Journal of Organometallic Chemistry, 402 (1991) 313–318
Elsevier Sequoia S.A., Lausanne
JOM 21474

Synthesis of 2-silatranyl- and 2-(3,7,10-trimethyl)silatranylacetaldehydes

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(Received July 20th, 1990)

Abstract

2-Silatranyl-2-bromoethanols, $N(CH_2CHRO)_3SiCH(Br)CH_2OH$ (R = H, Me), have been obtained by bromohydroxylation of silatranylethylenes, which react with triethylmethoxystannane to give 2-silatranylacetaldehydes, $N(CH_2CHRO)_3SiCH_2CHO$, in high yields.

Introduction

The much-studied pentacoordinated silicon compounds known as silatranes include some compounds that have carbofunctional substituents on the silicon atom and these are of special interest in respect of their structure, reactivity, and biological activity [1]. However, compounds containing a carbonyl group α to the silicon have not previously been reported. Such compounds would also belong to the general class of α-silyl carbonyl compounds, $R_3SiCH_2COR^1$ with R = alkyl and aryl, which possess a labile Si–C bond and can undergo a practically irreversible thermal and catalytic transformation into *O*-silyl-enols [2]. There is undoubted interest in studying the influence of silicon bearing a transannular coordinative Si–N bond on the stability and reactivity of this type of compound.

At present several methods have been proposed for the synthesis of α-silylaldehydes with bulky groups attached to the silicon atom, and triphenyl- [3], tripropyl- [4], dimethyl-tert-butylsilylacetaldehydes [5–7] and α-dimethyl-tert-butylsilyloctanal [6,7] have been isolated. The trimethylsilyl- and triethyl-silylacetaldehydes, however, were not isolated as pure substances [8].

Results and discussion

We have developed a multi-step route to α-silatranylacetaldehydes starting from the readily accessible silatranylethylenes:

$$(AcO)_3SiCH{=}CH_2 \xrightarrow[-3AcOH]{N(CH_2CHROH)_3} N(CH_2CHRO)_3SiCH{=}CH_2 \qquad (1)$$

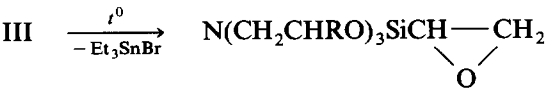
(I)

$$\mathrm{I} \xrightarrow{NBS/H_2O} N(CH_2CHRO)_3SiCH(Br)CH_2OH \qquad (2)$$

(II)

$$\mathrm{II} \xrightarrow[-MeOH]{Et_3SnOMe} [N(CH_2CHRO)_3SiCH(Br)CH_2OSnEt_3] \qquad (3)$$

(III)



$$\mathrm{III} \xrightarrow[-Et_3SnBr]{t^0} N(CH_2CHRO)_3\underset{O}{SiCH{-}CH_2} \qquad (4)$$

(IV)

$$\mathrm{IV} \xrightarrow{t^0} N(CH_2CHRO)_3SiCH_2CHO \qquad (5)$$

(V)

(a: R = H; b: R = Me)

Heating of a mixture of 2-silatranyl-2-bromoethanol (IIa) with small excess of triethylmethoxystannane to 100 ° C (reaction 3), followed by the removal of triethylbromostannane by distillation (reactions 4 and 5) gave 2-silatranylacetaldehyde (Va) in practically quantitative yield and containing only a small amount (5%) of the intermediate silatranyloxirane IVa. The presence of IVa was revealed by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectrum the protons of the oxirane ring gave signals in the form of an ABX system with δ 2.0–2.2 (H_x) and δ 2.7–2.8 (H_a, H_b) ppm; the protons of the "atrane" fragment gave two triplets with δ 2.89 (NCH_2) and 3.83 (OCH_2) ppm and J 5.6 Hz. The ^{13}C NMR spectrum of oxirane IVa contains four signals with δ 44.6 (CH), 45.3 (CH_2), 51.09 (CH_2N) and 57.28 (CH_2O) ppm. Recrystallization of the product from chloroform/n-pentane gave (Va) in 92% yield. An analogous procedure gave, 2-(3,7,10-trimethyl)silatranylacetaldehyde (Vb) in quantitative yield as a mixture of almost equal amounts of the two diastereomers having different orientations of the methyl groups relative to the axial Si–N bond.

Interaction of 2-trialkylsilyl-2-bromoethanol with trialkylmethoxystannane was previously shown [8] to give a mixture of three isomers with an overall yield of 40–50%, namely trialkylsilyloxiranes (20–30% of the mixture), trialkylvinyloxysilanes (10%) and trialkylsilylacetaldehydes (60–70%) and it was not possible to isolate the trialkylsilylacetaldehydes. When the mixture was heated at 190 ° C in the presence of tripropylbromostannane the triethylsilyloxirane formed isomerized to triethylsilylacetaldehyde and the latter finally to triethylvinyloxysilane. In contrast, in the present work no formation of vinyloxysilatranes was observed during the reaction; even after 4 h of heating at 200 ° C the silatranylacetaldehyde (Va) was not isomerised to the corresponding vinyloxysilatrane.

The starting compounds, the silatranylethylenes (Ia, Ib), were prepared as previously described [9], by interaction of triacetoxyvinylsilanes with the corresponding trialkanolamines (reaction 1). (3,7,10-Trimethyl)silatranylethylene (Ib) was prepared

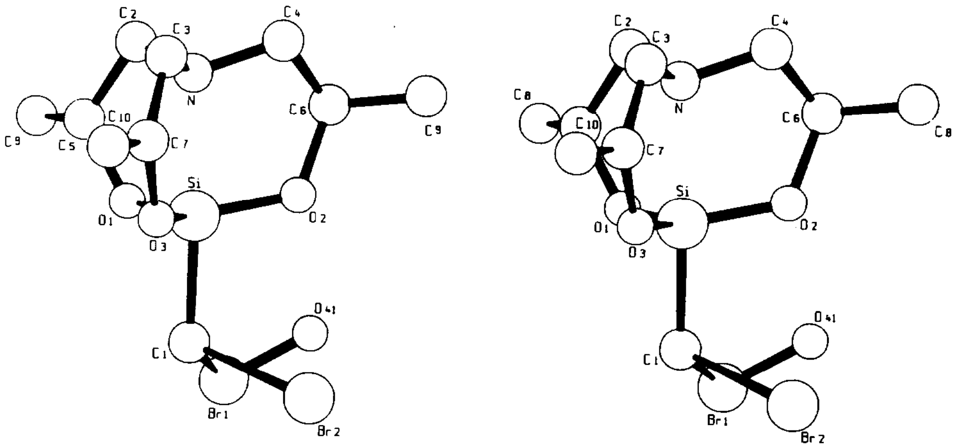


Fig. 1. SCHAKAL [14] stereo plot of one of the two diastereomeric structures of compound IIb.

by this method and identified by comparison of the physical data with those previously reported [10] and its structure further confirmed by NMR spectroscopy, which showed it to be a mixture of two diastereomers. The mixed isomers of 2-silatranyl-2-bromoethanol (IIa, b) were obtained in yields of > 80% from the exothermic reaction of silatranylethylenes (Ia, b) with *N*-bromosucciniimide in the presence of water [11] (reaction 2). These compounds (II) are stable white crystalline substances, very soluble in $CHCl_3$.

The results we obtained were somewhat surprising since it is known that reaction of *N*-bromosuccinimide with 1-organosilatranes, e.g. arylsilatranes, in methanol or in dichloromethane, affords only 1-bromosilatranes [12]. It is known that the carbon–silicon bond in vinylsilatrane is cleaved by electrophilic reagents, e.g. phosphorylsulfenyl chlorides [13]. The ^{13}C NMR spectrum of compound (IIb) shows it to be a mixture of four diastereomers: δ (CHBr), 45.16; 45,45; 45,63 and 45.69 pm.

The X-ray diffraction study of compounds IIb (Fig. 1) showed that the bond lengths and bond angles are almost identical to those in 1-chloromethylsilatrane [1]: Si–N 212.3; Si–C 192.8; Si–O 165.5; C–O 142.0; C–C 144.0; C–N 149.0 pm; N–Si–C 177.6; O–Si–C 95.8; O–Si–O 119; C–N–C 113.3; N–C–C 109° (Table 2).

Experimental

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian XR-400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. IR spectra were recorded in Nujol on a Zeiss UR-20 spectrometer.

2-Silatranylacetaldehyde (Va)

A mixture of 2-silatranyl-2-bromoethanol (IIa) (0.7 g, 2.3 mmol) and triethylmethoxystannane (0.6 g, 2.5 mmol) was kept at 100°C for 0.5 h, during which methanol (0.073 g) evaporated off. From the residue which contained mainly compound IIIa, triethylbromostannane (0.65 g, 98%) was separated by further heating and continuous distillation *in vacuo* (b.p. 98–100 ° C at 1 Torr). The residual solid was washed with n-pentane and dried *in vacuo* and shown to be Va (0.46 g 92%), m.p. 127–128 ° C. IR (ν, cm^{-1}): 1692 (C=O). ^1H NMR ($CDCl_3$, δ, ppm): 2.13 (d, 2H, CH_2, J 4.6 Hz); 9.65 (t, 1H, CH=O, J 4.6 Hz); 2.88 (t, 6H, NCH_2, J 6 Hz); 3.8 (t, 6H, OCH_2, J 6 Hz). ^{13}C NMR: 40.76 (CH_2); 51.01 (NCH_2); 57.45 (OCH_2); 204.13 (C=O). Analyses. Found: C, 44.00; H, 6.80; Si, 13.29. $C_8H_{15}NO_4Si$ calcd.: C, 44.22; H, 7.09; Si 12.92%.

2-(3,7,10-Trimethyl)silatranylacetaldehyde (Vb)

This was made analogously in quantitative yield, m.p. 92–93 ° C. IR (ν, cm^{-1}). 1700 (C=O). ^1H NMR: 2.11 (d, 2H, CH_2), 2.13 (d, 2H, CH_2), 9.28 (t, 1H, CH=O), 9.64 (t, 1H, CH=O) ppm, J 4,6 Hz (for all couplings). ^{13}C NMR: 41.05, 41.11 (CH_2); 204.57, 204.45 (C=O) ppm (two diastereomers). Analyses. Found: C, 50.93; H, 8.06; Si, 10.40. $C_{11}H_{21}NO_4Si$ calcd.: C, 50.93; H, 8.16; Si, 10.83%.

(3,7,10-Trimethyl)silatranylethylene (Ib)

To a solution of triacetoxyvinylsilane (23.3 g, 100 mmol) in 100 ml chloroform was added dropwise during 25 min at 0 ° C a solution of 19.1 g (100 mmol) of triisopropanolamine in 100 ml of chloroform. The mixture was stirred for 1 h and the acetic acid then removed by azeotropic distillation with toluene. n-Pentane (25 ml) was added and the precipitate filtered off and dried *in vacuo*. Yield of Ib 20 g (82%), m.p. 104–105 ° C; lit. [10]: 103.3–104.5 ° C. ^{13}C NMR: 20.36, 20.48, 20.69, 23.37 (CH_3); 129.28, 129.62 (CH_2=); 139.95, 140.19 (CH=); 58.91, 61.64, 61.70, 63.26, 64.81, 64.87, 65.14, 66.57 (NCH_2, OCH) (two diastereomers).

Table 1

Positional parameters and their estimated standard deviations for compound IIb [a]

Atom	x	y	z	B ($Å^2$)
Br	0.1489(3)	0.000	0.1770(3)	4.42(5)
Br′	0.1459(4)	0.2728(3)	0.1694(4)	6.68(8)
Si(1)	0.5091(3)	0.1390(7)	0.2983(3)	3.09(5)
O(1)	0.5404(8)	0.0121(8)	0.2206(9)	4.5(2)
O(2)	0.5027(6)	0.142(2)	0.4830(6)	3.9(1)
O(3)	0.5485(8)	0.2717(8)	0.2257(8)	4.1(2)
O(4)	0.203(2)	0.017(2)	0.364(2)	8.2(5)
O(4)′	0.169(1)	0.273(1)	0.263(2)	18.0(5)
N(1)	0.7780(7)	0.141(2)	0.4507(8)	3.5(2)
C(1)	0.2657(9)	0.114(2)	0.156(1)	3.7(2)
C(2)	0.838(2)	0.013(2)	0.407(3)	13.2(6)
C(3)	0.840(1)	0.250(1)	0.415(1)	3.9(3)
C(4)	0.801(1)	0.155(2)	0.623(1)	5.2(3)
C(5)	0.709(2)	−0.019(2)	0.245(2)	6.4(4)
C(6)	0.651(1)	0.104(1)	0.634(1)	4.8(4)
C(7)	0.708(2)	0.326(1)	0.291(2)	11.7(5)
C(8)	0.635(1)	0.154(3)	0.788(1)	9.5(4)
C(9)	0.713(2)	−0.145(1)	0.183(2)	8.0(4)
C(10)	0.735(2)	0.426(1)	0.218(2)	6.0(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $\exp[-2P_{1,2}\{h^2a^2U_{1,1}+k^2b^2U_{2,2}+l^2c^2U_{3,3}+2hkabU_{1,2}+2hlacU_{1,3}+2klbcU_{2,3}\}]$ where a, b and c are reciprocal lattice constants. Hydrogen atoms were refined isotropically.

Table 2

Selected bond lengths (pm) and bond angles (°) for IIb

Br-O(4)	151.1(15)	O(3)-C(7)	138.3(15)
Br-C(1)	193(2)	O(4)′-C(1)	209(2)
Br′-O(4)′	76(2)	N(1)-C(2)	160(3)
Br′-C(1)	179(2)	N(1)-C(3)	141(2)
Si(1)-O(1)	162.3(11)	N(1)-C(4)	145.7(13)
Si(1)-O(2)	166.1(7)	C(2)-C(5)	142(2)
Si(1)-O(3)	168.1(11)	C(3)-C(7)	144(2)
Si(1)-N(1)	212.3(6)	C(4)-C(6)	147(2)
Si(1)-C(1)	192.8(7)	C(5)-C(9)	149(2)
O(1)-C(5)	144(2)	C(6)-C(8)	153(2)
O(2)-O(6)	144.5(11)	C(7)-C(10)	134(2)
O(4)-Si-N(1)	85.8(6)		
O(4)-Br-C(1)	95(1)	C(2)-N(1)-C(4)	116.0(2)
O(4)′-Br′-C(1)	101(9)	C(3)-N(1)-C(4)	105.0(2)
O(1)-Si(1)-O(2)	121.4(9)	Br-C(1)-Br′	106.3(5)
O(1)-Si(1)-O(3)	118.1(5)	Br-C(1)-Si(1)	113.0(1)
O(1)-Si(1)-N(1)	85.8(6)	Br-C(1)-O(4)′	99.5(6)
O(1)-Si(1)-C(1)	95.4(7)	Br′-C(1)-Si(1)	119.0(1)
O(2)-Si(1)-O(3)	117.5(9)	Br′-C(1)-O(4)′	21.0(5)
O(2)-Si(1)-N(1)	83.8(3)	Si(1)-C(1)-O(4)′	106.0(8)
O(2)-Si(1)-C(1)	97.4(4)	N(1)-C(2)-C(5)	105.0(1)
O(3)-Si(1)-N(1)	82.8(6)	N(1)-C(3)-C(7)	113.5(9)
O(3)-Si(1)-C(1)	94.7(7)	N(1)-C(4)-C(6)	108.5(9)
N(1)-Si(1)-C(1)	177.6(9)	O(1)-C(5)-C(2)	113.0(2)
Si(1)-O(1)-C(5)	119.8(8)	O(1)-C(5)-C(9)	111.0(1)
Si(1)-O(2)-C(6)	119.4(8)	C(2)-C(5)-C(9)	118.0(1)
Si(1)-O(3)-C(7)	123.3(8)	O(2)-C(6)-C(4)	107.0(1)
Br′-O(4)′-C(1)	57.0(1)	O(2)-C(6)-C(8)	108.0(1)
Si(1)-N(1)-C(2)	103.4(9)	C(4)-C(6)-C(8)	111.0(1)
Si(1)-N(1)-C(3)	107.1(9)	O(3)-C(7)-C(3)	113.0(1)
Si(1)-N(1)-C(4)	105.1(6)	O(3)-C(7)-C(10)	120.0(1)
C(2)-N(1)-C(3)	119.0(1)	C(3)-C(7)-C(10)	125.0(1)

Crystal structure determination

Data for IIb were collected on an Enraf-Nonius CAD 4 diffractometer (Mo-K_α radiation, graphite monochromator (ψ-scan)). White crystals of the compound were obtained by procedure described previously [11]. The crystals have space group $P2_12_12_1$ with a unit cell $a = 875.3(3)$, $b = 1090.9(4)$, $c = 884.7(3)$ pm, $\beta = 111.69(2)°$, $Z = 2$, $V = 754.8$ Å^3. A total of 1762 unique reflections were collected in the range $\theta < 30°$, and 1117 of those had $I > 3\sigma(I)$.

The structure was solved by direct methods (MULTAN); refinement of the nonhydrogen atoms was carried out in anisotropic full matrix version. The hydrogen atoms were held at the fixed positions found in the difference Fourier synthesis and eventually refined with anisotropic temperature factors; the final residual factor was R = 0.053. The atomic coordinates are shown in Table 1 and the bond lengths and angles in Table 2 *.

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* Lists of observed and calculated structure factors are available from Dr. Tafeenko, c/o Prof. L.A. Aslanov, Department of Chemistry, Moscow State University, Moscow 119 899, USSR.

Compound IIb is a mixture of 4 diastereomers, and two enantiomeric molecular forms were present in the crystal. Two bromine atoms Br and Br′ and two oxygen atoms O(4) and O(4)′ are disordered between two positions, and as a result carbon atoms bonded to C(1) could not be located. The atoms Si(1), N(1) and C(1) are at distances of 17, 195 and 210 pm, respectively from a plane defined by the oxygen atoms O(1), O(2) and O(3).

Acknowledgments

We gratefully acknowledge the assistance of Dr. Tafeenko with the X-ray diffraction study.

Extensive editorial efforts by Prof. Eaborn to streamline this paper are gratefully acknowledged.

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