A Novel 1,3-Migration of a Silyl Group from Carbon to Oxygen in a Silanolate Ion

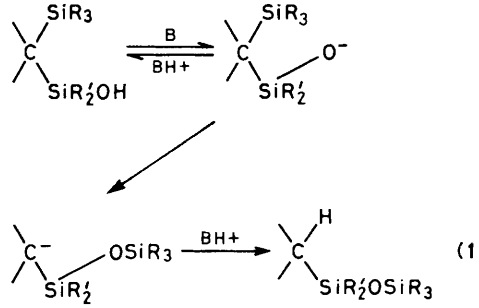
Robert Damrauer,*[a] Colin Eaborn,*[b] Duncan A. R. Happer,[b] and Abdulrahman I. Mansour[b]

[a] *Chemistry Department, University of Colorado at Denver, 1100 Fourteenth Street, Denver, Colorado 80202, U.S.A.*

[b] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.*

The silanols $(Me_3Si)_3CSiMe_2OH$, $(Me_3Si)_2C(SiMePh_2)(SiMe_2OH)$, and $(PhMe_2Si)_3C(SiMe_2OH)$ undergo rearrangement in MeONa–MeOH to give $(Me_3Si)_2CH(SiMe_2OSiMe_3)$, $(Me_3Si)_2CH(SiMe_2OSiMePh_2)$, and $(PhMe_2Si)_2CH(SiMe_2OSiMe_2Ph)$, respectively.

Anionic rearrangements involving migration of R_3Si groups from C to a negatively charged oxygen centre are well known, but a recent comprehensive review gives no examples of such migration from carbon to the oxygen of a silanolate ion, *i.e.* in $R_3SiC{\sim\sim}SiO^-$ systems, and includes a comment that surprisingly few anionic 1,3-silyl migrations of any kind have been reported.[1] We present below evidence for 1,3-migrations from carbon to the oxygen of a silanolate ion, as depicted in equation (1).



(1)

The first indications of the occurrence of such rearrangements were (a) the reaction of $(Me_3Si)_3CSiPh_2Br$ with Bu^n_4PCl (evidently containing some Bu^n_4POH and/or H_2O) gave, along with the substitution product $(Me_3Si)_3CSiPh_2Cl$, the siloxane $(Me_3Si)_2CH(SiPh_2OSiMe_3)$, which might have been formed by rearrangement of initially produced $(Me_3Si)_3CSiPh_2OH$;[2] (b) treatment of $(Me_3Si)_3CSiMe_2OH$ with potassium in boiling benzene gave $(Me_3Si)_2CH(SiMe_2OSiMe_3)$.[3]† We have now obtained clear evidence for such rearrangements.

A solution of $(Me_3Si)_3CSiMe_2OH$ in 0.5 M methanolic sodium methoxide was boiled under reflux for 2 h, then added to water. Extraction with hexane, followed by separation, washing, drying ($MgSO_4$), and evaporation of the extract left an oil, which was shown by ^1H n.m.r. spectroscopy and g.l.c. analysis to contain $(Me_3Si)_3CSiMe_2OH$ (48%), $(Me_3Si)_2CH(SiMe_2OSiMe_3)$ (38%), and $(Me_3Si)_2CH(SiMe_2OMe)$ (14%). (Authentic samples of the products were available.)[3,4] When the reaction was carried on for 6 h the same compounds were present in 10:25:65 ratio, and a separate experiment confirmed that $(Me_3Si)_2CH(SiMe_2OSiMe_3)$ was converted into $(Me_3Si)_2CH(SiMe_2OMe)$ under the conditions used.

The closely related silanol $(Me_3Si)_2C(SiMePh_2)(SiMe_2OH)$ was found to undergo rearrangement much more readily, the reaction being complete within 0.5 h at room temperature (*ca.* 22 °C) in 0.2 M NaOMe–MeOH. The product was shown by its mass spectrum to be isomeric with the original silanol (base peak m/z 415, $[M-Me]^+$), and was identified as $(Me_3Si)_2CH(SiMe_2OSiMePh_2)$ from its ^1H n.m.r. spectrum: δ (CCl_4) −0.60 (s, 1H, CH), 0.08 (s, 18H, $SiMe_3$), 0.10 (s, 6H, $SiMe_2$), 0.62 (s, SiMe, 3H), and 7.0—8.0 (m, 10H, Ph). G.l.c. revealed less than 3% of impurity, and it seems that effectively only the Ph_2MeSi group migrates; this is possibly related to the much greater ease of reaction of $(Me_3Si)_2C(SiMePh_2)(SiMe_2OH)$ than of $(Me_3Si)_3CSiMe_2OH$.

The silanol $(PhMe_2Si)_3C(SiMe_2OH)$ also reacted completely within 0.5 h in 0.2 M NaOMe–MeOH at room temperature. The dominant product (which was indicated by g.l.c. to constitute 90% of the product mixture) was isolated as a low-melting solid by preparative g.l.c. (20% OV101 on Chromosorb P), and shown by its mass spectrum (base peak m/z 477, $[M-Me]^+$) to be isomeric with the original silanol. The ^1H n.m.r. spectrum is consistent with the formula $(PhMe_2Si)_2CH(SiMe_2OSiMe_2Ph)$ if the signals from the $CSi\mathit{Me}_2Ph$ protons are assumed to be split because these Me groups are in different environments whatever the conformation: δ (CCl_4) (with tentative assignments) −0.03 (s, 6H, $CSi\mathit{Me}_2Ph$), 0.19 (s, 1H, CH), 0.21 (s, 6H, $CSi\mathit{Me}_2Ph$), 0.31 (s, 6H, $CSiMe_2O$), 0.34 (s, 6H, $OSi\mathit{Me}_2Ph$), and 6.8—7.2 (m, 15H, Ph).

The rearrangements discussed above are probably facilitated by (a) relief of steric strain, and (b) stabilisation of the formed carbanion by the three attached silicon atoms (see ref. 5). The acidities of the silanols must be important in determining the rates of reaction in a given basic medium, but the relative reactivities of the three silanols considered may be influenced mainly by the respective magnitudes of the relief of steric strain.

In the light of the results described above, it seems very likely that the formation of $(Me_3Si)_2CH(SiPh_2OSiMe_3)$ in the reaction of $(Me_3Si)_3CSiPh_2Br$ with Bu^n_4PCl does, indeed, involve rearrangement of initially formed $(Me_3Si)_3CSiPh_2OH$.[2] The results also raise the possibility that the formation of $(Me_3Si)_2CHSiR_2OMe$ species in the reaction of $(Me_3Si)_3CSiR_2X$ (R = Me or Ph; X = F, Cl, Br, I) with MeONa–MeOH[4] also involves initial formation of $(Me_3Si)_3CSiR_2OH$ (from traces of water), but, for reasons which will be discussed elsewhere, we think this unlikely.

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† The significance of this result was obscured by the fact that Me_3SiCl was added after the dissolution of the potassium (ref. 3). We have now confirmed that the Me_3SiCl is unnecessary.