*Inorganica Chimica Acta*, 45 (1980) L229–L230
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

# Synthesis of Cyclic Hydroxylamines: Crystal Structure of $[(Me_3C)_2SiONH]_2$

DIETER BENTMANN, WILLIAM CLEGG, UWE KLINGEBIEL and GEORGE M. SHELDRICK*

*Anorganisch-Chemisches Institut der Universität Göttingen, Tammannstrasse 4, D-3400 Göttingen, F.R.G.*

Received June 23, 1980

Unlike chlorosilanes, fluorosilanes do not undergo substitution reactions with hydroxylamine [1–3]. Here we report a preparative method for fluorosilyl-substituted hydroxylamines. The presence of two functional groups in such molecules leads to the possibility of further reaction to give cyclic hydroxylamines, a class of compounds hitherto unknown.

## Preparation

Substitution of the hydroxyl H atom of $H_2NOH$ by $R_2SiF$ results from reaction of $H_2NOH \cdot HCl$ with amino-fluorosilanes $R_2SiFNHCMe_3$ [4] in THF and n-pentane at room temperature, to give $R_2SiFONH_2$. The by-product $Me_3CNH_2 \cdot HCl$ is precipitated from solution. When R = $CH_3$, the product cannot be isolated because it polymerises on removal of the solvent; when R = $CMe_3$, the product can be distilled at reduced pressure.

IR and $^1H$ NMR spectra of the products indicate that there is no substitution at N [5]. Further reaction with $ClSiMe_3$ and trimethylamine does, however, produce substitution at N. $Me_2SiF \cdot ONH_2$, prepared in solution as above, reacts to give $Me_2SiF \cdot ONHSiMe_3$, with precipitation of $Et_3N \cdot HCl$. The product can be isolated and purified by distillation at reduced pressure.

TABLE I. Atomic Coordinates ($\times 10^4$) for II.[a]

| *Atom* | *x* | *y* | *z* |
|---|---|---|---|
| Si(1) | −1084(2) | 1200(1) | 6225(1) |
| Si(2) | 485(2) | 2691(1) | 6222(1) |
| N(1) | −2600(7) | 1834(2) | 6054(1) |
| N(2) | 2005(7) | 2022(2) | 6132(1) |
| O(1) | 1274(6) | 1496(2) | 6396(1) |
| O(2) | −2065(5) | 2411(2) | 6288(1) |
| C(11) | −748(9) | 680(3) | 5749(2) |
| C(12) | 861(10) | 976(3) | 5441(2) |
| C(13) | 153(10) | 42(3) | 5863(2) |
| C(14) | −2909(10) | 593(3) | 5519(2) |
| C(15) | −2291(10) | 818(3) | 6700(2) |
| C(16) | −648(10) | 405(3) | 6932(2) |
| C(17) | −3055(12) | 1325(3) | 7001(2) |
| C(18) | −4291(10) | 413(3) | 6589(2) |
| C(21) | 1134(10) | 3118(3) | 6724(2) |
| C(22) | 1537(12) | 2644(3) | 7071(2) |
| C(23) | −739(10) | 3525(3) | 6872(2) |
| C(24) | 3144(11) | 3531(4) | 6687(2) |
| C(25) | 762(9) | 3168(3) | 5731(2) |
| C(26) | −256(10) | 3819(3) | 5769(2) |
| C(27) | 3164(10) | 3226(3) | 5606(2) |
| C(28) | −409(10) | 2832(3) | 5364(2) |

[a] Estimated standard deviations are given in parentheses.

These substituted hydroxylamines contain two functional groups: N–H and Si–F. In aminofluorosilanes, the same groups can lead to ring formation when treated with bases [6]. Here, too, reaction with

TABLE II. Ring Geometry for II.

| | | | |
|---|---|---|---|
| Bond lengths (Å): | | | |
| Si(1)–N(1) | 1.732(4) | Si(2)–N(2) | 1.729(5) |
| Si(1)–O(1) | 1.677(4) | Si(2)–O(2) | 1.694(4) |
| N(1)–O(2) | 1.476(6) | N(2)–O(1) | 1.475(6) |
| Bond angles (°): | | | |
| N(1)–Si(1)–O(1) | 106.1(2) | N(2)–Si(2)–O(2) | 103.5(2) |
| Si(1)–N(1)–O(2) | 111.7(3) | Si(2)–N(2)–O(1) | 111.5(3) |
| Si(1)–O(1)–N(2) | 111.3(3) | Si(2)–O(2)–N(1) | 115.9(3) |
| Torsion angles (°): | | | |
| O(1)–Si(1)–N(1)–O(2) | −29.7(4) | O(2)–Si(2)–N(2)–O(1) | −38.5(4) |
| N(2)–O(1)–Si(1)–N(1) | −37.5(4) | N(1)–O(2)–Si(2)–N(2) | −30.8(4) |
| Si(1)–N(1)–O(2)–Si(2) | 65.4(4) | Si(2)–N(2)–O(1)–Si(1) | 74.0(4) |

---

*Author to whom correspondence should be addressed.

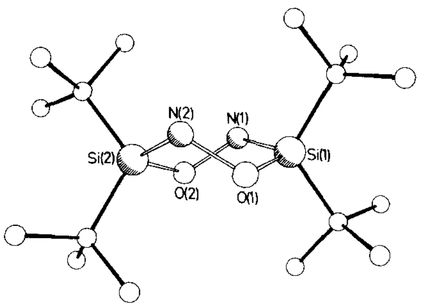
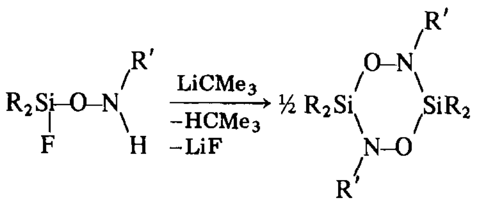


Fig. 1. Molecular structure of $[(Me_3C)_2SiONH]_2$.

$LiCMe_3$ eliminates LiF and isobutane, and previously unknown cyclic silylhydroxylamines are formed.



I, II

I : R = Me, R' = $SiMe_3$
II : R = $CMe_3$, R' = H

The compound II is obtained as long colourless needles by recrystallisation from $CH_2Cl_2$.

## Crystal Structure of II

Crystal data: $C_{16}H_{38}N_2O_2Si_2$, orthorhombic, $a$ = 6.163(2), $b$ = 21.306(7), $c$ = 31.977(10) Å. Space group $Pbca$, $Z$ = 8. $R$ = 0.066 (0.069 weighted) for 1348 unique reflections with $7° \leqslant 2\theta \leqslant 4.2°$ and $I \geqslant 2\sigma(I)$, measured with a Stoe-Siemens AED diffractometer and Mo-$K_\alpha$ radiation ($\lambda$ = 0.71069 Å) [7].

Final coordinates are given in Table I. The molecular structure is shown in Fig. 1. H atoms are omitted for clarity. Those for the Me groups were included in the refinement with C–H and H–C–H constrained to 0.96 Å and 109.5° respectively. H atoms attached to N were not located, but N and O atoms could be distinguished by their relative thermal parameters when the various possible arrangements were tested, and by the Si–N and Si–O bond lengths.

The bond lengths, bond angles and torsion angles of the (SiNO)2 ring are given in Table II. The ring is far from planar, and has a twist conformation [8].

## Acknowledgement

We thank the Verband der Chemischen Industrie for financial support.

## References

1 U. Wannagat and J. Pump, *Monatsh. Chem.*, *94*, 141 (1963).
2 P. Boudjouck and R. West, *Intra-Sci. Chem. Reports*, *7*, 65 (1973).
3 U. Klingebiel and M. Northe, *J. Organometal. Chem.*, *179*, 391 (1979).
4 U. Klingebiel and A. Meller, *Z. Anorg. Allg. Chem.*, *430*, 234 (1977).
5 H. Bürger, K. Burczyk and O. Smrekar, *Monatsh. Chem.*, *100*, 766 (1969).
6 U. Klingebiel and A. Meller, *Z. Anorg. Allg. Chem.*, *428*, 27 (1977).
7 W. Clegg, *Acta Cryst.*, *36A*, in press.
8 R. Bucourt and D. Hainaut, *Bull. Soc. Chim. France*, 1366 (1965).