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The First Organobismuth Rings: $(RBi)_3$ and $(RBi)_4$, R = $(Me_3Si)_2CH$[**]

Hans Joachim Breunig,[*] Roland Rösler, and Enno Lork

Dedicated to Professor Bernt Krebs
on the occasion of his 60th birthday

Monocyclic oligomers $(RE)_n$, R = organo group, $n = 3 - 6$, are only well known for the three central elements of the fifth main group (E = P, As, Sb). The existence of the corresponding organobismuth rings is questionable. Compounds such as $(PhBi)_x$,[1] and $(2,4,6\text{-}Ph_3C_6H_2Bi)_x$,[2] which are described in the literature are possibly rings but their structures have not been proven. The first fully characterized organobismuth(I) compound is a dibismuthene: $(RBi)_2$ (R = 2,4,6-$[(Me_3Si)_2CH]_3C_6H_2$).[3]

Inorganic bismuth compounds have a tendency to form cyclic structures, for example, in the element bismuth, in polycyclic cations such as Bi_9^{5+}[4] and Bi_5^{3+},[5] and in bismutides such as Bi_4^{2-}.[6] Here we report the synthesis and the structure of the trimeric and tetrameric compounds **1** and **2**, the first organobismuth rings.

R_3Bi_3 R_4Bi_4 (R = $(Me_3Si)_2CH$)
1 **2**

Compounds **1** and **2** were synthesized by reduction of $RBiCl_2$[7] with magnesium filings in THF at −35 °C. In solution there is an equilibrium between the two organobismuth rings [Eq. (1)]. The equilibrium constant $K = [R_3Bi_3]^4/[R_4Bi_4]^3$ is $40 \pm 5\,mol\,L^{-1}$ in C_6D_6 at 23 °C. As

$$4\,R_3Bi_3 \rightleftharpoons 3\,R_4Bi_4 \qquad (1)$$

expected, the equilibrium is shifted in favor of the four-membered ring when the solution is cooled. Black crystals of **2** were grown from a solution in petroleum ether at low temperatures. When the crystals were dissolved in hydrocarbons fascinating color changes were observed: first the four-membered ring dissolved to give an intensive green solution. Within a few minutes the ring – ring equilibrium was established and the red color associated with the three-membered ring predominated in the solution. At low temperatures the fraction of **2** increased again and the solutions became first brown and then black on cooling. Both solutions of **1** and **2**, as well as the crystals of **2** are air-sensitive and thermolabile. In the absence of light and air, solutions in C_6D_6 decompose at ambient temperature with first-order kinetics to give R_3Bi[8] and bismuth. At 23 °C the concentrations of the rings decreased with half-life periods of 20.2 ± 2.0 h for **2** and 31.6 ± 2.7 h for **1**. At −28 °C the crystals of **2** and the solutions of **1** and **2** are stable for several months.

The structure of **1** can be derived from the NMR spectra. It is a tribismirane with $(Me_3Si)_2CH$ groups in *cis – trans* positions. The ^1H NMR spectrum shows singlets for the methine protons, with an intensity ratio 1:2. As a consequence of the diastereotopy at the substituents in the *cis* positions there are three signals of equal intensity for the methyl protons. The ^{13}C NMR spectrum contains three signals for the carbon atoms of the methyl groups and two broad signals for the carbon atoms of the methine groups. The line broadening is a consequence of the interactions with the quadrupole moment of the bismuth nucleus. Similar signal patterns are also found in the NMR spectra of the antimony analogue of **1**, which was recently characterized by X-ray crystallography.[9] The ^1H and ^{13}C NMR spectra of **2** in C_6D_6 show two signals each, corresponding to an *all-trans* arrangement of the alkyl substituents. To date **1** and **2** could not be characterized by mass spectrometry; even with soft ionization techniques only signals of decomposition products (R_3Bi, R_4Bi_2) could be identified. A single-crystal X-ray structure analysis for **2** confirmed the *all-trans* configuration of the tetrabismethane in the solid state (Figure 1).[10]

The structure contains a folded four-membered bismuth ring. The bismuth – bismuth bond lengths lie between 297.0(5) and 304.4(2) pm. Similar Bi – Bi bond lengths were also measured for dibismuthanes Ph_4Bi_2 (299.0(2)[11]) and $(Me_3Si)_4Bi_2$ (303.5(3)[12]). The anionic ring Bi_4^{2-} has slightly shorter bonds (293.6(2), 294.1(2) pm).[6] The double bond in the dibismuthene $[\{2,4,6\text{-}[(Me_3Si)_2CH]_3C_6H_2Bi\}_2]$ (Bi – Bi 282.06(8) pm) is even shorter.[3] The Bi – C distances in **2** vary between 233(2) and 239(2) pm. They are a little longer on average than in R_3Bi (R = $(Me_3Si)_2CH$, Bi–C 230.6(13) – 234.7(13) pm).[8] The Bi-Bi-Bi bond angles in **2** lie between 78.97(8)and 79.93(6)°; in contrast the Bi-Bi-C angles are relative large (range between 93.9(6) and 109.5(5)°). The larger Bi–Bi distances and Bi-Bi-C angles may be related to repulsive interactions of the alkyl substituents in the mole-

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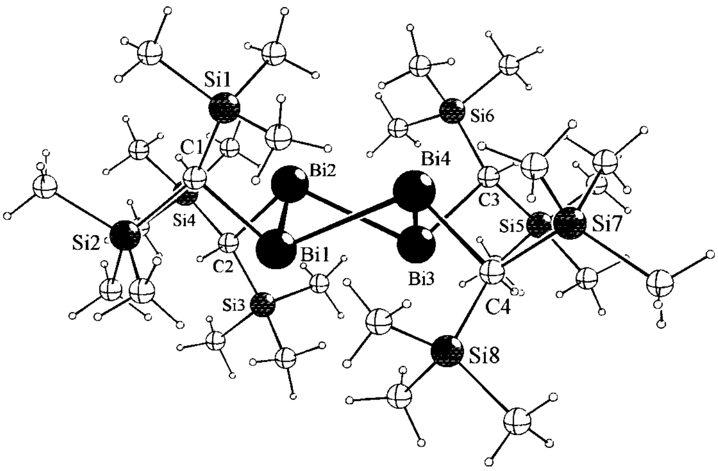

Figure 1. Structure of **2** in the crystal. Selected bond lengths [pm] and angles [°]: Bi(1)−Bi(2) 298.4(5), Bi(2)−Bi(3) 304.4(2), Bi(3)−Bi(4) 297.0(5), Bi(1)−Bi(4) 302.3(2), Bi(1)−C(1) 233(2), Bi(2)−C(2) 234.0(16), Bi(3)−C(3) 239.0(19), Bi(4)−C(4) 232(2), Bi(1)···Bi(3) 383.4, Bi(2)···Bi(4) 385.9; Bi(2)-Bi(1)-Bi(4) 79.93(6), Bi(1)-Bi(2)-Bi(3) 78.97(8), Bi(2)-Bi(3)-Bi(4) 79.82(8), Bi(1)-Bi(4)-Bi(3) 79.52(8), C(1)-Bi(1)-Bi(2) 93.9(6), C(1)-Bi(1)-Bi(4) 109.5(5), C(2)-Bi(2)-Bi(1) 97.9(5), C(2)-Bi(2)-Bi(3) 109.4(4), C(3)-Bi(3)-Bi(4) 97.1(5), C(3)-Bi(3)-Bi(2) 108.2(5), C(4)-Bi(4)-Bi(1) 107.5(5), C(4)-Bi(4)-Bi(3) 95.9(5); mean torsion angles Bi-Bi-Bi-Bi ± 46.12(8); mean fold angle between the Bi-Bi-Bi planes 112.7.

cules. As a consequence of the considerable folding of the four-membered ring, the Bi-Bi-Bi bond angles are surprisingly small for three-coordinate bismuth compounds. The fold angles are 112.6° and 112.9°. As in all four-membered rings $(RE)_n$ with *cis–trans* configuration the folding results from repulsive interactions of the substituents in 1,3-positions and from the tendency to avoid eclipsed conformations. The repulsive interactions should decrease with increasing bond lengths. Consequently, the folding decreases clearly from the phosphorus four-membered ring to the four-membered antimony ring (mean fold angles: $(RP)_4$ 109.8°,[13] $(RSb)_4$ 115.4°;[14] R = $(Me_3Si)_2CH$). An opposing effect is exerted by stabilising transannular E···E interactions.[15] The small increase of folding on the transition to the bismuth ring **2** may be related to transannular Bi···Bi contacts. The corresponding Bi−Bi distances are 383.4 and 385.9 pm. They clearly lie within the sum of the van der Waals radii of 480 pm.[16] For comparison with the analogous antimony ring $(RSb)_4$, the ratio E···E/E−E of the shortest E···E contact distance and the E–E bond length may be used.[12] The E···E/E−E ratio is 1.31 in $(RSb)_4$[14] but 1.29 in $(RBi)_4$ and displays the expected decrease for the heavier element. However, the difference from the corresponding antimony ring is minor and the prevailing impression is of a close relationship of the two structures.

Experimental Section

1 and **2**: All operations were carried out with careful exclusion of air in an argon atmosphere. At −80 °C a solution of $(Me_3Si)_2CHBiCl_2 \cdot 0.5\,Et_2O$ (1.48 g, 3.11 mmol) in THF (20 mL) was added dropwise with stirring to magnesium filings (0.25 g, 10.28 mmol) activated with 1,2-dibromoethane in THF (10 mL). Thereafter the mixture was warmed to −35 °C, stirred for 6 h at −35 °C and 1 h at −15 °C. The solvent was removed in vacuo and the residue was extracted with petroleum ether (250 mL). The dark brown solution was filtered at −10 °C through a frit and concentrated to dryness. After removal of the solvent a dark brown solid consisting of **1** and **2** remained. Yield 0.78 g, 68 %. Large black crystals of **2**, m.p. 89–91 °C, grew from a solution of the cyclobismuthane mixture in petroleum ether −28 °C in several weeks. Elemental analysis of $C_{28}H_{76}Bi_4Si_8$ (**2**): calcd. C 22.82, H 5.20; found: C 22.10, H 5.16; ^1H NMR (200 MHz, C_6D_6, 23 °C): **1**: $\delta = 0.25$ (s, $^2J(Si,H) = 6.4$ Hz, 18 H; *trans*-CH_3), 0.28 (s, $^2J(Si,H) = 6.2$ Hz, 18 H; *cis*-CH_3^a), 0.40 (s, $^2J(Si,H) = 6.3$ Hz, 18 H; *cis*-CH_3^b), 1.87 (s, $^2J(Si,H) = 7.7$ Hz, 1 H; *trans*-CH), 2.20 (s, $^2J(Si,H) = 7.5$ Hz, 2 H; *cis*-CH); **2**: $\delta = 0.33$ (s, $^2J(Si,H) = 6.3$ Hz, 18 H; CH_3), 2.31 (s, $^2J(Si,H) = 8.0$ Hz, 1 H; CH); ^{13}C NMR (50 MHz, C_6D_6, 23 °C): **1**: $\delta = -2.37$ (br, *cis*-CH), −0.70 (br, *trans*-CH), 4.53 (*cis*-CH_3^b), 5.50 (*trans*-CH_3), 6.02 (*cis*-CH_3^a); **2**: $\delta = 3.78$ (br, CH), 6.20 (CH_3). C,H correlation with HSQC and HMBC spectra; the indices a and b refer to the diastereotopic methyl groups. MS (CI+, NH_3): *m*/*z* (%): 1071 (5) $[[(Me_3Si)_2CH]_4Bi_2 + NH_4^+]$, 918 (6), 1071 (5) $[[(Me_3Si)_2CH]_2Bi + NH_4^+]$, 687 (15) $[[(Me_3Si)_2CH]_3Bi^+]$, 671 (23) $[[(Me_3Si)_2CH]_3Bi^+ - CH_3]$, 627 (100) $[[(Me_3Si)_2CH]_2Bi^+]$.

The decomposition of a mixture of **1** and **2** (115 mg) in C_6D_6 (1 mL) at 23 °C was monitored by ^1H NMR spectroscopy, with 60 $mmol\,L^{-1}$ TMS as reference. The equilibrium constant was determined from the ratio of intensities of the signals of **1** and **2**. The decomposition products are $[(Me_3Si)_2CH]_3Bi$[8] and elemental Bi. $[(Me_3Si)_2CH]_3Bi$: ^1H NMR (200 MHz, C_6D_6, 23 °C): $\delta = 0.29$ (s, $^2J(Si,H) = 6.2$ Hz, 18 H; CH_3), 1.37 (s, $^2J(Si,H) = 8.6$ Hz, 1 H; CH); ^{13}C NMR (50 MHz, C_6D_6, 23 °C): $[(Me_3Si)_2CH]_3Bi$ $\delta = 5.05$ (br; CH_3), 8.73 (br; CH).

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[10] X-ray structure analysis of **2** ($C_{28}H_{76}Bi_4Si_8$), $M_r = 1473.53$; crystal size $0.7 \times 0.6 \times 0.4$ mm^3; triclinic, space group $P\bar{1}$, $a = 1242(2)$, $b = 1307.1(7)$, $c = 1678.5(9)$ pm, $\alpha = 107.74(4)$, $\beta = 91.71(7)$, $\gamma = 102.56(6)$°, $V = 2.519(5)$ nm^3, $Z = 2$, $\rho_{calcd} = 1.943$ $Mg\,m^{-3}$, $\mu = 14.136$ mm^{-1}. A suitable single crystal was fixed with Kel-F oil on a glass fiber and measured on a Siemens P4 four-circle diffractometer at −100 °C. With graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm) in $\omega/2\theta$ scan mode 7334 intensities were collected ($2.56° < \theta < 22.50°$); 6149 reflections ($R_{int} = 0.0549$) remained after averaging. After Lp correction the structure was solved by direct methods. The refinement converged after an absorption correction (DIFABS)[17] at $wR_2 = 0.1447$ (refinement against F^2) for all the 6149 reflections and 387 variables ($R1 = 0.0562$ for 4308 reflections with $I > 2\sigma(I)$). Heavy atoms obtained individual anisotropic displacement parameters. The hydrogen atoms were refined with a riding model and a common isotropic temperature factor. Max/min residual electron density: 1771/−1748 $e\,nm^{-3}$. The structure solution and refinement was carried out using SHELX-97.[18] For the figure the Diamond program was used.[19] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101535. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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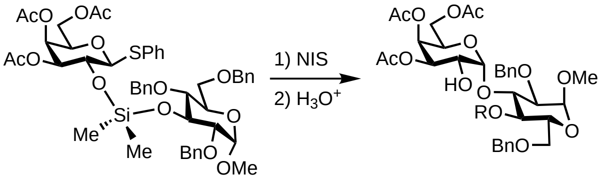
A New Intramolecular Reaction for the Regioselective Debenzylation or Protection of Alcohols**

Jacob Madsen and Mikael Bols*

In an earlier study of silicon-tethered intramolecular glycosidation reactions it was observed that treatment of compound **1** with *N*-iodosuccinimide (NIS) gave both the expected glycoside **2** and an unexpected debenzylated product **2a** (Scheme 1).[1] Originally we believed that this debenzylation reaction followed an intramolecular pathway involving silicon during the glycosidation procedure. We came to this conclusion for two reasons: The reaction was regioselective, and if the reaction mixture was not treated with acid after the glycosidation, a debenzylated, silicon-bridged product was isolated (Figure 1).[1a]



1

2 R = Bn
2a R = H

Scheme 1. Intramolecular glycosidation with formation of two products. Bn = benzyl.

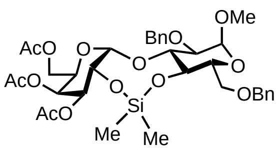
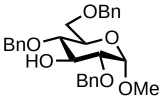
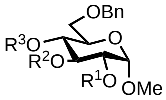
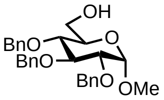
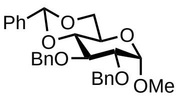
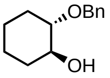
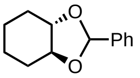
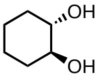
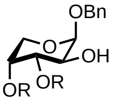
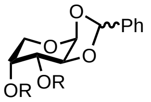
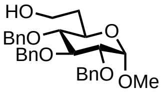
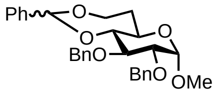


Figure 1. Compound isolated when the reaction mixture from Scheme 1 was not treated with acid.

We have now reinvestigated the reaction (Scheme 1) and have come to the conclusion that the debenzylation apparently is not connected to the glycosidation process. In fact treatment of compound **2** with NIS in $MeNO_2$ gave compound **2a** (Table 1). This indicated an intermolecular reaction and indeed no participation by silicon. On the other hand the regioselectivity of the debenzylation suggested an intramolecular reaction and in that case the only possibility seemed to be participation of the free OH group at C-2 in the galactose unit.

Table 1. Reaction of benzylated compounds containing free OH groups with NIS.[11]

Reactant	Product	Solvent/Equiv. NIS	Yield [%]
2	**2a**	$MeNO_2$/2.5	36[a]
 **4**	 **5** R^1 = Bn, R^2 = R^3 = H **6** R^1 = R^2 = H, R^3= Bn	$MeNO_2$/2.5[b]	80 (32) (48)
 **7**	 **8**	$MeNO_2$/5[c]	74
 **9**	 **10**	CH_2Cl_2/2.5[d]	49
9	 **11**	CH_2Cl_2/2.5[b, d]	66
 **12** R = H **14** R, R = CMe_2	 **13** R = H **15** R, R = CMe_2	CH_3CN/5	41–44
 **16**	 **17**	$MeNO_2$/5	84

[a] Not optimized. The crude product was a 2:1 mixture of **2** and **2a**, respectively, so the recovered yield was very high. [b] Treatment with TFA/H_2O 5/1. [c] Reaction with 20 equiv NIS gave **8** in 76% yield. [d] Reaction at room temperature.

The presence of the unprotected alcohol was found to be essential. When glucose derivative **3**[2] (Scheme 2) was treated with NIS (5 equiv), no reaction was observed even on addition of water or methanol. In contrast, when readily available alcohol **4**[3] was refluxed for 2 h in $MeNO_2$ with NIS (2.5 equiv) quantitative conversion to less polar products was observed (by thin-layer chromatography) with simultaneous formation of iodine (Table 1). These products could not be purified by chromatography due to their instability, but on

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