PREPARATION OF SUBSTITUTED 9,10-DIHYDRO-9-SILA-3-AZAANTHRACENES AND THEIR DERIVATIVES

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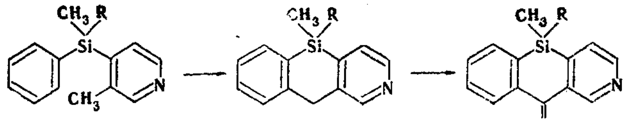
3-Methyl-4-dimethylphenylsilylpyridine and 3-methyl-4-methyldiphenylsilylpyridine, which were obtained from β-picoline and dimethylphenylchlorosilane and methyldiphenylchlorosilane, respectively, were converted by catalytic dehydrocyclization to 9,9-dimethyl-9,10-dihydro-9-sila-3-azaanthracene and 9-methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthracene. The corresponding silaazaanthrones were obtained from them and were converted to tertiary silaazaanthrols with a methyl or phenyl group attached to the C_{10} atom. On the basis of an analysis of data from the PMR spectra of the silaazaanthracenes it was assumed that they exist in the form of an equilibrium mixture of "boat" conformations. 9-Methyl-9-phenyl-10-methylene-9,10-dihydro-9-sila-3-azaanthracene was obtained in the form of a stable crystalline substance by dehydration of the corresponding silaazaanthrol. Potassium tert-butoxide cleaves the Si–C bond in the silaazaanthrone system; this was confirmed by isolation of 1,2-dimethyl-1,2-diphenyl-1,2-bis(2-nicotinoylphenyl)disiloxane.

Until recently, dihydrosilaazaanthracenes, silicon- and nitrogen-containing heterocycles, were unknown compounds. A brief communication was devoted to the synthesis of 2-methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthracene, the first representative of compounds of this sort [1]. It was obtained by catalytic dehydrocyclization of 2,5-dimethyl-4-triphenylsilylpyridine. The accessibility of silyl-substituted pyridine bases that contain an arylsilyl group and a methyl group in the α position relative to it, as well as the relatively simple method for their conversion to silaazaanthracenes, made it possible to begin a more detailed study of this heterocyclic system. We obtained new (with respect to the character of substitution at the silicon atom) dihydrosilaazaanthracenes, which were converted successively to silaazaanthrones and silaazaanthrols.

9,9-Dimethyl- and 9-methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthracenes (III, IV) were obtained by dehydrocyclization of 3-methyl-4-dimethylphenylsilyl- and 4-methyldiphenylsilylpyridines (I, II), respectively, on a K-16 industrial dehydrogenating catalyst. The products were converted to 9,9-dimethyl- and 9-methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthrones (V, VI) in 90% yield by oxidation with potassium permanganate in acetone. Compounds III-VI are crystalline substances, and their structures were confirmed by means of analytical and spectral data.



I, II   III, IV   V, VI

I, III, V R=CH$_3$; II, IV, VI R=C$_6$H$_5$

In analogy with dihydrosilaanthracenes [2-4], dihydrosilaazaanthracenes III and IV exist in the form of an equilibrium mixture of boat–boat conformations.

Their conformational interconversions proceed very rapidly, as a consequence of which the signals of the protons attached to the C_{10} atom and of the methyl groups attached to the silicon atom in the PMR spectra of silaazaanthracenes III and IV are distinct singlets.

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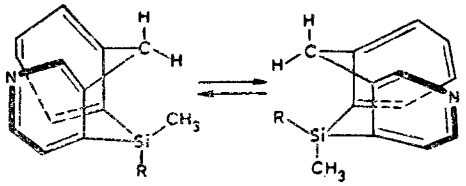
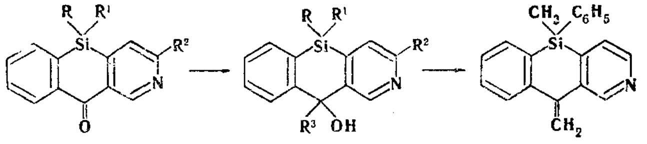


When the temperature is lowered to −65°C, a small degree of broadening of the signal of the protons attached to the C_{10} atom is observed in the PMR spectrum of silaazaanthracene III. However, in the case of silaazaanthracene IV the signal of the protons attached to the C_{10} atom is a typical AB system (J = 14 Hz) under these conditions. The equilibrium is evidently shifted to favor the thermodynamically more favorable conformation with a pseudoaxial phenyl group in this case when the temperature is lowered [5, 6].

Silaazaanthrols VIII-XIII were obtained in the reaction of silaazaanthrones V and VI, as well as the previously obtained [1] 2-methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthrone (VII), with methylmagnesium iodide, as well as with phenylmagnesium bromide. According to data from the PMR spectra, azaanthrol X is a mixture (1:1) of two isomers with cis- and trans-oriented methyl groups attached to the silicon and C_{10} atoms; this indicates the planar structure of dihydrosilaazaanthrone system VI.



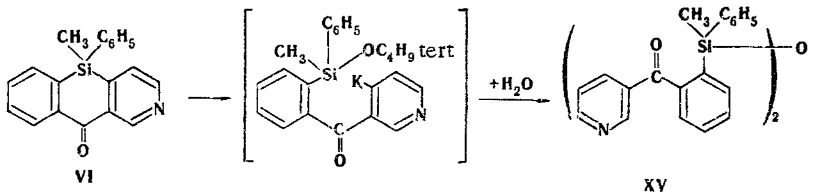
V-VII VIII-XIII XIV

V, VIII, IX $R=R^1=CH_3$, $R^2=H$; VI, X, XI $R=CH_3$, $R^1=C_6H_5$, $R^2=H$; VII, XII, XIII $R=R^1=C_6H_5$, $R^2=CH_3$; VIII, X, XII $R^3=CH_3$; IX, XI, XIII $R^3=C_6H_5$

A band of stretching vibrations of a hydroxy group tied up in an intermolecular hydrogen bond is observed in the IR spectra of silaazaanthrols VIII-XII at 3148-3300 cm^{-1}. A band of a free hydroxy group at 3600 cm^{-1}, the position of which in the IR spectra of solutions ($1.43 \cdot 10^{-2}$ and $7.15 \cdot 10^{-3}$ mole/liter) remains virtually constant (3605 cm^{-1}), is observed in the IR spectrum of silaazaanthrol XIII as a consequence of the steric hindrance created by three phenyl groups.

Dehydration of silaazaanthrol X was realized by means of phosphorus pentoxide in refluxing xylene. 9-Methyl-9-phenyl-10-methylene-9,10-dihydro-9-sila-3-azaanthracene (XIV), the structure of which was confirmed by spectral data, was isolated in the form of a stable crystalline substance. A singlet signal of methylene protons is located at 5.61 ppm in the PMR spectrum of XIV. Bands of stretching vibrations of an exocyclic double bond and of deformation vibrations of a CH bond are found at 1608 and 915 cm^{-1}, respectively, in its IR spectrum.

The Si—C bond is cleaved when silaazaanthrone VI is heated with potassium tert-butoxide in alcohol. 1,2-Dimethyl-1,2-diphenyl-1,2-bis(2-nicotinoylphenyl)disiloxane (XV) was isolated from the reaction products.



VI XV

A band of stretching vibrations of a carbonyl group and a band of stretching vibrations of Si—O bonds are found in the IR spectrum of disiloxane XV at 1650 and 1010 cm^{-1}, respectively. The fragmentation of XV under the influence of electron impact also confirms its structure. Its mass spectrum contains a molecular-ion (M^+) peak with m/e 620 (1%), which corresponds to its empirical formula. The ions with m/e 605 (77%) and 543 (100%) are due to detachment of methyl and phenyl groups from M^+, while the ions with m/e 318 (1.5%) and 302 (50%) are due to its cleavage at the Si—O bond. The bands at 1425-1430 and 1105-1113 cm^{-1} in the IR spectra of the synthesized compounds are due to vibrations of the Si—C_6H_5 bond, while the bands at 1250-1260 and 796-805 cm^{-1} are due to vibrations of the Si—CH_3 bond.

TABLE 1. Physicochemical and Spectral Characteristics of Substituted 9-Sila-9,10-dihydro-3-azaanthracenes (III, IV), Anthrones (V, VI), and Anthrols (VIII-XIII)

Compound	mp, °C (solvent)	M^+	R_f[a]	PMR spectra, δ, ppm	Found, %			Empirical formula	Calc., %			Yield, %
					C	H	N		C	H	N	
III	86—86,5[b]	225	0,35	8,54, s, 1H (4-H); 8,42, d, 1H (2-H); 4,12, s, 2H (CH_2); 0,5, s, 6H (CH_3)	74,4	6,9	6,4	$C_{14}H_{15}NSi$	74,7	6,7	6,4	54[c]
IV	132—133[b]	289	0,45	8,52, s, 1H (4-H); 8,41, d, 1H (2-H); 7,5, m, 1H (5-H); 4,06, s, 2H (CH_2); 0,82, s, 3H (CH_3)	78,9	5,95	5,0	$C_{19}H_{17}NSi$	79,0	6,0	4,9	37[c]
V	149—150[b]	239	0,22	10,37, s, 1H (4-H); 8,73, d, 1H (2-H); 7,36, d, 1H (1-H); 0,56, s, 6H (CH_3)	70,1	5,7	5,6	$C_{14}H_{13}NOSi$	70,2	5,4	5,85	90
VI	100—101[b]	301	0,5	9,38, s, 1H (4-H); 8,67, d, 1H (2-H); 8,36, m, 1H (5-H); 0,92, s, 3H (CH_3)	75,9	5,3	4,6	$C_{19}H_{15}NOSi$	76,0	5,0	4,7	90
VIII	128,5—129[d]	255	0,23	8,88, m, 2H (4-H, 2-H); 5,1, s, 1H (OH); 2,4, s, 3H (10-CH_3); 1,3, s, 3H (CH_3); 1,1, s, 3H (Si—CH_3)	70,3	6,8	5,4	$C_{15}H_{17}NOSi$	70,5	6,6	5,4	30
IX	158—159[e]	317	0,3	9,0, s, 1H (4-H); 7,9, d, 1H (2-H); 4,5, s, 1H (OH); 0,46, s, 6H (CH_3)	75,5	6,2	4,5	$C_{20}H_{19}NOSi$	75,7	6,0	4,4	60
X[f]	152—153[e]	317	0,23	8,66, s, —(4-H); 8,62, s, —(4-H); 7,8, d, —(2-H); 7,6, d, —(2-H); 1,17, s, —(10-CH_3); 0,91, s, —(10-CH_3); 0,24, s, —(Si—CH_3); 0,22, s, —(Si—CH_3)	76,0	6,0	4,4	$C_{20}H_{19}NOSi$	75,7	6,0	4,4	75
XI	195—196[e]	379	0,33	8,07, d, 1H (2-H); 5,0, s, 1H (OH); 0,06, s, 3H (Si—CH_3)	79,0	5,4	3,5	$C_{25}H_{21}NOSi$	79,1	5,5	3,6	32
XII	238—239[e]	393	0,21	8,78, s, 1H (4-H); 3,17, s, 1H (OH); 2,13, s, 3H (2-CH_3), 1,1, s, 3H (10-CH_3)	79,7	6,2	3,4	$C_{26}H_{23}NOSi$	79,4	5,9	3,6	60
XIII	230—232[e]	455	0,41	9,0, s, 1H (4-H); 2,5, s, 3H (CH_3)	81,4	5,2	3,2	$C_{31}H_{25}NOSi$	81,7	5,4	3,0	50

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[a] The following systems were used: ethyl acetate—heptane (1:4) for III and V, ethyl acetate—heptane (1:3) for IV and VI, and ether for VIII-XIII. [b] From heptane. [c] The yield based on the converted pyridine base. [d] From alcohol—hexane—ethyl acetate. [e] From heptane—ethyl acetate. [f] A mixture of two isomers.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in $CDCl_3$ (tetrachloroethane in the case of X) were obtained with a Tesla BS-487 spectrometer with tetramethylsilane as the internal standard. The mass spectra were measured with an MKh-1303 mass spectrometer. Column chromatography and thin-layer chromatography (TLC) were carried out on activity II Al_2O_3. The characteristics of the synthesized compounds are presented in Table 1.

3-Methyl-4-dimethylphenylsilyl- and 4-Methyldiphenylsilylpyridines (I, II). A solution of 102 g (0.64 mole) of dimethylphenylchlorosilane in 300 ml of freshly distilled (over sodium) tetrahydrofuran (THF) was added in a stream of nitrogen in the course of 2 h to 13.2 g (2 g-atom) of finely cut lithium in 500 ml of absolute THF, and the mixture was stirred for 3 h. It was then transferred by means of nitrogen to a solution of 137 g (1.2 moles) of β-picoline in 70 ml of THF, which was cooled to 0°C. The mixture was stirred at 20°C for 1 h and refluxed for 1 h, after which it was neutralized with respect to Congo red with 18% hydrochloric acid and refluxed for 1.5 h. The THF was removed by distillation, and the neutral substances were extracted with ether (two 100-ml portions). The aqueous solution was treated with a concentrated solution of alkali, and the organic bases were extracted with ether. The extract was dried with magnesium sulfate, the ether was removed by distillation, and the residue was fractionated to give 102.2 g (45%) of pyridine base I with bp 160-165°C (5 mm), n_D^{20} 1.6819, and R_f 0.5 [ethyl acetate—hexane (1:4)]. Found: C 73.8; H 7.6; N 5.8%; M^+ 227. $C_{14}H_{17}NSi$. Calculated: C 74.0; H 7.4; N 6.2%; M 227. The picrate had mp 128-129°C (from acetone). Found: N 12.1%. $C_{14}H_{17}NSi \cdot C_6H_3N_3O_7$. Calculated: N 12.3%.

Similarly, the reaction of β-picoline and methyldiphenylchlorosilane gave silyl-substituted piperidine II with bp 210-215°C (2 mm), mp 72-74°C (from heptane), and R_f 0.59 [ethyl acetate—hexane (1:3)] in 60% yield. Found: C 79.1; H 5.7; N 5.2%; M^+ 289. $C_{19}H_{19}NSi$. Calculated: C 79.0; H 6.2; N 4.9%; M 289. The picrate had mp 170-172°C (from acetone). Found: N 11.1%. $C_{19}H_{19}NSi \cdot C_6H_3N_3O_7$. Calculated: N 10.9%.

9,9-Dimethyl- and 9-Methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthracenes (III, IV). A solution of 10 g (0.042 mole) of pyridine base I in 50 ml of benzene was passed at a constant rate for 3 h over a K-16 catalyst (20 cm³) at 560-570°C. At the end of the experiment, 60 ml of benzene was passed at the same temperature, after which 150 ml of benzene was passed at 100°C. A total of 1 liter of gas (at 20°C and 758 mm) was collected. The benzene was removed from the catalyzate by distillation, and the residue (6.4 g) was dissolved in 30 ml of acetone. The acetone solution was treated with a solution of 7 g of picric acid in 20 ml of acetone to give 7.8 g of the picrate of silaazaanthracene III, which was decomposed in a chromatographic column (elution with boiling chloroform). Crystallization from heptane gave 3.2 g of III in the form of colorless crystals. The picrate of III had mp 208-210°C (from alcohol). Found: N 11.9%. $C_{14}H_{15}NSi \cdot C_6H_3N_3O_7$. Calculated: N 12.2%.

Similarly, the reaction of silyl-substituted pyridine base II gave IV. The picrate of IV had mp 190-192°C (from alcohol). Found: N 10.9%. $C_{19}H_{17}NSi \cdot C_6H_3N_3O_7$. Calculated: N 11.0%.

9,9-Dimethyl- and 9-Methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthrones (V, VI). A 4.2-g (0.026 mole) sample of potassium permanganate was added in small portions with stirring to a solution of 2.8 g (0.012 mole) of III in 200 ml of acetone, and the mixture was maintained at room temperature for 24 h. The manganese dioxide was removed by filtration and washed with hot acetone. The acetone was removed by filtration, and the residue was crystallized from hexane to give 2.6 g of ketone V in the form of colorless crystals.

Ketone VI was obtained by similar oxidation of IV.

9,9,10-Trimethyl- and 9,10-Dimethyl-9-phenyl-9,10-dihydro-9-sila-3-aza-10-anthrols (VIII, X) and 2,10-Dimethyl-9,9-diphenyl-9,10-dihydro-9-sila-3-aza-10-anthrol (XII). A solution of 1.34 g (0.005 mole) of ketone V in 50 ml of ether was added gradually to methylmagnesium iodide obtained from 2 g (0.08 g-atom) of magnesium and 9.12 g (0.06 mole) of methyl iodide in 200 ml of absolute ether, and the mixture was refluxed for 2 h. It was then decomposed with 20 ml of a saturated solution of ammonium chloride. The ether extract was dried with magnesium sulfate, the ether was removed by distillation, and the residue (1.3 g) was crystallized from heptane—ethyl acetate to give 0.6 g of silaazaanthrol VIII in the form of colorless crystals.

Compound X was similarly obtained from ketone VI, and alcohol XII was obtained from ketone VII.

9,9-Dimethyl-10-phenyl- and 9-Methyl-9,10-diphenyl-9,10-dihydro-9-sila-3-aza-10-anthrols (IX, XI) and 2-Methyl-9,9,10-triphenyl-9,10-dihydro-9-sila-3-azaanthrol (XIII). A solution of 1.3 g (4.3 mmole) of ketone VI in 80 ml of ether was added to phenylmagnesium bromide obtained from 7.8 g (0.052 mole) of bromobenzene and 1.6 g (0.07 g-atom) of magnesium in 100 ml of ether, and the mixture was refluxed for 2 h. It was then decomposed with 20 ml of a saturated solution of ammonium chloride. The residue (0.9 g) from the ether solution was chromatographed; successive elution with heptane and ether gave 0.5 g of starting ketone VI and 0.4 g of silaazaanthrol XI (colorless crystals).

Compound IX was similarly obtained from ketone V, while alcohol XIII was obtained from ketone VII.

9-Methyl-9-phenyl-10-methylene-9,10-dihydro-9-sila-3-azaanthracene (XIV). A 0.8-g (2.5 mmole) sample of silaazaanthrol X was refluxed for 11 h in 20 ml of xylene with 2.5 g (0.02 mole) of phosphoric anhydride, after which 10 ml of water was added, and the mixture was made alkaline to pH 12 with ammonium hydroxide. The xylene solution was dried with magnesium sulfate, the xylene was removed by distillation, and the residue (0.5 g) was chromatographed [elution with heptane—ethyl acetate (5:1)] to give 0.14 g (18%) of XIV as colorless crystals with mp 130-132°C (from heptane) and R_f 0.72 [ethyl acetate—hexane (1:4)]. PMR spectrum (in $CDCl_3$), δ: 0.83 ppm (3H, s, CH_3). Found: C 79.9; H 5.6; N 4.6%; M^+ 299. $C_{20}H_{17}NSi$. Calculated: C 80.3; H 5.7; N 4.7%; M 299.

1,2-Dimethyl-1,2-diphenyl-1,2-bis(2-nicotinoylphenyl)disiloxane (XV). A 0.08-g (0.002 g-atom) sample of potassium was dissolved in 1.5 ml of absolute tert-butyl alcohol, after which a solution of 0.3 g (1.3 mmole) of azaanthrone VI in 40 ml of absolute alcohol was added, and the mixture was refluxed for 1 h. Water (1 ml) was added, the alcohol was removed by distillation, and the residue (0.25 g) was chromatographed [h = 30 cm, d = 2 cm, elution with heptane—ethyl acetate (4:1)] to give 0.1 g (32%) of disiloxane XV as colorless crystals with mp 154-155°C and R_f 0.76 [ethyl acetate—hexane (1:4)]. PMR spectrum (in $CDCl_3$), δ: 8.6 (4H, m, α-H of the pyridine ring), 7.7 (2H, dd, γ-H of the pyridine ring), and 0.57 ppm (6H, s, CH_3). Found: N 4.4%; M^+ 620. $C_{38}H_{32}N_2O_3Si_2$. Calculated: N 4.5%; M 620.

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PREPARATION AND IONIC HYDROGENATION OF SUBSTITUTED 4-(3-OXOPROPYL)-5-PYRAZOLONES

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4-(3-Oxopropyl)-5-pyrazolone derivatives were obtained under mild conditions of alkaline catalysis by condensation of 1-phenyl-3-methyl-5-pyrazolone and substituted chalcones. During ionic hydrogenation of the products they undergo heterocyclization with the formation of 5,6-dihydropyrano[3,2-d]pyrazoles.

Individual data on the ability of 1-phenyl-3-R-5-pyrazolones to undergo the Michael reaction with α,β-unsaturated compounds has recently begun to appear in the literature more and more frequently [1-4], whereas data on the heterocyclization of the resulting 4-(3-oxopropyl)-5-pyrazolones are virtually absent. We set out to study the ability of 1-phenyl-3-R-5-pyrazolones (I, II) to react with chalcones III-VI and the behavior of the resulting 1,5-dicarbonyl compounds under ionic hydrogenation conditions.

Fusion of the starting 3-R-5-pyrazolones with chalcones at 160°C for 3 h is used in most cases as the principal method of carrying out the Michael reaction [2, 4]. Heating of an alcohol solution of the components in the presence of NaOH can also be used in the case of 1,3-diphenyl-5-pyrazolone [2], while refluxing of equimolar amounts of the substances in the presence of sodium ethoxide for 3 h is proposed for the condensation of 1-phenyl-3-methyl-5-pyrazolone [4].

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