DEHYDRATION OF 10,10-DIMETHYL-9-ALLYL-9,10-DIHYDRO-10-SILA-2-AZAANTHROL-9

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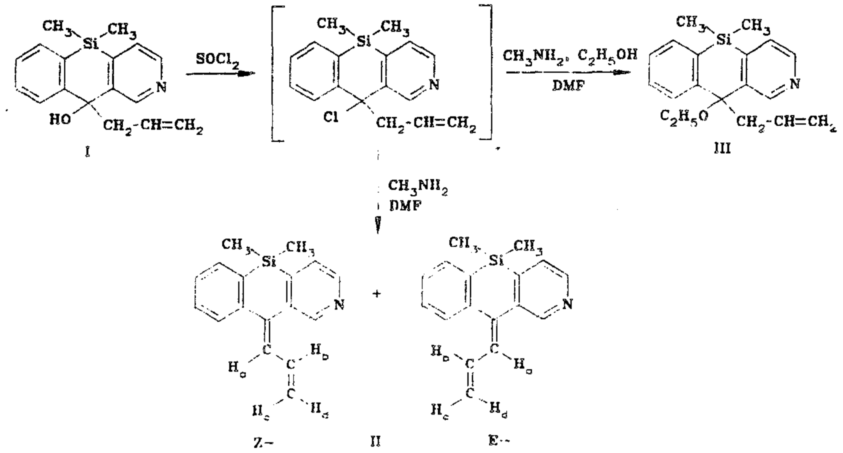
Dehydration under various conditions of the tertiary alcohol 10,10-dimethyl-9-allyl-9,10-dihydro-10-sila-2-azaanthrol-9 yielded the following compounds: Z- and E-isomers of 10,10-dimethyl-9-propenyldiene-9,10-dihydro-10-sila-2-azaanthracene; 10,10-dimethyl-9-allyl-9-ethoxy-9,10-dihydro-10-sila-2-azaanthracene; 1,1,3,3-tetramethyl-1,3-di(3'-propenylidenebenzylpyridyl-4')-disiloxane; 1-methyl-3-(4'-dimethyloxysilylpyridyl-3')indene.

With the development of a synthesis of 9,10-dihydro-10,10-diorganosilyl-2-azaanthrenes [1] it became possible to systematically study this relatively new heterocyclic system. The present work is devoted to the dehydration of 10,10-dimethyl-9-allyl-9,10-dihydro-10-sila-2-azaanthrol-9 (I) [2]. The $C_{(9)}$-propenylidene derivative thus obtained is of interest both as a synthone for new heterocycles, e.g., spiro compounds with a dihydrosilaazaanthracene segment, and as a material for the study of the geometrical isomerism of this series of compounds.

Only one publication has been devoted to the dehydration of silaazaanthrol-9 compounds [1], viz., to the synthesis of 9-methylene-10-methyl-10-phenyl-9,10-dihydro-10-sila-2-azaanthracene by dehydration of the corresponding silaazaanthrol by phosphorus pentoxide.

Alcohol I was dehydrated by two methods. In one, sila-azaanthrol was treated with thionyl chloride, and then with methylamine in DMFA. A mixture of Z- and E-isomers (depending on the location of the vinyl group with respect to the ring containing nitrogen) of 10,10-dimethyl-9-propenylidene-9,10-dihydro-10-sila-2-azaanthracene (II) was obtained. According to the PMR spectrum the Z:E ratio is 1.4:1.5.



The insignificant difference between the chemical shifts of the Z- and E-isomers of compound II hindered the interpretation of the PMR spectrum of the mixture. Use of the two-dimensional spectrum (2M) of the nuclear Overhauser effect — NOESY [3] — permitted this problem to be solved. From the cross peaks present in the 2M spectrum, due to the pairs of $H_{(a)}$–8-H and $H_{(a)}$–1-H protons, we identified the signals corresponding to the 8-H protons in the Z-isomer and the 1-H proton in the E-isomer. For assignment of the remain-

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TABLE 1. Chemical Shifts of Protons in PMR Spectra of Dihydrosilaazaanthracenes II and VII in $CDCl_3$

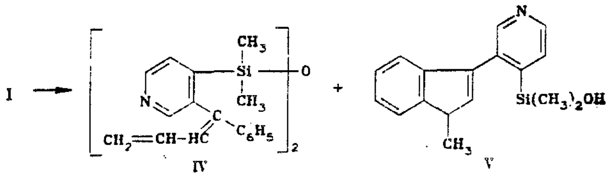
Compound		1-H	3-H	4-H	5-H	6-H	7-H	8-H	$H_{(a)}$	$H_{(c)}$	$H_{(c)}$	$H_{(d)}$	$Si(CH_3)_2$	$CH_2=$
II*	Z	8,70	8,51	7,50	7,52	7,43	7,32	7,63	6,68	6,85	5,51	5,31	0,45	—
	E	8,79	8,49	7,41	7,61	7,42	7,34	7,57	6,63	6,82	5,49	5,32	0,45	—
VII†		8,89	8,57	7,40...7,80					—	—	—	—	0,48	5,74

*Spectrum recorded at 400 MHz.
†Spectrum recorded at 80 MHz.

ing proton signals (Table 1), we used the two-dimensional homonuclear correlational COSY-4S spectrum [4]. The chemical shifts of olefinic protons in the isomers were asssigned using the PMR data for butadiene [5]. When we consider the large vicinal SSCC, $^3J_{ab}$ = 11.1 Hz, it can be assumed that the butadiene segment has S-trans configuration [5]. The signal of the $Si-CH_3$ protons at 20°C is a very broad singlet at 0.45 ppm; by analogy with the data of [6] this indicates a retarded interconversion of the bath–bath conformations of the central ring.

When dehydration is carried out with alcoholic methylamine the main product is 10,10-dimethyl-9-allyl-9-ethoxy-9,10-dihydro-10-sila-2-azaanthracene (III) (39%). This ethoxy derivative is apparently formed by replacement of the chlorine in 9,10-dihydro-9-chloro-10,10-dimethyl-9-allyl-10-sila-2-azaanthracene by the ethoxy anion of the ammonium base that forms when methylamine dissolves in ethanol. It is also necessary to consider that the respective solvate can also take part in the substitution.

Alcohol I undergoes dehydration with 55% sulfuric acid at 50°C, with cleavage of the central silicon-containing ring at the $Si-C_{phenyl}$ bond. The main reaction product, obtained in 32% yield, is 1,1,3,3-tetramethyl-1,3-di(3'-propenylidenebenzylpyridyl-4')-disiloxane (IV); this compound apparently is formed by condensation of 1-phenyl-1-(4'-dimethyloxysilylpyridyl-3')butadiene-1,3, which is the product of dehydration and cleavage of the Si–C bond of compound I.



Beside compound IV, 1-methyl-3-(4'-dimethyloxysilyl-pyridyl-3')indene (V) was separated from the reaction mixture in 4% yield. Possibly the pyridyl substituted indene V is also formed from the phenylpyridyl substituted butadiene-1,3 by cyclization in acid medium.

The structures of IV and V were established from their spectral data. In the IR spectrum of IV the band at 1055 cm^{-1} is due to Si–O–Si vibrations. Its mass spectrum lacks the peak of the molecule-ion. But it shows fragment ions at 264* (53) and 280 (2.5) that are due to cleavage of IV at the Si–O bond, as confirmed by the respective metastable ions. In the PMR spectrum the $Si-CH_3$ and the 1-H and 6-H signals of the pyridine segment could definitely be assigned, as well as the complex spectrum of the propenylidene protons in the 5.38-5.94 ppm region.

The mass spectrum of pyridylindene V shows the peak of the molecule-ion at 281, which corresponds with its empirical formula; the main direction of fragmentation thereof is the elimination of a water molecule to form an ion of weight 263. The presence of the hydroxyl group in V is also confirmed by the bands at 3090 cm^{-1} (the bonded OH) at 910 cm^{-1} (vibration of the Si–O bond in Si–OH [7]) in the IR spectrum. The PMR data confirm the presence of $Si-CH_3$ and $1-CH_3$, and 1-H and 2-H protons.

9,10,10-Trimethyl-9,10-dihydro-10-sila-2-azaanthrol-9 (VI) was dehydrated with thionyl chloride.

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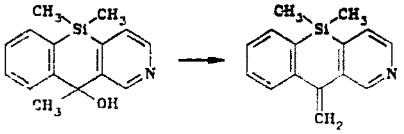
*Here and subsequently m/z (relative intensity, %) is given.



VI VII

An analog of 10,10-dimethyl-9-methylene-9,10-dihydroanthracene, viz., 10,10-dimethyl-9-methylene-9,10-dihydro-10-sila-2-azaanthracene (VII), was separated as a stable crystalline material in 44% yield. The PMR data that confirm the structure of VII are given in Table 1. Its mass spectrum shows a molecule-ion peak at 237 (72); the main direction of the fragmentation thereof is the detachment of a methyl from silicon to form an ion at 222 (100).

EXPERIMENTAL

IR spectra of the synthesized compounds were obtained with a UR-20 spectrophotometer in KBr tablets. PMR spectra were obtained with WP-80 and WM-400 spectrometers at 80 and 400 MHz, respectively, with RMS internal standard. Mass spectra were measured with a MX-1303 mass spectrometer at 70 eV ionizing voltage. For thin layer chromatography we used Silufol UV-254 silica gel in 1:1 ethyl acetate—heptane; for column chromatography, grade L 100/250 silica gel and aluminum oxide of Brockman activity grade II.

10,10-Dimethyl-9-propenylidene-9,10-dihydro-10-sila-2-azaanthracene (II). A solution of 0.6 g (2.13 mmoles) of alcohol I in 8 ml of thionyl chloride was stirred at 30°C for 6 h. Thionyl chloride was distilled off, and the residue was rubbed with 15 ml of absolute ether, then dissolved in 20 ml of absolute DMFA. Into the solution at 20° was passed a stream of gaseous methylamine until the pH was 10-11. After 4 h the mixture was poured into 50 ml of water. The reaction products were extracted (3 × 50 ml) with ether, and the extract was dried with magnesium sulfate. The ether was distilled off, and the residue was chromatographed on a silica gel column (ℓ = 45 cm, d = 2 cm) and eluted with 10:1 hexane—ethyl acetate. A mixture of Z- and E-isomers of compound II (0.22 g, 39.6%) was separated. Yellowish liquid, R_f 0.52 and 0.45. Found, %: C 77.8; H 6.8; N 5.1; M^+ 263. $C_{17}H_{17}NSi$. Calculated, %: C 77.6; H 6.5; N 5.3; M 263.

Elution with the same solvents in 3:1 ratio gave 0.14 g (23%) of the starting silaazaanthrol I. MP-143-144°. A mixed melting point with the ethanolic sample gave 142-143°C.

10,10-Dimethyl-9-allyl-9-ethoxy-9,10-dihydro-2-aza-10-silaanthracene (III). A solution of 1 g (3.56 mmoles) of alcohol I in 10 ml of thionyl chloride was stirred for 6 h at 30°C. The reaction mixture was treated as described above. The residue was dissolved in 20 ml of absolute DMFA. To the solution at 20°C over 5 min was added 10 ml of a solution of methylamine in ethanol (saturated at 20°C). After 5 h the mixture was poured into 50 ml of water. The reaction products were extracted (4 × 50 ml) with ether and the extract was dried with magnesium sulfate. After the ether was distilled off the residue was chromatographed on an aluminum oxide column (ℓ = 40 cm, d = 2 cm), and eluted with 10:1 heptane—ethyl acetate. Compound III, 0.43 g (39.1%), was separated. Oily yellow material, R_f 0.68. PMR spectrum ($CDCl_3$): 9.05 (1H, d, 1-H, $J_{1,4}$ = 0.8); 8.52 (1H, d, 3-H, $J_{3,4}$ = 4.7); 7.87 (1H, m, 8-h); 7.30-7.50 (4H, m, 4-H-7-H); 4.50-5.22 (3H, m $CH{=}CH_2$); 3.09 (2H, q, CH_2O); 2.79 (2H, d, CH_2, J = 7.2); 1.19 (3H, t, CH_3); 0.48 (3H, s, $SiCH_3$); 0.39 ppm (3H, s, $SiCH_3$). Found, %: C 73.4; H 7.5; N 4.4. $C_{19}H_{23}NOSi$. Calculated, %: C 73.8; H 7.4; N 4.5.

1,1,3,3-Tetramethyl-1,3-di(3'-propenylidenebenzylpyridyl-4')-disiloxane (IV) and 1-methyl-3-(4'-dimethoxyloxysilylpyridyl-3')indene (V). Alcohol I, 2 g (7.1 mmoles), was heated in 33 ml of 55% sulfuric acid at 60-70°C for 3 h. The solution was neutralized with saturated sodium carbonate solution and the reaction products were extracted (4 × 50 ml) with ether. The extract was dried with magnesium sulfate, the ether was distilled off, and the residue was chromatographed on a column of aluminum oxide. Disiloxane IV, 0.64 g (32%), was washed off with 1:10 ethyl acetate—heptane. Oily material, R_f 0.60. PMR spectrum ($CDCl_3$): 8.97 (1H, s, 2-H); 8.72 (1H, d, 6-H, $J_{6,5}$ = 4.5); 5.38-5.94 (4H, m, $CH_2{=}CH{-}CH{=}$); 0.63 ppm (6H, s, $Si(CH_3)_2$). Found, %: N 4.7. $C_{34}H_{36}N_2OSi_2$. Calculated, %: N 5.1.

The indene V was eluted by a 1:5 ratio of the same solvents (0.06 g, 4.0%). Colorless crystals, mp 149-150°C (from heptane—ethylacetate), R_f 0.12. PMR spectrum ($CDCl_3$): 8.50-7.05 (7H, m, arom. protons); 6.02 (1H, s, 2-H); 4.85 (1H, m, 1-H); 2.19 (3H, d, CH_3); 0.56 ppm (6H, s, $Si(CH_3)_2$). Found, %: C 72.7; H 5.7; N 4.9; M^+ 281. $C_{17}H_{18}NOSi$. Calculated, %: C 72.6; H 6.0; N 5.0; M 281.

10,10-Dimethyl-9-methylene-9,10-dihydro-2-aza-10-silaanthracene (VII). Alcohol VI, 0.5 g (2 mmoles) was boiled in 10 ml of thionyl chloride for 1 h. The thionyl chloride was boiled off and the residue was heated with 20 ml of triethylamine for 3 h. The reaction mixture was poured into 50 ml of water, and the reaction products were extracted (3 × 20 ml) with ether. The extract was dried with magnesium sulfate and the ether was distilled off. The residue was chromatographed on a silica gel column ($\ell = 30$ cm, $d = 2$ cm) and eluted with 10:1 hexane–ethyl acetate to give 0.2 g (44%) of compound VII. Colorless crystals, mp 75-76°C (from hexane). Found, %: C 76.2; H 6.1; N 6.0. $C_{15}H_{15}NSi$. Calculated, %: C 75.9; H 6.3; N 5.9; M 237.

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