

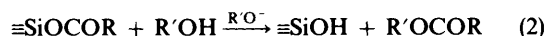
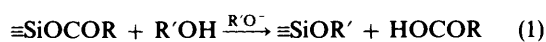
Acyl-Oxygen Fission in Reactions of Organosilicon Carboxylates with Sodium Methoxide in Methanol

Ramadan I. Damja, Colin Eaborn* and Anil K. Saxena

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The compounds $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{O}_2\text{CR}$ [$\text{R} = \text{Me}, \text{CH}_2\text{Cl}, \text{CF}_3, \text{Ph}, \text{C}_6\text{H}_4\text{NO}_2\text{-}p, \text{C}_6\text{H}_3(\text{NO}_2)_{2-3,5}$] and $\text{Bu}^t_3\text{SiO}_2\text{CCF}_3$, in which there is serious steric hindrance to nucleophilic attack at silicon, react with 0.20M-NaOMe in MeOH to give the corresponding silanols, $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{OH}$ and Bu^t_2SiOH ; *i.e.*, exclusive acyl-oxygen fission occurs rather than the normal silicon-oxygen fission. With both trifluoroacetates the reaction is complete within *ca.* 1 min at room temperature. For the $(\text{Me}_3\text{Si})_3\text{CSiMe}_2\text{O}_2\text{CR}$ species the reactivity sequence is $\text{R} = \text{CF}_3 > \text{C}_6\text{H}_3(\text{NO}_2)_{2-3,5} > \text{CH}_2\text{Cl} > \text{C}_6\text{H}_4\text{NO}_2\text{-}p > \text{Me} > \text{Ph}$.

Because of the great ease of nucleophilic attack at silicon, solvolysis of organosilicon carboxylates under the type of conditions used for base-catalysed hydrolysis or alcoholysis (ester exchange) of organic esters normally involves Si-O bond cleavage rather than the acyl-O cleavage observed with organic esters. For example, alcoholysis, with or without base, normally proceeds as in equation (1) rather than as an equation (2).



However, it is known that when there is steric hindrance to attack at the silicon atom, reaction by route (2) can be observed under such conditions alongside that by route (1); *e.g.*, in the reaction of $\text{Bu}^t\text{Me}_2\text{SiOCOMe}$ with Bu^nOH containing Bu^nONa , $\text{Bu}^t\text{Me}_2\text{SiOBu}^n$ and $\text{Bu}^t\text{Me}_2\text{SiOH}$ are formed in a 4:1 ratio.¹ (Under other conditions, and with some other types of nucleophile, attack at the carbonyl carbon can greatly predominate.¹) We have now found that acyl-oxygen cleavage occurs exclusively when $\text{Bu}^t_3\text{SiO}_2\text{CCF}_3$ and compounds of the type $\text{TsiSiMe}_2\text{O}_2\text{CR}$ [where Tsi denotes the very bulky 'trisilyl group, $(\text{Me}_3\text{Si})_3\text{C}$] react with sodium methoxide in methanol.

Results and Discussion

The trisilyl-silicon compounds $\text{TsiSiMe}_2\text{O}_2\text{CR}$, with $\text{R} = \text{Me}, \text{CH}_2\text{Cl}, \text{CF}_3, \text{Ph}, \text{C}_6\text{H}_4\text{NO}_2\text{-}p$, and $\text{C}_6\text{H}_3(\text{NO}_2)_{2-3,5}$, all gave silanol $\text{TsiSiMe}_2\text{OH}$ when treated with MeOH containing 0.2M-NaOMe, the ease of the reaction varying markedly with R. Thus for the trifluoroacetate ($\text{R} = \text{CF}_3$) (initially 0.025M) complete reaction had taken place at room temperature (*ca.* 21 °C) by the time (within *ca.* 1 min) the ¹H n.m.r. spectrum could be recorded. For the chloroacetate ($\text{R} = \text{CH}_2\text{Cl}$) reaction at 25–35 °C was *ca.* 50% complete after 2 min and *ca.* 85% complete after 7 min; reaction at 15 °C was *ca.* 50% complete after 5 min and 80% complete after 20 min. The acetate ($\text{R} = \text{Me}$) was considerably less reactive, reaction being 50% complete after *ca.* 42 min at 60 °C or *ca.* 9 h at 35 °C.

The benzoate ($\text{R} = \text{Ph}$) was even less reactive, reaction at 60 °C being *ca.* 50% complete after 7 h and 80% after 20 h. As expected, the *p*-nitrobenzoate ($\text{R} = \text{C}_6\text{H}_4\text{NO}_2\text{-}p$) was markedly more reactive, and (since the base was in *ca.* four-fold excess) a good first-order plot with a half-life of *ca.* 31 min at 35 °C was obtained up to 70% completion of the reaction; in this case the reaction was also carried out on a larger scale, and the solid product isolated shown to be a 1:1 mixture of $\text{TsiSiMe}_2\text{OH}$ and *p*-O₂NC₆H₄CO₂Me by comparison with a mixture of authentic samples. The reaction of the 3,5-dinitrobenzoate [$\text{R} = \text{C}_6\text{H}_3$ -

(NO₂)_{2-3,5}] at 15 °C was *ca.* 50% complete after 3 min and *ca.* 80% after 7 min. The sequence of reactivity of the $\text{TsiSiMe}_2\text{O}_2\text{CR}$ species is thus given by $\text{R} = \text{CF}_3 > \text{C}_6\text{H}_3(\text{NO}_2)_{2-3,5} > \text{CH}_2\text{Cl} > \text{C}_6\text{H}_4\text{NO}_2\text{-}p > \text{Me} > \text{Ph}$.

Reaction of $\text{Bu}^t_3\text{SiO}_2\text{CCF}_3$ under similar conditions at room temperature was complete before the first measurement could be made (*i.e.* within *ca.* 1 min). The product was exclusively Bu^t_2SiOH .

It is noteworthy that the less hindered compound $\text{TsiSiPh(H)(O}_2\text{CMe)}$ reacts fairly slowly with MeOH alone to give the methoxide TsiSiPh(H)OMe and much more rapidly with 0.2M-NaOMe in MeOH to give very predominantly the hydroxide TsiSiPh(H)OH along with a minor amount, perhaps 5–10%, of the methoxide.² The amount of the methoxide formed is too great to be accounted for by reaction with the solvent, and it seems that attack of the MeO^- ion at the carbonyl carbon is only some 10–20 times as fast as that at the silicon atom, showing how strong must be the preference for attack at the silicon atom in the absence of such severe steric hindrance. It is thus somewhat surprising that the much less hindered $\text{Bu}^t\text{Me}_2\text{SiO}_2\text{CMe}$ gives $\text{Bu}^t\text{SiMe}_2\text{OH}$ and $\text{Bu}^t\text{Me}_2\text{SiOBu}^n$ in a 1:4 ratio on treatment with NaOBu^n in Bu^nOH ; ¹ possibly the change in the reagent from MeO^- to BuO^- has a marked effect.

The results indicate that (alkyl)₃SiO⁻ anions are quite good leaving groups, in line with the fact that trialkylsilanols have acidities comparable to those of phenols.³

Experimental

Organosilicon Carboxylates.—The preparations of $\text{TsiSiMe}_2\text{O}_2\text{CCF}_3$ ⁴ and $\text{Bu}^t_3\text{SiO}_2\text{CCF}_3$ ⁵ have been previously described. The other $\text{TsiSiMe}_2\text{O}_2\text{CR}$ compounds were made by treatment of $\text{TsiSiMe}_2\text{OH}$ with the appropriate RCOCl ; details will be given in a forthcoming publication.

Methanolysis.—(a) For rate studies the $\text{TsiSiMe}_2\text{OCOR}$ compound (10 mg; 0.02–0.03 mmol) was dissolved in a drop of CCl_4 in an n.m.r. tube and 0.20M-NaOMe in MeOH (1 cm³) was added. The tube was fitted with a cap, shaken, then either (i) placed in the n.m.r. probe at the appropriate temperature [$\text{R} = \text{CF}_3, \text{CH}_2\text{Cl}, \text{C}_6\text{H}_4\text{NO}_2\text{-}p, \text{C}_6\text{H}_3(\text{NO}_2)_{2-3,5}$], or (ii) kept in a bath at 60 °C and transferred into the probe at intervals for recording of the n.m.r. spectra ($\text{R} = \text{Me}, \text{Ph}$). The heights of the singlets from the Me_3Si and Me_2Si protons of the $\text{TsiSiMe}_2\text{O}_2\text{CR}$ and $\text{TsiSiMe}_2\text{OH}$ were used to estimate the extent of reaction, with the results described in the main text. After appropriately prolonged reaction complete conversion into the silanol had occurred in each case.

(b) A solution of $\text{TsiSiMe}_2\text{O}_2\text{CC}_6\text{H}_4\text{NO}_2\text{-}p$ (0.37 g) in 0.2M-

NaOMe in MeOH (5 cm³) was kept at room temperature for 24 h then added to water. After extraction with diethyl ether the ethereal layer was separated, washed, dried (MgSO₄), and evaporated. The solid residue was shown to be a 1:1 mixture of TsiSiMe₂OH and *p*-O₂NC₆H₄CO₂Me by comparison of the n.m.r. spectrum of its solution in CCl₄ with that of a solution of a 1:1 mixture of authentic samples.

(c) A little Bu¹₃SiO₂CCF₃ (0.10 g, 0.032 mmol) was dissolved in a drop of CCl₄ in an n.m.r. tube and 0.2M-NaOMe in MeOH was added. The ¹H n.m.r. spectrum at 90 MHz was recorded (*ca.* 1 min after mixing) and the position of the peak for the Bu¹ protons showed that complete conversion into Bu¹₃SiOH had taken place. The identity of the product was confirmed by addition of a little authentic Bu¹₃SiOH, which increased the height of the peak. The spectrum of the solution after this addition was then re-examined at 300 MHz and found still to show only one Bu¹ peak, whereas two distinct peaks could be seen for a mixture of authentic Bu¹₃SiOH and Bu¹₃SiOMe under the same conditions.

Acknowledgements

One of us (R. I. D.) thanks the Libyan Government for a scholarship. We thank the S.E.R.C. for support, the Dow Corning Co., Ltd., for gifts of organosilicon chemicals, and Mr. R. W. Bott for valuable comments.

References

- 1 P. F. Hudrlik and R. Feasley, *Tetrahedron Lett.*, 1972, 1781.
- 2 Z. H. Aiube, personal communication.
- 3 C. Eaborn and W. Stańczyk, *J. Chem. Soc., Perkin Trans. 2*, 1984, 2009.
- 4 C. Eaborn, D. A. R. Happer, S. P. Hopper, and K. D. Safa, *J. Organomet. Chem.*, 1980, **188**, 179.
- 5 C. Eaborn and A. K. Saxena, *J. Organomet. Chem.*, 1984, **271**, 33.

Received 30th July 1984; Paper 4/1336