_2SiBu(OEt)_2$ FT-IR (KBr, cm^{-1}), (C-O-Si) 1030, (C-Si) 1250. FT-^{1}H NMR ($CDCl_3$) -0.5 (d, 2H, Si-CH_2), 0.1 (s, 9H, $SiMe_3$), 0.5–1.5 (m, 9H, Bu);. 1–1.5 (m, 6H, Me-C), 3.85 ppm (q, 4H, CH_2-Me). *m/z* (EI): 262(1%, $[M]^+$), 247(2), 205(40), 203(62), 189(100), 175(18), 173(10), 73(20).

3.9. Preparation of $TsiSiBr_3$

Br_2 (1 g, 6.25 mmol) was added to a solution of $TsiSiH_3$ (0.55 g, 2.09 mmol) in benzene (50 ml) in the presence of aluminium powder (0.3 g, 11.11 mmol). The mixture was stirred for 6 h. Then worked up with a solution of sodium thiosulfate and petroleum ether (40–60), the organic layer separated, dried ($MgSO_4$), evaporated and washed several times with cold ethanol (50%) mp>340°C. FT-IR (KBr. cm^{-1}). (C-H aliphatic)3000, 2963 (Si-C) 1261, 859, (Si-Br) 620–690. FT-^{1}H NMR ($CDCl_3$) 0.15 ppm (d, 27H, Tsi). *m/z* (EI): 487(10%, $[M\text{-}Me]^+$), 485(18), 483(15), 481(8), 441(2), 419(2), 351(30), 331(50), 265(20), 241(95), 221(25), 127(18), 73(100). (Found: C, 25.0; H, 5.8. $C_{10}H_{27}Br_3Si_4$ calculated: C, 24.1; H, 5.4). $TsiSiBr_3$ also was obtained from reaction of $TsiSiCl_3$ with Br_2 in the presence of aluminium powder

3.10. Reaction of $TsiSiBr_3$ with NaOMe/MeOH

A solution of $TsiSiBr_3$ (2 g, 4 mmol) in 0.1 M NaOMe/MeOH (150 ml) was refluxed for 2 h. The methanol was evaporated. Cyclohexane was added and the cyclohexane solution washed, dried (Na_2SO_4), and evaporated. The resulting liquid product mixture was subjected to preparative TLC (Silicagel, 2:1, dichloromethane: cyclohexane as eluent) to give the following products:

i) $TsiSiBr_2OMe$, FT-^{1}H NMR ($CDCl_3$) 0.32 (s, 27H, Tsi), 3.77 ppm (s, 3H, OMe). *m/z* (EI): 452 (15%, $[M]^+$), 450(14%, $[M]^+$), 448(16%, $[M]^+$), 421(20), 379(25), 369(28), 353(30), 73(100). (Found: C, 29.8; H, 6.8. $C_{11}H_{30}Br_2OSi_4$ calculated: C, 29.3; H, 6.7%).

ii) $TsiSiBr(OMe)_2$, FT-^{1}H NMR ($CDCl_3$) 0.23 (s, 27H, Tsi), 3.61 ppm (s, 6H, OMe). *m/z* (EI): 402 (20%, $[M]^+$), 387(2), 369)(22), 355(2), 339(10), 58(100). (Found: C, 36.0; H, 8.1. $C_{12}H_{33}BrO_2Si_4$ calculated: C, 35.9; H, 8.2%).

iii) $(Me_3Si)_2CHSi(OMe)_3$ FT-^{1}H NMR ($CDCl_3$) −0.71 (s, 1H, CH), 0.05 (s, 18H, $SiMe_3$), 3.75 ppm (s, 9H, OMe). *m/z* (EI) 280(2%, $[M]^+$), 265(2), 249(2), 236(80), 221(10), 192(15), 145(50).

3.11. Reaction of $TsiSiBr_3$ with NaOEt/EtOH

A solution of $TsiSiBr_3$ with NaOEt/EtOH (2 g. 4 mmol) in 0.1 M NaOEt/EtOH (150 ml) was refluxed for 2.5 h. The ethanol was evaporated. Cyclohexane was added and the organic layer washed dried (Na_2SO_4), and evaporated. The resulting product mixture was subjected to preparative TLC (Silicagel, 3:2, dichloromethane : cyclohexane as eluent) to give the following products:

i) $TsiSiBr_2OEt$ FT-^{1}H NMR ($CDCl_3$) 0.25 (s, 27H, Tsi), 1.03 (t, 3H, Me-C), 3.84 ppm (q, 2H, OCH_2). *m/z* (EI): 466(5%, $[M]^+$), 451(20), 439(5), 422(4), 395(7), 384(2), 337(6), 323(8), 73(100). (Found: C, 31.2; H, 7.2, $C_{12}H_{32}Br_2OSi_4$ calculated: C, 31.0; H, 6.9%).

ii) $TsiSiBr(OEt)_2$ FT-^{1}H NMR ($CDCl_3$) 0.13 (s, 27H, Tsi); 1.17 (t, 6H, Me-C); 3.75 (q, 4H, OCH_2). *m/z* (EI): 415(20%, $[M\text{-}Me]^+$), 350(3), 340(2), 284(2), 199(3), 73(100). (Found: C, 39.3; H, 8.5. $C_{14}H_{37}BrO_2Si_4$ calculated: C, 39.2; H, 8.6%).

iii) $(Me_3Si)_2CHSi(OEt)_3$ FT-^{1}H NMR ($CDCl_3$) –0.30 (s, 1H, CH), 0.22 (s, 18H, $SiMe_3$), 1.05 (t, 9H, CH_3) 3.78 ppm (q, 6H, OCH_2) *m/z* (EI): 222(25%, $[M]^+$), 207(3), 149(50), 97(15), 73(100), 45(3). (Found: C, 48.5; H, 10.4. $C_{13}H_{34}O_3Si_3$ calculated: C, 48.4; H, 10.6%).

3.12. Reaction of $TsiSiBr_3$ with $NaO^iPr/^iPrOH$

A solution of $TsiSiBr_3$ (2 g, 4 mmol) in 0.1 M $NaO^iPr/^iPrOH$ (150 ml) was refluxed for 3.5 h. The isopropanol was evaporated. Cyclohexane was added and the cyclohexane solution washed, dried (Na_2SO_4), and evaporated. The resulting product mixture was subjected to preprative TLC (Silicagel. 1:1, dichloromethane : cyclohexane as eluent) to give the following products:

i) $TsiSiBr_2O^iPr$ FT-^{1}H NMR ($CDCl_3$) 0.09 (s, 27H, Tsi), 1.95 (d, 6H, C-CH_3) 3.55 ppm (m, 1H, CH-Me). *m/z* (EI): 480 (20%, $[M]^+$), 478(18), 476(15), 465(21), 425(7), 417(26), 398(10), 323(40), 280(32), 279(75), 251(45), 73(50), 43(100). (Found: C, 32.6; H, 7.2. $C_{13}H_{34}OSi_4$ calculated: C, 32.6; H, 7.1%).

ii) $(Me_3Si)_2CHSi(O^iPr)_3$ FT-^{1}H NMR ($CDCl_3$) –0.42 (s, 1H, CH-Si), 0.09 (s, 18H, $SiMe_3$), 1.80 (d, 18H, Me-C), 3.65 (m, 3H, CH-Me). *m/z* (EI): 364(6%, $[M]^+$), 349(20), 334(19), 294(21), 291(23), 233(2), 218(15), 205(2), 105(17), 73(100). (Found: C, 52.9; H, 11.1. $C_{16}H_{40}O_3Si_3$ calculated: C, 52.8; H, 11.0%).

3.13. Preparation of $TsiSi(C_6H_4OMe\text{-}p)MeF$

$(C_6H_4OMe\text{-}p)SiMeCl_2$ (22 g, 0.1 mol), KHF_2 (16g, 0.2 mol), and *n*-heptane (50 ml) were mixed at 70–80 °C for 1 h, then KF filtered and from the cold solution, the separated solid recristallized to give $(C_6H_4OMe\text{-}p)SiMeF_2$ (70%). $(C_6H_4OMe\text{-}p)SiMeF_2$ (9.4 g, 50 mmol) was added to a solution of TsiLi (50 mmol) inTHF (100 ml) and the mixture was refluxed for 3 h. The solution was treated with an aqueous solution of NH_4Cl, the organic layer was separated, dried (Na_2SO_4), and the solvent was removed. The pure product was obtained from recrystallization of EtOH to give TsiSi(C_6H_4OMe-*p*)MeF (70%), mp 109 °C. FT-^{1}H NMR ($CDCl_3$) 0.25 (s. 27H, Tsi), 0.39 (s. 3H, SiMe), 3.82 (s, 3H, OMe-aryl) 6.8–7.8 ppm (m, 4H, aryl-H). *m/z* (EI): 385(22%, $[M\text{-}Me]^+$), 293(18), 205(80), 201(100), 185(65).

3.14. Reaction of TsiSi(C_6H_4OMe-*p*)MeF with NaOMe/MeOH

TsiSi(C_6H_4OMe-*p*)MeF (1.2 g, 3 mmol) was refluxed in 1.5 M NaOMe/MeOH solution (50 ml) for 10 h. The solution was added to cyclohexane, the organic layer was washed several times with water, the organic layer was separated, dried (Na_2SO_4), filtered, the solvent evaporated, and the liquid residue was purified by preparative TLC (Silicagel, cyclohexane as eluent) to give $(Me_3Si)_2$CH-Si(C_6H_4OMe-*p*)(OMe)(Me) (30%). FT-^{1}H NMR ($CDCl_3$) –0.21 (s, 1H, CH), 0.07 (d, 18H, $SiMe_3$), 0.45 (s, 3H, SiMe), 3.26 (s, 3H, Si-OMe), 3.82 (s, 3H, OMe-aryl), 6.8–7.8 ppm (m, 4H, aryl-H). *m/z* (EI): 325(30%, $[M\text{-}Me]^+$), 293(18), 205(80), 201(90), 185(65).

Acknowledgements

We thank Professor C. Eaborn for helpful comments.

References

[1] C. Eaborn, D.A.R. Happer, K.D. Safa and D.R.M. Walton, J. Organometal Chem., **157**, C50, (1978).
[2] S.S. Dua, C. Eaborn, D.A.R. Happer, S.P. Hopper, K.D. Safa and D.R.M Walton, J. Organometal. Chem., **178**, 75, (1979).
[3] C. Eaborn, D.A.R. Happer. S.P. Hopper and K.D. Safa, J. Organometal. Chem., **170**, C9, (1979).
[4] C. Eaborn and S.P. Hopper. J. Organometal. Chem., **170**, C51, (1979).
[5] C. Eaborn. D.A.R. Happer, S.P. Hopper and K.D. Safa, J. Organometal. Chem.. **188**, 1790, (1980).
[6] D.B. Azarian, C. Eaborn and P.D. Lickiss, J. Organometal. Chem., **330**, 1-7, (1987).
[7] C.Eaborn, D.A.R. Happer and K.D. Safa, J. Organometal. Chem., **191**, 355–362, (1980).
[8] M. Kumada, K. Tamao, M. Ishikawa and M. Matsuno, J. Chem. Soc. Chem. Commun., **614**, (1968).
[9] K.D. Safa, A. Asadi, M. Sargordan, J. Organometal Chem., **545–546**, 61–65, (1997).