SHORT PAPER

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Reactions of the highly sterically hindered silanols (Me$_3$Si)$_3$CSiMe(C$_6$H$_4$R-*p*)OH with acid chlorides[†]

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The silanol TsiSiMe(C$_6$H$_4$Me-*p*)OH (Tsi = (Me$_3$Si)$_3$C) has been shown to react with some acid chlorides RCOCl (R = Me , Et , ClCH$_2$) and acetic acid anhydride (MeCO)$_2$O to give the related carboxylates TsiSiMe(C$_6$H$_4$Me-*p*)OCOR. It also reacts with 4-O$_2$NC$_6$H$_4$COCl and a mixture of Cl$_2$CHCOCl and AlCl$_3$ to give TsiSiMe[C$_6$H$_3$-3-(CO-C$_6$H$_4$NO$_2$-p)-4-Me]OCOC$_6$H$_4$NO$_2$-p and TsiSiMe[C$_6$H$_3$-3-(COCHCl$_2$- 4-Me)]OCOCHCl$_2$ respectively. The reaction of the silanol TsiSiMe(C$_6$H$_4$OMe-p)OH with acid chloride RCOCl (R = Me or Et) gives TsiSiMeClOCOR and TsiSiMe(RCO)OCOR, while in the presence of pyridine gives the normal carboxylate TsiSiMe(C$_6$H$_4$OMe-p)OCOR.

Keywords: silicon, trisyl, silanol, carboxylate

Some reactions of the silanol TsiSiRR′OH (*e.g.* R= R′= Me, Et or Ph ; R=Me , R′=Ph) where Tsi denotes the bulky ligand (Me$_3$Si)$_3$C have been described previously.(1-4) We have now extended this reaction to TsiSiRR′OH (R=C$_6$H$_4$Me-p, R′=Me; R=C$_6$H$_4$OMe-p, R′=Me) with acid chlorides RCOCl (R=Me, Et, ClCH$_2$, 4-O$_2$NC$_6$H$_4$) which involve breaking of the O–H bond (breaking of the Si–O bond is inhibited by severe steric hindrance to nucleophilic attack at silicon).

Results and discussion

The reaction of TsiSiMe(C$_6$H$_4$Me-p)OH with an excess of neat MeCOCl was found to be complete within 11h at reflux temperature and gave the expected acetate.

$$\mathrm{TsiSiMe(C_6H_4Me\text{-}p)OH + MeCOCl} \longrightarrow \mathrm{TsiSiMe(C_6H_4Me\text{-}p)OCOMe}$$

The silanol was also converted into the acetate TsiSiMe(C$_6$H$_4$Me-p)OCOMe by reaction with acetic acid anhydride (MeCO)$_2$O. The reaction was slower than that with acetyl chloride and the reaction was not even completed when the silanol and an excess of neat (MeCO)$_2$O was kept at 100 °C for 6 days. The hydroxide TsiSiMe(C$_6$H$_4$Me-p)OH was satisfactorily converted into the acetate TsiSiMe(C$_6$H$_4$Me-p)OCOCHCl$_2$ by reaction with neat H$_2$CClCOCl at 75°C for 21h and for EtCOCl the reaction was carried out under reflux for 24h (though they may in some cases have been completed in shorter times).

When the mixture of the silanol TsiSiMe(C$_6$H$_4$Me-p)OH with excess of neat 4-O$_2$NC$_6$H$_4$COCl was kept at 200 °C (above the melting point of the chloride) for 24h, the product was found to be TsiSiMe[C$_6$H$_3$-3-(CO-C$_6$H$_4$NO$_2$-p)-4-Me]OCOC$_6$H$_4$NO$_2$-p. Evidently the initially-formed normal carboxylate TsiSiMe(C$_6$H$_4$Me-p)OCO(C$_6$H$_4$NO$_2$-p) reacts further with 4-O$_2$NC$_6$H$_4$COCl to give the above-mentioned product. The reaction of Cl$_2$CHCOCl was carried out in the presence of AlCl$_3$ at 90 °C for 5h to give TsiSiMe[(C$_6$H$_3$-3-COCHCl$_2$)-4-Me]OCOCHCl$_2$. It seems possible that the silanol reacts with one molar proportion of Cl$_2$CHCOCl to give the corresponding acetate TsiSiMe(C$_6$H$_4$Me-p)OCOCHCl$_2$. The acetate in turn reacts with a further molar proportion of Cl$_2$CHCOCl to give the product.

However, when the silanol TsiSiMe(C$_6$H$_4$OMe-p)OH itself is treated with an excess of neat MeCOCl or EtCOCl the products are a mixture of TsiSi(RCO)MeOCOR and TsiSiClMeOCOR. The different outcome of the reactions of TsiSiMe(C$_6$H$_4$OMe-p)OH may possibly associated with the fact that there is one molar proportion of HCl present that cleaves the C$_6$H$_4$OMe group on Si very rapidly, then the products would be TsiSi (RCO)MeOCOR and TsiSiClMeOCOR. In the light of this observation the reaction of TsiSiMe(C$_6$H$_4$OMe-p)OH with RCOCl (R=Me or Et) and small portion of pyridine (to neutralise the HCl generated in the course of the reaction) was carried out. The products were the normal expected carboxylate TsiSiMe(C$_6$H$_4$OMe-p) OCOR (R=Me or Et).

Experimental

General: The HNMR spectra were recorded on Perkin Elmer at 80 MHz with CDCl$_3$ as a solvent and CHCl$_3$ as internal standard. The FT-IR spectra were recorded with KBr disk on a Shimadzu-DR-408 instrument. Melting points are uncorrected and were determined with a 9100 Electrothermal apparatus and mass spectra were recorded on a Shimadzu QP-100x spectrometer. Acetyl chloride, monochloroacetyl chloride and propionyl chloride were distilled immediately before use.

Preparation of TsiSi(C$_6$H$_4$R-p)MeOH (R=Me, OMe): A mixture of 0.5 g (1.3 mmol) of TsiSi(C$_6$H$_4$R-p)MeI, H$_2$O(4ml), DMSO (25ml) and CH$_3$CN(12ml) was refluxed for 24h. The solution was then cooled to room temperature and the produced iodine was neutralised with a 5% solution of Na$_2$S$_2$O$_3$. Then extraction with ether, followed by separation, washing, drying and evaporation of the extract left a solid which was recrystallized from ethanol.[16]

Preparation of TsiSi(C$_6$H$_4$Me-p)MeOCOMe: A mixture of TsiSi(C$_6$H$_4$Me-p)MeOH (0.14g 0.36 mmol) and pure acetyl chloride (10ml) was refluxed for 11h. The progress of the reaction was monitored by TLC. When the silanol had disappeared, the reaction was stopped and the resulting mixture stirred with an excess of aqueous NaHCO$_3$. Extraction with ether, followed by drying (MgSO$_4$) and evaporation of the extract left a solid, which was sublimed (70 °C/2mmHg) to give TsiSi(C$_6$H$_4$Me-p)MeOCOMe (90%), m.p. = 78 °C; υ(C=O)1742.2 cm^{-1}; δ(H) 0.1ppm(s,27H, SiMe$_3$), 0.7(s,3H,SiMe), 2.15(s,3H,C$_6$H$_4$-Me-p), 0.2(s,3H,COMe), 7–8 (m,4H,C$_6$H$_4$); *m/z* 409.2 [M-Me]$^+$,43[COMe]$^+$, 73 [SiMe$_3$]$^+$, 367.2, 333.1, 275, 263, 193, 186, 148.9, 91.

Reaction of TsiSiMe(C$_6$H$_4$Me-p)OH with (MeCO)$_2$O: A mixture of TsiSiMe(C$_6$H$_4$Me-p)OH (0.1g, 0.26 mmol) and freshly distilled (MeCO)$_2$O (10ml) was kept at 100 °C for 6 days. The progress of the reaction was monitored by TLC. When the reaction was completed, volatile material was removed under reduced pressure and the residue was sublimed (70 °C/2 mmHg) to give TsiSiMe(C$_6$H$_4$Me-p)OCOMe (45%) with properties identical to those listed above.

Preparation of TsiSi(C$_6$H$_4$Me-p)MeOCOCH$_2$Cl: A mixture of TsiSi(C$_6$H$_4$Me-p)MeOH (0.1g, 0.26 mmol) and pure monochloroacetyl chloride (10ml) was stirred at 75 °C for 21h. The

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

progress of the reaction was monitored by TLC. When the silanol had disappeared, the reaction was stopped and the product stirred with an excess of aqueous $NaHCO_3$. Extraction with ether, followed by drying ($MgSO_4$) and evaporation of the extract left a solid that separated with preparative TLC (silicagel, cyclohexane-dichloromethane in 3:1 ratio as eluant) (80%), m.p. = 95 °C; υ(C=O)1757.5 cm^{-1}; δ(H) 0.3ppm (s,27H, $SiMe_3$), 0.7(s,3H,SiMe), 2.15(s,3H,C_6H_4-Me-p), 3.9(s,2H,$COCH_2Cl$), 7–8(m,4H,C_6H_4); *m/z* 443 [M-Me]$^+$, 73 [$SiMe_3$]$^+$, 275, 187, 149, 105, 73.

Preparation of TsiSi(C_6H_4Me-p)MeOCOEt: A mixture of TsiSi(C_6H_4Me-p)MeOH (0.1g, 0.26 mmol) and pure EtCOCl (10ml) was refluxed for 24h. The progress of the reaction was monitored by TLC. When the silanol had disappeared at TLC the reaction was stopped and the product stirred with an excess of aqueous $NaHCO_3$. Extraction with ether, followed by drying ($MgSO_4$) and evaporation of the extract left a solid that separated with preparative TLC (silicagel, cyclohexane-dichloromethane in 3:1 ratio as eluant) (90%), m.p. = 104 °C; υ(C=O)1734 cm^{-1}; δ(H) 0.1ppm(s,27H, $SiMe_3$), 0.7(s,3H,SiMe), 2.15(s,3H,C_6H_4-Me-p), 0.95(t,3H, CH_2CH_3), 2.25(q,2H,CH_2), 7-8(m,4H,C_6H_4); *m/z* 438.9 [M]$^+$, 423.4 [M-Me]$^+$, 57 [COEt]$^+$, 73 [$SiMe_3$]$^+$, 367, 350, 334.9,278.1, 275.7, 263, 186.8, 148.9, 132.8.

Preparation of TsiSi[(C_6H_3-3-$COCHCl_2$)-4-Me]$MeOCOCHCl_2$: A mixture of $AlCl_3$ (0.2g) and of pure $CHCl_2COCl$ (10 ml) was stirred at room temperature for 1h then TsiSi(C_6H_4Me-p)MeOH (0.1g, 0.26mmol) was added and the mixture kept at room temperature for 5h. It was then filtered and the excess of $Cl_2CHCOCl$ was evaporated under vacuum, and the residue was purified and separated with preparative TLC silicagel, cyclohexane-dichloromethane in 3:1 ratio as eluant) (80%), m.p. = 127 °C; υ(C=O)1711.35 cm^{-1}; δ(H) 0.1ppm(s,27H, $SiMe_3$), 0.35(s,3H,SiMe), 2.15(s,3H,C_6H_4-Me-p), 4.2(s,1H, $COCHCl_2$), 7-8(m,4H,C_6H_4); *m/z* 604 [M]$^+$, 589 [M-Me]$^+$, 112 [Cl_2CHCO]$^+$, 73 [$SiMe_3$]$^+$, 552, 538, 395, 97, 57.

Preparation of TsiSi[C_6H_3-3-(CO-C_6H_4-NO_2-p)-4-Me] $MeOCOC_6H_4$-NO_2-p: A mixture of TsiSi(C_6H_4Me-p)MeOH (0.2g, 0.52mmol) and 4-$O_2NC_6H_4COCl$ (1g, 5.39mmol) was kept at 150 °C (above the melting point of the chloride) for 24h (though this reaction may have been completed in shorter time), then cooled and stirred with an excess of aqueous $NaHCO_{3.}$ Extraction with ether, followed by drying ($MgSO_4$) and evaporation of the extract left a solid, which was separated with preparative TLC (silicagel, cyclohexane-dichloromethane in 3:1 ratio as eluant) (75%), m.p. = 165 °C; υ(C=O)1742.22 cm^{-1}; δ(H) 0.4ppm(s,27H, $SiMe_3$), 1(s,3H,SiMe), 1.4(s,3H,C_6H_4-Me-p), 9.1(m,11H,C_6H_3, 2C_6H_4-NO_2-p); *m/z* 681 [M]$^+$, 666 [M-Me]$^+$, 149 [C_6H_4-NO_2-p]$^+$, 73 [$SiMe_3$]$^+$, 564, 437, 275, 195.

Reaction of TsiSi(C_6H_4OMe-p)MeOH with EtCOCl: A mixture of TsiSi(C_6H_4OMe-p)MeOH (0.2g, 0.5mmol) and EtCOCl (15ml) was refluxed for 16h. Excess of propionyl chloride was removed under reduced pressure and the residue was purified and separated with preparative TLC (silicagel, cyclohexane-dichloromethane in 3:1 ratio as eluant) to give two sticky products as follows

(a) TsiSiMeCl(OCOEt): FT-IR (KBr, cm^{-1}) υ(C=O)1749, ^{1}H NMR ($CDCl_3$) 0.2(s, 27H, Tsi), 0.87(s, 3H, Si–Me), 0.95(t, 3H, Me) and 2.25ppm(q, 2H, CH_2). *m/z*(EI) 367(41.9%, [M–Me]$^+$), 311(16.7), 275(77.0), 187(18.6), 73(54.0), 57(100.0).

(b) TsiSi(EtCO)Me(OCOEt): FT-IR (KBr, cm^{-1}) υ(C=O)1749, ^{1}H NMR ($CDCl_3$) 0.23(s, 27H, Tsi), 0.8 (s, 3H, Si–Me), 1.1(t, 6H, 2Me) and 2.3ppm(q, 4H, $2CH_2$). *m/z*(EI) 405(5.2%, [M]$^+$), 348(1.4), 275(4.7), 73(55.2), 57(100.0).

Preparation of TsiSi(C_6H_4OMe-p)Me(OCOEt): A mixture of TsiSi(C_6H_4OMe-p)MeOH (0.1g, 0.25mmol), EtCOCl (10ml) and pyridine (0.1ml) was refluxed for 15h. The mixture then was filtered, the excess of EtCOCl was evaporated under reduced pressure and the residue was purified with preparative TLC (silicagel, cyclohexane-dichloromethane in 1:2 ratio as eluant) (90%). FT-IR (KBr, cm^{-1}) υ(C=O)1742. ^{1}H NMR ($CDCl_3$) 0.1(s, 27H, Tsi), 0.7(s, 3H, Si–Me), 1.0(t, 3H, CH_3), 2.1(q, 2H, CH_2), 3.7(s, 3H, Aryl-OMe) and 6.6–7.6ppm(m, 4H, Aryl-H). *m/z*(EI) 439(14.9%, [M-Me]$^+$), 366(6.7), 347(5.7), 275(47.7), 187(14.0), 73(100.0), 57(67.9).

Reaction of TsiSi(C_6H_4OMe-p)MeOH with CH_3COCl: A mixture of TsiSi(C_6H_4OMe-p)MeOH (0.2g, 0.5mmol) and MeCOCl(12 ml) was refluxed for 14h. Excess of the acetyl chloride was evaporated under reduced pressure and the residue was purified and separated with preparative TLC (silicagel, cyclohexane-dichloromethane in 3:1 ratio as eluant) to give two sticky products as follows

(a) TsiSiMeCl(OCOMe): FT-IR (KBr, cm^{-1}) υ(C=O)1749. ^{1}H NMR ($CDCl_3$) 0.2(s, 27H, Tsi), 0.7(s, 3H, Si–Me) and 1.9ppm(s, 3H, CO–Me). *m/z*(EI) 368(1.3%, [M]$^+$), 353(37.3%, [M–Me]$^+$), 275(99.4), 245(10.5), 187(24.4), 73(63.0), 43(100.0).

(b) TsiSi(MeCO)Me(OCOMe): FT-IR (KBr, cm^{-1}) υ(C=O)1742. ^{1}H NMR ($CDCl_3$) 0.2(s, 27H, Tsi), 0.6(s, 3H, Si-Me) and 1.8ppm(s, 6H, CO-Me). Unfortunately, the mass spectrum was not recorded but by comparison of this reaction with that of EtCOCl reaction products mentioned above, it was tentativily attibuted to Tsi(MeCO)SiMe(OCOMe).

Preparation of TsiSi(C_6H_4OMe-p)Me(OCOMe): A mixture of TsiSi(C_6H_4OMe-p)MeOH (0.1g, 0.25mmol), MeCOCl (10ml) and pyridine(0.1ml) was refluxed for 12h. The mixture was then filtered, the excess of MeCOCl was evaporated under reduced pressure and the residue was purified with preparative TLC (silicagel, cyclohexane-dichloromethane in 1:2 ratio as eluant) to give TsiSi(C_6H_4OMe-p)MeOCOMe (85%). FT-IR (KBr, cm^{-1}) υ(C=O)1742. ^{1}H NMR ($CDCl_3$) 0.3 (s, 27H, Tsi), 0.87 (s, 3H, Si–Me), 2.2 (s, 3H, CO–Me), 3.8 (s, 3H, Aryl-OMe) and 6.8–7.7 ppm (m, 4H, Aryl-H). *m/z*(EI) 440 (2.4%, [M]$^+$), 425 (67.4%, [M-Me]$^+$), 381(17.8), 275(100.0), 187(17.2), 73(63.9), 43(95.5).

Preparation of TsiSi(C_6H_4OMe-p)MeNCO: TsiSi(C_6H_4OMe-p)MeI (0.15g, 0.3mmol) and AgOCN (0.18g, 1.2mmol) in dichloromethane (30ml) was stirred for 50h at room temperature. The mixture was filtered, the solvent was removed under reduced pressure and the residue was purified with preparative TLC (silicagel, cyclohexane-dichloromethane in 1:1 ratio as eluant) (80%).m.p. 90–93°C. FT-IR (KBr, cm^{-1}) υ(Si-NCO)2289. ^{1}H NMR ($CDCl_3$) 0.1(s, 27H, Tsi), 0.35(s, 3H, Si–Me), 3.6(s, 3H, Aryl-OMe) and 6.6-7.6ppm(m, 4H, Aryl-H). *m/z*(EI) 423(8.0%, [M]$^+$), 408(48.5%, [M-Me]$^+$), 365(31.7), 243(21.6), 73(100.0).

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