

Direct displacement of chlorine or iodine in reactions of $(\text{Me}_3\text{Si})_3\text{CSiRR}'\text{X}$ with metal salts

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Abstract

Direct nucleophilic displacement of halide X (X = Cl or I) takes place when the compounds $(\text{Me}_3\text{Si})_3\text{CSiRR}'\text{X}$ with R = Me, R' = (C₆H₄Me-*p*), (C₆H₄OMe-*p*), CH₂=CH R = Bu, R' = Cl, or R = Ph, R' = Ph are treated with solutions of KOCN, KSCN, KCN, or NaN₃ in CH₃CN or MeOH, and H₂O in DMSO, or CH₃CN. © 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 TsiSiR₂X species take place through bridged silicocationic intermediates. When the steric hindrance at the functional silicon centres is reduced, or linear nucleophiles like N₃[−], SCN[−], OCN[−] and CN[−] are used, direct bimolecular displacement takes place. Earlier work had indicated that nucleophilic substitution, while relatively easy for TsiSiMe₂X, was very slow for TsiSiPh₂I [2–5]. But we have now shown that under suitable conditions such substitution reactions provide a satisfactory route to TsiSiPh₂X 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=CH₂)Cl and TsiSi-BuCl₂ undergo direct nucleophilic reactions to give the corresponding products. The chlorides (C₆H₄OMe-*p*)-SiMeHCl and (C₆H₄Me-*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 N₃[−], 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 TsiSiAn₂I by the reaction of TsiSiAn₂H with ICl was unsuccessful [1]. An attempt to make TsiSi(C₆H₄Me-*p*)₂F by reaction of TsiLi with (C₆H₄Me-*p*)₂SiF₂ was also unsuccessful. For that reason in order to reduce steric hindrance we have chosen methylanisyl and methyltolyl derivatives to prepare TsiSi(C₆H₄OMe-*p*)MeI and TsiSi(C₆H₄Me-*p*)MeI, respectively and studied the reaction of the iodides with electrophiles, nucleophiles and alkoxides. When steric hindrance 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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When Me is substituted with a bulky anisyl group in $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)_2\text{H}$ the iodide derivative $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)\text{MeI}$ was successfully prepared by the reaction of $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)\text{MeH}$ 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 $\text{TsiSiRR}'X$

These compounds were obtained by reaction of TsiLi with (a) $n\text{-BuSiCl}_3$; (b) $(\text{C}_6\text{H}_4\text{OMe-}p)\text{SiMeHCl}$; (c) $(\text{C}_6\text{H}_4\text{Me-}p)\text{SiMeHCl}$; (d) $\text{CH}_2=\text{CHSiMeCl}_2$; (e) Ph_2SiF_2 .

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

(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 $\text{TsiSiMe}(\text{CH}=\text{CH}_2)\text{Cl}$ was found to react with KSCN , NaN_3 , KCN , and KOCN in CH_3CN to give $\text{TsiSiMe}(\text{CH}=\text{CH}_2)\text{Y}$ ($\text{Y} = \text{NCS}, \text{NCO}, \text{N}_3, \text{CN}$).

(iii) The methyltolyl and methylanisyl compounds $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeI}$, $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)\text{MeI}$ were reacted with KSCN in CH_3CN , and H_2O in DMSO , CH_3CN [6–9]. The hydrides $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeH}$, $\text{TsiSi}(\text{C}_6\text{H}_4\text{OMe-}p)\text{MeH}$ were subsequently made by the treatment of TsiLi with $(\text{C}_6\text{H}_4\text{Me-}p)\text{MeSiHCl}$ and $(\text{C}_6\text{H}_4\text{OMe-}p)\text{MeSiHCl}$, respectively.

(iv) The diphenyl compound $\text{TsiSiPh}_2\text{I}$ was found to react with KSCN , KOCN in CH_3CN containing crown ether and NaN_3 in MeOH containing crown ether. The reaction of $\text{TsiSiPh}_2\text{I}$ 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 $\text{TsiSiPh}_2\text{I}$ did not react with KCN in MeOH . The reaction of the $\text{TsiSi}(\text{C}_6\text{H}_4\text{-Me-}p)\text{MeI}$, $\text{TsiSi}(\text{C}_6\text{H}_4\text{-OMe-}p)\text{MeI}$ with H_2O , DMSO , CH_3N give the silanol derivatives, $\text{TsiSi}(\text{C}_6\text{H}_4\text{-Me-}p)\text{MeOH}$, $\text{TsiSi}(\text{C}_6\text{H}_4\text{-OMe-}p)\text{MeOH}$.

3. Experimental

3.1. Solvents and reagents

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

3.2. Spectra

The $^1\text{H-NMR}$ 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 trisyl diphenylisocyanato silane $\text{TsiSiPh}_2\text{NCO}$

A mixture of $\text{TsiSiPh}_2\text{I}$ (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 ($\text{KBr}, \text{cm}^{-1}$) $\nu(\text{Si-NCO})$ 2278.1, (C-Si) 1245. $^1\text{H-NMR}$ (CDCl_3): 0.12 (s, 27H, Tsi), and 7.13–7.50 ppm (m, 10H, Aryl-H). m/z (EI): 440 (20%, $[\text{M-Me}]^+$), 413 (38%, $[\text{M-NCO}]^+$), 335 (100%, $[\text{M-Ph-SiMe}]^+$), 247 (60%, $[\text{M-2Ph-CH}_2\text{SiC}]^+$), 197 (38%, $[\text{M-Tsi-Si}]^+$). (Found: C, 60.2; H, 8.1; N, 3.02, $\text{C}_{23}\text{H}_{37}\text{Si}_4\text{NO}$ Calc.: C, 60.66; H, 8.13; N, 3.07%).

3.4. Preparation of trisyl azidodiphenylsilane $\text{TsiSiPh}_2\text{N}_3$

A mixture of $\text{TsiSiPh}_2\text{I}$ (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 (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 recrystallized from EtOH . (83%); m.p. 137.5–138.5°C. FTIR ($\text{KBr}, \text{cm}^{-1}$) $\nu(\text{Si-N}_3)$ 2143.3. $^1\text{H-NMR}$ (CDCl_3): 0.112 (s, 27H, Tsi), and 7.12–7.65 ppm (m, 10 H, Aryl-H). m/z (EI): 440 (8%, $[\text{M-Me}]^+$), 397 (2%, $[\text{M-N}_3]^+$), 335 (41%, $[\text{M-Ph-SiMe}]^+$), 247 (25%, $[\text{M-2Ph-CH}_2\text{SiC}]^+$), 197 (12%, $[\text{M-Tsi-Si}]^+$), 175 (15%, $[\text{M-2}(\text{SiMe}_3)\text{-PhMe-3N}]^+$). (Found: C, 58.2; H, 8.4; N, 8.7. $\text{C}_{22}\text{H}_{37}\text{Si}_4\text{N}_3$ Calc.: C, 58.02; H, 8.13; N, 9.2%).

3.5. Preparation of trisyl diphenylisothiocyanatosilane $\text{TsiSiPh}_2\text{NCS}$

A mixture of $\text{TsiSiPh}_2\text{I}$ (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, $^1\text{H-NMR}$ (CDCl_3): 0.99 (s, 27H, Tsi), and 7.12–7.62 ppm (m, 10H, Aryl–H). m/z (EI): 456 (48%, $[\text{M-Me}]^+$), 397 (40%, $[\text{M-Me}_3\text{SiH}]^+$), 378 (72%, $[\text{M-Ph-CH}_4]^+$), 340 (15%, $[\text{M-Me}_3\text{Si-NCS}]^+$), 325 (15%, $[\text{M-(Me}_3\text{Si)}_2]^+$), 145 (11%, $[\text{M-SiMe}_3\text{-CSiPh}_2\text{-NCS}]^+$), 135 (85%, $[\text{SiMe}_3\text{Ph}]^+$), 135 (85%, $[\text{M-Tsi-SiPh}]^+$). (Found: C, 58.3; H, 7.9; N, 3.2. $\text{C}_{23}\text{H}_{37}\text{Si}_4\text{SN}$ Calc.: C, 58.5; H, 7.8; N, 3.0%).

3.6. Preparation of trisylmethylvinylchlorosilane $\text{TsiSi}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{Cl}$

Dichloromethylvinylsilane $\text{Cl}_2\text{Si}(\text{CH}_3)(\text{CH}=\text{CH}_2)$ (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 $\text{TsiSi}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{Cl}$ (55%), m.p. 340°C FTIR (KBr, cm^{-1}), ($=\text{C-H}$) 3061.5, (C-H aliphatic) 2962.2, 2987.2, ($\text{C}=\text{C}$) 1592.5. $^1\text{H-NMR}$ (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%, $[\text{M-Me}]^+$), 301 (4%, $[\text{M-Cl}]^+$), 213 (100%, $[\text{M-Me}_3\text{SiCl-Me}]^+$), 105(5%, $[\text{M-Tsi}]^+$). (Found: C, 46.4; H, 9.7. $\text{C}_{13}\text{H}_{33}\text{Si}_4\text{Cl}$ Calc.: C, 46.4; H, 9.8%).

3.7. Preparation of trisylisothiocyanatomethylvinylsilane $\text{TsiSi}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{NCS}$

A mixture of $\text{TsiSi}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{Cl}$ (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, $^1\text{H NMR}$ (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%, $[\text{M-Me}]^+$), 301 (2%, $[\text{M-NCS}]^+$), 285 (39%, $[\text{M-Me}_3\text{Si}]^+$), 256 (15%, $[\text{M-Me}_3\text{Si-Me}]^+$), 213 (46%, $[\text{M-(Me}_3\text{Si)}_2]^+$), 154 (19%, $[\text{M-(Me}_3\text{Si)}_2\text{-NCS}]^+$). (Found: C, 46.2; H, 8.9; N, 3.7. $\text{C}_{14}\text{H}_{33}\text{Si}_3\text{NS}$ Calc.: C, 46.9; H, 9.2; N, 3.9%).

3.8. Preparation of trisylazidomethylvinylsilane $\text{TsiSi}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{N}_3$

A mixture of $\text{TsiSi}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{Cl}$ (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, $^1\text{H-NMR}$ (CDCl_3): 0.27 (s, 27 H, Tsi), 0.57 (s, 3H, Si–Me) and 5.7–6.5 ppm (m, 3H, $\text{CH}=\text{CH}_2$). m/z (EI): 328 (12%, $[\text{M-Me}]^+$), 284 (8%, $[\text{M-N}_3\text{-CH}_4]^+$), 228 (14%, $[\text{M-Me}_3\text{SiN}_3]^+$), 200 (18%, $[\text{M-Me}_3\text{SiN}_3\text{-(CH}=\text{CH}_2)]^+$).

3.9. Preparation of trisylcyanidomethylvinylsilane $\text{TsiSi}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{CN}$

A mixture of $\text{TsiSi}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{Cl}$ (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, $^1\text{H-NMR}$ (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%, $[\text{M-Me}]^+$), 285 (28%, $[\text{M-(CH}=\text{CH}_2)\text{-Me}]^+$), 224 (24%, $[\text{M-Me}_3\text{Si-2Me}]^+$), 213 (99%, $[\text{M-Me}_3\text{Si-Me-CN}]^+$), 201 (46%, $[\text{M-Tsi-2Me}]^+$), 155 (33%, $[\text{M-(Me}_3\text{Si)}_2\text{-CN}]^+$).

3.10. Preparation of trisylisocyanatomethylvinylsilane $\text{TsiSi}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{NCO}$

A mixture of $\text{TsiSi}(\text{CH}_3)(\text{CH}=\text{CH}_2)\text{Cl}$ (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, $^1\text{H-NMR}$ (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%, $[\text{M-Me}]^+$), 285 (10%, $[\text{M-NCO-CH}_4]^+$), 240 (20%, $[\text{M-Me}_3\text{Si-2Me}]^+$), 213 (58%, $[\text{M-Me}_3\text{SiNCO-Me}]^+$), 201 (20%, $[\text{M-Tsi-2Me}]^+$). (Found: C, 47.2; H, 9.5; N, 3.9, $\text{C}_{14}\text{H}_{33}\text{Si}_3\text{NO}$ Calc.: C, 49.1; H, 9.6; N, 4%).

3.11. Preparation of trisyl(*p*-methylphenyl)methylsilane $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-}p)\text{MeH}$

$(\text{C}_6\text{H}_4\text{Me-}p)\text{SiMeHCl}$ (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, $^1\text{H-NMR}$ (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%, $[\text{M}]^+$), 365 (4%, $[\text{M-H}]^+$), 351 (18%, $[\text{M-Me}]^+$), 275 (5%, $[\text{M-tolyl}]^+$), 261 (22%, $[\text{M-tolyl-Me}]^+$), 73(100), 45 (18). (Found: C, 58.5; H, 10.2. $\text{C}_{18}\text{H}_{38}\text{Si}_4$ Calc.: C, 59.0; H, 10.3%).

3.12. Preparation of trisyl(*p*-methylphenyl)-methylidosilane $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-p})\text{MeI}$

A solution of iodine monochloride (0.24 g, 1.4 mmol), in carbon tetrachloride (20 cm^3), was added dropwise to $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-p})\text{MeH}$ (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 $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-p})\text{MeI}$, (90%), m.p. 179°C. FTIR (KBr, cm^{-1}), (C–Si) 1245, 850, $^1\text{H-NMR}$ (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%, $[\text{M-Me}]^+$), 386 (5%, $[\text{M-Me-tolyl}]^+$), 365 (90%, $[\text{M-I}]^+$). (Found: C, 44.4; H, 7.6. $\text{C}_{18}\text{H}_{37}\text{ISi}_4$ Calc.: C, 43.9; H, 7.5%).

3.13. Preparation of trisyl(*p*-methylphenyl)-hydroxymethylsilane $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-p})\text{MeOH}$

A mixture of $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-p})\text{MeI}$ (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, $^1\text{H-NMR}$ (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%, $[\text{M-Me}]^+$), 352 (18%, $[\text{M-Me-tolyl}]^+$). (Found: C, 56.6; H, 9.9. $\text{C}_{18}\text{H}_{38}\text{OSi}_4$ Calc.: C, 56.5; H, 9.9%).

3.14. Preparation of trisyl (*p*-methylphenyl)-methylisothiocyanatosilane $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-p})\text{MeNCS}$

A mixture of $\text{TsiSi}(\text{C}_6\text{H}_4\text{Me-p})\text{MeI}$ (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, $^1\text{H-NMR}$ (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%, $[\text{M-Me}]^+$), 350 (35%, $[\text{M-Me}_3\text{Si}]^+$), 377 (5%, $[\text{M-2}(\text{Me}_3\text{Si})]^+$), 365

(10%, $[\text{M-SCN}]^+$), 347 (30%, $[\text{M-Ph}]^+$), 201 (18%, $[\text{M-tolyl-Me}_3\text{Si-SCN}]^+$). (Found: C, 53.8; H, 8.7; N, 3.4. $\text{C}_{19}\text{H}_{37}\text{NSi}_4$ Calc.: C, 53.9; H, 8.7; N, 3.3%).

3.15. Preparation of trisylbutyldichlorosilane TsiSiBuCl_2

n-BuSiCl₃ (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, $^1\text{H-NMR}$ (CDCl_3) 0.347 (s, 27H, Tsi) and 0.4–1.5 ppm (m, 9H, Bu). *m/z* (EI): 386 (5%, $[\text{M}]^+$), 371 (95%, $[\text{M-Me}]^+$), 315 (65%, $[\text{M-2Cl}]^+$), 221 (70), 73 (87), 45 (38). (Found: C, 42.6; H, 9.3. $\text{C}_{10}\text{H}_{36}\text{Cl}_2\text{Si}_4$ Calc.: C, 43.1; H, 9.3%).

3.16. Preparation of trisylbutyldiisothiocyanatosilane $\text{TsiSiBu}(\text{SCN})_2$

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, $^1\text{H-NMR}$ (CDCl_3) 0.348 (s, 27H, Tsi), and 0.5–1.5 ppm (m, 9H, Bu). *m/z* (EI): 417 (100%, $[\text{M-Me}]^+$), 374 (60%, $[\text{M-SCN}]^+$), 361 (20), 244 (42), 73 (82), 45 (10). (Found: C, 44.1; H, 8.5; N, 6.0. $\text{C}_{16}\text{H}_{36}\text{S}_2\text{N}_2\text{Si}_4$ Calc.: C, 44.4; H, 8.3; N, 6.0%).

3.17. Preparation of trisylbutyldiazidosilane $\text{TsiSiBu}(\text{N}_3)_2$

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–N₃) 2120, $^1\text{H-NMR}$ (CDCl_3) 0.304 (s, 27H, Tsi) and 0.5–1.5 ppm (m, 9H, Bu). *m/z* (EI): 385.5 (18%, $[\text{M-Me}]^+$), 358.5 (100%, $[\text{M-N}_3]^+$), 330 (25), 172 (40), 73 (30), 45 (5). (Found: C, 40.3; H, 9.0; N, 20.4. $\text{C}_{14}\text{H}_{36}\text{N}_6\text{Si}_4$ 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 cm³) 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 NH₄Cl was added and the organic material was extracted with Et₂O. The extract dried (Na₂SO₄), 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, ¹H-NMR (CDCl₃) 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–SiMe₃]⁺). (Found: C, 54.0; H, 10.0. C₁₈H₃₈OSi₄ Calc.: C, 56.5; H, 9.9%).

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

A solution of iodine monochloride (0.93 g, 6 mmol) in carbon tetrachloride (10 cm³) was added dropwise to one of TsiSi(C_6H_4OMe-p)MeH (1.4 g, 4 mmol) in carbon tetrachloride (20 cm³) 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, ¹H-NMR (CDCl₃) 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(Me₃Si)]⁺), 277 (12%, [M–Tsi]⁺). (Found: C, 42.3; H, 7.3. C₁₈H₃₇IOSi₄ 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 CH₃CN (50 cm³) was refluxed for 10 days, then was treated with water and petroleum ether (40–60), the organic layer separated, dried (Na₂SO₄) and evaporated. The residue recrystallised from EtOH (50%).m.p. 130°C. FTIR (KBr, cm⁻¹), (Si–NCS) 270, (Si–C) 1245, ¹H-NMR (CDCl₃) 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–SiMe₃]⁺), 365 (45%, [M–SiMe₂–O]⁺).

3.21. Preparation of trisyldichloro (*p*-methoxyphenyl)silane TsiSi (C_6H_4OMe-p)Cl₂

(C_6H_4OMe-p)SiCl₃ (12 g, 50 mmol) was added dropwise with stirring to a solution of TsiLi (50 mmol) in THF (100 cm³) 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 NH₄Cl was added and the organic material was extracted with Et₂O. The extract dried (Na₂SO₄), 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, ¹H-NMR (CDCl₃) 0.3160 (s, 27H, Tsi), 3.8254 (s, 3H, OMe–anisole), 6.9261 (m, 4H, C₆H₄). *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–(Me₃Si)–CH₄–2H]⁺), 260 (25%, [M–Ar–H]⁺), 187 (16%, [M–3(Me₃Si)–Ar–H]⁺). (Found: C, 46.5; H, 7.8. C₁₇H₃₄Cl₂OSi₄ 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)Cl₂ (0.3 g, 0.6 mmol), KSCN (0.1 g, 1 mmol) and CH₃CN (50 cm³) was refluxed for 10 days. Then was treated with water and petroleum ether (40–60), the organic layer separated, dried (Na₂SO₄) and evaporated. The residue recrystallised from EtOH (40%) m.p. 130°C. FTIR (KBr, cm⁻¹), (Si–NCS) 2070, (Si–C) 1245, ¹H-NMR (CDCl₃) 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. C₁₉H₃₄N₂OS₂Si₄ Calc.: C, 47.3; H, 7.00; N, 5.8%).

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