Synthesis of new highly sterically hindered organosilicon compounds via displacement reaction of $TsiSiCl_3$

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The displacement reaction of $TsiSiCl_3$ with nucleophiles does not take place, but in this work we did this reaction with some alcohols and phenols in the presence of base, to product silyl ethers of the type $TsiSiCl_2OR$, $TsiSiCl_2OAr$, (R= *n*-Pr, *i*-Bu, *i*-Am, $PhCH_2$, and Ar = Ph, C_6H_4OMe-*p*, $C_6H_4NH_2$-*p*, $C_6H_4NO_2$-*p*, C_6H_4COOMe-*o*, $C_6H_4NHCOOMe$-*p*).

Keywords: displacement; silylether; sterically hindrance; trisyl, organosilicon

Introduction

The very bulky tris (trimethylsilyl) methyl ligand, $(Me_3Si)_3C$, commonly denoted Tsi, in organosilicon chemistry can cause some interesting results in that its direct displacement does not take place easily.[1–3] Because the normal reaction path is forbidden, such compounds display unusual reactions.[4–7] For example reactions of halogen derivatives with sodium alkoxides give fragmentation products.[8] Also unusual rearrangement and migration reactions in compounds of the type $TsiSiR_2X$ take place, when they react with some electrophiles such as AgOAC, Hg $(OAC)_2$, or ICl. Only when the steric hindrance of the functional silicon centres is reduced, or linear nucleophiles such as N_3^-, SCN^-, OCN^-, and CN^- are used, can direct bimolecular displacement take place.[9] In this work we did direct displacement reactions of $TsiSiCl_3$ with alcohols and phenols that has not been previously observed.

Results and discussion

In some recent work it was reported that displacement of chlorine in $TsiSiCl_3$ with nucleophiles such as alkoxide dos not take place easily, and a fragmentation reaction was observed, because steric hindrance of the functional silicone centres prevents this reaction.[10] We now did these reactions for $TsiSiCl_3$ by using suitable methods and have synthesised some displacement products. Tris (trimethylsilyl) methyl trichlorosilane was obtained by reaction of $SiCl_4$ with TsiLi in one molar proportion. It has been reported that this compound is stable towards alcohols, and reacts slowly with NaOMe,[4] but we have now shown that under suitable condition such a substitution reaction can proceed. We have used alkoxides in low molaratio, or some bases such as NaH in THF as a solvent, with $TsiSiCl_3$ in the presence of base and have synthesised aliphatic and aromatic silyl ethers of the type $TsiSiCl_2OR$, $TsiSiCl_2OAr$, (R= *n*-Pr, *iso*-Bu, *iso*-amyl, benzyl, Ar = Ph, C_6H_4OMe-*p*, $C_6H_4NH_2$-*p*, $C_6H_4NO_2$-*p*, C_6H_4COOMe-*o*, $C_6H_4NHCOOMe$-*p*). In the reaction of phenols with $TsiSiCl_3$ the presence of electron – donating and electron withdrawing groups does not seem important, but sterical effects are an important factor, for example, the reaction of methylsalicylate takes place slower than other species that have electron donating or withdrawing groups. The other importance of our work is that we have prepared not only novel organosilicon compounds, but also silyl ethers of two drugs, *i.e.* methylsalicylate, and acetaminophen. Silylethers are important compounds which can act as protecting agents for alcohols and phenols.

$$Me_3SiCl + CHCl_3 + Li \longrightarrow TsiH$$

$$Tsi\text{–}H + MeLi \longrightarrow TsiLi$$

$$TsiLi + SiCl_4 \xrightarrow{THF} TsiSiCl_3$$

$$TsiSiCl_3 + ROH \longrightarrow TsiSiCl_2OR$$

$$TsiSiCl_3 + ArOH \longrightarrow TsiSiCl_2OAr$$

Scheme 1 Preparation and reaction of $TsiSiCl_3$.

Reaction conditions for reactions of $TsiSiCl_3$ with alcohols and phenols are shown in Table 1.

Experimental

Solvent and reagents: Reactions involving lithium metal, or organolithiums were carried out under dry argon. Solvents were dried by standard methods.

Spectra: The ^1H NMR spectra were recorded using an FT- H NMR Bruker (400 MHz) spectrometer in $CDCl_3$. The IR spectra were recorded on an FTIR, DR.8001-S Bruker spectrometer. Mass spectra were obtained with a Finnigan-Mat model 8400, 70 eV. Melting points were determined with a 9100-electro thermal apparatus.

Preparation of [tris (trimethyl silyl) methyl] dichloro propoxy silane TsiSiCl$_2$(Opr): A mixture of $TsiSiCl_3$ (0.15 g, 0.4 mmol) and 0.07 M NaOPr in PrOH (30 cm^3) was refluxed for 7 h. NaCl formed was separated with filtration from the organic layer. Solvent was evaporated and the residue purified by preparative TLC (silica gel, *n*-hexane as eluant) (14%); m.p. 206°C. FT-IR (KBr, cm^{-1}): 2960, 1269, 1073, 891, 856. FT-^1H NMR ($CDCl_3$): 0.33 (s, 27H, Tsi),

Table 1

Entry	Starting material	Alkoxides/Bases	Products	Time/h
1	PrOH	NaOPr/*n*- PrOH	$TsiSiCl_2O$ *n*-Pr	7
2	*i*-BuOH	NaOBu/*i*-BuOH	$TsiSiCl_2O$ *i*-Bu	7
3	*i*- AmOH	NaOAm/*i*-AmOH	$TsiSiCl_2O$ *i*-Am	7
4	$PhCH_2OH$	$NaOCH_2Ph$/PhCH2 OH	$TsiSiCl_2OCH_2Ph$	4.5
5	PhOH	NaH/THF	$TsiSiCl_2OPh$	5.5
6	$C_6H_4NH_2$-*p*-OH	NaH/THF	$TsiSiCl_2OC_6H_4NH_2$	7
7	C_6H_4OMe-*p*-OH	NaH/THF	$TsiSiCl_2OC_6H_4OMe$	7
8	$C_6H_4NO_2$-*p*-OH	NaH/THF	$TsiSiCl_2OC_6H_4NO_2$	8—9
9	$C_6H_4NHCOCH_3$-*p*-OH	NaH/THF	$TsiSiCl_2OC_6H_4NHCOCH3$	7
10	$C_6H_4COOCH_3$-*o*-OH	NaH/THF	$TsiSiCl_2OC_6H_4COOCH3$	60

* Correspondence.

0.95 (t, 3H, CH3), 1.64 (m, 2H, CH2), 3.8 (t, 2H, OCH2). *m/z* (EI): 373 (16%, $[M-Me]^+$), 352 (80), 241(86), 72 (100).

Preparation of [tris (trimethyl silyl) methyl] dichloro isobutoxy silane TsiSiCl$_2$ (O ^{i}Bu): A mixture of $TsiSiCl_3$ (0.17 g, 0.46 mmol) and 0.07M NaO^iBu in BuOH (30 cm^3) was refluxed for 7 h. NaCl formed and was separated by filtration from the organic layer and solvent was evaporated. The residue was purified by preparative TLC (silica gel, *n*-hexane as eluant (16%); m.p. 103°C. FT-IR (KBr, cm^{-1}): 2960, 1269, 1073, 891, 856. FT-^{1}H NMR ($CDCl_3$): 0.33 (s, 27H, Tsi), 0.93─0.95 (d, 6H, CH_3), 1.86 (m, 1H, CH), 3.62 (d, 2H. OCH_2). *m/z* (EI): 359(6%, $[M-Pr]^+$), 299(44), 294(38), 72 (40), 56(6).

Preparation of [tris (trimethyl silyl) methyl] dichloro isoamiloxy silane TsiSiCl$_2$ (O ^{i}Am): A mixture of $TsiSiCl_3$ (0.15 g, 0.4 mmol) and 0.07M NaO^iAm in ^{i}AmOH (30 cm^3) were refluxed for 7 h. NaCl formed was separated by filtration from the organic layer and the solvent was evaporated. The residue was purified with preparative TLC (silica gel, *n*-hexane as eluant) (15%); m.p. 107°C. FT-IR (KBr, cm^{-1}): 2962, 1261, 1100, 884, 838. FT-^{1}H NMR ($CDCl_3$): 0.34 (s, 27H,Tsi), 0.9 (d, 6H, CH_3), 1.5 (q, 2H, CH_2), 1.7 (m, 1H, CH), 3.8 (t, 2H, OCH_2). *m/z* (EI): 401(4%, $[M-Me]^+$), 351(74), 241(100), 72(100), 56(46).

Preparation of [tris (trimethyl silyl) methyl] dichloro benzyloxy silane TsiSiCl$_2$ (OBn): A mixture of $TsiSiCl_3$ (0.36 g, 1 mmol) and 0.07M NaOBn in BnOH (30 cm^3) was refluxed for 4.5 h. NaCl formed and was separated with filtration from the organic layer and the solvent was evaporated. The residue was purified with preparative TLC (silica gel, *n*- hexane as eluant) (25%); m.p. 78°C. FT-IR (KBr, cm^{-1}): 3050, 2963, 1497, 1378, 1260, 1217, 830. FT-^{1}H NMR ($CDCl_3$): 0.30 (s, 27H, Tsi), 4.89 (s, 2H, CH_2), 7.36 (s, 5H, aryl–H). *m/z* (EI): 91(100), 78(30).

Preparation of [tris (trimethyl silyl) methyl] dichloro phenoxy silane TsiSiCl$_2$ (OPh): A mixture of PhOH (0.08 g, 0.8 mmol) and NaH (0.02 g, 0.8 mmol) in THF (40 cm^3) was stirred. $TsiSiCl_3$ (0.15 g, 0.4 mmol) in THF (10 cm^3) was added drop wise to the mixture and it was refluxed for 5.5 h. Salt and organic layer separated with filtration and solvent was evaporated. The residue was purified with preparative TLC (silica gel, *n*-hexane as eluant) (20%). m.p. 172.5°C. FT-IR (KBr, cm^{-1}): 3050, 2962, 1495, 1595, 1260, 1072, 834. FT-^{1}H NMR ($CDCl_3$): 0.4 (s, 27H, Tsi), 7.1─7.3 ppm (d, 5H, aryl─H). *m/z* (EI): 408(100%, $[M-Me]^+$), 300(6), 191(6), 72(8).

Preparation of [tris (trimethyl silyl) methyl] dichloro para amino phenoxy silane TsiSiCl$_2$ (OC$_6$H$_4$-NH$_2$-p): A mixture of *para* amino phenol (0.09 g, 0.8 mmol) and NaH (0.02 g, 0.8 mmol) in THF (40 cm^3) was stirred. $TsiSiCl_3$ (0.15 g, 0.4 mmol) in THF (10 cm^3) was added drop wise to the mixture which was refluxed for 7 h. Salt and organic layer separated by filtration and solvent was evaporated. The residue was purified with preparative TLC (silica gel, dichloromethane and petroleum ether as eluant 1:1) (18%); m.p.175°C. FT- IR (KBr, cm^{-1}): 3373, 3451, 3100, 2985, 1508, 1622, 1410, 1260, 834. FT-^{1}H NMR ($CDCl_3$): 0.39 (s, 27H, Tsi), 1.6 (broad, 2H, NH_2), 7─7.3 ppm (m, 4H, aryl─H). *m/z* (EI): 423(14%, $[M-Me]^+$), 221(56), 72(100).

Preparation of [tris (trimethyl silyl) methyl] dichloro para methoxy phenoxy silane TsiSiCl$_2$ (OC$_6$H$_4$-OMe- p): A mixture of *para* methoxy phenol (0.12 g, 1 mmol) and NaH (0.03 g, 1.2 mmol) in THF (40 cm^3) was stirred. $TsiSiCl_3$ (0.25 g, 0.6 mmol) in THF (10 cm^3) drop wise added to mixture and refluxed for 7 h. Salt and organic layer separated with filtration and solvent was evaporated. The residue was purified with preparative TLC (silica gel, dichloromethane and cyclohexane as eluant 1:1) (18%); m.p. 137°C. FT- IR (KBr, cm^{-1}): 3050, 2962, 1506, 1442, 1261, 1181, 1232, 831. FT-^{1}H NMR ($CDCl_3$): 0.4 (s, 27H, Tsi), 3.77 (s, 3H, OMe), 6.8─7.0 (d, 4H, aryl─H). *m/z* (EI): 437(54%, $[M-Me]^+$), 221(64), 91(100), 72(68).

Preparation of [tris (trimethyl silyl) methyl] dichloro para nitro phenoxy silane TsiSiCl$_2$ (OC$_6$H$_4$-NO2-p): A mixture of *para* nitro phenol (0.14 g, 1 mmol) and NaH (0.03 g, 1.2 mmol) in THF (40 cm^3) was stirred. $TsiSiCl_3$ (0.25 g, 0.6 mmol) in THF (10 cm^3) was added drop wise to the mixture and refluxed for 8─9 h. Salt and organic layer separated by filtration and solvent was evaporated. The residue was purified by preparative TLC (silica gel, dichloromethane as eluant) (16%). m.p. 116°C. FT- IR (KBr, Cm^{-1}): 3050, 2962, 2924, 1594, 1497, 1411, 1344, 1261, 1024, 899. FT-^{1}H NMR ($CDCl_3$): 0.41(s, 27H, Tsi), 7.2─8.2 ppm (d, 4H, aryl─H). *m/z* (EI): 453(100%, $[M-Me]^+$), 346(6), 222(105), 93(8), 72(26), 46(6).

Preparation of [tris (trimethyl silyl) methyl] dichloro para acetanilide phenoxy silane TsiSiCl$_2$ (OC$_6$H$_4$-NHCOCH3-p): A mixture of *para* acetanilide phenol (0.2 g, 1.3 mmol) and NaH (0.03 g, 1.2 mmol) in THF (40 cm^3) was stirred. $TsiSiCl_3$ (0.25 g, 0.6 mmol) in THF (10 cm^3) was added drop wise to the mixture and refluxed for 7 h. Salt and organic layer separated by filtration and solvent was evaporated. The residue was purified by preparative TLC (silica gel, dichloromethane as eluant) (17%); m.p. 246°C. FT- IR (KBr, cm^{-1}): 3299, 3050, 2963, 1610, 1540, 1663, 1260, 832.FT-^{1}H NMR ($CDCl_3$): 0.39 (s, 27H, Tsi), 2.1 (s, 3H, $COCH_3$), 3.4 (broad, 1H, NH), 7.0─7.3 ppm (d, 4H, aryl─H). *m/z* (EI): 464(100%, $[M-Me]^+$), 222(40), 72(60).

Preparation of [tris (trimethyl silyl) methyl] dichloro ortho methylsalicyloxy silane TsiSiCl$_2$ (OC$_6$H$_4$-COOCH3-o): A mixture of methylsalicylate (0.2 g, 1.3 mmol) and NaH (0.03 g, 1.2 mmol) in THF (40 cm^3) was stirred. $TsiSiCl_3$ (0.25 g, 0.6 mmol) in THF (10 cm^3) was added drop wise to the mixture and refluxed for 60 h. Salt and organic layer separated by filtration and solvent was evaporated. The residue was separated by preparative TLC (silica gel, dichloromethane as eluant) (18%); m.p. 78°C. FT- IR (KBr, cm^{-1}): 3050, 2961, 1738, 1490, 1602, 1447, 1261, 1082, 833. FT-^{1}H NMR ($CDCl_3$): 0.42 (s, 27H, Tsi), 3.8 (s, 3H, CH_3OCO), 7.1─7.5 (t, 4H, aryl─H). *m/z* (EI): 465(70%, $[M-Me]^+$), 345(36), 249(8), 72(80), 91(10).

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