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Synthesis and reactions of [tris(trimethylsilyl)methyl]ethyl dichlorosilane

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Abstract

The crowded dichlorosilane $TsiSiEtCl_2$, (1), (Tsi = $(Me_3Si)_3C$) was prepared from the reaction between $EtSiCl_3$ and TsiLi, then it was reduced with $LiAlH_4$ to give $TsiSiEtH_2$, (2). The hydride (2) was then treated with two equivalents of ICl/CCl_4 or Br_2/CCl_4 to produce $TsiSiEtI_2$, (3), and $TsiSiEtBr_2$, (4), respectively. The reaction of compound (2) with one equivalent of ICl/CCl_4 gives TsiSiEtHI, (5). This product reacted with H_2O/dioxane in the presence of $AgClO_4$ or with dry MeOH to produce TsiSiEtHOH, (6), and TsiSiEtHOMe, (7), respectively. The compound (3) reacted with H_2O in DMSO/CH_3CN to give $TsiSiEt(OH)_2$, (8), and the compound TsiSiEtIOMe, (9), was prepared from the reaction of the compound (7) with ICl/CCl_4. When the dichloride (1) was treated with NaOMe/MeOH it gave $(Me_3Si)_2CHSiEt(OMe)_2$. It is suggested that the reaction proceeds through an elimination–addition mechanism. The dichloride (1) was also treated with KSCN, NaN_3 or NaOCN in CH_3CN to give S_N2 substitution products. All the new products were characterized by FTIR, ^1H NMR, and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis.

Keywords: Silicon; Steric hindrance; Trisyl; Organosilicon

1. Introduction

Much novel chemistry has emerged from studies of the reactions of highly sterically hindered organosilicon compounds of the type $TsiSiRX_2$ (R = Me, Ph, Bu and X = Cl, Br, I) where Tsi denotes the bulky ligand $(Me_3Si)_3C$ [1–9]. Since the derivatives of $TsiSiEtCl_2$ had not been synthesized, we thought it would be worthwhile to make them in order to study the reactivity of this crowded dichloride. It has been shown that when the steric hindrance at the functional silicon centers is reduced or linear nucleophiles like N_3^-, SCN^- and OCN^- are used, direct bimolecular displacement takes place [10]. Studies have already revealed that nucleophilic attack by alkoxide at a silicon center bearing the $(Me_3Si)_3C$ group is inhibited because of the steric hindrance; instead they react with one of the less hindered Me_3Si groups to yield fragmentation products by a mechanism involving silaolefin (silene) intermediates [11].

2. Results and discussion

Tris(trimethylsilyl)methyl silicon compounds of the type $TsiSiRX_2$ have been shown to posses unusual properties, which can be attributed to the very large steric hinderance to nucleophilic attack at the silicon atom of the Si–X bond. The observation of unusual mechanisms of reaction at silicon centers in trisyl-silicon compounds is made possible mainly by the marked steric inhibition of direct bimolecular attack. However, with suitable nucleophiles such substitutions do take place.

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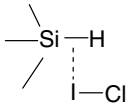
It has been shown previously that TsiLi reacts with $MeSiCl_3$, $BuSiCl_3$ and $PhSiCl_3$ to give the crowded disilanes $TsiSiMeCl_2$, $TsiSiBuCl_2$ and $TsiSiPhCl_2$, respectively, and we have now extended this reaction to the preparation of related $TsiSiEtCl_2$ and the study some of its reactions. The dichlorosilane, $TsiSiEtCl_2$, was prepared by the reaction of TsiLi with $EtSiCl_3$. Then direct replacement of the chloride by the small hydride ligand was effected by treatment with $LiAlH_4$, and direct nucleophilic substitution by reaction with pseudohalide salts such as NaN_3, NaOCN or KSCN in MeCN or MeOH (although the reactions in MeOH are accompanied by some formation of elimination–addition products) (Scheme 2). In the case of the reactions with KSCN, when the reaction was carried out for 48 h under reflex, the isolated product was exclusively the thiocyanate, $TsiSiEt(SCN)_2$, as indicated by the appearance of a bond at 2200 cm^{-1} in the IR spectrum. When the reaction was followed by IR, the spectrum showed that with a reaction time of 3 days both isomers were present in the mixture with the appearance of bonds at 2200 and 2073 cm^{-1} corresponding to SCN, NCS groups, respectively. Then the reaction was carried out 5 days under reflux, the isolated product was exclusively the thermodynamically more stable NCS derivative, $TsiSiEt(NCS)_2$. The reactions of $TsiSiEtCl_2$ with alkali metal salts in MeCN appear to be S_N2 nucleophilic displacements involving a five-coordinate intermediate; similar behavior was observed by Eaborn et al. [12,13] in the case of $TsiSiMe_2X$. The compound $TsiSiEtCl_2$ is cleaved by NaOMe/MeOH to give $(Me_3Si)_2CHSiEt(OMe)_2$. We postulate this reaction proceeds initially by the reaction of $TsiSiEtCl_2$ with NaOMe/MeOH to give $(Me_3Si)_2CHSiEtClOMe$. This type of reaction was also observed for all of the compounds $TsiSiMe_2X$ with X = Cl, Br and $TsiSiPh_2X$ with X = F, Cl, Br and I [2,14]. Direct nucleophilic displacement of chloride with methoxide gives $(Me_3Si)_2CHSiEt(OMe)_2$ (Scheme 1).

The initial process is analogous to an E_2 elimination from organic halides but with attack at a β-silicon rather than a β-hydrogen. That the nucleophile attacks at Me_3Si rather than at the electronically favored $EtCl_2Si$ center can be attributed to the fact that attack at the former results in relief of more steric strain [2]. We also observed that treatment of $TsiSiEtH_2$ with a molar proportion of ICl in CCl_4 gave the iodide TsiSiEtHI, which was converted into the di-iodide by a further molar proportion of ICl. Similar behavior was observed in the case of $TsiSiMeH_2$ [15]. However, it was shown previously that when TsiSiPhHI is treated with a one molar proportion of ICl the product is a 35:65 mixture of TsiSiPhClI and $TsiSiPhI_2$ [16]. The mode halogenation of TsiSiEtHI can be attributed to the presence of the sterically-undemanding hydrogen substituent in the transition state. The reaction essentially involves interaction of the electrophile with the electrons of the Si–H bond, and so attack by the positive end of the I–Cl dipole, as in. This concept was developed by Sommer for reactions with BrCl in terms of rate-determining formation of an intermediate ionic intermediate as in **II**, [16] which then rapidly breaks down by separation of HCl. The compound TsiSiEtIOMe was prepared from the reaction of the compound TsiSiEtHOMe with ICl/CCl_4.



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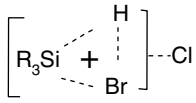
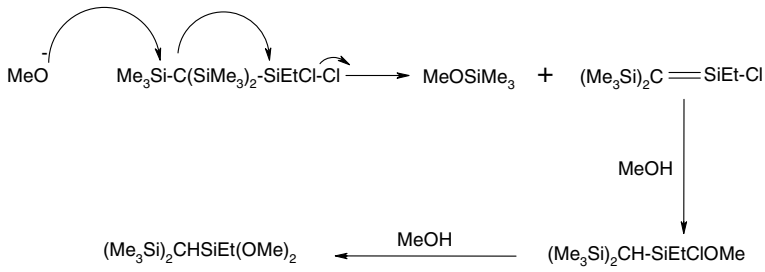


II

The hydride $TsiSiEtH_2$ has been reacted with two equivalent of Br_2 in CCl_4 to give the corresponding dibromide. The reaction of $TsiSiEtH_2$ with Br_2 or ICl (uncatalized by light) in CCl_4 is fast, and occurs with retention [17]. For the compounds of the type $TsiSiR_2X$ with R = Me or Ph, X = F, Cl, Br, I, there is no reaction with methanol alone, but with sodium methoxide in methanol fragmentation occurs (presumably driven by release of steric strain) to give products of the type $(Me_3Si)_2CH$-SiR_2OMe, seemingly via the silaolefins $(Me_3Si)_2C = SiR_2$ [11]. Replacement of one of the groups R by hydrogen reduce the steric hindrance considerably and our results for TsiSiEtHI show that nucleophlic substitution takes place readily. Mechanisms involving initial formation of a five-coordinate silicon complex have commonly been assumed in discussion of displacements at silicon atom in organosilicon compounds. Steric hindrance by the trisyl group would be expected to prevent backside approach and force displacement from the same side as the leaving group and the observed substitution at silicon in TsiSiEtHI by MeOH and H_2O may



Scheme 1.

involve flank attack. The iodide TsiSiEtHI reacted with H_2O in dioxan in the presence of $AgClO_4$, and with dry MeOH to produce TsiSiEtHOH and TsiSiEtHOMe respectively by direct bimolecular displacement reactions. Finally, the compound $TsiSiEtI_2$ reacted with H_2O in DMSO/MeCN to give $TsiSiEt(OH)_2$ during 24 h under reflux in 6/3/1 (vol./vol.) Me_2SO/MeCN/H_2O (the MeCN being added to increase the solubility of the iodide). This observation was of considerable significance, not only because it made the hydroxide available but also, more importantly, because the absence of rearranged product showed that the solvolysis did not proceed through a cationic intermediate [2]. It seems likely that formation of a five-coordinated intermediate is rate-determining (Scheme 2).

The 400 MHz NMR spectra of most of our compounds gave non-first-order ethyl resonances, as found previously for compounds $TsiSiEt_2X$ and TsiSiEtMeX [16,17], but in those for $TsiSiEtX_2$ (X = I, OH, SCN, N_3) and TsiSiEtIOMe the CH_3 and CH_2 resonances were clearly resolved.

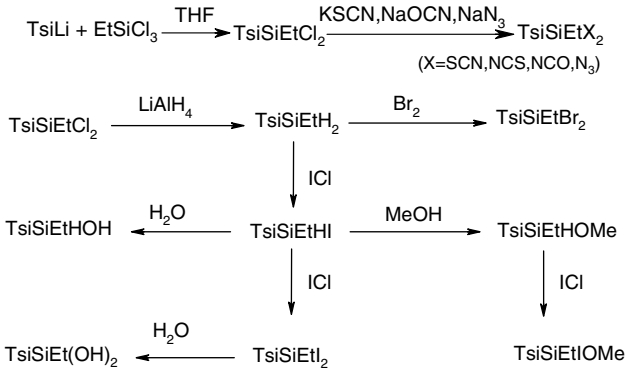
3. Experimental

3.1. Solvents and reagents

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

3.2. Spectra

Melting points were taken on an Electromental 9100-digital melting point apparatus.The ^1H NMR and ^{13}C NMR spectra were recorded with a NMR Bruker. FT-400 MHz spectrometer at room temperature using $CDCl_3$ as a solvent. The mass spectra were obtained with a Finnigan–Mat model 8400, operating at 70 ev. The IR spectra were recorded on an FTIR, DR.8001-Shimadzu spectrometer. Elemental analyses were carried out with a Heareus CHN-ORAPID instrument.



Scheme 2.

3.3. Prepartion of $TsiSiEtCl_2$

$EtSiCl_3$ (8.17 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 (ll.5 g, 50 mmol) with MeLi (0.84 g, 120 mmol) (Prepared as described by Eaborn and his co-workers [18]). 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 very pure product for elemental analysis was obtained by preparative TLC (silica gel, hexane as eluant) to give $TsiSiEtCl_2$ (62%), m.p. 308 °C. FTIR (KBr, cm^{-1}), (C–H aliphatic) 2960, (C–Si) 1250, 850, (Si–Cl) 675. ^1H NMR ($CDCl_3$) 0.34 (s, 27H, Tsi) and 1–1.25 ppm (m, 5H, Et). ^{13}C NMR ($CDCl_3$) 1.7 (C–$SiMe_3$), 3.8 (CH_3Si), 6.0 (CH_3), 16.2 ppm (CH_2). *m/z* (EI): 344 (100%, $[M - Me]^+$), 330(5%, $[M - Et]^+$), 140 (5%), 128(20%), 73(20%). (Found: C, 39.8; H, 8.8. $C_{11}H_{32}Cl_2Si_4$ Calc.: C, 40.1; H, 8.9%).

3.4. Preparation of $TsiSiEt(SCN)_2$

A mixture of $TsiSiEtCl_2$ (0.5 g, 1.4 mmol), KSCN (1.4 g, 14 mmol) and CH_3CN (100 mL) was refluxed for 48 h. The mixture was treated with water and Et_2O, the organic layer was separated, dried ($MgSO_4$), and filtered. Solvent was evaporated from the filtrate and the residue was purified by TLC (silica gel, *n*-hexane as eluent), (72%). m.p. 286 °C. FTIR (KBr, cm^{-1}), (SCN) 2200. ^1H NMR ($CDCl_3$). 0.24 (s, 27H, Tsi), 0.99–1.05 (q, 2H, CH_2), 1.14–1.18 ppm (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$), 0.8 (C–$SiMe_3$), 3.2 (CH_3–Si), 6.0 (CH_3), 11.8 ppm (CH_2). *m/z* (EI): 390 (30% $[M - Me]^+$), 73 (100%, $[Me_3Si]^+$), 259 (10%), 204 (5%), 130 (10%). (Found: C, 41.2; H, 7.8; N, 6.7. $C_{14}H_{32}S_2N_2Si_4$ Calc.: C, 41.5; H, 7.9; N, 6.9%).

3.5. Preparation of $TsiSiEt(NCS)_2$

A mixture of $TsiSiEtCl_2$ (0.5 g, 1.4 mmol) KSCN (1.4 g, 14 mmol) and MeCN (l00 mL) was refluxed for 5 days. The mixture was treated with water and Et_2O. The organic layer was separated, dried ($MgSO_4$) and filtered. Solvent was evaporated from the filtrate and the residue was purified by TLC (Silica gel, *n*-hexane as eluent), (65%). m.p. 290 °C. FTIR (KBr, cm^{-1}), (NCS) 2073. ^1H NMR ($CDCl_3$), 0.28 (s, 27H, Tsi), 1.12–1.26 ppm (m, 5H, Et). ^{13}C NMR ($CDCl_3$), 1.8 (C–$SiMe_3$), 3.3 (CH_3–Si), 5.9 (CH_3), 11.5 ppm (CH_2). *m/z* (EI): 390 (20% $[M - Me]^+$), 259 (15%), 204 (10%), 73 (100%, $[Me_3Si]^+$). (Found: C, 41.4; H, 7.8; N, 6.8 $C_{14}H_{32}S_2N_2Si_4$ Calc.: C, 41.5; H, 7.9; N, 6.9%).

3.6. Preparation of $TsiSiEt(NCO)_2$

A mixture of $TsiSiEtCl_2$ (0.5 g, 1.4 mmol), NaOCN (0.9 g, 14 mmol) in MeCN (100 mL) was refluxed for l0 days. The mixture was treated with Et_2O and water, separated the organic layer was separated, dried ($MgSO_4$) and filtered. Solvent was evaporated from the filtrate and residue was purified by TLC (Silica gel, *n*–hexane as eluent), (53%). m.p. 303 °C. FTIR (KBr, cm^{-1}), (NCO) 2271. ^1H NMR ($CDCl_3$) 0.34 (s, 27H, Tsi), 1.12–1.21 ppm (m, 5H, Et). ^{13}C NMR ($CDCl_3$), 2.2 (C–$SiMe_3$), 3.8 (Tsi), 8.5 (CH_3), 12.8 ppm (CH_2). *m/z* (EI): 372 (5% $[M - Me]^+$), 359 (10%), 243 (5%), 73 (100%, $[Me_3Si]^+$). (Found: C, 45.2; H, 8.5; N, 7.6. $C_{14}H_{32}O_2N_2Si_4$ Calc.: C, 45.1; H, 8.6; N, 7.5%).

3.7. Preparation of $TsiSiEt(N_3)_2$

A mixture of $TsiSiEtCl_2$ (0.5 g, 1.4 mmol) and NaN_3 (0.9 g, 14 mmol) in MeCN (100 mL) was refluxed for 3 days. The mixture was treated with water and Et_2O, the organic layer was separated, dried ($MgSO_4$) and filtered. Solvent was evaporated from the filtrate and residue was purified by TLC (Silica gel, *n*-hexane as eluent), (82%). m.p. 312 °C. FTIR (KBr, cm^{-1}), (N_3) 2100. ^1H NMR ($CDCl_3$) 0.28 (s, 27H, Tsi), 0.99–1.05 (q, 2H, CH_2), 1.14–1.18 ppm (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$), 2.8 (C–$SiMe_3$), 4.4 (Tsi), 7.0 (CH_3), 12.5 ppm (CH_2). *m/z* (EI): 358 (10%, $[M - Me]^+$), 246 (10%), 131 (25%), 73 (100%, $[Me_3Si]^+$). (Found: C, 38.5; H, 8.7; N, 22.7. $C_{12}H_{32}N_6Si_4$ Calc.: C, 38.6; H, 8.6 N, 22.5%).

3.8. Preparation of $(Me_3Si)_2CHSiEt(OMe)_2$

$TsiSiEtCl_2$ (1 g, 2.8 mmol) was refluxed in 2 M $NaOCH_3/CH_3OH$ solution (30 mL) for 24 h. The solution was added to petroleum ether, the organic layer was washed several times with water, the organic layer was separated, dried ($MgSO_4$) and filtered. Solvent was evaporated from the filtrate and the residue was purified by TLC (silica gel, 90:10 *n*-hexane:dichloromethane as eluent) to give $(Me_3Si)_2CHSiEt(OMe)_2$. ^1H NMR ($CDCl_3$): 0.1(s, 18H, Me_3Si), −0.6 (s, 1H, C–H), 0.5–1.5 (m, 5H, Et), 3.5 ppm (s, 1H, OMe). ^{13}C NMR ($CDCl_3$), 0.0 (C–H), 1.7(Me_3Si), 5.1 (CH_3), 12.6 (CH_2), 49.2 ppm (OMe). *m/z* (EI): 278 (30%, $[M]^+$), 263 (80%, $[M - Me]^+$), 182 (100%), 107 (20%), 77 (5%). (Found: C, 47.1; H, 10.5. $C_{11}H_{30}Si_3O_2$, Calc.: C, 47.5; H, 10.8%).

3.9. Preparation of $TsiSiEtH_2$

$LiAlH_4$ (6 g, 0.158 mol) was gradually added with stirring to a solution of $TsiSiEtCl_2$ (6 g, 16.7 mmol) in dried THF (150 mL). The mixture was refluxed for 2 days. After cooling of the mixture in ice water, aqueous saturated NH_4Cl was slowly added, the solution was extracted with Et_2O, then the extract was dried ($MgSO_4$) and filtered. Solvent was evaporated from the filtrate and the residue was recrystallized from EtOH to give $TsiSiEtH_2$ (82.5%). m.p. 210 °C. FTIR (KBr, cm^{-1}), (C–H) 2904, (Si–H) 2112, (C–Si) 1254, 850. ^1H NMR ($CDCl_3$): 0.18 (s, 27H, Tsi), 0.76–1.04 (m, 5H, Et), 3.76–3.78 ppm (m, 2H, SiH_2) ^{13}C NMR ($CDCl_3$) 2.1 (C–$SiMe_3$), 2.3 (CH_3–Si), 2.5 (CH_3), 8.8 ppm(CH_2). *m/z* (EI): 289 (30%, $[M - H]^+$), 275(100%, $[M - Me]^+$), 273(80%), 242(40%), 201(50%). (Found: C, 49.8, H, 11.6. $C_{12}H_{34}Si_4$ Calc.: C, 49.6; H, 11.7%).

3.10. Preparation of $TsiSiEtBr_2$

A solution of Br_2 (0.55 g, 3.34 mmol) in CCl_4 (25 ml) was added dropwise during a period of 30 min with stirring to a solution of $TsiSiEtH_2$ (0.5 g, 1.72 mmol) in CCl_4 (10 mL) cooled in an ice bath. Then the mixture was stirred for an additional 30 min. at room temperature. Solvent was removed under reduced pressure (20 Torr) to leave a white residue, which was sublimed under reduced pressure (5 Torr) to give $TsiSiEtBr_2$ (85%). m.p. 162 °C. ^1H NMR ($CDCl_3$) 0.37 (27H, Tsi), 1.12–1.17 (t, 3H, CH_3) 1.20–1.37 ppm (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$) 4.0 (C–$SiMe_3$), 4.1 (CH_3–Si), 6.7 (CH_3) 18.4 ppm (CH_2). *m/z* (EI): 433 (15%$[M - Me]^+$), 389 (100%, $[M - Et - 2Me]^+$), 343 (20%), 288 (70%,$[M - 2Br]^+$), 221 (40%). (Found: C, 32.5, H, 7.6. C_{11} H_{32} Br_2 Si_4 Calc.: C, 32.1; H, 7.2%).

3.11. Preparation of TsiSiEtHI

A solution of ICl (1.12 g, 6.9 mmol) in CCl_4 (30 mL) was added dropwise with stirring to a solution of $TsiSiEtH_2$ (2 g, 6.89 mmol) in CCl_4 (20 mL). The mixture was stirred for 30 min and the solvent removed under reduced pressure (20 Torr) to leave a white residue, which was sublimed under reduced pressure (5 Torr) to give TsiSiEtHI (92%). m.p. 267 °C. FTIR (KBr, cm^{-1}), (Si–H) 2133. ^1H NMR ($CDCl_3$) 0.32 (s, 27H, Tsi), 1.05–1.09 (t, 3H, CH_3) 1.10–1.23 (m, 2H, CH_2), 4.60–4.61 ppm (d, 1H, Si–H). ^{13}C NMR ($CDCl_3$) 2.2 (C–$SiMe_3$), 3.3 (CH_3–Si), 8.3 (CH_3), 12.5 ppm (CH_2). *m/z* (EI): 416 (5%, $[M]^+$), 401 (90%, $[M - Me]^+$), 313 (20%), 290 (100% $[M - I]^+$), 72 (30%). (Found: C, 35; H, 8.1. $C_{11}H_{33}ISi_4$ Calc.: C, 34.6; H, 7.9%).

3.12. Preparation of TsiSiEtHOH

A mixture of $AgClO_4$ (0.1 g), TsiSiEtHI (0.5 g, 1.2 mmol) dioxane (30 mL) and H_2O (5 mL) was refluxed for 2 h. The flask was covered with aluminum foil to avoid light. The mixture was cooled and filtered and

water (10 mL) was added. The organic material was extracted with *n*-hexane. The extract was dried (Na_2SO_4) and filtered. Solvent was evaporated from the filtrate and the residue was purified by TLC (Silica gel, 1:1 *n*-hexane: dichloromethane as eluent), (54%). m.p. 150 °C. FTIR (KBr, cm^{-1}), (OH) 3446, (Si–H) 2133. ^1H NMR ($CDCl_3$) 0.22 (S, 27H, Tsi), 0.74–0.85 (m, 2H, CH_2) 1.05–1.59 (t, 3H, CH_3), 1.54 (s, 1H, O–H), 4.68–4.69 pm (d, 1H, Si–H). ^{13}C NMR ($CDCl_3$) 2.6 (C–$SiMe_3$), 3.5 (Tsi), 5.4 (CH_3), 10.2 ppm (CH_2). *m/z* (EI): 306 (5%, $[M]^+$), 291 (80%, $[M - Me]^+$), 289 (100%, $[M - OH]^+$), 275 (40%), 173 (10%), 72 (10%). (Found: C, 47.3; H; 10.8. $C_{11}H_{34}OSi_4$ Calc.: C, 47.1; H, 11.5%).

3.13. Preparation of TsiSiEtHOMe

A mixture of TsiSiEtHI (0.5 g, 1.2 mmol) and methanol (40 mL) was refluxed for 48 h. The solvent was removed and the solid product was recrystallized from MeOH to yield TsiSiEtHOMe (89%). m.p. 235 °C. FTIR (KBr, cm^{-1}), (Si–H) 2089, (Si–O) 1095. ^1H NMR ($CDCl_3$) 0.19 (s, 27 H, Tsi), 0.73–0.89 (m, 2H, CH_2) 1.08–1.12 (t, 3H, CH_3), 3.51. (s, 3H, OCH_3), 4.54–4.55 ppm (d, 1H, Si–H). ^{13}C NMR ($CDCl_3$) 2.8 (C–$SiMe_3$), 3.1 (Tsi), 8.2 (CH_3) 9.6 (CH_2), 52.2 ppm (OMe). *m/z* (EI): 305 (100% $[M - Me]^+$), 289 (20% $[M - Me]^+$), 201 (20%), 72 (10%). (Found: C, 48.8; H; 10.9. $C_{12}H_{36}OSi_4$ Calc.: C, 48.7; H, 11.2%).]

3.14. Preparation of TsiSiEtI(OMe)

A solution of ICl (0.15 g, 0.94 mmol) in CCl_4 (15 mL) was added dropwise with stirring to a solution of TsiSiEtH(OMe) (0.3 g, 0.94 mmol) in CCl_4 (15 mL). The mixture was stirred for 30 min and the solvent removed under reduced pressure (20 Torr) and leave a white residue. A pure product was obtained by preparative TLC (silica gel, *n*-hexane as eluant), (71%) m.p. 319 °C. ^1H NMR ($CDCl_3$), 0.32 (s, 27H, Tsi), 1.06–1.14 (t, 3H, Me) 1.38–1.42 (q, 2H, CH_2), 3.51 ppm (s, 3H, OMe). ^{13}C NMR ($CDCl_3$) 5.7 (C–$SiMe_3$), 6.0 (CH_3–Si), 10.2 (CH_3), 20.5 (CH_2), 54.7 ppm (OMe). *m/z* (EI): 431 (20%, $[M - Me]^+$), 320 (100%, $[M - I]^+$), 319 (20%), 290 (10%, $[M - I - Et]^+$), 129 (10%), 72 (20%). (Found: C, 35.2; H; 7.8. $C_{12}H_{35}IOSi_4$, Calc.: C, 34.9; H, 7.8%).

3.15. Preparation of TsiSiEtI$_2$

A solution of ICl (0.56 g, 3.45 mmol) in CCl_4 (25 mL) was added dropwise with stirring to a solution of TsiSiEtH_2 (0.5 g, 1.72 mmol) in CCl_4 (10 mL). The mixture was stirred for 30 min and the solvent removed under reduced pressure (20 Torr). A very pure product for elemental analysis was obtained by preparative TLC (silica gel, *n*-hexane as eluent), (94%). m.p. 280 °C. ^1H NMR ($CDCl_3$) 0.44 (s, 27H, Tsi) 1.08–1.12 (t, 3H, CH_3), 1.56–1.61 ppm (q, 2H, CH_2). ^{13}C NMR ($CDCl_3$) 4.3(C–Me_3), 4.9 (CH_3–Si), 9.9 (CH_3) 18.4 ppm (CH_2). *m/z* (EI): 542(2%, $[M]^+$), 541(10%, $[M - H^+]$), 527(100%, $[M - Me]^+$), 513 (20%), 440 (60%), 416 (95%), (Found: C, 26.7; H, 6.2. $C_{11}H_{32}I_2Si_4$ Calc.: C, 26.5; H, 5.5%).

3.16. Preparation of TsiSiEt(OH)$_2$

A mixture of TsiSiEtI_2 (0.5 g, 0.93 mmol), DMSO (30 mL), H_2O (5 mL) and MeCN (15 mL) was refluxed for 24 h. The solution was treated with water (50 mL)and *n*-hexane (50 mL), dried (Na_2SO_4) and evaporated. A pure product was obtained by preparative TLC (Silica gel, dichloromethane as eluent), (64%). m.p. 255 °C. FTIR (KBr, cm^{-1}) (O–H) 3465. ^1H NMR ($CDCl_3$) 0.25 (s, 27H, Tsi), 0.73–0.79 (q, 2H, CH_2) 0.99–1.02 (t, 3H, CH_3), 1.97 ppm (s, 2H, OH). ^{13}C NMR ($CDCl_3$) 2.9 (C–$SiMe_3$), 3.5 (Tsi), 5.8 (CH_3), 10.5 ppm (CH_2). *m/z* (EI): 307 (10%, $[M - Me]^+$), 290 (100%, $[M - Me–OH]^+$) 276 (10%, $[M - Et - OH]^+$), 187 (10%), 72 (30%). (Found: C, 46.6, H, 10.5. $C_{11}H_{34}O_2Si_4$ Calc.: C, 44.70; H, 10.5%).

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