9-DIAZO-10,10-DIMETHYL-9,10-DIHYDRO-10-SILA-2-AZAANTHRACENE AND 10,10-DIMETHYL-4'-OXOSPIRO[9,10-DIHYDRO-10-SILA-2-AZAANTHRACENE-9,2'-AZETIDINE]

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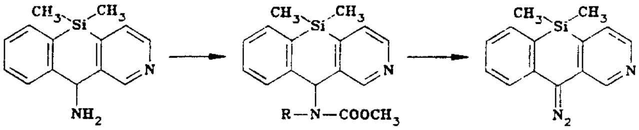
The synthesis of the first representative of diazo compounds in the dihydrosilaazaanthracene series and a spiro compound with dihydrosilaazaanthracene and azetidine fragments was realized.

9-Amino-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (I), which was obtained by reduction of the oxime of the corresponding silaazaanthrone [1], has been used in syntheses of relatively little-studied derivatives of silaazaanthracenes, as well as to obtain a new heterocyclic system — the spirodihydrosilaazaanthraceneazetidine system. Diazo compounds are unknown in the dihydrosilaazaanthracene series. In the present paper we describe the synthesis of one of them, for which amine I was used.

The reaction of amine I with methyl chlorocarbonate gave 9-N-methoxycarbonylamino-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (II), which was converted to 9-(N-nitroso-N-methoxycarbonyl)amino derivative III. Alkaline cleavage of the latter with sodium isopropoxide in absolute ether gave diazo compound IV (26% yield) — a crystalline pinkish-lilac substance that is stable on storage at 0-4°C.



I II, III IV

II R=H, III R=NO

The IR spectrum of IV contains a band of stretching vibrations of a diazo group at 2070 cm^{-1}. A molecular-ion peak M^+ at 251 (14),* which corresponds to its empirical formula, is observed in the mass spectrum. The M^+ ion subsequently eliminates a molecule of nitrogen (which is characteristic for the dissociative ionization of diazo compounds [2]) and a methyl group. The peak of the $[M - N_2, -CH_3]^+$ ion has the maximum intensity.

9-N-Chloroacetamido-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (V) was obtained in the acylation of amine I with chloroacetyl chloride. 10,10-Dimethyl-4'-oxospiro[9,10-dihydro-10-sila-2-azaanthracene-9,2'-azetidine] (VI) was obtained from V under the influence of sodium hydride in a mixture of dimethylformamide with benzene as a result of intramolecular cyclization.

The structure of spiro compound VI was confirmed by spectral data. A signal of a 9-H proton is absent in the ^1H NMR spectrum, while signals at 3.13 and 8.62 ppm, which correspond to the protons of the CH_2 and NH groups of the azetidine fragment with long-range spin-spin coupling constant (SSCC) ${}^4J_{(1',3')} = 1.7$ Hz, are observed. In the ^{13}C NMR spectrum without proton decoupling there is a broad singlet signal of the $C_{(9)}$ nucleus at 58.88 ppm. A trip-

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*The numbers that characterize the ions are the m/z values; the relative intensities of the ion peaks in percent of the maximum peak are given in parentheses.

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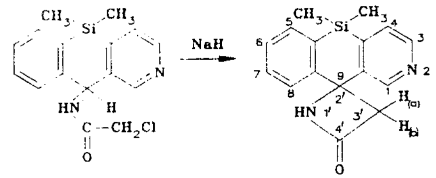
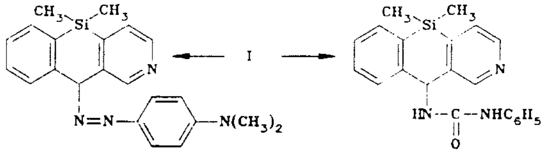
let of doublets of a $C_{(3)}$ nucleus is located at 58.13 ppm ($^1J_{CH}$ = 143.2 Hz; $^3J^{C(3')NH}$ = 11.7 Hz). The IR spectrum contains a band of stretching vibrations of an NH group at 3258 cm^{-1}. An M^+ peak at 280 (26), which corresponds to its empirical formula, is observed in the mass spectrum. The fragmentation of the M^+ ion of spiro compound VI is characterized by the successive splitting out of a hydrogen atom and a molecule of CO with the formation of the maximally intense peak of an $[M - H, -CO]^+$ ion at 251 (100). The $[M - NHCO]^+$ fragment ion at 237 (9) and $[M - CH_2CO]^+$ fragment ion at 238 (4) confirm the presence of a β-lactam ring [3]. These ions subsequently eliminate a methyl group. It should be noted that splitting out of acyl, acylamino, and methyl (from the silicon atom) radicals with the formation of high-intensity peaks of the corresponding ion is characteristic for the dissociative ionization of the M^+ ions of 9-acylamino-substituted dihydrosilaazaanthracenes [4].



V

VI

9-(4'-Dimethylaminophenyl-1'-azo)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (VII) — a yellow azo dye — was obtained by condensation of amine I with p-nitrosodimethylaniline. 9-N-Phenylcarbmoylamino-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (VIII) is formed in the reaction of amine I and phenyl isocyanante.



VII

VIII

The nitrosation of VIII leads to the formation of diazo compound IV and products of its transformations — 10,10-dimethyl-10-sila-2-aza-9-anthrone and 10,10-dimethyl-9,10-dihydro-10-sila-2-aza-9-anthrol.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The ^1H and ^{13}C NMR spectra of solutions of the compounds in $CDCl_3$ were recorded with WP-80 and WM-400 spectrometers with tetramethylsilane (TMS) as the internal standard. The mass spectra were obtained with an MKh-1303 spectrometer. Thin-layer chromatography was accomplished on Silufol UV-254 plates; 100/250 brand silica gel was used for column chromatography.

9-N-Methoxycarbonylamino-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (II). A solution of 2.8 g (29.6 mmole) of methyl chlorocarbonate in 10 ml of absolute ether was added at 20°C in the course of 30 min to a solution of 4 g (16.7 mmole) of amine I and 2 g (19.8 mmole) of triethylamine in 150 ml of absolute ether. After 5 h (monitoring by TLC), the precipitate was removed by filtration and washed with 100 ml of ether, and the ether layer was separated and dried with magnesium sulfate. Removal of the ether by distillation gave 0.73 g of II. The precipitate on the filter was washed with 150 ml of water and dried to give another 3 g of II (for an overall yield of 75%). The colorless crystals had mp 172-174°C (heptane—ethyl acetate) and R_f 0.42 (ethyl acetate) [1].

9-(N-Nitroso-N-methoxycarbonyl)amino-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (III, $C_{16}H_{17}N_3O_3Si$). A 5-g (72.5 mmole) sample of sodium nitrite was added in portions at −2°C to −3°C in the course of 2 h (monitoring by TLC) to 1 g (3.36 mole) of urethane II in a mixture of 5 ml of acetic acid and 40 ml of acetic anhydride, after which the reaction mass was poured into 50 ml of water, and the acid was neutralized with 10% sodium carbonate solution. The mixture was extracted with ether (four 35-ml portions), and the extract was dried with magnesium sulfate. The ether was removed by distillation, and the residue was crystallized from hexane to give 1 g (92%) of yellow crystals of nitroso compound III with mp 110-112°C and R_f 0.82 [ethyl acetate—hexane (1:1)]. IR spectrum: 820 and 1260 [$Si(CH_3)_2$], 1450

(N=O), 1780 cm^{-1} (CO). ^1H NMR spectrum: 0.44 (3H, s, $SiCH_3$), 0.71 (3H, s, $SiCH_3$), 3.96 (3H, s, OCH_3), 8.23 (1H, broad, s, NH), 8.50 ppm (1H, broad s, 3-H).

9-Diazo-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (IV, $C_{14}H_{13}N_3Si$). A mixture of 0.5 g (1.53 mmole) of nitroso compound III and 0.18 g (2.17 mmole) of sodium isoproxide in 30 ml of absolute ether was maintained at 20°C in a stream of nitrogen until the starting III had vanished according to TLC. Water (50 ml) was added, and the ether layer was separated and dried with magnesium sulfate. The ether was removed by distillation, and the residue was chromatographed with a column (30 × 1.5 cm) packed with silica gel by elution with ether to give 0.1 g (26%) of diazo compound IV in the form of pinkish-lilac crystals with mp 60-62°C (from hexane), R_f 0.56 [ethyl acetate—hexane (1:1)], and M^+ 251.

9-(Chloroacetamido)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (V, $C_{16}H_{17}ClN_2OSi$). A 0.4-g (3.8 mmole) sample of chloroacetyl chloride in 10 ml of absolute ether was added at 20°C in the course of 30 min to a solution of 0.8 g (3.33 mmole) of amine I and 0.47 g (4.6 mmole) of triethylamine in 50 ml of absolute ether. After 6 h (monitoring by TLC), the precipitate was removed by filtration and washed on the filter with ether (50 ml) and water (100 ml). The ether layer was separated from the filtrate and dried with magnesium sulfate. The ether was removed by distillation, and the residue was combined with the residue on the filter and recrystallized from a mixture of heptane with ethyl acetate to give 0.85 g (83%) of V in the form of colorless crystals with mp 200-202°C and R_f 0.45 (ethyl acetate). IR spectrum: 1700 (CO), 3200 cm^{-1} (NH). ^1H NMR spectrum: 0.52 (3H, s, $SiCH_3$), 0.55 (3H, s, $SiCH_3$), 3.91 (2H, s, CH_2), 6.15 (1H, d, $J_{NH,9H}$ = 8 Hz, 9-H), 6.72 (1H, d, NH), 8.40 (1H, d, 3-H), 8.68 ppm (1H, s, 1-H). Mass spectrum: M^+ 316/318 (M 316 was calculated for the ^{35}Cl isotope).

10,10-Dimethyl-4'-oxospiro[9,10-dihydro-10-sila-2-azaanthracene-9,2'-azetidine] (VI, $C_{16}H_{16}N_2OSi$). A 0.5-g (1.58 mmole) sample of chloroacetamide V and 0.08 g (3.3 mmole) of sodium hydride were heated at 80°C in a stream of nitrogen in a mixture of 50 ml of absolute benzene and 10 ml of absolute DMF. The course of the reaction was monitored by TLC. Water (100 ml) was added, the benzene layer was separated, and the aqueous layer was extracted with benzene (two 35-ml portions). The combined extract was dried with magnesium sulfate, the benzene was removed by distillation, and the residue was chromatographed with a column (30 × 2 cm) packed with silica gel by elution with a mixture of hexane with ethyl acetate (1:1) to give 0.3 g (68%) of spiro compound VI in the form of white crystals with mp 190-192°C (hexane—ethyl acetate) and R_f 0.26 (ethyl acetate). IR spectrum: 1720 and 1757 (CO), 3258 cm^{-1} (NH). ^1H NMR spectrum: 0.38 (3H, s, $SiCH_3$), 0.67 (3H, s, $SiCH_3$), 3.13 (2H, d, $J_{1',3'}$ = 1.7 Hz, CH_2), 7.33 (1H, t, 6-H), 7.42 (1H, t, 7-H), 7.50 (1H, d, $J_{3,4}$ = 4.5 Hz, 4-H), 7.62 (1H, d, $J_{5,6}$ = 7.5 Hz, 5-H), 7.79 (1H, d, $J_{7,8}$ = 8 Hz, 8-H), 8.59 (1H, d, 3-H), 8.62 (1H, t, NH), 9.02 ppm (1H, s, 1-H). ^{13}C NMR spectrum: −1.27 (CH_3), −4.70 (CH_3), 58.13 [$C_{(3')}$], 58.88 [$C_{(9)}$], 122.65 [$C_{(8)}$], 126.98 [$C_{(6)}$], 130.05 [$C_{(7)}$], 132.94 [$C_{(10a)}$], 133.83 [$C_{(5)}$], 143.31 [$C_{(1)}$], 143.52 [$C_{(9a)}$], 145.13 [$C_{(4a)}$], 147.75 [$C_{(3)}$], 148.00 [$C_{(8a)}$], 166 ppm [$C_{(4')}$]. Mass spectrum, m/z (%): 280 (26), 279 (34), 265 (3), 251 (100), 239 (3.5), 238 (4), 237 (8.6), 223 (58.7), 222 (13.6); M^+ 280.

9-(4'-Dimethylaminophenyl-1'-azo)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (VII, $C_{22}H_{24}N_4Si$). A 0.5-g (2.08 mmole) sample of amine I and 0.38 g (2.10 mmole) of p-nitrosodimethylaniline were refluxed in 30 ml of glacial acetic acid, after which the mixture was poured into 50 ml of water, and the aqueous mixture was neutralized with sodium carbonate. The reaction products were extracted with ether (four 35-ml portions), and the ether extract was dried with magnesium sulfate. The ether was removed by distillation, and the residue was chromatographed on silica gel (40 × 2 cm) by elution with a mixture of petroleum ether with ethyl acetate (5:1) to give 0.32 g (40%) of diazo compound VII in the form of dark-orange crystals with mp 122-125°C (hexane—ethyl acetate) and R_f 0.5 (ethyl acetate). IR spectrum: 1630 cm^{-1} (N=N).

9-(N-Phenylcarbamoylamino)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (VIII, $C_{21}H_{21}N_3OSi$). A 1.2-g (5 mmole) sample of amine I, 2 ml (1.8 mmole) of triethylamine, and 0.7 g (5.8 mmole) of phenyl isocyanate were refluxed for 5 h in 40 ml of absolute benzene (monitoring by TLC). The precipitate was removed by filtration and crystallized from a mixture of hexane with ethyl acetate to give 1.7 g (95%) of carbamoyl derivative VIII in the form of white crystals with mp 195-197°C and R_f 0.4 (ethyl acetate). IR spectrum: 1720 (CO), 3220 and 3400 cm^{-1} (NH). ^1H NMR spectrum: 0.43 (3H, s, $SiCH_3$), 0.48 (3H, s, $SiCH_3$), 5.32

(1H, d, $J_{NH,9H}$ = 8 Hz, NH), 6.25 (1H, d, 9-H), 8.50 (1H, d, $J_{3,4}$ = 4.5 Hz, 3-H), 8.86 ppm (1H, s, 1-H). Mass spectrum: M^+ 359.

Nitrosation of 9-(N-Phenylcarbamoylamino)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene. A 2-g (28.9 mmole) sample of sodium nitrite was added in portions in the course of 2 h at 0°C to 0.5 g (1.4 mmole) of VIII in a mixture of 20 ml of acetic anhydride and 5 ml of glacial acetic acid. After 1.5 h (monitoring by TLC), the reaction mass was poured into 50 ml of water, and the aqueous mixture was neutralized with 15% sodium carbonate solution. The reaction products were extracted with ether (three 20-ml portions), and the extract was dried with magnesium sulfate. The residue was chromatographed on silica gel (45 × 2 cm) by elution with a mixture of hexane with ethyl acetate (1:10). Initially we isolated 0.1 g (28%) of diazo compound IV ($C_{14}H_{13}N_3Si$) in the form of pinkish-lilac crystals with mp 59-61°C (from hexane) and R_f 0.56 (ethyl acetate), and M^+ 251; no melting-point depression was observed for a mixture of this product with a genuine sample. Next we isolated 0.1 g (30%) of 10,10-dimethyl-10-sila-2-azaanthrone in the form of colorless crystals with mp 149-150°C (from heptane); no melting-point depression was observed for a mixture of this product with a genuine sample. Finally we eluted 0.05 g (16%) of 10,10-dimethyl-9,10-dihydro-10-sila-2-aza-9-anthrol ($C_{14}H_{15}NOSi$) in the form of colorless crystals with mp 182-184°C (from ethyl acetate) and M^+ 241; no melting-point depression was observed for a mixture of this product with a genuine sample.

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