EXPERIMENTAL

Compounds I-XII were prepared according to known methods [11, 12]. Their constants agreed with published data.

The mass spectra were obtained with a Hewlett-Packard 5985 instrument at an ionization tension of 70 eV. The temperature of the ionic source was 200°C in a direct input regime. The temperature of the setting system was 150-220°C. A thermogravimetric investigation of compounds I-XII by the material evaporation curves in the mass spectrometer and according to DTA curves, taken with a derivatograph manufactured by MOM (Hungary), showed that in the conditions used for recording the mass spectra the investigated substances did not pyrolyze.

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Z,E-ISOMERS OF 10,10-DIMETHYL-9-BENZYLIDENE-9,10-DIHYDRO-10-SILA-2-AZAANTHRACENE AND REACTIONS OF 10,10-DIMETHYL-9,10-DIHYDRO-10-SILA-2-AZAANTHRACENE UNDER CONDITIONS OF BASIC CATALYSIS

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UDC 547.836:546.287

The synthesis of 9-benzylidenesilaazaanthracenes has been achieved, and the configurations of their Z- and E-isomers have been established. The reactions of silaazaanthracene in the presence of aromatic aldehydes and bases have been studied; these result in dimerization, oxidation, cleavage of the Si–C bond, and desilylation of the heterocyclic system.

We have previously synthesized various examples of dihydrosilaazaanthracenes and have studied their conformational states [1-3]. Based on the feasibility of the existence of their 9-benzylidene derivatives in the form of geometric isomers, differing from one another in the position of the phenyl group of the benzylidene fragment relative to the pyridine ring,

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TABLE 1. PMR Spectra of Silaazaanthracenes IIa, b, V

Compound	Chemical shifts, δ, ppm ($CDCl_3$, 20°C, TMS as internal standard)									
	1-H	3-H	4-H	5-H	6-H	7-H	8-H	CH	$Si-CH_3$	phenylene protons
IIa	8,39	8,42	7,51	7,61	7,35	7,46	7,78	7,07	0,53	7,10—7,25
IIb	8,95	8,52	7,44	7,63	7,26	7,11	7,28	6,97	0,53	7,15—7,25
V	7,41	8,34	7,49	7,66	7,21	6,90	6,20	4,05*	0,66 0,80	—

	Spin-spin coupling constant, J, Hz							
	1—4	3—4	5—6	5—7	5—8	6—7	6—8	7—8
IIa	0,8	4,7	7,3	1,5	0,8	7,6	1,1	7,9
IIb	0,8	4,7	7,3	1,6	0,8	7,6	1,2	7,8
V	—	4,8	7,5	1,6	~1,0	7,5	1,1	7,5

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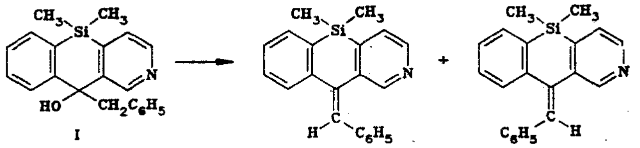
*Signal of the 9-H proton.

we have now demonstrated the synthesis of these derivatives from 10,10-dimethyl-9-benzyl-9,10-dihydro-10-sila-2-azaanthracen-9-ol (I). Dehydration of this tertiary alcohol was accomplished by heating it in thionyl chloride followed by subsequent workup of the intermediate tertiary chloride derivative with pyridine. The Z and E isomers of 10,10-dimethyl-9-benzylidene-9,10-dihydro-10-sila-2-azaanthracene (IIa, b) were isolated chromatographically, in a 2:1 ratio, from the product mixture; these isomers differed from one another both in their chromatographic mobilities as well as in their melting points. An analogous relationship was observed in the case of the geometric isomers of 9-benzylideneazafluorenes [4].

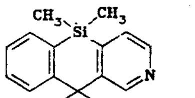
Extended reflux of silaazaanthrol I in thionyl chloride resulted in the isolation of the Z-isomer IIa in the form of its hydrochloride. 10,10-Dimethyl-9-bromo-9-(α-bromobenzyl)-9,10-dihydro-10-sila-2-azaanthracene (III) was prepared by bromination of the mixtures of isomers of compounds II.



I

Z, IIa

E, IIb



III

The structures of the geometric isomers of compound II were solved based on their PMR spectral data (Table 1). The high-field (by approximately 0.5 ppm) shifts of the 1-H proton signal in the Z-isomer and the 8-H proton signal in the E-isomer, due to the magnetic anisotropic effect of the phenyl ring in the benzylidene fragment, were especially useful in this regard (Table 1). PMR analysis also revealed that the central ring in the benzylidenesilaazaanthracenes IIa, b exists in a tub-shaped conformation, which undergoes rapid interconversion in solution at 20°C [5].

Treatment of 10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (IV) with aromatic aldehydes under base catalyzed conditions did not result in the formation of benzylidene derivatives analogous to compound II. Compound IV undergoes different reactions in the presence of N-nitrobenzaldehyde, depending on the reaction conditions. Upon heating in alcoholic sodium ethoxide solution with p-nitrobenzaldehyde compound IV gave di(10,10-dimethyl-10-sila-2-azaanthracen-9-yl) (V) in 30% yield. It is significant that this compound is not formed when silaazaanthracene IV is heated with sodium ethoxide in p-nitrobenzene solution. The PMR spectrum of compound V exhibited an anomalously greater high field shift of the 1-H (1.13 ppm) and 8-H (1.34 ppm) proton signals, compared to that observed for the corresponding

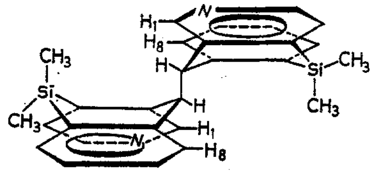
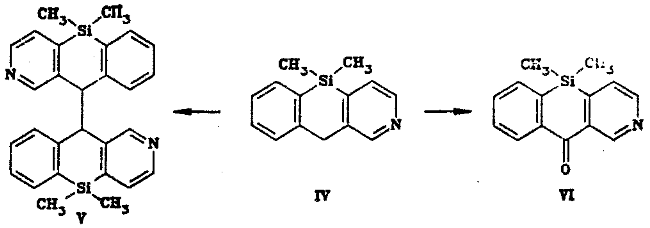


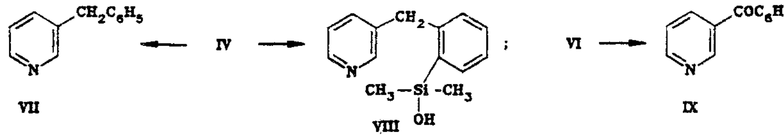
Fig. 1. Structure of di(silaazaanthracen-9-yl) V.

protons in silaazaanthracene IV; this may be explained in terms of the stereochemistry of the dimer. Diaxial annelation of silaazaanthracene fragments which exist in tub conformations apparently results in the conformer with an anti distribution of these two fragements being favored, due to steric hindrance (see Fig. 1). As a consequence, the 1-H and 8-H protons of one of the fragments will reside in the region of the diamagnetic ring current effect of the aromatic rings of the other fragment. In this type of conformation the methine 9-H proton also comes under the influence of the shielding zone; thus the chemical shift of this proton in the dimer V (4.05 ppm) occurs at higher field than the methylene protons in silaazaanthracene IV (4.20 ppm) (see Table 1).

The main product obtained upon treatment of silaazaanthracene IV with p-nitrobenzaldehyde in the presence of triethylamine, or benzaldehyde and anisyl aldehyde in the presence of sodium ethoxide in alcohol, as well as with Triton B in pyridine, was 10,10-dimethyl-10-sila-2-azaanthrone (VI).



More extensive degradative conversions of compound IV under conditions of basic catalysis have also been noted, namely, cleavage of the Si—C bonds and desilylation. The main product isolated upon heating compound IV with p-nitrobenzaldehyde in DMSO in the presence of potassium ethoxide was β-benzylpyridine (VII), whereas in the presence of veratric aldehyde in potassium tert-butoxide at 20°C compound IV was converted to 3-(o-dimethyloxysilylbenzyl)pyridine (VIII).



Silaazaanthrone VI was also desilylated under the influence of potassium ethoxide in DMSO to give 3-benzoylpyridine (IX) in 34% yield. The structure of silylbenzylpyridine VIII was proved based on its IR and mass spectra. The mass spectrum exhibited the molecular ion peak at m/z 243, corresponding to the correct molecular formula, as well as fragment ions which are attributed to elimination of water and OH, CH_3, and $Si(CH_3)_2OH$ groups. The IR spectrum of pyridine VIII contains a broad band at 3400 cm^{-1} for the bound hydroxyl group.

EXPERIMENTAL

PMR spectra were recorded on WP-80-SY (80 MHz) and WM-400 (400 MHz) spectrometers. IR spectra were obtained on a UR-20 spectrophotometer using KBr pellets. Mass spectra were measured on MX-1303 and Varian CH-8 spectrometers. TLC analyses were carried out using either Silufol UV-254 grade silica gel or activity II grade Al_2O_3. Column chromatography was carried out using either L100/160 grade silica gel or activity II grade Al_2O_3.

10,10-Dimethyl-9-benzyl-9,10-dihydro-10-sila-2-azaanthracen-9-ol (I). A solution of benzylmagnesium chloride, prepared from 9.4 g (7.5 mmole) benzyl chloride and 1.8 g (7.5 mmole) magnesium in 100 ml absolute ether, was treated with 4 g (1.7 mmole) of 10,10-dimethyl-10-sila-2-azaanthrone. The mixture was refluxed for 6 h, cooled, and decomposed by the addition of a saturated solution of ammonium chloride. The reaction products were extracted into ether. The ether extract was then dried over magnesium sulfate. The residue remaining after solvent evaporation was chromatographed on a column (h = 30 cm, d = 2 cm) with silica gel. Preliminary elution with hexane gave 0.3 g of the silaazaanthrone precursor; subsequent elution with a mixture of ethyl acetate and heptane (1:1) gave 4.9 g (89%) of silaazaanthrol I. White crystals, mp 185-186°C (from heptane); R_f 0.26 (Silufol, ethyl acetate—heptane, 1:4). PMR spectrum ($CDCl_3$): 8.80 (1H, s, 1-H); 8.02 (1H, d, 3-H); 4.0 (1H, br. s, OH); 3.00 (2H, s, CH_2); 0.45 (3H, s, Si—CH_3); 0.16 ppm (3H, s, Si—CH_3). Found, %: C 76.2; H 6.1; N 4.3; M^+ 331. $C_{21}H_{21}NOSi$. Calculated, %: C 76.1; H 6.3; N 4.2; M 331.

10,10-Dimethyl-9-benzylidene-9,10-dihydro-10-sila-2-azaanthracene (II). A. A solution of 2.15 g (6.5 mmole) silaazaanthrol I in 17.8 g (0.15 mole) thionyl chloride was refluxed for 1 h and 30 min. The residue remaining after distillation of excess thionyl chloride was heated with 15 ml pyridine. After removal of the pyridine and crystallization of the reaction mixture from heptane, 1.98 g (98%) of a mixture of isomers of silaazaanthracene II was obtained, which was chromatographed on a silica gel column (h = 60 cm, d = 2 cm) with a mixture of hexane—ethyl acetate, 10:1, as eluent. The Z-isomer IIa (1.03 g) eluted first. Colorless crystals, mp 83-84°C (from heptane—ethyl acetate), R_f 0.65 (Silufol, ethyl acetate—hexane, 1:3). Found, %: C 80.5; H 6.0; N 4.7; M^+ 313. $C_{21}H_{19}NSi$. Calculated, %: C 80.5; H 6.1; N 4.5; M 313. This was followed by 0.3 g of a mixture of isomers IIa, b. Finally, 0.48 g of the E-isomer IIb was eluted. Colorless crystals, mp 126-127°C (from heptane—ethyl acetate); R_f 0.45 (Silufol, ethyl acetate—hexane, 1:3). Found, %: C 80.5; H 6.3; N 4.6; M^+ 313. $C_{21}H_{19}NSi$. Calculated, %: C 80.5; H 6.1; N 4.5; M 313.

B. Silaazaanthrol I (1 g, 3 mmole) was dissolved in 8.3 g (70 mmole) thionyl chloride and the mixture was refluxed for 8 h. The residue remaining after distillation of thionyl chloride was triturated with absolute ether. Yield 0.91 g (86%) of the hydrochloride of silaazaanthracene IIa. Colorless crystals, mp 206-210°C (dec.); R_f 0.65. Found, %: C 72.1; H 5.6; Cl 9.9; N 3.6. $C_{21}H_{20}ClNSi$. Calculated, %: C 72.2; H 5.7; Cl 10.0; N 4.0.

10,10-Dimethyl-9-bromo-9-(α-bromobenzyl)-9,10-dihydro-10-sila-2-azaanthracene (III). To a solution of 0.4 g (1.3 mmole) of a mixture of isomers of compound II in 6 ml chloroform was added 0.6 g (3.3 mmole) bromine in 2 ml chloroform. The mixture was heated for 10 h on a steam bath. The course of the reaction was monitored by TLC. The residue after evaporation of chloroform was purified by column chromatography on Al_2O_3 (h = 10 cm, d = 2 cm) with a mixture of hexane—ethyl acetate as eluent. Yield 0.27 g (45%), viscous yellow liquid. Mass spectrum, m/z (%): $[M-Br]^+$ 392* (12); $[M-2Br]^+$ 313 (92); $[M-2Br-H]^+$ 312 (100). Found, %: Br 33.1; N 2.8. $C_{21}H_{19}Br_2NSi$. Calculated, %: Br 33.8; N 3.0.

Di(10,10-dimethyl-10-sila-2-azaanthracen-9-yl) (V). To a solution of sodium ethoxide, prepared from 1 g (43 mmole) sodium in 10 ml absolute alcohol, was added successively a solution of 2.09 g (9.3 mmole) silaazaanthracene IV in 10 ml absolute ethanol and a solution of 1.67 g (11 mmole) p-nitrobenzaldehyde in 20 ml absolute ethanol. The mixture was heated for 6 h at 60-65°C. Water (15 ml) was then added. The residue after evaporation of the ethanol was acidified with dilute (1:1) HCl. The neutral reaction products were extracted into ether. The residue, consisting of salts of organic bases, was treated with sodium hydroxide solution and also extracted with ether. The extract was dried over magnesium sulfate. The residue remaining after removal of ether was subjected to column chromatography on silica gel (h = 50 cm, d = 1.7 cm) with a mixture of heptane—ethyl acetate (1:2) as eluent. Yield 0.63 g (30%), colorless crystals, mp 274-275°C (from heptane—ethyl acetate), R_f 0.17 (Silufol, ethyl acetate—hexane, 1:1). Found: C 74.6; H 6.4; N 6.6%; M^+ 448. $C_{28}H_{28}N_2Si$. Calculated: C 75.0; H 6.3; N 6.3%; M 448.

10,10-Dimethyl-10-sila-2-azaanthrone (VI). A. A mixture of 0.5 g (2.2 mmole) silaazaanthracene IV, 0.34 g (2.3 mmole) p-nitrobenzaldehyde, and 5 ml triethylamine was refluxed for 11 h. The reaction mixture was poured into water and acidified with 18% HCl. The neutral reaction products were extracted with ether. The residue consisting of salts of nitrogen bases was decomposed with sodium hydroxide solution, extracted with ether, and dried over magnesium sulfate. After ether evaporation 0.45 g of nitrogen bases was obtained, which was crystallized from hexane. Yield 0.3 g (56.6%), colorless crystals, mp 147-149°C. A mixed melting point probe with an authentic sample did not exhibit a mp depression. Found: M^+ 239. $C_{14}H_{13}NOSi$. Calculated: M 239.

B. A solution of sodium ethoxide, prepared from 0.8 g (35 mmole) sodium in 20 ml absolute ethanol, was treated under a nitrogen stream with 2 g (8.8 mmole) silaazaanthracene IV,

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*Calculated based on the ^{79}Br isotope.

and subsequently, after 10 min, with a solution of 1.06 g (10 mmole) benzaldehyde in 5 ml absolute alcohol. The mixture was heated for 6 h at 60°C. The workup was carried out as described above. The organic bases were chromatographed on a silica gel column (h = 50 cm, d = 1.7 cm) with hexane–ethyl acetate, 5:1, eluent. Yield 0.58 g (27.4%), mp 149-150°C (from hexane–ethyl acetate).

C. Silaazaanthracene IV (0.5 g 2 mmole) was dissolved with 0.28 g (2.1 mmole) anisaldehyde in 5 ml absolute pyridine. A solution of 0.5 ml (50% solution in alcohol) Triton B in 5 ml absolute pyridine was added. The mixture was stirred for 5 h at 40-45°C and then poured into water. The reaction products were extracted into ether. The residue after evaporation of the ether was subjected to column chromatography on silica gel (h = 45 cm, d = 2 cm) with hexane–ethyl acetate eluent, 10:1. Yield 0.2 g (40%), mp 148-149°C. No melting point depression with an authentic sample.

3-Benzylpyridine (VII). Potassium ethoxide, prepared from 0.21 g (5.4 mmole) potassium, was treated with a solution of 0.3 g (1.3 mmole) dihydrosilaazaanthracene IV in 15 ml of dry DMSO. The mixture was heated to 60°C and a solution of 0.3 g (2 mmole) p-nitrobenzaldehyde in 5 ml DMSO was added. The reaction mixture was maintained at 60°C for 3 h. After being cooled the mixture was poured into 150 ml water. The reaction products were extracted with ether. The extract was dried over magnesium sulfate and the residue remaining after evaporation of the ether was subjected to column chromatography (h = 35 cm, d = 1.7 cm) on alumina with ethyl acetate–hexane, 1:2, as eluent. Yield 0.15 g (65%), mp 28-30°C (from hexane); according to [6], mp 34°C. PMR spectrum (in $CDCl_3$): 8.40 (1H, d of d, 6-H); 8.25 (1H, s, 2-H); 7.43 (1H, d of d, 4-H); 4.05 ppm (2H, s, CH_2). Found, %: N 8.2; M^+ 169. $C_{12}H_{11}N$. Calculated, %: N 8.3; M 169. Picrate: mp 117-118°C (from alcohol); according to [6], mp 119°C. Found, %: N 13.8. $C_{12}H_{11}N \cdot C_6H_3N_3O_7$. Calculated, %: N 14.1.

3-[o-(Dimethyloxysilyl)benzyl]pyridine (VIII). To a solution of 0.5 g (2 mmole) silaazaanthracene IV and potassium tert-butoxide, prepared from 0.17 g (4.4 mmole) potassium, in 15 ml absolute DMSO at 20°C under a dry nitrogen atmosphere was added 0.4 g (2.3 mmole) veratric aldehyde in 5 ml DMSO. After 1 h 30 min the reaction mixture was worked up as described above. Chromatography (alumina, with ethyl acetate–hexane, 1:10, eluent) gave 0.3 g (55%) of base VIII as a yellow, viscous liquid, R_f 0.33 (Al_2O_3, hexane–ethyl acetate, 2:1). IR spectrum (in KBr): 3400 (associated OH); 1250 and 845 [$Si(CH_3)_2$]; 1110 cm^{-1} (Si–O). Found, %: C 68.8; H 7.1; N 6.0; M^+ 243. $C_{14}H_{17}NOSi$. Calculated, %: C 69.1; H 7.0; N 5.8; M 243.

3-Benzoylpyridine (IX). A mixture of 0.5 g (2.1 mmole) silaazaanthrone VI and potassium ethoxide, prepared from 0.35 g (8.9 mmole) potassium, in 25 ml absolute DMSO was heated for 3 h at 60°C. The mixture was poured into 150 ml water and the reaction products were extracted with ether. The extract was dried over magnesium sulfate and the residue remaining after evaporation of the ether was chromatographed on a column of alumina with hexane–ethyl acetate, 2:1, as eluent. Yield 0.13 g (34%, mp 35-37°C (from hexane); according to [6], mp 42°C, R_f 0.50 (alumina, ethyl acetate–hexane, 1:2). IR spectrum (in KBr): 1655 cm^{-1} (C=O). Mass spectrum, m/z (%): 183 (M^+, 35); 105 [$C_6H_5CO^+$, 100]. Found, %: N 7.8. $C_{12}H_9NO$. Calculated: N 7.7%. Picrate: mp 158-159°C (from alcohol), according to [6], mp 161°C. Found: N 13.4%. $C_{12}H_9NO \cdot C_6H_3N_3O_7$. Calculated: N 13.6%.

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