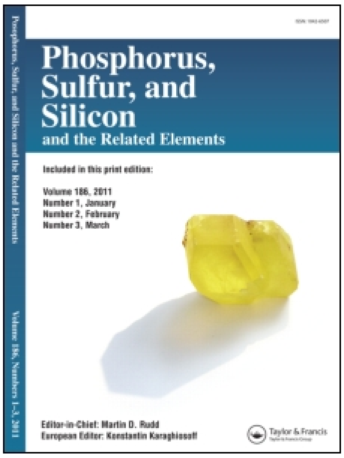

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND REACTIONS OF HIGHLY STERICALLY HINDEREID ORGANOSILICON COMPOUNDS OF THE TYPE $(Me_3Si)_3CSi(C_6H_4\text{-OMe-}p)MeX$ AND $(Me_3Si)_3CSi(C_6H_4\text{-Me-}p)MeX$

Kazem D. Safa[a]; Mohammad Bolourtchlan[a]; Mohammad G. Asadi[a]
[a] Faculty of chemistry, University of Tabriz, Tabriz, Iran

To cite this Article Safa, Kazem D. , Bolourtchlan, Mohammad and Asadi, Mohammad G.(1999) 'SYNTHESIS AND REACTIONS OF HIGHLY STERICALLY HINDEREID ORGANOSILICON COMPOUNDS OF THE TYPE $(Me_3Si)_3CSi(C_6H_4\text{-OMe-}p)MeX$ AND $(Me_3Si)_3CSi(C_6H_4\text{-Me-}p)MeX$', Phosphorus, Sulfur, and Silicon and the Related Elements, 149: 1, 229 — 236

To link to this Article: DOI: 10.1080/10426509908037034

URL: http://dx.doi.org/10.1080/10426509908037034

Phosphorus Sulfur and Silicon, 1999, Vol. 149, pp. 229-236
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SYNTHESIS AND REACTIONS OF HIGHLY STERICALLY HINDERED ORGANOSILICON COMPOUNDS OF THE TYPE $(Me_3Si)_3CSi(C_6H_4\text{-}OMe\text{-}p)MeX$ AND $(Me_3Si)_3CSi(C_6H_4\text{-}Me\text{-}p)MeX$

KAZEM D. SAFA*, MOHAMMAD BOLOURTCHIAN and MOHAMMAD G. ASADI

Faculty of chemistry, University of Tabriz, Tabriz, Iran

(Received 12 November, 1998; In final form 10 February, 1999)

Direct nucleophilic displacement of $TsiSi(C_6H_4\text{-}OMe\text{-}p)MeI$ and $TsiSi(C_6H_4\text{-}Me\text{-}p)MeI$ with nucleophiles take place. These compounds also react with electrophiles such as AgOAc and $AgNO_3$ to give rearrangment products, for example $(Me_3Si)_2C(SiMe_2OAC)SiMe_2(C_6H_4\text{-}Y\text{-}p)$ (Y = Me, OMe). The hydrides and bromides of these compounds were also synthesised.

Keywords: anisole; electrophiles; nucleophiles; organosilicon; sterically hindered; tolyl; trisyl

1. INTRODUCTION

Much interesting chemistry has emerged from studies of tris(trimethylsilyl)methyl ("trisyl") derivatives of the type $TsiSiR_2X$ ($Tsi{=}(Me_3Si)_3C$) in which is severe inhibition by steric hindrance to attack at the functional silicon centre[1]. For this reason the nucleophilic substitution reactions do not occur. When the steric hinderance of the functional silicon centres is reduced or linear nucleophiles like N_3^-, SCN^-, OCN^-, CN^- are used such bimolecular displacements take place. In the recent work, we synthesised highly sterically hindered organosilicon compound of the type $(Me_3Si)_3C(C_6H_4OMe)_2H$, but the iodide derivative of this compound is

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* Correspondence Author.

not obtained, because in the reaction of the hydride with ICI, or I_2 this highly sterically hindered compound was fragmentated[2]. Therefore we decided to synthesize the compounds with less steric hinderance at the functional silicon centres, in order to prepare the iodide derivative. Then we studied some nucleophilic, electrophilic, and fragmentation reactions of these compounds.

2. RESULTS AND DISCUSSION

In an attempt to make TsiSi(C_6H_4-Y-*p*)McH (Y=Me, OMe) we prepared (C_6H_4-Y-*p*)SiMeF_2 and then caused this to react with TsiLi to give TsiSi(C_6H_4-Y-*p*) MeF. But the reduction of this compound with LiAlH_4 in THF did not give TsiSi(C_6H_4-Y-*p*)MeH. For this reason we prepared MeSiH(C_6H_4-Y-*p*)Cl. Reaction of these compounds with TsiLi produced the novel organosilicon compounds with high steric hindrance, TsiSi(C_6H_4-Y-*p*)MeH. Reaction of TsiSi(C_6H_4-OMe-*p*)MeF with NaOMe in MeOH gave fragmetation products. The mechanism of this reaction is consistent with a silaolefin intermediate, then MeOH is added to give the product[3,4]. The reaction of TsiSi(C_6H_4-Y-*p*)MeH with ICl in dry CCl_4 gave the iodide derivatives. Reaction of the iodide derivatives with KSCN in CH_3CN and H_2O/DMSO/CH_3CN produced substitution products. We also carried out the reactions of these compounds with elecrtophiles such as $AgNO_3$, AgOAc. These reactions resulted in rearrangment products. The mechanism of these reactions involve the silicocation intermediate in which the Me is bridged[5–10].

3. EXPERIMENTAL

3.1. Solvents and reagents

Reactions involving lithium metal, organolithium or, organomagnesium and LiAlH_4 were carried out under dry argon. Solvents were dried by standard methods.

3.2. Spectra

The ^1H NMR spectra were recorded on FT-NMR Bruker (100 MHz) and FT-NMR 90 MHz spectrometers in $CDCl_3$ solution. The IR spectra were recorded on FT-IR, DR 8001-Shimadzu, Mass spectra were obtained with Finnigan-Mat model 8400, 70 eV. Melting points were determined on a 9100 Electrothermal apparatus.

3.3. Preparation of TsiSi(C_6H_4-Me-*p*)MeH

(C_6H_4-Me-*p*)SiMeHCl (8.52 g, 50 mmol) was added dropwise with stirring to a solution of TsiLi (50 mmol) in THF (100 ml) that had been made by reaction of TsiH (11.5 g, 60 mmol) with MeLi in ether (30 ml) made from iodomethane (8.5 g, 60mmol) and Li (0.84 g, 120mmol). The mixture was refluxed for 4h. An aqueous solution of NH_4Cl was added and the organic compound was extracted with Et_2O. The extract was dried ($MgSO_4$), filtered, evaporated, the residue recrystallized from EtOH and was purified with preparative TLC (silicagel, *n*-hexane as eluant), (45%), m.p. 107–108°C. FT-IR (KBr, cm^{-1}), (Si-H) 2107.7. FT-^1H NMR ($CDCl_3$) 0.213 (s, 27H, Tsi), 0.441 (d, 3H, Si-Me), 2.33 (s, 3H, Me-aryl), 4.58 (q, 1H, Si-H), 7.06–7.66 ppm (m, 4H, aryl-H). *m/z* (EI): 366(2%, $[M]^+$), 365(4%, $[M-H]^+$), 351(18%, $[M-Me]^+$), 275(5), 261(22), 73(100), 45(18). (Found: C, 58.5; H, 10.2. $C_{18}H_{38}Si_4$ calculated: C, 59.0; H, 10.3%).

3.4. Preparation of TsiSi(C_6H_4-Me-*p*)MeI

Iodine monochloride (0.24 g, 1.4 mmol), in carbontetrachloride (20 ml), was added dropwise to TsiSi(C_6H_4-Me-*p*)MeH (0.5 g, 1.0 mmol) in carbontetrachloride (10 ml) at room temperature. When the addition was complete, the solvent was removed and the solid product was recrystallized from EtOH to yield TsiSi(C_6H_4-Me-*p*)MeI, (90%), m.p. 179°C. FT-IR (KBr, cm^{-1}), (C-Si) 1245, 850. FT-^1H NMR ($CDCl_3$), 0.328 (s, 27H, Tsi), 1.38 (s, 3H, Me-Si), 2.35 (s, 3H, Me-aryl) and 7.6–7.7 ppm (m, 4H, aryl-H). *m/z* (EI): 477(10%, $[M-Me]^+$), 386(5), 365(90), 349(10), 73(30). (Found : C, 44.4; H, 7.6. $C_{18}H_{37}ISi_4$ calculated: C, 43.9; H, 7.5%).

3.5. Preparation of TsiSi(C_6H_4-Me-*p*)MeOH

A solution of TsiSi(C_6H_4-Me-*p*)MeI (0.5 g, 1.3 mmol), DMSO (25 ml), H_2O (4 ml), and CH_3CN (12 ml) was refluxed for 24 h. The solution was treated with water and petroleum ether, dried (Na_2SO_4) and evaporated. A pure sample was obtained by preparative TLC (silicagel: 1:1, cyclohexane, dichloromethane as eluant), (75%), m.p. 150°C. FT-IR (KBr, cm^{-1}), (Si-OH) 3600, (C-Si) 1245. FT-^1H NMR ($CDCl_3$), 0.25 (s, 27H, Tsi), 0.59 (s, 3H, Me-Si), 1.76 (s, b, 1H, OH), 2.34 (s, 3H, Me-aryl) and 7.0 - 7.7 ppm (m, 4H, aryl-H). *m/z* (EI): 367(30%. $[M-Me]^+$), 352(18), 275(78), 187(40). (Found: C, 56.6; H, 9.9. $C_{18}H_{38}OSi_4$ calculated: C, 56.5; H, 9.9%).

3.6. Preparation of TsiSi(C_6H_4-Me-*p*) MeNCS

TsiSi(C_6H_4-Me-*p*)MeI (0.5 g, 1.1 mmol) with KSCN (1 g, 10 mmol) in CH_3CN (50 ml) was refluxed for 10 days. Then the mixture was treated with water and petroleum ether (40-60), the organic layer seperated, dried (Na_2SO_4) and evaporated. The residue was recrystallized from EtOH. (70%), m.p. 128°C. FT-IR (KBr, cm^{-1}), (Si-NCS) 2080, (Si-C) 1245. FT-^1H NMR ($CDCl_3$) 0.273 (s, 27H, Tsi), 0.727(s, 3H, Me-Si), 2.361(s, 3H, Me-tolyl), and 7.0–7.7 ppm (m, 4H, aryl-H). *m/z* (EI): 408 (20%, $[M-Me]^+$), 350 (35) 377(5), 365(10), 347(30), 201(18). (Found: C, 53.8; H, 8.7; N, 3.4. $C_{19}H_{37}NSSi_4$ calculated: C, 53.9; H, 8.7; N, 3.3%).

3.7. Preparation of TsiSi(C_6H_4-OMe-*p*)MeH

(C_6H_4-OMe-*p*)SiMeHCl (9.3 g, 50 mmol) was added dropwise with stirring to a solution of TsiLi (50 mmol) in THF (100 ml) that had been made by reaction of TsiH (11.5 g, 60 mmol) with MeLi in ether (30 ml) made from iodomethane (8.5 g, 60 mmol) and Li (0.84 g, 120 mmol). The mixture was refluxed for 4h. An aqueous solution of NH_4Cl was added and the organic compound was extracted with Et_2O. The extract was dried (Na_2SO_4), filtered and evaporated, and the residue recrystallized from EtOH and was purified with preparative TLC (silicagel, *n*-hexane as eluant), (40%) m.p. 107–108°C. FT-IR (KBr, cm^{-1}), (Si-H) 2107.7. FT-^1H NMR ($CDCl_3$) 0.1959(s, 27H, Tsi), 0.4259(d, 3H, Me-Si), 3.7927(s, 3H, MeO-anisole), 4.5764(q, 1H, Si-H), and 6.5–7.5 ppm (m, 4H, aryl-H). *m/z* (EI): 382(5%,

[M]$^+$), 367(58%, [M-Me]$^+$), 366(28), 274(35), 260(5), 201(27). (Found: C, 54.0; H, 10.0. $C_{18}H_{38}OSi_4$ calculated: C, 56.5; H, 9.9%).

3.8. Preparation of TsiSi(C_6H_4-OMe-*p*)MeI

Iodine monochloride (0.93 g, 6 mmol) in carbontetrachloride (10 ml) was added dropwise to TsiSi(C_6H_4-OMe-*p*)MeH (1.4 g, 4 mmol) in carbontetrachloride (20 ml) at room temperature. When the addition was complete the solvent was removed and the solid product was recrystallized from EtOH to yield TsiSi(C_6H_4-OMe-*p*)MeI (90%), m.p. 182°C. FT-^{1}H NMR ($CDCl_3$) 0.2232(s, 27H, Tsi), 1.3020(s, 3H, Si-Me), 3.7079(s, 3H, MeO-anisole), and 6.5–7.5 ppm(m, 3H, aryl-H). *m/z* (EI): 493(4%, [M-Me]$^+$), 401(15), 381(65), 377(8), 365(16), 362(7), 277(12). (Found: C, 42.3; H, 7.3. $C_{18}H_{37}IOSi_4$ calculated: C, 42.5; H, 7.3%).

3.9. Preparation of TsiSi(C_6H_4-OMe-*p*)MeNCS

TsiSi(C_6H_4-OMe-*p*)MeI (0.1 g, 1 mmol) with KSCN (0.1 g, 1 mmol) in CH_3CN(50 ml) was refluxed for 10 days. Then the mixture was treated with water and peroleum ether (40-60), the organic layer seperated, dried (Na2SO4) and evaporated. The residue was recrystallized from EtOH(55%), m.p. 130°C. FT-IR(KBr, cm^{-1}), (Si-NCS)2070, (Si-C)1245. FT-^{1}H NMR ($CDCl_3$) 0.2220(s, 27H, Tsi), 1.2020(s, 3H, Si-Me), 3.6020(s, 3H, MeO-anisole), 6.5–7.5 ppm(m, 4H, aryl-H). *m/z* (EI): 439(3%, [M]$^+$), 424(65%, [M-Me]$^+$), 408(3), 381(20), 366(14)365(45).

3.10. Preparation of TsiSi(C_6H_4-OMe-*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 (100 ml) that had been made by reaction of TsiH (11.5 g, 50 mmol) with MeLi in ether (30 ml) made from iodomethane (8.5 g, 60 mmol) and Li (0.84 g, 120 mmol). The mixture was refluxed for 4h. An aqueous solution of NH_4Cl was added and the organic compound was extracted with Et_2O. The extract was dried (Na_2SO_4), filtered, evaporated and the residue recrystallized from EtOH and was sublimed in a sublimation apparatus at 100°C/0.1 mmHg, (60%)m.p. 165°C. FT-IR(KBr, cm^{-1}), (Si-C)1245. FT-^{1}H NMR ($CDCl_3$)

0.3160(s, 27H, Tsi), 3.8254(s, 3H, OMe-anisole), 6.9261 ppm (m, 4H, C_6H_4). *m/z* (EI): 368(5%, $[M]^+$), 353(96%, $[M\text{-}Me]^+$), 351(85), 337(4), 277(35), 280(25), 187(16). (Found: C, 46.5; H, 7.8. $C_{17}H_{34}Cl_2OSi_4$ calculated: C, 46.6; H. 7.8%).

3.11. Preparation of TsiSi(C_6H_4-OMe-*p*)($NCS)_2$

TsiSi(C_6H_4-OMe-*p*)Cl_2 (0.3 g, 0.6 mmol) with KSCN (0.1 g, 1.0 mmol) in CH_3CN (50 ml) was refluxed for 10 days. Then the mixture was treated with water and petroleum ether (40-60), the organic layer separated, dried(Na_2SO_4) and evaporated. The residue was recrystallized from EtOH (40%) m.p. 130°C. FT-IR (KBr, cm^{-1}), (Si-NCS) 2070, (Si-C) 1245. FT-^{1}H NMR ($CDCl_3$) 0.2398(s, 27H, Tsi), 3.7920(s, 3H, MeO-anisole), and 6.8–7.8 ppm (m, 4H, aryl-H). *m/z* (EI): 482(3%, $[M]^+$), 467(33%, $[M\text{-}Me]^+$), 409(28), 408(80), 351(5), 336(10), 277(20).

3.12. Preparation of TsiSi(C_6H_4-OMe-*p*)MeOH

A solution of TsiSi(C_6H_4-OMe-*p*)MeI (0.7 g, 1.3 mmol), DMSO (30 ml), H_2O (5 ml), CH_3CN (15 ml) was refluxed for 24 h. The solution was treated with sodium thiosulfate, cyclohexane, washed with water, extracted, dried (Na_2SO_4), and evaporated. A pure sample was obtained by preparative TLC (silicagel, 1:1, cyclohexane: dichloromethane as eluant), (60%), m.p. 120°C. FT-IR (KBr, cm^{-1}), (Si-OH) 3600, (C-Si) 1245. FT-^{1}H NMR ($CDCl_3$), 0.23(s, 27H, Tsi), 0.55 (s, 3H, Me-Si), 1.73(s, 1H, OH), 3.8(s, 3H, OMe-aryl) and 7.0–7.7 ppm (m, 4H, aryl-H). *m/z* (EI): 397(5%, $[M]^+$), 382(30%, $[M\text{-}Me]^+$), 290(40), 262(50).

3.13. Preparation of TsiSi(C_6H_4-OMe-*p*)MeBr

Bromine (0.25 g, 1 mmol) in carbontetrachloride (20 ml) was added dropwise to a solution of TsiSi(C_6H_4-OMe-*p*)MeH (0.3 g, 1 mmol) in carbontetrachloride (10 ml) at room temperature. When the addition was complete the solvent was removed and the solid product was recrystallized from EtOH to yield TsiSi(C_6H_4-OMe-*p*)MeBr (60%), m.p. 168°C. FT-^{1}H NMR ($CDCl_3$), 0.2 (s, 27H, Tsi), 1.00(s, 3H, Si-Me), 3.7(s, 3H, Me-anisole), 6.7–7.7 ppm (m, 4H, aryl-H). *m/z* (EI): 447(75%, [M-Me]$^+$), 431(5), 327(5). (Found: C, 46.3; H, 8.1. $C_{18}H_{37}BrOSi_4$ calculated: C, 46.8; H, 8.0%).

3.14. Preparation of $(Me_3Si)_2C(SiMe_2OAc)SiMe_2(C_6H_4\text{-}OMe\text{-}p)$

$TsiSi(C_6H_4\text{-}OMe\text{-}p)MeI$ (0.5 g, 1 mmol) with AgOAc (0.2 g, 1 mmol) in CH_3COOH (20 ml) was heated for 3 h. Then petroleum ether was added, the mixture decanted from the precipitate. washed several times with water, dried (Na_2SO_4), and evaporated to give $(Me_3Si)_2C(SiMe_2OAc)Si(C_6H_4\text{-}OMe\text{-}p)Me_2$. FT-IR (KBr, cm^{-1}), (C=O) 1720. FT-^{1}H NMR ($CDCl_3$), 0.2(s, 18H, $SiMe_3$), 0.3(S, 6H, $SiMe_2$), 0.4(s, 6H, $SiMe_2$-OAc), 2.1(s, 3H, OAc), 3.8(s, 3H, Me-aryl) and 6.7–7.7 ppm (m, 4H, aryl-H). *m/z* (EI): 440(3%, [M]$^+$), 425(30%, [M-Me]$^+$), 275(100), 209(17), 295(3).

3.15. Preparation of $(Me_3Si)_2C(SiMe_2OAc)Si(C_6H_4\text{-}Me\text{-}p)Me_2$

$TsiSi(C_6H_4\text{-}Me\text{-}p)MeI$ (0.47, 1 mmol) with AgOAc (0.2 g, 1 mmol) in CH_3COOH (20 ml) was heated for 1 h. Then petroleum ether was added, the mixture decanted from the precipitate, washed with water several times, dried (Na_2SO_4), and evaporated to give $(Me_3Si)_2C(SiMe_2OAc)Si(C_6H_4\text{-}Me\text{-}p)Me_2$. FT-IR(KBr, cm^{-1}), (C=O) 1720. FT-^{1}H NMR ($CDCl_3$), 0.27(s, 18H, $SiMe_3$), 0.37(s, 6H, $SiMe_2$-aryl), 0.5(s, 6H, $SiMe_2$-OAc), 2.14(s, 3H, OMe-aryl), 2.17(s, 3H, OAc) and 6.7–7.7 ppm (m, 4H, aryl-H). *m/z* (EI): 424(2%, [M]$^+$), 409(100%, [M-Me]$^+$), 365(98), 333(38), 275(55).

3.16. Preparation of $(Me_3Si)_2C(SiMe_2OMe)Si(C_6H_4\text{-}Me\text{-}p)Me_2$

$TsiSi(C_6H_4\text{-}Me\text{-}p)MeI$ (0.4 g, 1 mmol) with $AgNO_3$ (0.2 g, 1 mmol) in MeOH (40 ml) was refluxed for 1 h. Then cyclohexane was added, the mixture decanted from the precipitate, dried (Na_2SO_4) and evaporated to give $(Me_3Si)_2C(SiMe_2OMe)Si(C_6H_4\text{-}Me\text{-}p)Me_2$ (20%). A pure sample was obtained by TLC (silicagel, cyclohexane as eluant). FT-^{1}H NMR($CDCl_3$), 0.1167(s, 6H, $SiMe_2$-aryl), 0.20(s, 18H, $SiMe_3$), 2.33(s, 3H, Me-aryl), 3.4(s, 3H, Si-OMe), and 7–8 ppm (m, 4H, aryl-H). *m/z* (EI):

381(70%, [M-Me]$^+$), 365(22) 305(10), 277(20), 261(38), 217(40). (Found: C, 57.4;·H, 10.0. $C_{19}H_{40}OSi_4$ calculated: C, 57.5; H, 10.1 %).

Acknowledgements

We thank Professor C. Eaborn for helpful comments.

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