Anomalous rearrangements in the reaction of acylpolysilanes with $TMSNTf_2$

Malcolm B. Berry,[b] Russell. J. Griffiths,[a] Dmitrii S. Yufit[a] and Patrick G. Steel*[a]†

[a] *Department of Chemistry, University of Durham, Science Laboratories, South Road, Durham, UK DH1 3LE*
[b] *GlaxoWellcome Research and Development, Gunnels Wood Road, Stevenage, Herts, UK SG1 2NY*

Reaction of acylpolysilanes with silylbistriflimides (R_3SiNTf_2) leads to novel silanols *via* a pathway involving two 1,2-migrations of Me_3Si groups from silicon to carbon and one migration of a R_3SiO unit from carbon to silicon; the X-ray structure of one example is reported.

In the course of an investigation of the use of silenes as reagents for novel transformations in organic synthesis we had need to generate silenes from acylpolysilanes in what is effectively a 1,3 silyl migration.[1] This is normally achieved through either thermal (T = *ca*. 180 °C) or photochemical initiation.[1,2] Neither of these methods is compatible with the range of functionality which we wished to explore. Consequently, in order to determine whether it was possible to generate silenes through the Lewis acid promoted 1,3-silyl shift of acylpolysilanes, we investigated the reaction of benzoylpolysilane with silyl based Lewis acids (TMSOTf, $TMSNTf_2$). Here we report that there is no evidence for the formation of silenes in this process (neither silene adducts nor silene dimers are detected) but rather a series of 1,2-migrations occurs to generate a silenium ion intermediate which subsequently undergoes nucleophilic capture.

Initial experiments involved the addition of trimethylsilyl triflate (TMSOTf) to a mixture of the polysilane and piperylene. However, these reactions were complicated by extensive diene polymerisation. Consequently we turned to the use of the corresponding silylbistriflimides (R_3SiNTf_2), readily available from the corresponding allylsilane and bis(trifluoromethylsulfonyl)imide, which has been reported to be more tolerant with respect to alkene polymerisation.[3] Whilst this strategy proved to be no more successful than TMSOTf in inhibiting diene degradation, addition of $TMSNTf_2$ to a solution of the polysilane in CH_2Cl_2 at −78 °C afforded a deep red colour. After stirring at this temperature for 12 h, aqueous workup followed by flash column chromatography afforded a colourless crystalline material in near quantitative yield. Infra-red spectroscopy revealed the presence of an OH group, whilst mass spectroscopy showed a molecular ion at *m/z* 442 which corresponded to the starting material plus Me_3SiOH. Chemical analysis confirmed this formula. However it proved difficult to fit this data with the NMR spectra which showed four $SiMe_3$ units and five different silicon signals. Fortunately it proved possible to grow crystals suitable for X-ray diffraction,‡ which revealed the structure as the silanol **2a** (Fig. 1).§

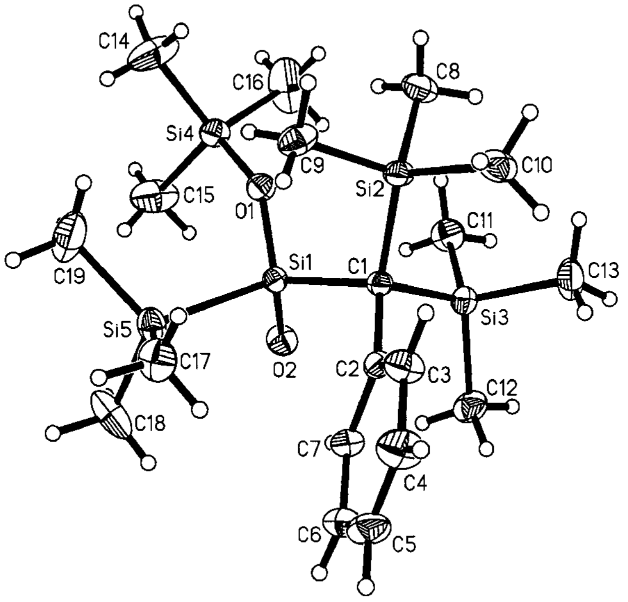
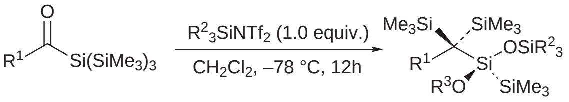


Fig. 1 Molecular structure of **2a**

In order to verify that this was a general procedure we then repeated this experiment with various other acylpolysilanes (Table 1). Whilst 4-trifluoromethylbenzoylpolysilane **1b** and acetylpolysilane **1d** gave similar products, pivaloylpolysilane **1e** failed to react and the 4-methoxyphenyl analogue **2c** underwent rapid decomposition on attempted isolation. To account for these observations we suggest that the reaction follows the pathway outlined in Scheme 1. Initial activation of the carbonyl group by the Lewis acid generates the oxacarbenium ion **5** which is stabilised by three β-Me_3Si units and R^1. In the situation in which the neighbouring alkyl group provides no stabilisation there is no reaction (R = Bu^t). Two successive 1,2 migrations of a trimethylsilyl group from silicon to carbon accompanied by a 1,2 shift of a trimethylsilyloxy group from carbon to silicon then occur. Similar migrations of trimethylsilyl groups from silicon to an adjacent cationic centre are precedented.[4–7] The precise order of these events is not clear and these may be either concerted or stepwise pathways. Whilst a silyl cation may be invoked as an intermediate in this process we have obtained no evidence for this and Lewis base coordinated species **6** and **8** (X = NTf_2^- or $RCOSiR'_3$) are probably more plausible. The resultant 'silenium ion' complex **8** is then hydrolysed by water on aqueous workup to produce the observed silanol. Use of MeOH in this final step leads to the

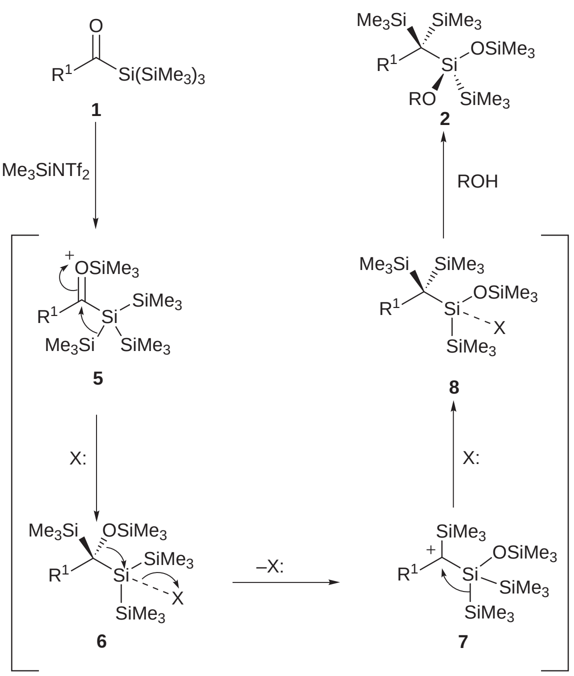
Table 1 Reaction of acylpolysilanes **1** with trialkylsilylbistriflimides



2 $R^2_3Si = Me_3Si$, R^3 = H
3 $R^2_3Si = Me_3Si$, R^3 = Me
4 $R^2_3Si = Bu^tMe_2Si$, R^3 = H

Entry	**1**	R^1	R^2_3Si	Product	Yield (%)[a,b]
1	**1a**	Ph	Me_3Si	**2a**	93
2	**1a**	Ph	Me_3Si^c	**2a**	9
3	**1a**	Ph	Me_3Si	**3a**	89[d]
4	**1a**	Ph	Bu^tMe_2Si	**4a**	84
5	**1b**	p-$CF_3C_6H_4$	Me_3Si	**2b**	82
6	**1c**	p-$MeOC_6H_4$	Me_3Si	**2c**	—[e]
7	**1d**	Me	Me_3Si	**2d**	77
8	**1e**	Bu^t	Me_3Si	**2e**	n.r.

[a] Yields refer to purified isolated compounds. [b] All products gave satisfactory spectroscopic and analytical data. [c] 10 mol% of $TMSNTf_2$ was used. [d] MeOH was added as the quenching agent. [e] Product decomposed on attempted isolation.



Scheme 1 Mechanistic pathway for the reaction of acylpolysilanes **1** with trialkylsilylbistriflimides

corresponding methoxide analogue **3a** in equally good yield (Table 1, entry 3). Further evidence in support of this pathway come from the use of TBMSOTf as the Lewis acid. As predicted this leads to complete incorporation of the TBDMS group at the silyloxy position (Table 1, entry 4) as confimed by ^{29}Si NMR spectroscopy (**4a**: $\mathrm{OSiBu^tMe_2}$ δ 9.48; **2a**: $\mathrm{OSiMe_3}$ δ 5.44). Furthermore, use of substoichiometric quantities of the initiator produces the same product in a corresponding yield together with recovered starting material (Table 1, entry 2).

Similar structures have been reported by Brook in the reaction of tertiary alkyl acylpolysilanes (R = Bu^t, adamantyl and bicyclo[2.2.2]octyl) with $TiCl_4$.[4] This was accounted for by a similar mechanistic pathway although, in this latter case, a 1,3 methyl shift from one of the trimethylsilyl groups to the 'silenium ion' also occurs. The reason for this difference between the $TiCl_4$ and the bistriflimide promoted pathways is not obvious at the present time.

In conclusion we report a novel rearrangement of acylpolysilanes on reaction with silyl triflates. Attempts to tune this reactivity to generate silenes in a convenient fashion are in progress and will be reported in due course.

We thank GlaxoWellcome and the EPSRC for financial support of this work (studentship to R. J. G. and funding for D. S. Y., repectively), the EPSRC mass spectrometry service at Swansea for accurate mass determinations, Dr A. M. Kenwright and Mr I. H. McKeag for assistance with NMR experiments and Dr M. Jones for mass spectra. The referees are thanked for helpful comments regarding the mechanism of this transformation.

Notes and References

† E-mail: p.g.steel@durham.ac.uk

‡ *Crystal data* for **2a**: $C_{19}H_{42}O_2Si_5$, M = 442.98, monoclinic, space group $P2_1/n$, a = 15.3270(1), b = 10.6851(1), c = 16.8596(1) Å, β = 105.50(1)°, U = 2659.5(9) Å^3, $F(000)$ = 968, Z = 4, D_c = 1.106 mg m^{-3}, μ = 0.28 mm^{-1} (Mo-Kα, λ = 0.71073 Å), T = 120(1) K, 33156 reflections (1.60 $\leqslant \theta \leqslant$ 30.5°) were collected on a Siemens SMART-CCD diffractometer (ω-scan, 0.3° per frame) yielding 7534 unique data (R_{merg} = 0.047). The structure was solved by direct-methods and refined by full-matrix least-squares on F^2 for all data using SHELXL software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were located on the difference map and refined isotropically. The H-atom of the OH group could not be located reliably and was not included in the refinement. Final $wR_2(F^2)$ = 0.1095 for all data (399 refined parameters), conventional $R(F)$ = 0.0411 for 5539 reflections with $I \geqslant 2\sigma$, GOF = 1.119. The largest peak on the residual map (0.62 e Å^{-3}) is located on the middle of one of the Si–Si bonds. CCDC 182/1000.

§ Attempts to achieve this transformation using TMSOTf afford a viscous oil which has similar spectroscopic properties to **2a** but whose structure is currently undefined. Details will be given in a full paper.

1 A. S. Batsanov, I. M. Clarkson, J. A. K. Howard and P. G. Steel, *Tetrahedron Lett.*, 1996, **37**, 2491.
2 A. G. Brook, J. W. Harris, J. Lennon and M. El Sheikh, *J. Am. Chem. Soc.*, 1979, **101**, 83.
3 B. Mathieu and L. Ghosez, *Tetrahedron Lett.*, 1997, **38**, 5497.
4 A. G. Brook, M. Hesse, K. M. Baines, R. Kumarathasan and A. J. Lough, *Organometallics*, 1993, **12**, 4259.
5 M. Kumada, J. Nakajima, M. Ishikawa and Y. Yamamoto, *J. Org. Chem.*, 1958, **23**, 292.
6 K. Sternberg, M. Michalik and H. Oehme, *J. Organomet. Chem.*, 1997, **533**, 265.
7 K. Sternberg and H. Oehme, *Eur. J. Inorg. Chem.*, 1998, 177.

Received in Liverpool, UK, 29th July 1998; 8/05966G