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1,3-Migration of triorganosilyl groups from carbon to oxygen in highly crowded organosilanols

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Abstract

The silanol $(Me_3Si)CSiMe_2OH$ has been shown to isomerize to $(Me_3Si)_2CH(SiMe_2OSiMe_3)$ (which reacts further to give $(Me_3Si)_2CH(SiMe_2OMe)$) in 0.5 *M* NaOMe/MeOH, the isomerization being ca. 90% complete after 6 h under reflux. Corresponding isomerizations of $(PhMe_2Si)_3CSiMe_2OH$ (to give $(PhMe_2Si)_2CH(SiMe_2OSiMe_2Ph)$), $(Me_3Si)_2C(SiMePh_2)SiMe_2OH$ (to give $(Me_3Si)_2CH(SiMe_2OSiMePh_2)$), and $(Me_3Si)_3CSiPh_2OH$ (to give $(Me_3Si)_2CH(SiPh_2OSiMe_3)$) take place much more readily, and are complete within ca. 2 min at room temperature in 0.10 *M* NaOMe/MeOH. The reactions involve 1,3-migration from carbon to oxygen within a silanolate ion to give a carbanion, which rapidly acquires a proton from the solvent. The migration is facilitated by relief of steric strain and stabilization of the forming carbanionic centre by the three attached silyl groups. The relative reactivities of the various silanols may be determined by the magnitude of the release of steric strain, by the inherent ease of nucleophilic attack at the relevant silicon centre, and, at least at low base concentrations, by the acidity of the silanol.

Treatment of $(Me_3Si)_3CSiPh_2OH$ with MeLi in Et_2O/THF gives, by the same rearrangement, the organolithium reagent $(Me_3Si)_2CLi(SiPh_2OSiMe_3)$, which on treatment with Me_2SiHCl gives $(Me_3Si)_2C(SiMe_2H)(SiPh_2OSiMe_3)$.

Introduction

A preliminary report appeared some seven years ago on the base-catalysed 1,3-migration of organosilyl groups from carbon to oxygen in the silanol $(Me_3Si)_3CSiMe_2OH$ and related species [1]. We present below details of the observations and the results of some related experiments.

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Results and discussion

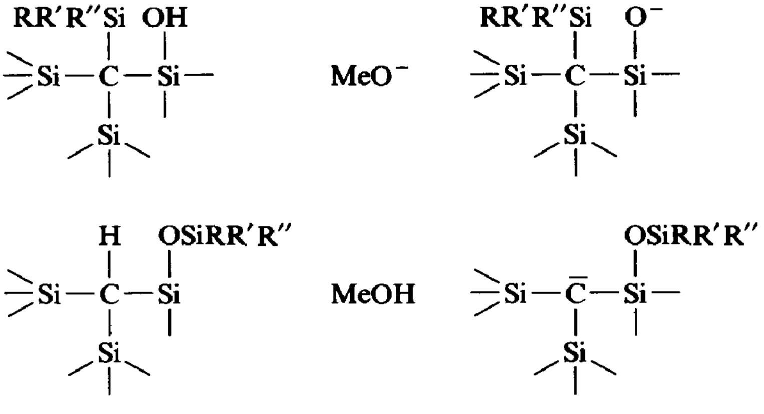
The first observation of the type of rearrangement under consideration involved the formation of the siloxane $(Me_3Si)_2CHSiMe_2OSiMe_3$ when $(Me_3Si)_3CSiMe_2OH$ was treated with potassium metal in boiling benzene [2]. That observation was somewhat complicated by the fact that after the dissolution of the potassium Me_3SiCl was added (in the expectation of trapping the generated anion), but we have confirmed that the same product is obtained when a similar procedure is carried out without addition of Me_3SiCl. The reaction involves the initial formation of the silanolate $(Me_3Si)_3CSiMe_2OK$, which rearranges to the organopotassium compound $(Me_3Si)_2C(K)SiMe_2OSiMe_3$, and this on work-up gives $(Me_3Si)_2CH$-$SiMe_2OSiMe_3$. It might seem surprising that in the experiment involving addition of Me_3SiCl the product was not $(Me_3Si)_3CSiMe_2OSiMe_3$, but the organolithium reagent $(Me_2PhSi)_3CLi$ is known not to react with Me_3SiCl [3], and we shall see below that $(Me_3Si)_2C(Li)SiPh_2OSiMe_3$ also fails to react with this chloride.

Rearrangement of $(Me_3Si)_3CSiMe_2OH$ was later found to take place in MeOH containing 0.50 *M* NaOMe. After a solution of the silanol in this medium had been boiled under reflux for 2 h, work-up showed that the unchanged silanol, the isomeric species $(Me_3Si)_2CHSiMe_2OSiMe_3$, and the methoxide $(Me_3Si)_2CHSi$-Me_2OMe were present in ca. 48/38/14 ratio, and after 6 h the same compounds were present in ca. 10/25/65 ratio. A separate experiment confirmed that the disiloxane $(Me_3Si)_2CHSiMe_2OSiMe_3$ was converted into the methoxide $(Me_3Si)_2CH$-$SiMe_2OMe$ under the conditions used.

The related silanol $(Me_3Si)_2C(SiMePh_2)(SiMe_2OH)$ (obtained by treatment of $(Me_3Si)_3CSiPh_2I$ with $AgClO_4$ in wet acetonitrile [4]) was found to undergo the same type of rearrangement much more readily. Thus rearrangement was found to be complete within 0.5 h in 0.20 *M* NaOMe/MeOH and to have given virtually exclusively $(Me_3Si)_2CHSiMe_2OSiMePh_2$, migration of the $SiMePh_2$ group being greatly favoured over that of an $SiMe_3$ group. Subsequently a reaction carried out in an NMR tube revealed that the rearrangement was complete within ca. 2 min at room temperature in 0.10 *M* NaOMe/MeOH.

The silanol $(PhMe_2Si)_3CSiMe_2OH$ (made by treatment of the iodide $(PhMe_2Si)_3CSiMe_2I$ with $AgOSO_2CF_3$ in moist ether [3]) was also found to have reacted completely within 0.5 h at room temperature in 0.20 *M* NaOMe/MeOH to give the expected disiloxane $(PhMe_2Si)_2CHSiMe_2OSiMe_2Ph$. Again reaction in an NMR tube indicated that rearrangement was complete within ca. 2 min in 0.10 *M* NaOMe/MeOH at room temperature.

The silanol $(Me_3Si)_3CSiPh_2OH$ reacted completely within 15 min in 0.20 *M* NaOMe/MeOH to give very predominantly the expected disiloxane $(Me_3Si)_2CHSi$-Ph_2OSiMe_3. Again reaction in an NMR tube showed that the rearrangement was actually complete within 2 min at room temperature in 0.1 *M* NaOMe/MeOH. (This rearrangement, under different conditions, had been observed previously by Damrauer and his colleagues [5].) It at one time appeared that this rearrangement took place in the absence of base during 3 h refluxing in MeOH that had been dried and distilled over $Mg(OMe)_2$ [6] (and this was mentioned in a publication dealing with the same type of rearrangement in a more complex system [7]). Reaction under these conditions was observed again during more recent work, but when Aldrich Anhydrous Gold Label MeOH was used no reaction was detected during 10 days



Scheme 1

under reflux. Furthermore, reaction in the home-dried MeOH, which presumably contained a trace of base, was completely inhibited by the presence of 0.10 *M* CF_3CO_2H. It is evident that base is needed to provide a sufficiently high concentration of the anion $(Me_3Si)_3CSiPh_2O^-$ for reaction to proceed at a detectable rate.

Corresponding rearrangements, followed by further reactions, have been reported for $(Me_3Si)_2C(SiMe_2OH)_2$ [8] and $C(SiMe_2OH)_4$ [7].

The course of the rearrangement can be represented as in Scheme 1.

The formation of an Si–O in place of an Si–C bond is energetically very favourable, but this is offset by going from a negative oxygen centre to a negative carbon centre, and an important feature is the stabilization of the carbanion by the three attached organosilyl groups. (The kinetic acidity of $(Me_3Si)_3CH$ is higher that that of Ph_3CH [9]). A factor of major importance is the relief of strain accompanying the migration in these highly crowded systems, and the differences in the ease of rearrangement of the various silanols studied probably arise mainly from this effect. This effect could account for the exclusive migration of the $SiMePh_2$ group in the isomerization of $(Me_3Si)_2C(SiMePh_2)(SiMe_2OH)$, but the inherent ease of nucleophilic attack at the relevant silicon centre must play some part, and we note that base-catalysed hydrolysis of Ph_3SiH is much faster than that of trialkylsilanes. At least at low base concentrations, the acidity of the silanol, which determines the concentration of the silanolate ion, must also be relevant, and the much greater ease of rearrangement of $(Me_3Si)_3CSiPh_2OH$ than of $(Me_3Si)_3CSiMeOH$ is probably partly attributable to higher acidity of the former.

In cases in which the rearranged disiloxanes are obtained fairly free from other products, the possibility of metallating the acidic CH centre gives them potential for further syntheses. The organolithium reagent $(Me_3Si)_2C(Li)(SiPh_2OSiMe_3)$ formed by treatment of $(Me_3Si)_3CSiPh_2OH$ with MeLi in Et_2O/THF was found (like $(PhMe_2Si)_3CLi$ [3]) not to react with Me_3SiCl, but it did react with the less hindered Me_2SiHCl to give the expected $(Me_3Si)_2C(SiMe_2H)(SiPh_2OSiMe_3)$.

Experimental

The silanols $(Me_3Si)_3CSiMe_2OH$ [10], $(PhMe_2Si)_3CSiMe_2OH$ [3], $(Me_3Si)_2C(SiMePh_2)(SiMe_2OH)$ [4], and $(Me_3Si)_3CSiPh_2OH$ [11] were made as previously described.

Methanol was dried over and distilled from $Mg(OMe)_2$. The solutions of NaOMe were made by dissolving Na in the MeOH and diluting to the required concentration.

Mass spectra (electron impact) were recorded at 70 eV. For analytical GLC a column of 5% OV101 on Chromasorb G was used in conjunction with a flame-ionization detector. The same packing was used in the linked GLC-mass spectrometry analyses.

The ^1H NMR spectra were recorded at 90 MHz with solutions in CCl_4 containing CH_2Cl_2 as lock and reference,

Reaction of $(Me_3Si)_3CSiMe_2OH$ with K in benzene

A stirred mixture of $(Me_3Si)_3CSiMe_2OH$ (1.0 g, 3.3 mmol) and K (0.30 g, 7.6 mmol) in anhydrous benzene (20 cm^3) was refluxed under nitrogen for 5 h, during which some of the metal disappeared. The mixture was cooled to room temperature and centrifuged, and the solution was decanted from the residue and treated very cautiously under nitrogen with wet benzene and then with water. The benzene layer was washed several times with water, dried ($MgSO_4$), filtered, and evaporated under vacuum. The residue was found by GLC to contain over 90% of a major product along with some minor impurities, and the ^1H NMR spectrum (δ −0.60 (s, 1H, CH), 0.06 (s, 9H, $OSiMe_3$), 0.08 (s, 18H, $SiMe_3$), and 0.16 (s, 6H, $SiMe_2$)) was identical with that of an authentic sample [2].

Reaction of $(Me_3Si)_3CSiMe_2OH$ with NaOMe/MeOH

A solution of the silanol (1.0 g) in 0.50 *M* NaOMe/MeOH (50 cm^3) was refluxed for 2 h under nitrogen then cooled to room temperature. Hexane was added, followed by a large excess of water. The organic layer was separated, washed several times with water, dried ($MgSO_4$), and evaporated under reduced pressure at room temperature to leave an oil, which was shown by GLC analysis to consist of the original silanol, the siloxane $(Me_3Si)_2CH(SiMe_2OSiMe_3)$, and the methoxide $(Me_3Si)_2CH(SiMe_2OMe)$ in ca. 48/38/14 ratio. (Authentic samples of these products were available.) The ^1H NMR spectrum was consistent with this composition.

When the experiment was repeated but with 6 h refluxing, the product contained the same components in ca. 10/25/65 ratio.

Reaction of $(Me_3Si)CH(SiMe_2OSiMe_3)$ with NaOMe/MeOH

A solution of the disiloxane (0.25 g) in 0.50 *M* NaOMe/MeOH (20 cm^3) was refluxed for 8 h then cooled to room temperature. Work-up as in the preceding experiment gave an oil, which from its retention time and ^1H NMR spectrum was identified as $(Me_3Si)_2CH(SiMe_2OMe)$.

Reaction of $(Me_3Si)_2C(SiMePh_2)(SiMe_2OH)$ with NaOMe/MeOH

(a) A solution of the silanol (1.0 g) in 0.20 *M* NaOMe/MeOH (50 cm^3) was stirred under nitrogen at room temperature (ca. 22 °C) for 0.5h. Work-up as in the preceding experiments gave an oil, which from GLC analysis appeared to consist of one major product with $< 5\%$ of impurities. Analysis by linked GLC-mass spectrometry showed the product to be isomeric with the original silanol (m/z 415 ($[M-Me]^+$)), and from its ^1H NMR spectrum (δ −0.60 (s, H, CH), 0.08 (s, 18H, $SiMe_3$), 0.10 (s, 6H, $SiMe_2$), 0.62 (s, 3H, SiMe), and 7.0–8.0 (m, 10H, SiPh)) it was judged to be $(Me_3Si)_2CH(SiMe_2OSiMePh_2)$.

(b) To $(Me_3Si)_2C(SiMePh_2)(SiMe_2OH)$ (0.03 g) in an NMR tube was added 0.10 *M* NaOMe/MeOH (0.5 cm^3). The solution was shaken for 1 min then placed in the probe of the NMR spectrometer. The spectrum showed that only $(Me_3Si)_2CH(SiMe_2OSiMePh_2)$ was present.

Reaction of $(PhMe_2Si)_3CSiMe_2OH$ with NaOMe/MeOH

A solution of the silanol (0.5 g) in 0.20 *M* NaOMe/MeOH (20 cm^3) was kept at room temperature for 0.5 h. Work-up as above gave an oil, which seemed from GLC to contain one very dominant product along with < 10% of impurities. The main product was isolated as a low-melting solid by preparative GLC (20% OV101 on Chromasorb P at 100–300°C). Its mass spectrum (m/z 477 ($[M-Me]^+$), 415 ($[M-Ph]^+$)) showed it to be an isomer of the original silanol. It was judged to be the expected $(PhMe_2Si)_2CH(SiMe_2OSiMe_2Ph)$ from its ^1H NMR spectrum: δ −0.03 (s, 6H, $SiMe_2O$), 0.19 (S, 1H, CH), 0.21 (s, 6H, $Si\mathit{Me}_2Ph$), 0.34 (s, 12H, $Si\mathit{Me}_2Ph$), and 6.8–7.2 (m, 15H, SiPh). (The appearance of two signals from the Me protons of the Me_2PhSi groups is attributable to the fact that the two Me groups in each Me_2PhSi group always lie between different groups on the central carbon atom.)

Reaction of $(Me_3Si)_3CSiPh_2OH$ with NaOMe/MeOH

(a) A solution of the silanol (0.30 g) in 0.20 *M* NaOMe/MeOH (5 cm^3) was kept at room temperature for 15 min. Work-up as above gave an oil, which from analysis by GLC appeared to consist of one very predominant product along with < 10% of impurities. The main product was shown by linked GLC-mass spectrometry to be isomeric with the starting silanol (m/z 415 ($[M-Me]^+$) and 353 ($[M-Ph]^+$)), and was judged to be $(Me_3Si)_2CH(SiPh_2OSiMe_3)$ from its ^1H NMR spectrum: δ −0.06 (s, 18H, $SiMe_3$), 0.02 (s, 1H, CH), 0.10 (s, 9H, $OSiMe_3$), and 7.0–7.5 (m. 10H, SiPh).

(b) To the silanol (0.03 g) in an NMR tube was added 0.10 *M* NaOMe/MeOH (0.5 cm^3). The tube was shaken for 1 min and placed in the spectrometer, and the spectrum showed that only $(Me_3Si)_2CH(SiPh_2OSiMe_3)$ was present.

Treatment of $(Me_3Si)_3CSiPh_2OH$ with MeOH

(a) A solution of the silanol (0.10 g) in MeOH (20 cm^3) which had been dried over and distilled from $Mg(OMe)_2$ was boiled under reflux for 3 h. The solvent was removed under reduced pressure to leave a solid, which was recrystallized from n-pentane and shown to be $(Me_3Si)_2CH(SiPh_2OSiMe_3)$ (0.086 g, 85%), with a ^1H NMR spectrum identical with that reported above.

(b) Anhydrous Gold Label methanol (0.35 cm^3) was added to a solution of the silanol (0.010 g) in CCl_4 (0.50 cm^3) in an NMR tube. The tube was capped and kept at 61°C. Recording of the spectrum at intervals revealed no change during 10 days. The solvent was evaporated off and the residual solid kept under vacuum for 2 h, then shown from its ^1H NMR spectrum in CCl_4 to be unchanged silanol.

(c) The procedure described under (b) was repeated but with 5 vol% of H_2O in the MeOH. There was again no reaction.

(d) The procedure described under (a) was repeated but with 0.10 *M* CF_3CO_2H in MeOH. There was no reaction.

Trapping of $(Me_3Si)_2C(Li)(SiPh_2OSiMe_3)$

(a) A solution of 1.0 *M* MeLi in Et_2O (2 cm^3) was added to one of $(Me_3Si)_3CSiPh_2OH$ (0.50 g, 1.16 mmol) in THF (10 cm^3) and the mixture was refluxed for 3 h. An excess of Me_2SiHCl (2.0 cm^3) was added and the mixture refluxed for a further 3 h (possibly unnecessarily). The volatile materials were removed under vacuum then light petroleum (b.p. 60–80 ° C) was added, followed by water. The organic layer was separated, dried ($MgSO_4$), filtered, and evaporated, to leave a solid (0.36 g, 65%), m.p. 108–110 ° C, which was judged to be $(Me_3Si)_2C(SiMe_2H)(SiPh_2OSiMe_3)$: δ_H 0.12 (d, *J*(SiH) 3.6 Hz, 6H, $SiMe_2$), 0.25 (s, 27H, $(Me_3Si)_2C$ and $OSiMe_3$), 4.9 (m, 1H, SiH), and 7.1–7.8 (m, 10H, Ph); *m/z* 488 (30%, $[M]^+$), 473 (100, $[M-Me]^+$), 415 (80, $[M-SiMe_3]^+$), 396 (100, $[M-Ph-Me]^+$), 323 (70), 246 (40), 216 (70), 173 (30), 73 (60).

(b) When the experiment was repeated, but with Me_3SiCl in place of Me_2SiHCl, the ^1H NMR spectrum of the product indicated that it was exclusively $(Me_3Si)_2CH(SiPh_2OSiMe_3)$.

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