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Direct displacement of chlorine or iodine in reactions of $(Me_3Si)_3CSiRR'X$ with metal salts

Kazem D. Safa *, Mohammad G. Asadi, Abdolreza Abri, Ali Mohammadpour, Hadi Kiae

Faculty of Chemistry, University of Tabriz, Tabriz, Iran

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Abstract

Direct nucleophilic displacement of halide X (X = Cl or I) takes place when the compounds $(Me_3Si)_3CSiRR'X$ with R = Me, R′ = $(C_6H_4Me\text{-}p)$, $(C_6H_4OMe\text{-}p)$, $CH_2{=}CH$ R = Bu, R′ = Cl, or R = Ph, R′ = Ph are treated with solutions of KOCN, KSCN, KCN, or NaN_3 in CH_3CN or MeOH, and H_2O in DMSO, or CH_3CN. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The effect of severe steric hindrance on direct nucleophilic attack at functional silicon centres bearing the bulky trisyl group (denoted here by Tsi) or a related group has allowed the observation of previously inaccessible mechanisms of reactions [1]. For example, unusual rearrangement and migration in $TsiSiR_2X$ species take place through bridged silicocationic intermediates. When the steric hindrance at the functional silicon centres is reduced, or linear nucleophiles like N_3^-, SCN^-, OCN^- and CN^- are used, direct biomolecular displacement takes place. Earlier work had indicated that nucleophilic substitution, while relatively easy for $TsiSiMe_2X$, was very slow for $TsiSiPh_2I$ [2–5]. But we have now shown that under suitable conditions such substitution reactions provide a satisfactory route to $TsiSiPh_2X$ and some related species.

We have also shown that with less hindered systems the chlorides can be satisfactorily used instead of iodides. For example, $TsiSiMe(CH{=}CH_2)Cl$ and $TsiSiBuCl_2$ undergo direct nucleophilic reactions to give the corresponding products. The chlorides $(C_6H_4OMe\text{-}p)$-SiMeHCl and $(C_6H_4Me\text{-}p)SiMeHCl$ react with TsiLi to give trisyl derivatives containing a hydride substituent. The presence of even one hydride ligand reduces the steric hindrance considerably and we have seen that for such compounds nucleophilic substitution takes place fairly readily.

In this work we synthesised new compounds with different groups and did some nucleophilic reactions on them with linear nucleophiles, namely N_3^-, SCN^-, OCN^- and CN^-, to examine the ease of reactions on Si bearing the bulky trisyl group.

2. Results and discussion

In our earlier work we have shown that the synthesis of $TsiSiAn_2I$ by the reaction of $TsiSiAn_2H$ with ICl was unsuccessful [1]. An attempt to make $TsiSi(C_6H_4Me\text{-}p)_2F$ by reaction of TsiLi with $(C_6H_4Me\text{-}p)_2SiF_2$ was also unsuccessful. For that reason in order to reduce steric hinderance we have chosen methylanisyl and methyltolyl derivatives to prepare $TsiSi(C_6H_4OMe\text{-}p)MeI$ and $TsiSi(C_6H_4Me\text{-}p)MeI$, respectively and studied the reaction of the iodides with electrophiles, nucleophiles and alkoxides. When steric hinderance of the functional silicon centre is reduced or linear nucleophiles such as NCS^-, NCO^-, CN^- are used, such bimolecular displacement reactions take place and no rearrangement is observed.

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* Corresponding author.

E-mail address: g-asadi@ank.tabriz.ac.ir (K.D. Safa)

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When Me is substituted with a bulky anisyl group in $TsiSi(C_6H_4OMe\text{-}p)_2H$ the iodide derivative $TsiSi(C_6H_4OMe\text{-}p)MeI$ was successfully prepared by the reaction of $TsiSi(C_6H_4OMe\text{-}p)MeH$ with ICl. So we think that by reducing steric hinderance around the Si centre, the cleavage of the Si–Aryl bond was not favoured.

2.1. Preparation of TsiSiRR′X

These compounds were obtained by reaction of TsiLi with (a) $n\text{-}BuSiCl_3$; (b) $(C_6H_4OMe\text{-}p)SiMeHCl$; (c) $(C_6H_4Me\text{-}p)SiMeHCl$; (d) $CH_2{=}CHSiMeCl_2$; (e) Ph_2SiF_2.

2.2. Reactions of TsiSiRR′X (R = Me, n-Bu, Ph, and R′ = p-C$_6$H$_4$OMe, p-C$_6$H$_4$Me, Cl, CH$_2$=CH)

(i) The butyl compound $TsiSiBuCl_2$ was only reacted with KSCN and KN_3 in CH_3CN. The difluoride derivative of this compound was prepared and unlike other derivatives of trisyl compounds is a liquid.

(ii) The vinyl compound $TsiSiMe(CH{=}CH_2)Cl$ was found to react with KSCN, NaN_3, KCN, and KOCN in CH_3CN to give $TsiSiMe(CH{=}CH_2)Y$ (Y = NCS, NCO, N_3, CN).

(iii) The methyltolyl and methylanisyl compounds $TsiSi(C_6H_4Me\text{-}p)MeI$, $TsiSi(C_6H_4OMe\text{-}p)MeI$ were reacted with KSCN in CH_3CN, and H_2O in DMSO, CH_3CN [6–9]. The hydrides $TsiSi(C_6H_4Me\text{-}p)MeH$, $TsiSi(C_6H_4OMe\text{-}p)MeH$ were subsequently made by the treatment of TsiLi with $(C_6H_4Me\text{-}p)MeSiHCl$ and $(C_6H_4OMe\text{-}p)MeSiHCl$, respectively.

(iv) The diphenyl compound $TsiSiPh_2I$ was found to react with KSCN, KOCN in CH_3CN containing crown ether and NaN_3 in MeOH containing crown ether. The reaction of $TsiSiPh_2I$ with KSCN in CH_3CN was previously reported requiring 30 days [10], but we found that it to be complete in 3 days in a mixture of CH_3CN and 18-crown-6. We also found that $TsiSiPh_2I$ did not react with KCN in MeOH. The reaction of the $TsiSi(C_6H_4\text{–}Me\text{-}p)MeI$, $TsiSi(C_6H_4\text{–}OMe\text{-}p)MeI$ with H_2O, DMSO, CH_3N give the silanol derivatives, $TsiSi(C_6H_4\text{–}Me\text{-}p)MeOH$, $TsiSi(C_6H_4\text{–}OMe\text{-}p)MeOH$.

3. Experimental

3.1. Solvents and reagents

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

3.2. Spectra

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

3.3. Preparation of trisyldiphenylisocyanato silane TsiSiPh$_2$NCO

A mixture of $TsiSiPh_2I$ (0.5 g, 0.93 mmol), KOCN (2 g, 24.7 mmol) and crown ether (0.2 g, 0.55 mmol) in CH_3CN (50 cm^3) was refluxed for 16 days. The mixture was treated with methanol (20 cm^3), n-hexane (40 cm^3), and a little NaCl aqueous solution, washed several times with water, and the organic layer was separated, dried ($MgSO_4$), evaporated and the residue recrystallised from EtOH (78%); m.p. 178–179°C FTIR (KBr, cm^{-1}) ν(Si–NCO)2278.1, (C–Si) 1245.^1H-NMR ($CDCl_3$): 0.12 (s, 27H, Tsi), and 7.13–7.50 ppm (m, 10H, Aryl–H). m/z (EI): 440 (20%, $[M\text{–}Me]^+$), 413 (38%, $[M\text{–}NCO]^+$), 335 (100%, $[M\text{–}Ph\text{–}SiMe]^+$), 247 (60%, $[M\text{–}2Ph\text{–}CH_2SiC]^+$), 197 (38%, $[M\text{–}Tsi\text{–}Si]^+$). (Found: C, 60.2; H, 8.1; N, 3.02, $C_{23}H_{37}Si_4NO$ Calc.: C, 60.66; H, 8.13; N, 3.07%).

3.4. Preparation of trisylazidodiphenylsilane TsiSiPh$_2$N$_3$

A mixture of $TsiSiPh_2I$ (0.5 g, 0.93 mmol), NaN_3 (2 g, 30.7 mmol) and crown ether (0.2 g, 0.55 mmol) in MeOH (50 cm^3) was refluxed for 14 days. The mixture was treated with methanol (20cm^3), n-hexane (40 cm^3), and a little NaCl aqueous solution, washed several times with water, and the organic layer was separated, dried ($MgSO_4$), evaporated and the residue recrystallized from EtOH. (83%); m.p. 137.5–138.5°C. FTIR (KBr, cm^{-1}), $\nu(Si\text{–}N_3)$ 2143.3. ^1H-NMR ($CDCl_3$): 0.112 (s, 27H, Tsi), and 7.12–7.65 ppm (m, 10 H, Aryl–H). m/z (EI): 440 (8%, $[M\text{–}Me]^+$), 397 (2%, $[M\text{–}N_3]^+$), 335 (41%, $[M\text{–}Ph\text{–}SiMe]^+$), 247 (25%, $[M\text{–}2Ph\text{–}CH_2SiC]^+$), 197 (12%, $[M\text{–}Tsi\text{–}Si]^+$), 175 (15%,$[M\text{–}2(SiMe_3)\text{–}PhMe\text{–}3N]^+$). (Found: C, 58.2; H, 8.4; N, 8.7. $C_{22}H_{37}Si_4N_3$ Calc.: C, 58.02; H, 8.13; N, 9.2%).

3.5. Preparation of trisyldiphenylisothiocyanatosilane TsiSiPh$_2$NCS

A mixture of $TsiSiPh_2I$ (0.5 g, 0.93 mmol), KSCN (0.9 g, 9.26 mmol) and crown ether (0.02 g, 0.05 mmol) in CH_3CN (50 cm^3) was refluxed for 3 days. The mixture was treated with methanol (20 cm^3), n-hexane (40 cm^3), and a little NaCl, washed several times with water, the organic layer was separated, dried ($MgSO_4$), evaporated and the residue recrystallised from EtOH. (87%); m.p. 139–141°C. FTIR (KBr, cm^{-1}), (Si–NCS) 2073.8. ^{1}H-NMR ($CDCl_3$): 0.99 (s, 27H, Tsi), and 7.12–7.62 ppm (m, 10H, Aryl–H). *m*/*z* (EI): 456 (48%, $[M–Me]^+$), 397 (40%, $[M–Me_3SiH]^+$), 378 (72%, $[M–Ph–CH_4]^+$), 340 (15%, $[M–Me_3Si–NCS]^+$), 325 (15%, $[M–(Me_3Si)_2]^+$), 145 (11%, $[M–SiMe_3–CSiPh_2$-$NCS]^+$), 135 (85%, $[SiMe_2Ph]^+$,), 135 (85%, $[M–Tsi–SiPh]^+$). (Found: C, 58.3; H, 7.9; N, 3.2. $C_{23}H_{37}Si_4SN$ Calc.: C, 58.5; H, 7.8; N, 3.0%).

3.6. Preparation of trisylmethylvinylchlorosilane $TsiSi(CH_3)(CH{=}CH_2)Cl$

Dichloromethylvinylsilane $Cl_2Si(CH_3)(CH{=}CH_2)$ (7.05 g, 50 mmol) was added dropwise with stirring to a solution of TsiLi (50 mmol) in THF (50 cm^3) that had been made by reaction of TsiH (11.5 g, 50 mmol) with MeLi (0.84 g, 120 mmol). The mixture was refluxed for 45 min. Then aqueous NH_4Cl was added and the organic compound was extracted with Et_2O. The extract was dried ($MgSO_4$), filtered and evaporated, and the residue recrystallized from EtOH, then purified by column chromatography (silica gel, *n*-hexane as eluant) to give $TsiSi(CH_3)(CH{=}CH_2)Cl$ (55%), m.p. 340°C FTIR (KBr, cm^{-1}), (=C–H) 3061.5, (C–H aliphatic) 2962.2, 2987.2, (C=C) 1592.5. ^{1}H-NMR ($CDCl_3$): 0.31 (s, 27H, Tsi), 0.702 (s, 3H, Si–Me), and 5.7–6.7 ppm (m, 3H, vinyl). *m*/*z* (EI) 321 (38%, $[M–Me]^+$), 301 (4%, $[M–Cl]^+$), 213 (100%, $[M–Me_3SiCl–Me]^+$), 105(5%, $[M–Tsi]^+$). (Found: C, 46.4; H, 9.7. $C_{13}H_{33}Si_4Cl$ Calc.: C, 46.4; H, 9.8%).

3.7. Preparation of trisylisothiocyanatomethylvinylsilane $TsiSi(CH_3)(CH{=}CH_2)NCS$

A mixture of $TsiSi(CH_3)(CH{=}CH_2)Cl$ (1 g, 3 mmol), KSCN (3.5 g, 36 mmol) in CH_3CN (150 cm^3), was refluxed for 3 h. The mixture was treated with petroleum ether and water, and the organic layer separated, dried ($MgSO_4$), evaporated and the residue was recrystallised from EtOH. (80%), m.p. 308°C. FTIR (KBr, cm^{-1}), (Si–NCS), 2076, ^{1}H NMR ($CDCl_3$): 0.29 (s, 27H, Tsi), 0.567 (s, 3H, Si–Me) and 5.7–6.3 ppm (m, 3H, vinyl). *m*/*z* (EI): 344 (98%, $[M–Me]^+$), 301 (2%, $[M–NCS]^+$) 285 (39%, $[M–Me_3Si]^+$), 256 (15%, $[M–Me_3Si–Me]^+$), 213 (46%, $[M–(Me_3Si)2]^+$), 154 (19%, $[M–(Me_3Si)_2–NCS]^+$). (Found: C, 46.2; H, 8.9; N, 3.7. C1$_4$H$_{33}$Si$_3$NS Calc.: C, 46.9; H, 9.2; N, 3.9%).

3.8. Preparation of trisylazidomethylvinylsilane $TsiSi(CH_3)(CH{=}CH_2)N_3$

A mixture of $TsiSi(CH_3)(CH{=}CH_2)Cl$ (1 g, 3 mmol), NaN_3 (2.8 g, 43.4 mmol) in CH_3CN (150 cm^3) was refluxed for 48 h. The mixture was treated with diethyl ether and water, the organic layer separated, dried ($MgSO_4$), evaporated and the residue recrystallised from EtOH (79%), m.p. 275°C. FTIR (KBr, cm^{-1}), (Si–N_3) 2139.4, ^{1}H-NMR ($CDCl_3$): 0.27 (s, 27 H, Tsi), 0.57 (s, 3H, Si–Me) and 5.7–6.5 ppm (m, 3H, $CH{=}CH_2$). *m*/*z* (EI): 328 (12%, $[M–Me]^+$), 284 (8%, $[M–N_3–CH_4]^+$), 228 (14%, $[M–Me_3SiN_3]^+$), 200 (18%, $[M–Me_3SiN_3–(CH{=}CH_2)]^+$).

3.9. Preparation of trisylcyanidomethylvinylsilane $TsiSi(CH_3)(CH{=}CH_2)CN$

A mixture of $TsiSi(CH_3)(CH{=}CH_2)Cl$ (1 g, 3 mmol), KCN (2 g, 43.4 mmol) in CH_3CN (150 cm^3) was refluxed for 38 h. The mixture was treated with diethyl ether and water, the organic layer separated, dried ($MgSO_4$), evaporated, and purified by column chromatography (Silicagel, *n*-hexane as eluant). (87%); m.p. 328°C. FTIR (KBr, cm^{-1}), (Si–CN) 2185.7, ^{1}H-NMR ($CDCl_3$): 0.33 (s, 27H, Tsi), 0.62 (s, 3H, Si–Me) and 5.6–6.4 ppm (m, 3H, vinyl). *m*/*z* (EI): 312 (38%, $[M–Me]^+$), 285 (28%, $[M–(CH{=}CH_2)–Me]^+$), 224 (24%, $[M–Me_3Si–2Me]^+$), 213 (99%, $[M–Me_3Si–Me–CN]^+$), 201 (46%, $[M–Tsi–2Me]^+$), 155 (33%, $[M–(Me_3Si)_2–CN]^+$).

3.10. Preparation of trisylisocyanatomethylvinylsilane $TsiSi(CH_3)(CH{=}CH_2)NCO$

A mixture of $TsiSi(CH_3)(CH{=}CH_2)Cl$ (1 g, 3 mmol), KOCN (3.5 g, 44 mmol) in CH_3CN (150 cm^3) was refluxed for 30 h. The mixture was treated with diethyl ether and water, separated the organic layer, dried ($MgSO_4$), evaporated, and the residue recrystallised from EtOH. (78%), m.p. 324°C. FTIR (KBr, cm^{-1}), (Si–NCO) 2284, ^{1}H-NMR ($CDCl_3$): 0.277 (s, 27H, Tsi), 0.52 (s, 3H, Si–Me) and 5.5–6.5 ppm (m, 3H, vinyl). *m*/*z* (EI): 328 (15%, $[M–Me]^+$), 285 (10%, $[M–NCO–CH_4]^+$), 240 (20%, $[M–Me_3Si–2Me]^+$), 213 (58%, $[M–Me_3SiNCO–Me]^+$), 201 (20%, $[M–Tsi–2Me]^+$). (Found: C, 47.2; H, 9.5; N, 3.9, $C_{14}H_{33}Si_3NO$ Calc.: C, 49.1; H, 9.6; N, 4%).

3.11. Preparation of trisyl(*p*-methylphenyl)methylsilane $TsiSi(C_6H_4Me\text{-}p)MeH$

(C_6H_4Me-*p*)SiMeHCl (8.52 g, 50 mmol) was added dropwise with stirring to a solution of TsiLi (50mmol)in THF (100 cm^3) that had been made by reaction of TsiH (11.5 g, 60 mmol) with MeLi (0.84 g, 120 mmol). The mixture was refluxed for 4 h. The aqueous NH_4Cl was added and the organic compound was extracted with Et_2O.The extract was dried ($MgSO_4$), filtered, evaporated, and the residue recrystallised from EtOH and was purified with preparative

TLC (silica gel, *n*-hexane as eluant), (45%), m.p. 107–108°C. FTIR (KBr, cm^{-1}), (Si–H) 2107.7, ^{1}H-NMR ($CDCl_3$) 0.21 (s, 27H, Tsi), 0.44 (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%, $[M–tolyl]^+$), 261 (22%, $[M–tolyl–Me]^+$), 73(100), 45 (18). (Found: C, 58.5; H, 10.2. $C_{18}H_{38}Si_4$ Calc.: C, 59.0; H, 10.3%).

3.12. *Preparation of trisyl(p-methylphenyl)-methyliodosilane TsiSi(C_6H_4Me-p)MeI*

A solution of iodine monochloride (0.24 g, 1.4 mmol), in carbon tetrachloride (20 cm^3), was added dropwise to TsiSi(C_6H_4Me-*p*)MeH (0.5 g, 10 mmol) in carbon tetrachloride (10 cm^3) at room temperature. When the addition was complete, the solvent was removed and the solid residue was recrystallised from EtOH to yield TsiSi(C_6H_4Me-*p*)MeI, (90%), m.p. 179°C. FTIR (KBr, cm^{-1}), (C–Si) 1245, 850, ^{1}H-NMR ($CDCl_3$), 0.328 (s, 27H, Tsi), 1.38 (s, 3H, Me–Si) and 2.35 ppm (s, 3H, Me–Aryl). *m/z* (EI): 477(10%, $[M–Me]^+$), 386 (5%, $[M–Me–tolyl]^+$), 365 (90%, $[M–I]^+$). (Found: C, 44.4; H, 7.6. $C_{18}H_{37}ISi_4$ Calc.: C, 43.9; H, 7.5%).

3.13. *Preparation of trisyl(p-methylphenyl)-hydroxymethylsilane TsiSi(C_6H_4Me-p)MeOH*

A mixture of TsiSi(C_6H_4Me-*p*)MeI (0.5 g, 1.3 mmol), DMSO (25 cm^3), H_2O (4 cm^3), and CH_3CN (12 cm^3) was refluxed for 24 h. The solution was treated with water and petroleum ether, dried (Na_2SO_4) and evaporated. A pure product was obtained by preparative TLC (silica gel, 1:1, cyclohexane: dichloromethane as eluant), (75%), m.p. 150°C. FTIR (KBr, cm^{-1}), (Si–OH) 3600, (C–Si) 1245, ^{1}H-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%, $[M–Me–tolyl]^+$). (Found: C, 56.6; H, 9.9. $C_{18}H_{38}OSi_4$ Calc.: C, 56.5; H, 9.9%).

3.14. *Preparation of trisyl (p-methylphenyl)-methylisothiocyanatosilane TsiSi(C_6H_4Me-p)MeNCS*

A mixture of TsiSi(C_6H_4Me-*p*)MeI (0.5 g, 1.1 mmol) with KSCN (1 g, 10 mmol) in CH_3CN (50 cm^3) was refluxed for 10 days. Then it was treated with water and petroleum ether (40–60), the organic layer separated, dried (Na_2SO_4) and evaporated. The residue recrystallised from EtOH. (70%), m.p. 128°C. FTIR (KBr, cm^{-1}), (Si–NCS) 2080, (Si–C) 1245, ^{1}H-NMR ($CDCl_3$) 0.27 (s, 27H, Tsi), 0.73 (s, 3H, Me–Si), and 2.36 ppm (s, 3H, Me–tolyl). *m/z* (EI): 408 (20%, $[M–Me]^+$), 350 (35%, $[M–Me_3Si]^+$), 377 (5%, $[M–2(Me_3Si)]^+$), 365 (10%, $[M–SCN]^+$), 347 (30%, $[M–Ph]^+$), 201 (18%, $[M–tolyl–Me_3Si–SCN]^+$). (Found: C, 53.8; H, 8.7; N, 3.4. $C_{19}H_{37}NSi_4$ Calc.: C, 53.9; H, 8.7; N, 3.3%).

3.15. *Preparation of trisylbutyldichlorosilane TsiSiBuCl$_2$*

n-BuSiCl$_3$ (9.575 g, 50 mmol) was added dropwise with stirring to a solution of TsiLi (50 mmol) in THF (50 cm^3) that had been made by reaction of TsiH (11.5 g, 50 mmol) with MeLi (0.84 g, 120 mmol). The mixture was refluxed for 30 min, then aqueous NH_4Cl was added and the organic layer was extracted with Et_2O. The extract was dried ($MgSO_4$), filtered, evaporated, and the residue recrystallised from EtOH. A pure product was obtained by preparative TLC (silica gel, hexane as eluant) to give TsiSiBuCl$_2$ (48%), m.p. 119°C. FTIR (KBr, cm^{-1}), (C–H aliphatic) 2961.2, (C–Si) 1250, 850, (Si–Cl) 675.2, ^{1}H-NMR ($CDCl_3$) 0.347 (s, 27H, Tsi) and 0.4–1.5 ppm (m, 9H, Bu). *m/z* (EI): 386 (5%, $[M]^+$), 371 (95%, $[M–Me]^+$), 315 (65%, $[M–2Cl]^+$), 221 (70), 73 (87), 45 (38). (Found: C, 42.6; H, 9.3. $C_{10}H_{36}Cl_2Si_4$ Calc.: C, 43.1; H, 9.3%).

3.16. *Preparation of trisylbutyldiisothiocyanatosilane TsiSiBu(SCN)$_2$*

A mixture of TsiSiBuCl$_2$ (1.5 g, 3.8 mmol), KSCN (3.5 g, 36 mmol) and CH_3CN (100 cm^3) was refluxed for 48 h. The mixture was treated with water and Et_2O, the organic layer separated, dried ($MgSO_4$), and evaporated. A pure product was obtained by preparative TLC (silica gel, *n*-hexane as eluent), (60%), m.p. 100°C. FTIR (KBr, cm^{-1}), (Si–NCS)2100, ^{1}H-NMR ($CDCl_3$) 0.348 (s, 27H, Tsi), and 0.5–1.5 ppm (m, 9H, Bu). *m/z* (EI): 417 (100%, $[M–Me]^+$), 374 (60%, $[M–SCN]^+$), 361 (20), 244 (42), 73 (82), 45 (10). (Found: C, 44.1; H, 8.5; N, 6.0. $C_{16}H_{36}S_2N_2Si_4$ Calc.: C, 44.4; H, 8.3; N, 6.0%).

3.17. *Preparation of trisylbutyldiazidosilane TsiSiBu(N$_3$)$_2$*

A mixture of TsiSiBuCl$_2$ (1.5 g, 3.8 mmol) and NaN_3 (2.8 g, 43.4 mmol) in CH_3CN (100 cm^3) was refluxed for 96 h. The mixture was treated with *n*-hexane and water, the organic layer was separated, dried ($MgSO_4$), evaporated, and the residue recrystallised from EtOH. A pure product was obtained by preparative TLC (silica gel, *n*-hexane as eluant), (40%), m.p. 136°C. FTIR (KBr, cm^{-1}), (Si–N$_3$) 2120, ^{1}H-NMR ($CDCl_3$) 0.304 (s, 27H, Tsi) and 0.5–1.5 ppm (m, 9H, Bu). *m/z* (EI): 385.5 (18%, $[M–Me]^+$), 358.5 (100%, $[M–N_3]^+$), 330 (25), 172 (40), 73 (30), 45 (5). (Found: C, 40.3; H, 9.0; N, 20.4. $C_{14}H_{36}N_6Si_4$ Calc.: C, 41.9; H, 9.0; N, 20.9%).

3.18. Preparation of trisyl (p-methoxy phenyl) methylsilane TsiSi (C_6H_4OMe-p)MeH

(C_6H_4OMe-*p*)SiMeHCl (9.3 g, 50 mmol) was added dropwise with stirring to a solution of TsiLi (50 mmol) in THF (100 cm^3) that had been made by reaction of TsiH (11.5 g, 60 mmol) with MeLi (0.84 g, 120 mmol). The mixture was refluxed for 4 h, the aqueous NH_4Cl was added and the organic material was extracted with Et_2O. The extract dried (Na_2SO_4), filtered and evaporated, and the residue recrystallised from EtOH, then was purified by preparative TLC (silica gel, *n*-hexane as eluant), (40%) m.p. 107–108°C. FTIR (KBr, cm^{-1}), (Si–H) 2107.7, ^{1}H-NMR ($CDCl_3$) 0.19 (s, 27 H, Tsi), and 0.42 (d, 3H, Me–Si), and 3.79 (s, 3H, MeO–anisole), and 4.57 (q, 1H, Si–H), and 6.50–7.50 (m, 4 H, aryl–H). *m/z* (EI): 382 (5%, $[M]^+$), 367 (58%, $[M–Me]^+$), 274 (35%, $[M–anisole]^+$), 260 (5%, $[M–anisole–Me]^+$), 201 (27%, $[M–anisole–SiMe_3]^+$). (Found: C, 54.0; H, 10.0. $C_{18}H_{38}OSi_4$ Calc.: C, 56.5; H, 9.9%).

3.19. Preparation of trisyl (p-methoxyphenyl) methyliodosilane TsiSi (C_6H_4OMe-p)MeI

A solution of iodine monochloride (0.93 g, 6 mmol) in carbon tetrachloride (10 cm^3) was added dropwise to one of TsiSi(C_6H_4OMe-*p*)MeH (1.4 g, 4 mmol) in carbon tetrachloride (20 cm^3) at room temperature. When the addition was complete the solvent was removed and the solid product was recrystallised from EtOH to yield TsiSi(C_6H_4OMe-*p)*MeI (90%), m.p. 182°C. FTIR (KBr, cm^{-1}), (Si–C) 1245, ^{1}H-NMR ($CDCl_3$) 0.22 (s, 27H, Tsi), 1.30 (s, 3H, Si–Me), 3.70 (s, 3H, MeO–anisole), and 6.5–7.5 ppm (m, 4H, aryl–H). *m/z* (EI): 493 (4%, $[M–Me]^+$), 401 (15%, $[M–anisole]^+$), 381 (65%, $[M–I]^+$), 366 (8%, $[M–Me–I]^+$), 362 (7%, $[M–Me–3(Me_3Si)]^+$), 277 (12%, $[M–Tsi]^+$). (Found: C, 42.3; H, 7.3. $C_{18}H_{37}IOSi_4$ Calc.: C, 42.5; H, 7.3%).

3.20. Preparation of trisyl (p-methoxyphenyl)-methylisothiosyanato silane TsiSi(C_6H_4OMe-p)MeNCS

A mixture of TsiSi (C_6H_4OMe-*p*)MeI (0.1 g, 1 mmol), KSCN (0.1 g, 1 mmol) and CH_3CN (50 cm^3) was refluxed for 10 days, then was treated with water and petroleum ether (40–60), the organic layer seperated, dried (Na_2SO_4) and evaporated. The residue recrystallised from EtOH (50%).m.p. 130°C. FTIR (KBr, cm^{-1}), (Si–NCS) 270, (Si–C) 1245, ^{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 (m, 4H, aryl–H) *m/z* (EI): 439 (3%, $[M]^+$), 424 (65%, $[M–Me]^+$), 408 (3%, $[M–OMe]^+$), 381 (20%, $[M–SCN]^+$), 366 (14%, $[M–SiMe_3]^+$), 365 (45%, $[M–SiMe_2–O]^+$).

3.21. Preparation of trisyldichloro (p-methoxyphenyl)silane 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 (100 cm^3) that had been made by reaction of TsiH (11.5 g, 50 mmol) with Li (0.84 g, 120 mmol). The mixture was refluxed for 4 h, the aqueous NH_4Cl was added and the organic material was extracted with Et_2O. The extract dried (Na_2SO_4), filtered, evaporated and the residue recrystallised from EtOH, then sublimed at 100°C/0.1 mmHg, (60%) m.p. 165°C. FTIR (KBr, cm^{-1}), (Si–C) 1245, ^{1}H-NMR ($CDCl_3$) 0.3160 (s, 27H, Tsi), 3.8254 (s, 3H, OMe–anisole), 6.9261 (m, 4H, C_6H_4). *m/z* (EI): 368 (5%, $[M]^+$), 367 (1.3%, $[M–H]^+$), 353 (96%, $[M–Me]^+$), 351 (85%, $[M–Me–2H]^+$), 337 (4%, $[M–OMe]^+$), 277(35%, $[M–(Me_3Si)–CH_4–2H]^+$), 260 (25%, [M–Ar–H] +), 187 (16%, $[M–3(Me_3Si)–$ Ar–H] +). (Found: C, 46.5; H, 7.8. $C_{17}H_{34}Cl_2OSi_4$ Calc.: C, 46.6; H, 7.8%).

3.22. Preparation of trisyldiisothiocyanato-(p-methoxyphenyl)silane TsiSi(C_6H_4OMe-p)$(NCS)_2$

A mixture of TsiSi (C_6H_4OMe-*p*)Cl_2 (0.3 g, 0.6 mmol), KSCN (0.1 g, 1 mmol) and CH_3CN (50 cm^3) was refluxed for 10 days. Then was treated with water and petroleum ether (40–60), the organic layer separated, dried (Na_2SO_4) and evaporated. The residue recrystallised from EtOH (40%) m.p. 130°C. FTIR (KBr, cm^{-1}), (Si–NCS) 2070, (Si–C) 1245, ^{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%, $[M–Me]^+$), 409 (28%, $[M–SCN–Me]^+$), 351 (5% $[M–(SCN)_2–Me]^+$). (Found: C, 46.6; H, 7.8; N, 5.8. $C_{19}H_{34}N_2OS_2Si_4$ Calc.: C, 47.3; H, 7.00; N, 5.8%).

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