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Rearrangement of silatranyl- and 3,7,10-trimethylsilatranyloxiranes to silatranylaldehydes and the crystal structure of silatranylacetaldehyde *

M. Nasim, V.S. Petrosyan, G.S. Zaitseva

Lomonosov University Moscow 119 899 Moscow (Russian Federation)

J. Lorberth, S. Wocadlo and W. Massa

Fachbereich Chemie, Philipps-Universität, W-3550 Marburg / Lahn (Germany)

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Abstract

Silatranylacetaldehyde $N(CH_2CH_2O)_3SiCH_2CHO$ and 3,7,10-trimethylsilatranylacetaldehyde $N(CH_2CHMeO)_3SiCH_2CHO$ were prepared in high yields by rearrangement of the corresponding silatranyloxiranes $N(CH_2CHRO)_3SiCHCH_2O$ ($R = H, Me$), with triethylbromostannane as a catalyst. An X-ray diffraction study of the parent silatranylacetaldehyde revealed the presence, along with the expected silatranylaldehyde, of some of the starting material silatranyl ethylene. Refinement of an appropriate disorder model for $C_6H_{12}NO_3Si(CH_2CHO)_{0.75}(CH=CH_2)_{0.25}$ led to $R/wR = 0.061/0.046$.

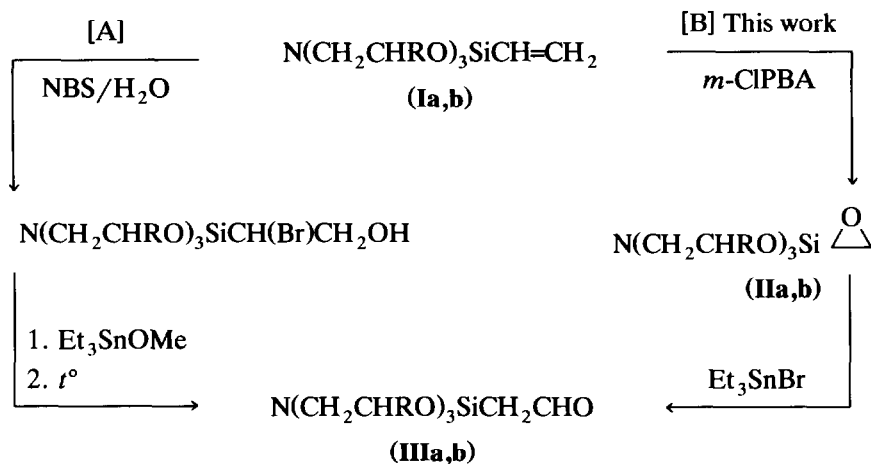
Results and discussion

Recently we started investigating the syntheses and chemical properties of functionalized silatranes and germatranes [1–5], large number of substituted functionalized silatranes having become available in earlier years [6,7]. However, until recently no α -silatranylcarbonyl derivatives were known except for the silatranylacetaldehydes [8] we made from the readily available silatranylethylenes [Scheme 1, route A].

This reaction was suggested to involve at one stage the assumption of an intermediate silatranyloxirane; the easy transformation of triphenylsilyloxirane into triphenylsilylacetaldehyde under the catalytic influence of a magnesium dibromide–ether complex supports this assumption [9,10]. We have now confirmed the correctness of this proposal by use of an alternative synthetic route B: by this route silatranyloxirane (IIa) and 3,7,10-trimethylsilatranyloxirane (IIb) are obtained in

Correspondence to: Dr. G.S. Zaitseva or Prof. Dr. J. Lorberth.

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Scheme 1. NBS, *N*-bromosuccinimide; R = H (a), Me (b).

yields greater than 80% via the oxidation of the precursor silatranylethylenes (**Ia**, **b**) with *m*-chloroperbenzoic acid (*m*-CIPBA) as described previously for the preparation of oxirane (**IIa**) [11].

The oxirane structures **IIa,b** were confirmed by ¹H, ¹³C NMR spectroscopy: in the ¹H NMR spectra the protons of the oxirane ring give rise to signals of an ABX system with $\delta = 2.07\text{--}2.11$ ppm (H_X) and $\delta = 2.2\text{--}2.8$ ppm for H_A and H_B. In the ¹³C NMR spectrum of oxirane **IIa**, signals for the ring carbon atoms appear at $\delta = 44.5$ (CH) and $\delta = 45.3$ (CH₂) ppm [12]. For the other oxirane, 3,7,10-trimethylsilatranyloxirane **IIb**, the ¹H and ¹³C NMR spectra revealed the presence of a mixture of four diastereomers [13,14].

Oxiranes **IIa,b** were isomerized at 100–110°C in the presence of triethylbromostannane as a catalyst; after distillation of the stannane *in vacuo* and crystallization of the solid residue silatranylaldehydes, **IIIa,b** were obtained in 92% and 88% yield with melting points and NMR data consistent with those in the literature [8].

Similar rearrangements have been detected previously in a few cases. Apart from the abovementioned example, there were reports on the thermal isomerization (170–310°C) of silyloxiranes into vinyloxysilanes without formation of silylaldehydes [15,16]. The rearrangement of triethylsilyloxirane into triethylvinyloxysilane in the reaction involving equimolar amounts of tripropylbromostannane at 190°C was monitored by IR spectroscopy and showed that it passes through a triethylsilyl-acetaldehyde as an intermediate [17].

The results presented in this paper show the complete absence of vinyloxysilanes in the reaction products. Moreover, the molecular and crystal structure of silatranylaldehyde **IIIa** has been determined by single crystal X-ray diffraction methods and confirms unambiguously the structure of a silatranylsubstituted aldehyde. The crystal structure revealed, however, that some of the starting material, silatranyl ethylene, was present in the crystal.

Crystal structure of **IIIa**

During the structure determination (see Tables 1–3) refinement of a pure silatranylaldehyde model resulted in poor residuals $R/wR = 0.071/0.055$ and high

Table 1

Details of the crystal structure determination of the disordered silatrane **IIIa** $C_6H_{12}NO_3Si(CH_2CHO)_{0.75}(CH=CH_2)_{0.25}$

<i>Crystal data</i>	
Crystal dimensions (mm ³)	<i>ca</i> 0.4 × 0.075 × 0.075
Absorption (cm ⁻¹)	$\mu = 19.9$ (numerical correction)
Min/max transmission	0.75/0.90
Space group	$P2_12_12_1$, $Z = 4$
Lattice constants (Å)	$a = 6.573(3)$
(Cu- K_α)	$b = 9.333(3)$
	$c = 16.610(10)$
Temperature (K)	193
Density (g cm ⁻³)	$d_c = 1.390$
<i>Data collection</i>	
Diffractometer	4-circle, CAD4 (Enraf–Nonius)
Radiation	Cu- K_α , graphite monochromator
Scan type	ω -scan
Scan width	(0.95 + 0.14 tg θ)° and 25% on the left hand and right hand side of a reflection for background determination
Measuring range (°)	$\theta = 2-55$, + h , + k , ± l
Reflections	1512, 1272 unique, 1077 > 3 $\sigma(F_o)$
<i>Computing</i>	
Program	SHELXTL-PLUS [18]
Solution	Direct methods
Atomic scattering factors for neutral atoms	$\Delta f'$, $\Delta f''$ from [19]
Refinement	Full matrix least squares, 136 parameters $\Sigma w(F_o - F_c)^2$ minimized, $w = 1/\sigma^2(F)$, hydrogen atoms riding with common isotropic U , anisotropic U for other atoms, except C2a
Correct polarity tested by η refinement	
Residuals	$R = 0.061$, $wR = 0.046$
Goodness of fit	2.71
Max. parameter shift	0.001 × e.s.d.
$\Delta\rho_{\max,\min}$ (e Å ⁻³)	0.64, -0.42

thermal parameters for the aldehyde group. Near C1, a weak maximum of electron density (0.82 e Å⁻³) indicated the presence of disorder. In addition, anomalous interatomic distances C1–C2 139 pm, C2–O4 124 pm suggested the partial statistical replacement of the aldehyde group by vinyl groups in two alternative orientations, one approximately along C1–C2 (I), the other along C1–C2a (II) (Fig. 1). After optimization of this disorder model including H-atoms in calculated positions, an occupation of 75% for the aldehyde function and 10% or 15% for the vinyl positions I and II, respectively, was found. The composition of the crystal is therefore $C_6H_{12}NO_3Si(CH_2CHO)_{0.75}(CH=CH_2)_{0.25}$. The presence of an oxirane species can be ruled out because the atoms C1, C2, C2a strongly deviate from the triangular geometry of an oxirane (C2 ··· C2a 1.94 Å). Now, R/wR dropped to 0.061/0.046. The final atomic parameters are collected in Table 2. The geometry

Table 2

Atomic fractional coordinates and equivalent isotropic temperature factors for the non-H atoms in **IIIa**
 $(U_{eq} = 1/3(\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j))$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Si	0.2538(3)	0.4229(2)	0.3705(1)	0.0387(6)
O1	0.5001(7)	0.4548(5)	0.3805(3)	0.048(2)
O2	0.1400(8)	0.3163(5)	0.4365(3)	0.045(2)
O3	0.1434(7)	0.4547(4)	0.2818(3)	0.044(2)
N	0.3500(9)	0.2301(6)	0.3165(3)	0.039(2)
C11	0.6464(12)	0.3628(8)	0.3473(4)	0.059(3)
C12	0.5662(11)	0.2174(8)	0.3410(5)	0.066(4)
C21	0.1657(12)	0.1646(7)	0.4354(4)	0.056(3)
C22	0.2195(11)	0.1179(7)	0.3532(4)	0.056(3)
C31	0.1390(12)	0.3492(8)	0.2213(4)	0.057(3)
C32	0.3187(11)	0.2532(9)	0.2303(4)	0.067(3)
C1	0.1646(12)	0.5985(8)	0.4185(5)	0.059(3)
C2	0.2171(17)	0.6171(10)	0.4988(6)	0.073(5) ^a
O4	0.0930(13)	0.6027(8)	0.5547(4)	0.089(4) ^b
C2a	0.247(7)	0.744(5)	0.4073(23)	0.045(12) ^c

Site occupation factors: ^a 0.85; ^b 0.75; ^c 0.15.

Table 3

Bond lengths (Å) and bond angles (°) in **IIIa**

Si–O1	1.654(5)	Si–O2	1.658(5)
Si–O3	1.669(5)	Si–N	2.108(6)
Si–C1	1.914(8)	O1–C11	1.402(9)
O2–C21	1.426(8)	O3–C31	1.406(8)
N–C12	1.483(9)	N–C22	1.484(9)
N–C32	1.464(9)	C11–C12	1.460(11)
C21–C22	1.476(10)	C31–C32	1.490(11)
C1–C2	1.390(13)	C1–C2a	1.47(4)
O4–C2	1.242(13)		
O1–Si–O2	118.8(3)	O1–Si–O3	118.8(2)
O1–Si–N	84.4(2)	O1–Si–C1	96.0(3)
O2–Si–O3	119.6(3)	O2–Si–N	84.5(2)
O2–Si–C1	95.8(3)	O3–Si–N	84.7(2)
O3–Si–C1	94.7(3)	N–Si–C1	179.4(3)
Si–O1–C11	121.4(4)	Si–O2–C21	122.3(4)
Si–O3–C31	121.0(4)	Si–N–C12	103.8(4)
Si–N–C22	104.7(4)	Si–N–C32	104.4(4)
C12–N–C22	112.6(5)	C12–N–C32	114.5(5)
C22–N–C32	115.1(5)	O1–C11–C12	110.4(6)
N–C12–C11	107.0(6)	O2–C21–C22	109.4(6)
N–C22–C21	108.1(5)	O3–C31–C32	109.5(6)
N–C32–C31	107.3(6)		
Si–C1–C2	115.5(6)	Si–C1–C2a	129(2)
O4–C2–C1	123(1)		

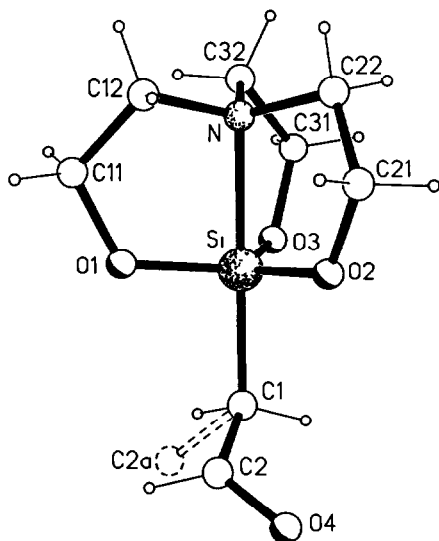


Fig. 1. An XP drawing [18] of a molecule of **IIIa** in the crystal showing the disorder between aldehyde and vinyl group II (dotted lines) on silicon.

of the silatranyl moiety is closely related to that of hitherto known silatranes [20]. The Si–N bond (2.11 Å) is relatively short and the angles N–Si–O thus close to 90° (mean 84.5°). The Si–C1 distance (1.91 Å) is the same as that in the Si–CH₂Cl compound. Because of the disorder, the bond lengths in the aldehyde moiety are subject to large error and are thus not to be discussed further [21]. The torsion angle Si–C1–C2–O4 (–105°) clearly shows that, in spite of the small C1–C2 distance (1.39 Å), this bond is essentially a single bond.

Experimental details

Melting points are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Varian XR-400 MHz spectrometer with TMS as an internal standard. IR spectra were recorded as Nujol mulls with a Zeiss UR-20 spectrometer.

1-Silatranyloxirane IIa

To a solution of 3.02 g (15 mmol) of silatranylethylene (**Ia**) in 25 ml of CH₂Cl₂ were added 4.0 g (38 mmol) of Na₂CO₃. The mixture was stirred for 5 min at ambient temperature and a solution of 7.5 g (43 mmol) of *m*-chloroperbenzoic acid in 25 ml of CH₂Cl₂ was added dropwise. Stirring was maintained for 4–5 days at room temperature. The solid was filtered off, and washed several times with *ca.* 15-ml portions of CH₂Cl₂. Most of the dichloromethane was removed and *n*-pentane was added. The precipitate was filtered and recrystallized from CH₂Cl₂/pentane, and dried *in vacuo* at 1 mm to give 2.72 g (83%) of silatranyloxirane (**IIa**); m.p. 189–190°C, lit. 141–142°C [11].

Anal. Found: C, 44.03; H, 6.62; N, 6.07; Si, 12.85. C₈H₁₅NO₄Si calc.: C, 44.22; H, 6.96; N, 6.45; Si, 12.92%. ¹H NMR: 2.89 (t, 6H, NCH₂); 3.84 (t, 6H, OCH₂); 2.07–2.1 (m, 1H, SiCH); 2.73–2.8 (m, 2H, CH₂-oxirane). ¹³C NMR: 44.57 (SiCH); 45.31 (CH₂); 51.11 (NCH₂); 57.30 (OCH₂).

3,7,10-Trimethylsilatranyloxirane (**IIb**)

IIb was prepared similarly; yield 83%, m.p. 131–132°C. Anal. Found: C, 50.85; H, 8.29; N, 5.36; Si, 10.53. C₁₁H₂₁NO₄Si calc.: C, 50.94; H, 8.16; N, 5.40; Si, 10.83%.

¹H NMR: 2.06–2.11 (m, 1H, SiCH); 2.25–2.44 (m, 2H, CH₂ oxirane). ¹³C NMR: 20.29, 20.41, 20.49, 20.50, 20.57, 20.58, 23.56, 23.62 (Me); 44.67, 44.77, 44.82, 44.90 (SiCH); 45.52, 45.78 (CH₂); 58.74, 59.09, 60.88, 61.00, 61.53, 61.89, 64.82, 64.93 (NCH₂); 63.03, 64.14, 64.34, 64.37, 64.44, 64.51, 66.04, 66.05 (OCH). These signals arise from four possible diastereomers.

Silatranylacetaldehyde (**IIIa**)

A mixture of 0.5 g (2.3 mmol) of silatranyloxirane **IIa** and 1.14 g (4 mmol) of triethylbromostannane was heated in a distillation apparatus for about 30 min at 100–110°C and the triethylbromostannane was then distilled off *in vacuo* at 62–63°C/1 Torr; 1.12 g (98%) of it was recovered. The solid residue was washed with *n*-pentane recrystallized from CH₂Cl₂/pentane, and dried *in vacuo* at 1 Torr to give 0.46 g (92%) of silatranylacetaldehyde (**IIIa**); m.p. 131–132°C; lit. 127–128°C [8].

3,7,10-Trimethylsilatranylacetaldehyde (**IIIb**)

IIIb was prepared similarly; yield 83%, m.p. 92–93°C; lit. 92–93°C [8].

Acknowledgements

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- 21 Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, stating the deposit number CSD-56705, the authors and the full literature citation.