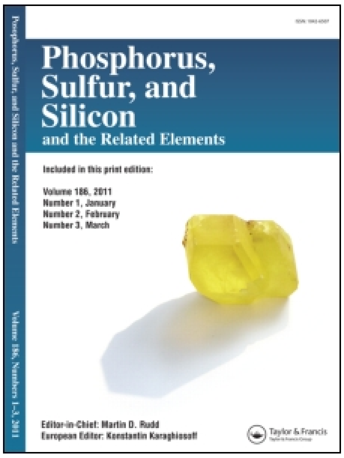

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Synthesis of Hindered Silyl Ethers via Fragmentation Reactions

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SYNTHESIS OF HINDERED SILYL ETHERS VIA FRAGMENTATION REACTIONS

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Reaction of alcoholic sodium alkoxides with $(Me_3Si)_3CSi(C_6H_4\text{-}OMe\text{-}p)MeX$ *have been performed. Main products are of the type:* $(Me_3Si)_2CHSi(An)Me(OR)$ *and* $Me_3SiCH_2Si(An)Me(OR)$*;* $An = (C_6H_4\text{-}OMe\text{-}p)$ *and OR = OEt, OPr,O iso-Pr, OBu, O iso-Bu,O iso-Amyl, OBenzyl, OAllyl, Ofurfuryl. It is suggested that the reaction proceeds through an elimination-addition mechanism.*

Keywords: Alkoxides; fragmentation; organosilicon

Because of the large bulk of the $(Me_3Si)_3C$ group (the "trisyl" group, often denoted below by Tsi), compounds of the type $(Me_3Si)_3CSiRR'X$ (e.g., X = halogen or H) undergo direct biomolecular nucleophilic displacement of X only with difficulty, and this permits observations of other reactions not normally encountered.[1–10] For example, the halides $(Me_3Si)_3CSi(C_6H_4OMe\text{-}p)MeX$ (X = F,Br,I) react with nucleophilic species such as alkoxides in alcoholic solvents to give, wholly or in part, fragmented products of the type $(Me_3Si)_2CHSi(C_6H_4OMe\text{-}p)Me(OR)$, $(Me_3Si)CH_2Si(C_6H_4OMe\text{-}p)Me(OR)$, or hydrolyzed products.[11,12]

The iodide $(Me_3Si)_3CSi(C_6H_4OMe\text{-}p)MeI$ reacts with a electrophilic reagent such as silver triflouroacetate to give a rearranged product of the type $(Me_3Si)_2C(SiMe_2I)(SiMe_2COOCF_3)$.

RESULT AND DISCUSSION

Our first observation was that all halides $TsiSi(C_6H_4OMe\text{-}p)MeX$ (X = halogen) undergo fragmentation reaction in refluxing sodium

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methoxide in methanol.[11] In this work we used 1.5–2.5 M of alkoxide solutions as reagents.

In an attempt to make TsiSi(C_6H_4OMe-*p*)MeF we prepared Si(C_6H_4OMe-*p*)MeCl_2 then reacted this with KHF_2 salt to give Si(C_6H_4OMe-*p*)MeF_2 and then this compound was treated with TsiLi to give TsiSi(C_6H_4OMe-*p*)MeF. The reduction of this compound with $LiAlH_4$ in THF did not give TsiSi(C_6H_4OMe-*p*)MeH. For this reason we prepared MeSiH(C_6H_4OMe-*p*)Cl.

Also, we prepared TsiSi(C_6H_4OMe-*p*)MeI from the reaction of TsiSi(C_6H_4OMe-*p*)MeH and ICl/CCl_4 at room temperature and TsiSi(C_6H_4OMe-*p*)MeBr from TsiSi(C_6H_4OMe-*p*)MeH with Br_2/CCl_4 at room temperature; the iodide and bromide derivatives were reacted with alkoxide solutions.

In this way, we prepared $(Me_3Si)_2$CHSi(C_6H_4OMe-*p*)Me(OR) and (Me_3Si)CH_2Si(C_6H_4OMe-*p*)Me(OR) compounds.

The mechanism of these reactions include two-steps: elimination and addition. In the first step with attack of alkoxide a silaolefin forms and in the later step solvolysis takes place. When the group of alkoxides is small the reaction of the iodide derivative is faster than the others, but when alkoxide was a large group the reaction of the fluoride derivatives was faster than the other halogens, because of the steric effect of alkoxide and the leaving group.

In this way we prepared novel organosilicon compounds. These reactions confirm the fragmentation mechanism. With increasing bulkiness of the alkoxide groups, the reaction was difficult to perform. Also, we used the new alkoxides that never were used later, and prepared fragmentation products of those alkoxides.

EXPERIMENTAL

Solvent and Reagents

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

Spectra

Melting points were taken on an electromental 9100-digital melting point apparatus. The ^{1}HNMR spectra were recorded with ^{1}HNMR Bruker FT-500 MHZ and NMR (80 MHZ). The mass spectra were run on a Shimadzu QP-100X spectrometer Finnigan, 70 ev.

TABLE I Reaction of TsiSi(C_6H_4-OMe-*p*)MeX

Substrate	Alkoxide solution	Time (h)	Product yield (%)
TsiSiAnMe F	EtONa/EtOH	7	52
TsiSiAnMe F	^{n}BuONa/^{n}BuOH	12	20
TsiSiAnMe F	^{i}AmONa/^{i}AmOH	28	22
TsiSiAnMe F	CH_2=CH—CH_2ONa/CH_2=CH—CH_2OH	8	51
TsiSiAnMe I	EtONa/EtOH	5	30
TsiSiAnMe I	^{n}BuONa/^{n}BuOH	18	10
TsiSiAnMe I	^{i}AmONa/^{i}AmOH	35	16
TsiSiAnMe I	CH_2=CH—CH_2Ona/CH_2=CH—CH_2OH	11	36
TsiSiAnMe Br	EtONa/EtOH	5	20

Preparation of TsiSi(C_6H4-OMe-*p*)MeF

(C_6H_4-OMe-*p*) $SiMeCl_2$ (0.22 g, 0.1 mmol), KHF_2 (16 g, 0.2 mmol), and *n*-heptan (150 ml) were mixed at 70–80°C for 1 h, then KF filtered and the solution cooled to form the solid, which was recrystallized to give (C_6H_4—OMe-*p*)$SiMeF_2$ (70%). (C_6H_4—OMe-*p*) $SiMeF_2$ (9.4 g, 59 mmol) was added to a solution of TsiLi (50 mmol) in THF (100 ml) and the mixture was refluxed for 3 h. The solution was treated with an aqueous solution of NH_4Cl, the organic layer was separated, dried (Na_2 SO_4), and the solvent was removed. The pure product was obtained from recrystalization in EtOH to give TsiSi(C_6H_4—OMe-*p*)MeF (70%), m.p. 109°C FT-^{1}HNMR ($CDCl_3$) 0.25(s, 27H, Tsi), 0.39(s, 3H, SiMe), 3.82(s, 3H, OMe-aryl), 6.8–7.8 ppm (m, 4H, C—H aryl), m/z (EI): 385(22%, $[M\text{-}Me]^+$), 293(18), 205(80), 201(100), 185(65). (Found: C, 53.5; H, 8.7. $C_{18}H_{37}Si_4FO$), (M_w = 400). (Calculated: C, 54; H, 9.2%).

Reaction of TsiSi(C_6H_4-OMe-*p*)MeF with NaOEt/EtOH

TsiSi (C_6H_4-OMe-*p*)MeF (0.5 g, 1.25 mmol) was refluxed in 2.5 M NaOEt/EtOH solution (30 ml) for 7 h. The solution was added to petroleum ether, the organic layer was washed several times with water, the organic layer was separated, dried (Na_2 SO_4), filtered, and the solvent evaporated and the residue was purified by TLC (silicagel, 60:40 dichloromethane: petroleum ether as eluent) to give the following products:

i) $(Me_3Si)_2$ CHSiMe(An)OEt FT-^{1}HNMR ($CDCl_3$) 0.27(s, lH, CH), −0.001(d, 18H, Me_3Si), 0.48. (s, 3H, Si—Me), 3.5(q, 2H, Si—OCH_2), 1.1(t, 3H, Si—OCH_2 CH_3), 3.82(s, 3H, OMe-aryl), 6.8–7.5 ppm (m, 4H, aryl). m/z (EI): 339(100%, $[M\text{-}Me]^+$), 309(12), 294(4), 266(4), 281(1).

(Found: C, 58; H, 9.7. $C_{17}H_{34}Si_3O_2$), ($M_w = 354$), (Calculated: C, 57.6; H, 9.6%).

ii) $Me_3SiCH_2SiMe(An)OEt$ FT-^{1}HNMR ($CDCl_3$) 0.2(s, 2H, CH_2), 0.09(s, 9H, Me_3Si), 0.4(s, 3H, Si—Me), 3.5(q, 2H, Si—OCH_2), 1.1(t, 3H, Si—OCH_2 CH_3), 3.82(s, 3H, OMe-aryl), 6.89–7.5 ppm (m, 4H aryl-H). m/z (EI): 282(6%, $[M]^+$), 267(10%, $[M\text{-}Me]^+$). (Found: C, 59.2; H, 8.9. $C_{14}H_{26}Si_2O_2$),($M_w = 282$). (Calculated: C, 59.5; H, 9.2%).

Reaction of TsiSi(C_6H_4-OMe-*p*)MeF with $NaO^nPr/^nPrOH$

A solution of TsiSi(C_6H_4-OMe-*p*)MeF (0.3 g, 0.75 mmol) in 2.5 M $NaO^nPr/^nPrOH$ (40 ml) was refluxed for 15 h, then worked up with a solution of water and petroleum ether. The organic layer was separated, washed several times with water, dried (Na_2 SO_4), filtered, and the filtrate evaporated. The resulting liquid product mixture was subjected to preparative TLC (silicagel, 50:50 dichloromethane: petroleum ether as eluent) to give $Me_3SiCH_2SiMe(An)O^nPr$.

FT-^{1}HNMR ($CDCl_3$), 0.0089(s, 9H, Me_3Si), 0.058(s, 2H, CH_2), 0.4(s, 3H, Si—Me), 0.87(t, 3H, CH_3), 1.5(m, 2H, CH_2), 3.5(t, 2H, O—CH_2), 3.82(s, 3H, OMe-aryl), 6.8–7.5 ppm (m, 4H arylC—H) m/z (EI): 296(2%, $[M]^+$), 281(8%, $[M\text{-}Me]^+$), 239(4), 209(6), 223(4), 131(100). (Found: C, 60.5; H, 9.2. $C_{15}H_{28}Si_2O_2$), ($M_w = 296$). (Calculated: C, 60.8; H, 9.4%).

Reaction of TsiSi(C_6H_4-OMe-*p*)MeF with $NaO^iPr/^iPrOH$

A solution of TsiSi(C_6H_4-OMe-*p*)MeF (0.3 g, 0.75 mmol) in 2.5 M $NaO^nPr/^nPrOH$ (50 ml) was refluxed for 15 h, then worked up with a solution of water and petroleum ether. The organic layer was separated, washed several times with water, dried (Na_2 SO_4), filtered, and the filtrate evaporated. The resulting liquid product mixture was subjected to preparative TLC (silicagel, 60:40 dichloromethane: petroleum ether as eluent) to give the following products:

i) $Me_3SiCH_2SiMe(An)O^iPr$ FT-^{1}HNMR ($CDCl_3$), −0.0029(s, 9H, Me_3Si), 0.05–0.1(s, 2H, CH_2), 0.4(s, 3H, Si—Me), 1.0–1.1(d, 6H, $CH(CH_3)_2$), 3.95(m, 1H, O—CH), 3.82(s, 3H, OMe-aryl), 6.9–7.5 ppm (m, 4H arylC—H). m/z (EI): 296(6%, $[M]^+$), 281 (10%, $[M\text{-}Me]^+$), 239(24), 223(1), 131(100). (Found: C, 61.1; H, 9.6. $C_{15}H_{28}Si_2O_2$), ($M_w = 296$). (Calculated: C, 60.8; H, 9.4%).

ii) $Me_3SiCH_2SiMe(An)OH$ FT-^{1}HNMR ($CDCl_3$), 0.034 (s, 9H, Me_3Si), 0.09–0.2(s, 2H, CH_2), 0.4(s, 3H, Si—Me), 1.6(s, 1H, OH), 3.82(s, 3H, OMe-aryl), 6.9–7.5 ppm (m, 4H aryl C—H). m/z (EI): 254(1%, $[M]^+$), 239(22%, $[M\text{-}Me]^+$), 223(2), 167(34). (Found: C, 56.4; H, 8.3. $C_{12}H_{22}Si_2O_2$), ($M_w = 254$). (Calculated: C, 56.7; H, 8.6%).

Reaction of TsiSi(C_6H_4-OMe-*p*)MeF with $NaO^nBu/^n$ BuOH

A solution of TsiSi(C_6H_4-OMe-*p*)MeF (0.3 g, 0.75 mmol) in 2.5 M $NaO^nBu/^nBuOH$ (30 ml) was refluxed for 30 h, then worked up with a solution of water and petroleum ether. The organic layer was separated, washed several times with water, dried (Na_2 SO_4), filtered, and the filtrate evaporated. The resulting liquid product mixture was subjected to preparative TLC (silicagel, 60:40 dichloromethane: petroleum ether as eluent) to give $Me_3SiCH_2SiMe(An)O^nBu$.

FT-^{1}HNMR ($CDCl_3$), 0.01(s, 9H, Me_3Si), −0.009(s, 2H, CH_2), 0.4(s, 3H, Si—Me), 0.9(t, 3H,CH_3), 1.1(m, 2H, CH_2), 1.3(m, 2H, CH_2), 3.9(t, 2H, O—CH_2), 3.82(s, 3H, OMe-aryl), 6.9–7.5 ppm (m, 4H, C—H aryl). m/z (EI): 295(6%, $[M\text{-}Me]^+$), 279(14), 278(20), 277(72), 205(48), 72(100). (Found: C, 61.5; H, 9.4. $C_{16}H_{30}Si_2O_2$), ($M_w = 310$). (Calculated: C, 61.9; H, 9.6%).

Reaction of TsiSi(C_6H_4-OMe-*p*)MeF with $NaO^iBu/^iBuOH$

TsiSi(C_6H_4-OMe-*p*)MeF (0.5 g, 1.25 mmol) was refluxed in 2.5 M $NaO^iBu/^iBuOH$ solution (30 ml) for 7 h. The solution was added to petroleum ether, the organic layer was washed several times with water, the organic layer was separated, dried (Na_2 SO_4), filtered, the solvent evaporated and the residue was purified by TLC (silicagel, 60:40 dichloromethane: petroleum ether as eluent) to give $Me_3SiCH_2SiMe(An)O^iBu$.

FT-^{1}HNMR ($CDCl_3$) −0.04(s, 9H, Me_3Si), 0.04–0.09(s, 2H, Si—CH_2), 0.39(s, 3H, Si—Me), 0.89(d, 6H,$CH(CH_3)_2$), 1.78(m, 1H, CH), 3.3(d, 2H, O—CH_2), 3.84(s, 3H, OMe-aryl), 6.9–7.5 ppm (m, 4H, C—H aryl). m/z (EI): 310(4%, $[M]^+$), 295(36%, $[M\text{-}Me]^+$), 240(24), 239(98), 131(100). (Found: C, 61; H, 9.4. $C_{16}H_{30}Si_2O_2$), ($M_w = 310$). (Calculated: C, 61.9; H, 9.6%).

Reaction of TsiSi(C_6H_4-OMe-*p*)MeF with $NaO^iAm/^iAmOH$

A solution of TsiSi(C_6H_4-OMe-*p*)MeF (0.2 g, 0.5 mmol) in 2.5 M $NaO^iAm/^iAmOH$ (30 ml) was refluxed for 48 h, then worked up with a solution of water and petroleum ether. The organic layer was separated, washed several times with water, dried (Na_2 SO_4), filtered, and the filtrate evaporated. The resulting liquid product mixture was subjected to preparative TLC (silicagel, 1:1 dichloromethane: cyclohexane as eluent) to give $Me_3SiCH_2SiMe(An)$ O^iAm.

FT-^{1}HNMR ($CDCl_3$) −0.05(s, 9H, Me_3Si), 0.09(s, 2H, Si—CH_2), 0.37(s, 3H, Si—Me), 0.85(d, 6H,$CH(CH_3)_2$), 1.4–1.5 (m, 2H, CH_2), 0.9(m, 1H, CH), 3.54(t, 2H, O—CH_2), 3.8(s, 3H, OMe-aryl), 6.8–7.4 ppm (m, 4H, C—H aryl). m/z (EI): 309(6%, $[M\text{-}Me]^+$), 239(8), 237(4), 207(4), 147(18), 131(100). (Found: C, 62.7; H, 9.6. $C_{17}H_{32}Si_2O_2$),($M_w = 324$). (Calculated: C, 62.9; H, 9.8%).

Reaction of TsiSi(C_6H_4-OMe-*p*)MeF with $CH_2CH{=}CH_2ONa/CH_2\text{-}CHCH_2OH$

TsiSi(C_6H_4-OMe-*p*)MeF (0.37 mmol) was refluxed in 2 M $CH_2CH{=}CH_2ONa/CH_2{=}CHCH_2OH$ solution (30 ml) for 8 h. The solution was added to petroleum ether, the organic layer was washed several times with water, the organic layer was separated, dried ($Na_2\ SO_4$), filtered, the solvent evaporated, and the residue was purified by TLC (silicagel, 60:40 dichloromethane: petroleum ether as eluent) to give the following products:

i) $(Me_3Si)_2CHSiMe(An)OCH_2CH{=}CH_2$ FT-^{1}HNMR ($CDCl_3$) −0.2(s, 1H, CH), −0.04–0.1 (d, 18H, Me_3Si), 0.48(s, 3H, Si—Me), 3.9(d, 2H, OCH_2), 4.9–5.2 (m, 2H, $=CH_2$), 5.8(m, 1H, =CH), 3.82(s, 3H, OMe-aryl), 6.9–7.4 ppm (m, 4H, aryl). m/z (EI): 351(12%, $[M\text{-}Me]^+$), 309(1), 236(2), 221(2), 203(100). (Found: C, 59.3; H, 9.2. $C_{18}H_{34}O_2$), ($M_w = 366$). (Calculated: C, 59; H, 9.3%)

ii) $Me_3SiCH_2SiMe(An)OCH_2CH{=}CH_2$ FT-^{1}HNMR ($CDCl_3$) 0.095(s, 2H, CH_2), −0.04(s, 9H, Me_3Si), 0.39(s, 3H, Si—Me), 4.1(d, 2H, OCH_2), 5.1–5.3 (m, 2H, $=CH_2$), 5.9(m, 1H, =CH), 3.82(s, 3H, OMe-aryl), 6.9–7.4 ppm (m, 4H, aryl). m/z (EI): 294(4%,$[M]^+$), 279(8%,$[M\text{-}Me]^+$), 239(24), 207(10), 131(100). (Found: C, 61.6; H,8.6. $C_{15}H_{26}Si_2O_2$), ($M_w = 294$). (Calculated: C, 61.2; H, 8.8%).

Reaction of TsiSi(C_6H_4-OMe-*p*)MeF with $NaOCH_2Ph/PhCH_2OH$

A solution of TsiSi(C_6H_4-OMe-*p*)MeF (0.5 g, 1.25 mmol) in 2.5 M $NaOCH_2Ph/PhCH_2OH$ (30 ml) was refluxed for 75 h, then worked up with a solution of water and petroleum ether. The organic layer was separated, washed several times with water, dried ($Na_2\ SO_4$), filtered, and the filtrate evaporated. The resulting liquid product mixture was subjected to preparative TLC (silicagel, 1:1 dichloromethane: cyclohexane as eluent) to give $Me_3Si\ CH_2SiMe(An)OCH_2Ph$.

FT-^{1}HNMR ($CDCl_3$), −0.01(s, 9H, Me_3Si), 0.01–0.2 (s, 2H, Si—CH_2), 0.4(s, 3H, Si—Me), 3.85(s, 3H, OMe-aryl), 4.6(s, 2H, OCH_2), 6.9–7.5 ppm (m, 9H, C—H aryl). m/z (EI): 344(1%, $[M]^+$), 329(0.5%, $[M\text{-}Me]^+$), 336(6), 257(0.5), 131(68), 91(100). (Found: C, 66.3;H, 8.1.$C_{19}H_{28}Si_2O_2$), ($M_w = 344$). (Calculated: C, 66.2; H, 8.1%).

Reaction of TsiSi(C_6H_4-OMe-*p*)MeF with Furfuryloxy Sodium, Furfuryalcohol

TsiSi(C_6H_4-OMe-*p*)MeF (0.25 mmol) was refluxed in 1.5 M furfuryloxy sodium, furfurylalcohol solution (25 ml) for 7 h. The solution was added to petroleum ether, the organic layer was washed several times with water, the organic layer was separated, dried (Na_2 SO_4), filtered, the solvent evaporated, and the residue was purified by TLC (silicagel, 60:40 dichloromethane: petroleum ether as eluent) to give Anisolemethylfurfuryloxymethyltrimethylsilylsilane.

FT-^{1}HNMR ($CDCl_3$) −0.03(s, 9H, Me_3Si), 0.04–0.2 (s, 2H, CH_2), 0.42(s, 3H, Si—Me), 3.85(s, 3H, OMe-aryl), 4.6 ppm (s, 2H, OCH_2), 6.3(m, 1-αH, Furfuryl alcohol), 6.9–7.5 (m, 4H, aryl), 7.4(m, $2-\beta$H, Furfuryl alcohol). m/z (EI): 332(4%, $[M\text{-}2H]^+$), 261(4), 247(1), 237(12), 222(6), 165(100). (Found: C, 60.8; H, 7.5. $C_{17}H_{26}Si_2O_3$), ($M_w = 334$). (Calculated: C, 61.1; H, 7.7%).

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