Synthesis and unusual rearrangement of 2-organyl-4,4,6,6-tetramethyl-5-chloro-6λ^5-sila-Δ^2-dihydro-1,3,4λ^4-oxadiazinium chlorides

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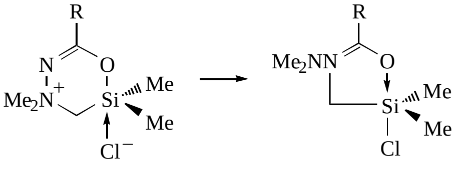
The reactions of *O*-TMS derivatives of 1,1-dimethylhydrazides of trifluoroacetic and benzoic acids with $Me_2Si(CHCl_2)Cl$ give 2-organyl-4,4,6,6-tetramethyl-5-chloro-6λ^5-sila-Δ^2-dihydro-1,3,4λ^4-oxadiazinium chlorides which in $CDCl_3$ solution exhibit unexpected decomposition with the formation of Me_2SiCl_2, DMF and the corresponding organylcyanide.

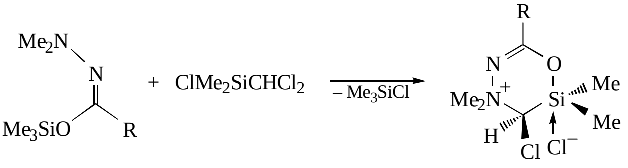
A recent study of 2-organyl-4,4,6,6-tetramethyl-6λ^5-sila-Δ^2-dihydro-1,3,4λ^4-oxadiazinium chlorides **1** showed that these six-membered silaheterocycles, of unusual zwitterionic structure with coordinative Si←Cl bonds, are unstable and isomerize on melting or heating and prolonged storage in solution to five-membered (O–Si)chelate dimethyl[2-(1,1-dimethyl-2-acyl-hydrazino)methyl]chlorosilanes **2** *via* a Vavzonec-type rearrangement[1–3] (Scheme 1):



1 **2**

Scheme 1

We have now succeeded in preparing two 5-chloro-derivatives of compounds **1**, 2-trifluoromethyl- and 2-phenyl-4,4,6,6-tetramethyl-5-chloro-6λ^5-sila-Δ^2-dihydro-1,3,4λ^4-oxadiazinium chlorides **3a**,**b**, from the reactions of dimethyl(dichloromethyl)chlorosilane with an equimolar amount of the *O*-TMS derivative of 1,1-dimethylhydrazides of trifluoroacetic and benzoic acids, respectively[†] (Scheme 2):



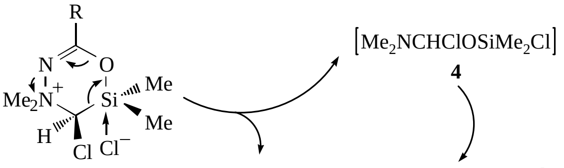
3a R = CF_3
3b R = Ph

Scheme 2

Hypervalent silicon chiral heterocycles **3a**,**b** gave satisfactory elemental analyses and the expected NMR spectra.[‡] Thus, pentacoordination at the silicon atom in **3a**,**b** is revealed by a strong (by 58 ppm) high field shift of their ^{29}Si NMR signals with respect to those observed in the spectrum of the parent tetracoordinated compound, $ClMe_2SiCHCl_2$. The chirality of the C-5 atom results in diastereotopy of the methyl groups at the N-4 and Si atoms, as detected by ^{1}H and ^{13}C NMR spectroscopy, though two Me_2Si proton singlets are broadened at ambient temperature and coalesce at higher temperature perhaps due to dissociation–association and pseudorotation at trigonal-bipyramidal silicon.[6] Finally, the ammonium character of the N-4 atom provides high values of the ^{1}H and ^{13}C NMR chemical shifts in the NMe_2 fragments.

Heterocycles **3a**,**b** are also thermodynamically unstable but the direction of their spontaneous transformation in solution differs drastically from that observed for the progenitor compounds **1a**,**b** which have no C–Cl bond. In $CDCl_3$ 5-chloro-substituted derivatives **3a**,**b** undergo an unusual rearrangement decomposition to yield dimethyldichlorosilane, *N*,*N*-dimethylformamide (DMF) and the nitrile of the corresponding carboxylic acid. These compounds were detected by NMR and GLC-MS spectroscopy[§] as the exclusive and major (70% yield) products of the decay of heterocycles **3a** and **3b**, respectively. From the NMR monitoring data, the half-life of compounds **3a**,**b** at room temperature is about 3 days.

The mechanism of the decomposition of compounds **3a**,**b** cannot be established unambiguously at this time. It can be preliminary described as a total combination of various concerted acts (Scheme 3):



3

Scheme 3

These involve the heterolytic cleavage of the N–N$^+$ and C–O bonds, formation of a covalent Si–C bond and insertion of the oxygen atom into the endocyclic Si–C bond leading to formation of the corresponding organonitrile and unobserved, transient dimethyl[(*N*,*N*-dimethylamino)chloromethoxy]chlorosilane **4** which yields DMF and dimethyldichlorosilane from a fast

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[†] *Synthesis of* 2-*trifluoromethyl*- and 2-*phenyl*-4,4,6,6-*tetramethyl*-5-*chloro*-6λ^5-*sila*-Δ^2-*dihydro*-1,3,4λ^4-*oxadiazinium chlorides*. A mixture of 1,1-dimethylhydrazone of trimethylsiloxy-2,2,2-trifluoroethanone[4] (3.82 g, 16.7 mmol) and dimethyl(dichloromethyl)chlorosilane (3.35 g, 18.9 mmol) in 30 ml of dry diethyl ether was kept for 8 h in an evacuated sealed ampoule at room temperature. The solvent and volatile compounds were then evaporated *in vacuo* and the residue was recrystallized from dry diethyl ether and dried *in vacuo*. The yield of **3a** was 2.76 g (55.5%), mp 93 °C (evacuated capillary).

Compound **3b** was prepared similarly from the reaction of $ClMe_2SiCHCl_2$ with *O*-trimethylsilylated 1,1-dimethyl-2-benzoylhydrazine[5] in dry Et_2O in 89% yield, mp 101.5 °C (evacuated capillary).

[‡] The NMR spectra were run for 20% solutions of compounds in $CDCl_3$ in evacuated sealed NMR tubes on a JEOL FX 90Q spectrometer. TMS was used as internal standard. ^{13}C and ^{29}Si NMR spectra were recorded with proton decoupling, the latter being obtained by use of the INEPT pulse sequence.

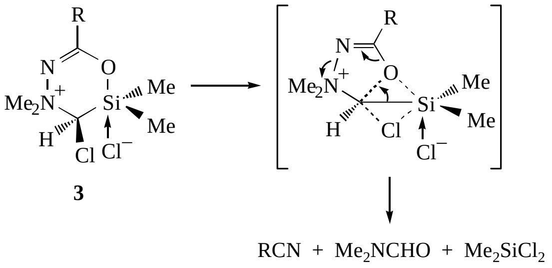
Compound **3a**: ^{1}H NMR (–20 °C) δ: 0.74 and 0.90 (s, 6H, Me_2Si), 3.57 and 3.62 (s, 6H, NMe_2), 5.61 (s, 1H, CHCl); ^{13}C NMR δ: 8.4 and 8.8 (Me_2Si), 52.7 and 55.5 (NMe_2), 80.4 (CHCl), 116.9 (q, CF_3, $^1J_{CF}$ 283.7 Hz), 159.1 (q, CO, $^1J_{CF}$ 37.7 Hz); ^{29}Si NMR δ: –40.2.

Compound **3b**: ^{1}H NMR δ: 0.86 and 1.05 (s, 6H, Me_2Si), 3.67 and 3.73 (s, 6H, NMe_2), 6.06 (s, 1H, CHCl), 7.4–8.0 (m, 5H, Ph); ^{13}C NMR δ: 6.9 and 8.0 (Me_2Si), 52.4 and 57.3 (NMe_2), 77.4 (CHCl), 127.5 (C-2′,6′), 128.0 (C-3′,5′), 131.1 (C-1′), 132.0 (C-4′), 164.5 (CO); ^{29}Si NMR δ: –36.1.

[§] Mass spectra of the products of decomposition of **3a**,**b** were detected on a Hewlett-Packard instrument equipped with a HP 5890 chromatograph and a HP 5971A mass-selective detector.

β-decomposition. However, the rearrangement of the transition species, $Me_2NCHClSi(O^+)Me_2Cl^-$, into **4** raises doubts. Owing to the more nucleophilic nature of the methyl carbon than that of an endocyclic C_α, this rearrangement should instead lead to a stable product, $Me_2NCHClSiMe(OMe)Cl$.

The second and more probable scheme for the decomposition of **3a**,**b** might involve the double migration of an O atom from Si to C_α and a Cl atom from C_α to Si with the aid of chloride ion, with concerted or subsequent heterolytic cleavage of the N–N⁺ and C–Si bonds in the resulting transition complex (Scheme 4):



Scheme 4

The proposed 1,2-sigmatropic shift resembles the well-known fluorine-induced relay of the nucleophile from silicon to its adjacent carbon in thermodynamically controlled reactions of the nucleophilic substitution of $ClSiMe_2CH_2Cl$ with PhEH (E = O or NMe).[7] A more detailed study of compounds **3** is in progress.

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References

1 I. D. Kalikhman, V. A. Pestunovich, B. A. Gostevskii, O. B. Bannikova and M. G. Voronkov, *J. Organomet. Chem.*, 1988, **338**, 169.
2 A. A. Macharashvili, V. E. Shklover, Yu. T. Struchkov, B. A. Gostevskii, I. D. Kalikhman, O. B. Bannikova, V. A. Pestunovich and M. G. Voronkov, *J. Organomet. Chem.*, 1988, **340**, 23.
3 A. A. Macharashvili, V. E. Shklover, Yu. T. Struchkov, B. A. Gostevskii, I. D. Kalikhman, O. B. Bannikova, V. A. Pestunovich and M. G. Voronkov, *J. Organomet. Chem.*, 1988, **356**, 23.
4 I. D. Kalikhman, E. N. Medvedeva, O. B. Bannikova, N. G. Fabina, M. F. Larin, V. A. Lopyrev and M. G. Voronkov, *Zh. Obshch. Chem.*, 1984, **54**, 477 (*Chem. Abstr.*, 1984, **101**, 55156).
5 I. D. Kalikhman, O. B. Bannikova, L. I. Volkova, B. A. Gostevskii, T. I. Yushmanova, V. A. Lopyrev and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 460 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 378).
6 Vad. V. Negrebetsky, A. G. Shipov, E. P. Kramarova, V. V. Negrebetsky and Yu. I. Baukov, *J. Organomet. Chem.*, 1997, **530**, 1 and references cited therein.
7 J. J. Eisch and C. S. Chiu, *J. Organomet. Chem.*, 1988, **358**, C1.

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