Synthesis and crystal structure of 7,7,10-trimethyl-7-silabenzo[*a*]anthrone

V. M. Polosin,[a] *A. A. Astakhov,*[b] *M. A. Ryashentseva,*[c]* *and V. A. Tafeenko*[d]

[a]*State Scientific Research Institute of Reagents and Extra Pure Chemicals,*
3 Bogorodsky val, 107076 Moscow, Russian Federation.
Fax: 007 (095) 963 7525
[b]*Russian People's Frendship University,*
6 ul. Miklukho-Maklaya, 117198 Moscow, Russian Federation.
Fax: 007 (095) 954 1271
[c]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: 007 (095) 135 5328
[d]*Department of Chemistry, M. V. Lomonosov Moscow State University,*
Vorob'evy Gory, 119899 Moscow, Russian Federation.
Fax: 007 (095) 936 3654

Skeletal isomerization of arylsilanes that occurs under conditions of catalytic dehydrocyclization and is accompanied by migration of the triorganosilyl group was additionally confirmed by dehydrocyclization of dimethyl(2,4-dimethylphenyl)(1-naphthyl)silane on chromium-containing oxide catalysts.

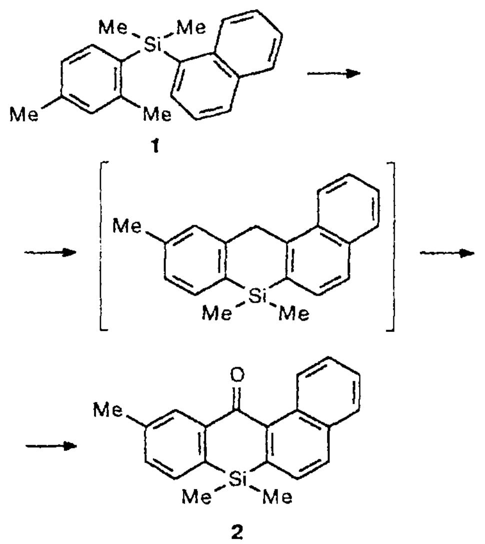
Key words: catalytic dehydrocyclization, 7,7,10-trimethyl-7-silabenzo[*a*]anthrone, X-ray structural analysis.

In the study of catalytic dehydrocyclization of 2-thienyl- and 2-benzo[*b*]thienyltriorganosilanes on aluminochromium oxide catalysts, we found an unusual skeletal isomerization of the initial compounds, which was accompanied by migration of the triorganosilyl substituent from the α position to the β position of the thiophene fragment of the molecule with simultaneous dehydrocyclization.[1—4] It was suggested that aromatic compounds that contain a silyl substituent and a free *ortho* position should undergo analogous conversions. To confirm this hypothesis, in this work we studied high-temperature catalytic dehydrocyclization of dimethyl(2,4-dimethylphenyl)(1-naphthyl)silane (**1**) (Scheme 1).

The initial silane **1** was prepared by successive treatment of 1-bromonaphthalene with butyllithium and dimethyl(2,4-dimethylphenyl)chlorosilane in ether. Dehydrocyclization of compound **1** was carried out in a flow system in a quartz reactor (d = 30 mm, l = 250 mm) using a catalyst of the following composition (wt. %): 5 Cr_2O_3, 1 K_2O, 5 Ln_xO_y (2.7 CeO_2, 1.3 La_2O_3, 0.75 Nd_2O_3, 0.25 Pr_6O_{11}), 89 γ-Al_2O_3 (A-1 grade)[5] and an IM-2204 industrial catalyst for dehydrogenation. The yield of liquid products of this reaction was 75—85%. The reaction products (without prior separation) were oxidized with $KMnO_4$ in acetone. Product **2** was isolated by column chromatography in 8% yield. No other cyclic products were detected in the reaction mixture.

The results of X-ray structural analysis of single crystals of compound **2** (Fig. 1) provide evidence that, as in the case of 2-thienyl- and 2-benzo[*b*]thienylsilanes, dehydrocyclization of silane **1** proceeds with isomerization of the initial molecule. It was demonstrated that the molecule of compound **2** is nonplanar. Substantial deformation is caused by repulsion between the hydrogen atom at C(11) and the oxygen atom. As a result, the angle between the planes of the naphthalene and benzene fragments is 27.7°. The oxygen and the silicon atoms deviate from the plane of the benzene ring by 0.65

Scheme 1



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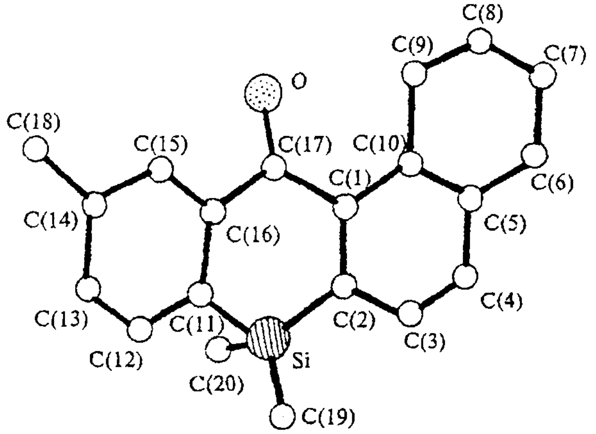

Fig. 1. Overall view of molecule **2** (H atoms are omitted).

and 0.14 Å, respectively. The geometric parameters of the aromatic fragments of the molecule and the bond lengths and bond angles at the silicon atom are close to the corresponding tabular values.[6]

Experimental

The IR spectra were recorded on an IR-435 instrument (KBr pellets and films). The mass spectra were measured on a Hitachi M-80A instrument. The purity of the resulting compound was monitored by TLC on Silufol UV-254 plates in a 5 : 1 hexane—ethyl acetate system; visualization was carried out with iodine vapor.

1-Bromonaphthalene of chemically pure grade was used. Dimethyl(2,4-dimethylphenyl)chlorosilane was prepared according to a known procedure.[7]

Dimethyl(2,4-dimethylphenyl)(1-naphthyl)silane (1). 1-Bromonaphthalene (16.6 g, 80 mmol) was added to a mixture of *n*-butyllithium (5.5 g, 85 mmol) in hexane (80 mL) and diethyl ether (150 mL) under a flow of dry argon at −10 °C. The reaction mixture was stirred for 20 min. Then a solution of dimethyl(2,4-dimethylphenyl)chlorosilane (15.9 g, 80 mmol) in ether (20 mL) was added. The reaction mixture was stirred for 5 h, kept for ~12 h, and treated with an aqueous solution of NH_4Cl. The organic layer was separated and dried with $MgSO_4$. The solvent was evaporated, and the residue was fractionated. Compound **1** was obtained as a vitreous oil in a yield of 15.7 g (68%), b.p. 160—162 °C (2 Torr), n_D^{20} 1.6138. Found (%): C, 82.73; H, 7.59. $C_{20}H_{22}Si$. Calculated (%): C, 82.75; H, 7.58. IR, ν/cm^{-1}: 1255, 820 ($SiMe_2$). Mass spectrum (EI, 70 eV), *m/z* (I_{rel} (%)): 290 $[M]^+$ (100), 275 $[M-Me]^+$ (65).

7,7,10-Trimethyl-7-silabenzo[*a*]anthrone (2). A solution of compound **1** (13 g, 44 mmol) in benzene (30 mL) was passed over a catalyst at a rate of v_w = 0.5—1.0 h^{-1} at 560—580 °C. After completion of the reaction, benzene (10 mL) was passed over the catalyst to wash off the reaction products from the catalyst. The catalyzate was concentrated. The residue (10.2 g) was dissolved in acetone (150 mL), and

Table 1. Atomic coordinates (×10^4; for H, ×10^3) in molecule **2**

Atom	*x*	*y*	*z*
Si	3199(2)	1577.5(8)	1636.3(4)
O	1295(5)	396(2)	406(1)
C(1)	685(6)	451(2)	1231(1)
C(2)	1555(6)	709(3)	1645(1)
C(3)	1152(6)	291(3)	2079(2)
C(4)	−70(7)	−317(3)	2099(2)
C(5)	−1038(6)	−572(3)	1691(2)
C(6)	−2350(7)	−1196(3)	1713(2)
C(7)	−3260(7)	−1438(3)	1322(2)
C(8)	−2916(7)	−1049(3)	866(2)
C(9)	−1638(6)	−451(3)	839(2)
C(10)	−651(6)	−185(2)	1244(2)
C(11)	2559(6)	2154(1)	1092(1)
C(12)	3012(6)	2981(3)	1003(2)
C(13)	2613(6)	3368(3)	579(2)
C(14)	1777(6)	2941(3)	216(2)
C(15)	1339(6)	2122(3)	289(2)
C(16)	1702(5)	1729(2)	721(1)
C(17)	1232(6)	825(2)	760(1)
C(18)	1391(7)	3348(3)	−260(2)
C(19)	2974(8)	2245(4)	2179(2)
C(20)	5512(7)	1171(4)	1583(2)
H(3)	180(5)	45(2)	236(1)
H(4)	−33(5)	−62(2)	237(1)
H(6)	−257(7)	−139(3)	201(2)
H(7)	−432(6)	−188(3)	134(2)
H(8)	−362(6)	−117(3)	60(2)
H(9)	−151(7)	−15(3)	55(2)
H(12)	356(5)	328(2)	126(1)
H(13)	299(5)	394(2)	53(1)
H(15)	79(4)	180(2)	5(1)
H(181)	78(7)	386(3)	−18(2)
H(182)	55(7)	309(3)	−46(2)
H(183)	216(7)	359(3)	−34(2)
H(191)	319(6)	191(2)	245(2)
H(192)	178(7)	244(3)	219(2)
H(193)	388(7)	241(3)	216(2)
H(201)	565(7)	80(3)	183(2)
H(202)	553(7)	78(3)	133(2)
H(203)	628(6)	162(3)	153(2)

Table 2. Bond lengths (*d*) in molecule **2**

Bond	*d*/Å
Si—C(2)	1.863(4)
Si—C(11)	1.848(4)
Si—C(19)	1.870(5)
Si—C(20)	1.860(5)
O—C(17)	1.210(5)
C(1)—C(2)	1.395(6)
C(1)—C(10)	1.432(6)
C(1)—C(17)	1.508(5)
C(2)—C(3)	1.420(6)
C(3)—C(4)	1.341(7)
C(3)—H(3)	0.96(4)
C(4)—C(5)	1.414(6)
C(4)—H(4)	0.93(3)
C(5)—C(6)	1.407(7)
C(5)—C(10)	1.429(6)
C(6)—C(7)	1.349(8)
C(6)—H(6)	0.90(4)
C(7)—C(8)	1.396(8)
C(7)—H(7)	1.07(5)
C(8)—C(9)	1.365(7)
C(8)—H(8)	0.97(4)
C(9)—C(10)	1.416(6)
C(9)—H(9)	0.95(5)
C(11)—C(12)	1.395(6)
C(11)—C(16)	1.400(6)
C(12)—C(13)	1.376(6)
C(12)—H(12)	0.95(4)
C(13)—C(14)	1.377(6)
C(13)—H(13)	0.97(4)
C(14)—C(15)	1.374(6)
C(14)—C(18)	1.514(7)
C(15)—C(16)	1.392(6)
C(15)—H(15)	0.94(3)
C(16)—C(17)	1.500(5)
C(18)—H(181)	0.97(5)
C(18)—H(182)	0.93(5)
C(18)—H(183)	0.73(5)
C(19)—H(191)	0.96(4)
C(19)—H(192)	0.95(5)
C(19)—H(193)	1.01(6)
C(20)—H(201)	0.93(5)
C(20)—H(202)	0.94(5)
C(20)—H(203)	0.93(5)

Table 3. Bond angles (ω) in molecule **2**

Angle	ω/deg
C(2)—Si—C(11)	102.4(2)
C(2)—Si—C(19)	111.1(2)
C(2)—Si—C(20)	110.8(2)
C(11)—Si—C(19)	111.1(2)
C(11)—Si—C(20)	110.6(2)
C(19)—Si—C(20)	110.5(3)
C(2)—C(1)—C(10)	121.3(4)
C(2)—C(1)—C(17)	118.8(4)
C(10)—C(1)—C(17)	119.8(3)
Si—C(2)—C(1)	121.4(3)
Si—C(2)—C(3)	120.5(3)
C(1)—C(2)—C(3)	118.1(4)
C(2)—C(3)—C(4)	121.7(4)
C(2)—C(3)—H(3)	117(2)
C(4)—C(3)—H(3)	121(2)
C(3)—C(4)—C(5)	121.9(4)
C(3)—C(4)—H(4)	124(2)
C(5)—C(4)—H(4)	114(2)
C(4)—C(5)—C(6)	122.0(4)
C(4)—C(5)—C(10)	118.6(4)
C(6)—C(5)—C(10)	119.4(4)
C(5)—C(6)—C(7)	121.6(5)
C(5)—C(6)—H(6)	115(3)
C(7)—C(6)—H(6)	124(3)
C(6)—C(7)—C(8)	119.2(5)
C(6)—C(7)—H(7)	123(2)
C(8)—C(7)—H(7)	118(2)
C(7)—C(8)—C(9)	121.9(5)
C(7)—C(8)—H(8)	122(3)
C(9)—C(8)—H(8)	116(3)
C(8)—C(9)—C(10)	120.2(4)
C(8)—C(9)—H(9)	120(3)
C(10)—C(9)—H(9)	119(3)
C(1)—C(10)—C(5)	118.3(4)
C(1)—C(10)—C(9)	124.1(4)
C(5)—C(10)—C(9)	117.6(4)
Si—C(11)—C(12)	124.2(3)
Si—C(11)—C(16)	119.2(3)
C(12)—C(11)—C(16)	116.3(4)
C(11)—C(12)—C(13)	122.2(4)
C(11)—C(12)—H(12)	117(2)
C(13)—C(12)—H(12)	121(2)
C(12)—C(13)—C(14)	120.8(4)
C(12)—C(13)—H(13)	119(2)
C(14)—C(13)—H(13)	120(2)
C(13)—C(14)—C(15)	118.5(4)
C(13)—C(14)—C(18)	121.5(4)
C(15)—C(14)—C(18)	120.0(4)
C(14)—C(15)—C(16)	121.2(4)
C(14)—C(15)—H(15)	122(2)
C(16)—C(15)—H(15)	117.2(2)
C(11)—C(16)—C(15)	121.0(4)
C(11)—C(16)—C(17)	121.8(3)
C(15)—C(16)—C(17)	117.2(3)
O—C(17)—C(1)	120.1(4)
O—C(17)—C(16)	118.9(4)
C(1)—C(17)—C(16)	121.0(3)
C(14)—C(18)—H(181)	104(3)
C(14)—C(18)—H(182)	117(3)
C(14)—C(18)—H(183)	111(4)
H(181)—C(18)—H(182)	101(5)
H(181)—C(18)—H(183)	91.5(5)
H(182)—C(18)—H(183)	125(5)
Si—C(19)—H(191)	108(3)
Si—C(19)—H(192)	108(3)
Si—C(19)—H(193)	109(3)
H(191)—C(19)—H(192)	108(4)
H(191)—C(19)—H(193)	110(4)
H(192)—C(19)—H(193)	114(4)
Si—C(20)—H(201)	106(3)
Si—C(20)—H(202)	108(3)
Si—C(20)—H(203)	109(3)
H(201)—C(20)—H(202)	97(4)
H(201)—C(20)—H(203)	124(4)
H(202)—C(20)—H(203)	113(4)

$KMnO_4$ was added portionwise until the solution developed a steady pink color. The precipitate of MnO_2 was filtered off, the acetone was evaporated, and the residue was chromatographed on a column packed with SiO_2 (a 1 : 5 ethyl acetate—hexane mixture as the eluent). The initial compound **1** (R_f 0.84) was isolated in a yield of 6.1 g. Compound **2** (R_f 0.53) was obtained as pale-yellow crystals in a yield of 1.2 g (8%), m.p. 109—110 °C (from hexane). Found (%): C, 79.50; H, 5.98. $C_{20}H_{18}OSi$. Calculated (%): C, 79.47; H, 5.96. IR, ν/cm^{-1}: 1250 ($SiMe_2$); 1630 (C=O); 3035 (C—H). Mass spectrum (EI, 70 eV), m/z (I_{rel} (%)): 302 $[M]^+$ (40), 287 $[M-Me]^+$ (25), 227 $[M-SiMe_2-OH]^+$ (100).

X-ray structural analysis of compound 2. Crystals of compound **2** are orthorhombic, at 20 °C, a = 7.504(2) Å, b = 16.075(3) Å, c = 28.026(3) Å, V = 3380 $Å^3$, Z = 8, space group *Pbca*. The unit cell parameters and intensities of reflections were measured on an automated four-circle CAD-4 Enraf Nonius diffractometer (Mo-Kα radiation, graphite monochromator, ω scanning technique). A total of 2131 nonzero reflections were collected in the region $\theta \le 25$ °, of which 1402 reflections with $I > 3\,\sigma(I)$ were used in the refinement of positional and thermal parameters of the molecule, whose structure was solved by direct methods with the use of the MULTAN program from the SDP program package. Positional and thermal parameters of nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method. The positions of the hydrogen atoms were located from Fourier syntheses and refined isotropically. The final value of the R factor was 4.3%.

Molecule **2** (H atoms are omitted) is shown in Fig. 1. The atomic coordinates are given in Table 1. The bond lengths and bond angles are listed in Tables 2 and 3, respectively.

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