9-(2-OXO-1-AZETIDINYL)-10,10-DIMETHYL-9,10-DIHYDRO-10-SILA-2-AZAANTHRACENES

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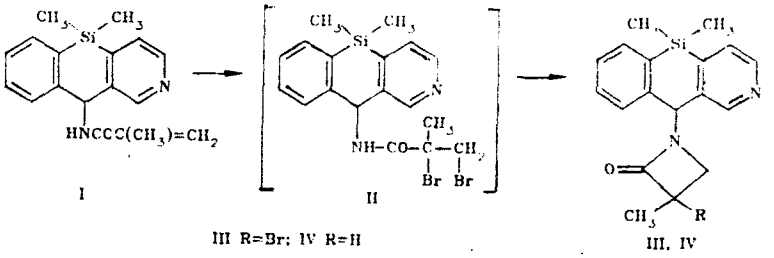
9-(3-Methyl-3-bromo-2-oxo-1-azetidinyl)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene was obtained in the form of a mixture of two diastereomers by intramolecular cyclization of the corresponding 9-(α,β-dibromoisobutyrylamino)dihydrosilaazaanthracene in the presence of sodium hydride, as well as Triton B. It was established by two-dimensional nuclear Overhauser effect (NOE) spectroscopy that the azetidinyl substituent in the 9 position has a pseudoaxial orientation vis-à-vis a boat conformation of the central silicon-containing ring.

It has been previously shown [1] that spiro[dihydrosilaazaanthracene-9,4'-azetidinone] is formed in the intramolecular cyclization of 9-(chloroacetylamino)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene in the presence of sodium hydride. In the present research we studied the cyclization under the same conditions of a similar compound with an α,β-dibromoisobutyrylamino group attached to the $C_{(9)}$ atom.

The acylation of 9-amino-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene [2] with methacrylyl chloride gave 9-(methacrylylamino)dihydrosilaazaanthracene I, which was converted to 9-(α,β-dibromoisobutyryl)amino derivative II by bromination.



Dibromo derivative II was not obtained in individual form, since quaternary salts involving the pyridine fragment of the molecule formed during attempts to isolate it. Theoretically, aziridine, azetidine, and pyrrolidine rings may be formed as a result of the intramolecular cyclization of II due to the participation of bromine and the NH and 9-H hydrogen atoms. It was demonstrated by means of TLC that only one compound is formed in the cyclization of dibromo derivative II in the presence of sodium hydride or Triton B. 9-(3-Bromo-3-methyl-2-oxo-1-azetidinyl)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (III) was isolated from the reaction mixture in 25-30% yield by chromatography. Triton B is less active in this cyclization reaction than sodium hydride. The low yield of III is due to the fact that it is oxidized during chromatography to give 10,10-dimethyl-9,10-dihdyro-10-sila-2-aza-9-anthrone, the yield of which was 70% in separate experiments. Compound III was reduced quantitatively with activated zinc in alcohol to azetidinyldihydrosilaazaanthracene IV, which proved to be stable during chromatography.

In the mass spectra* of III and IV we observed low-intensity molecular-ion peaks at 388 (2.5)† and 308 (11), which correspond to their empirical formulas. The maximally intense peak is the peak of a fragment ion at 224 due to the detachment of an azetidinone fragment from the M^+ ion. This sort of pathway of fragmentation of the molecular ion is characteristic for 9-acylamino-substituted dihydrosilaazaanthracenes [3].

The IR spectra of III and IV are characterized by the presence of an intense absorption band at, respectively, 1770 and 1780 cm^{-1} due to the stretching vibrations of the CO group of a β-lactam ring [4].

Paired signals with similar chemical shifts and multiplicities corresponding to two diastereomers with IIIA:IIIB = 1.2:1.0 and IVA:IVB = 1.4:1.0 are observed in the PMR spectra of III and IV (see Table 1). The presence of an azetidinone fragment in the III and IV molecules is confirmed by the geminal spin-spin coupling constants (SSCC) of the 4'-CH_2 group (J = 5.9 Hz for IIIA,B and J = 5.1 Hz for IVA,B) and the vicinal SSCC $^3J_{3'4'}^{cis}$ = 5.1 Hz and $^3J_{3'4'}^{trans}$ = 2.4 Hz for IVA,B. The structure of IV was additionally confirmed by the ^{13}C NMR spectra (see Table 2).

*Here and subsequently, the m/z values (I, percent relative to I_{max}) are presented for the ion peaks.
†Based on the ^{81}Br isotope.

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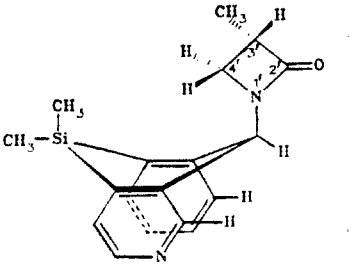
TABLE 1. PMR Spectra of Diastereomers IIIA,B and IVA,B

Diastereomer	Chemical shifts, ppm												
										Azetidinone			
	1-H	3-H	4-H	5-H	6-H	7-H	8-H	9-H	10-CH_3	3′-H	3′-CH_3	4′-H	4″-H
III A	8,77	8,59	7,49	7,59	7,42	7,51	7,63	6,32	0,49; 0,53	—	1,80	3,18	3,05
III B	8,81	8,57	7,49	7,59	7,42	7,49	7,63	6,29	0,50; 0,54	—	1,77	3,17	3,04
IV A	8,77	8,57	7,47	7,56	7,38	7,46	7,60	6,29	0,47; 0,50	3,04	1,18	2,93	2,38
IV B	8,77	8,55	7,47	7,55	7,39	7,48	7,60	6,29	0,46; 0,50	3,06	1,16	2,91	2,38

It is known that the central ring of substituted 10,10-dimethyl-9,10-dihydrosilaazaanthracenes is characterized by a boat conformation [5]. To establish the orientation of the azetidinonyl substituent in the 9 position we obtained the two-dimensional nuclear Overhauser effect (NOESY) spectrum of a mixture of the IV diastereomers, in which nondiagonal cross peaks from 1-H–9-H, 8-H–9-H, 3′-CH_3–10-CH_3, and 4′-H–10-CH_3 proton pairs are observed. The set of indicated NOE cross peaks provides unambiguous evidence for a pseudoaxial orientation of the azetidinonyl substituent vis-à-vis the boat conformation of the central six-membered ring.



The result obtained is in agreement with the conclusion in [6] that in 9,10-dihydroanthracenes substituents with high conformational energies in the 9 and 10 positions prefer to take on a pseudoaxial orientation because of repulsion on the part of the aromatic rings.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions in $CDCl_3$ were obtained with a WM-400 spectrometer with tetramethylsilane (TMS) as the internal standard. The mass spectra were obtained with an MKh-1303 spectrometer. Thin-layer chromatography was accomplished on Silufol plates; L 100/250 silica gel was used for column chromatography.

The results of analysis for C, H, and N were in agreement with the calculated values.

9-Methacrylylamino-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (I, $C_{18}H_{20}N_2OSi$). A 1.9-g (18 mmole) sample of methacrylyl chloride in 20 ml of absolute ether was added at 20°C in the course of 0.5 h to a solution of 4 g (17 mmole) of 9-amino-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene and 1.8 g (18 mmole) of triethylamine in 100 ml of absolute ether. After 2 h (monitoring by TLC), the precipitate was removed by filtration and washed on the filter with 50 ml of ether and water. The ether layer was separated 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 heptane–ethyl acetate to give 4.72 g (92%) of colorless crystals of I with mp 154-155°C and R_f 0.43 (ethyl acetate). IR spectrum: 1650 ($C{=}CH_2$), 1690 (CO), 3200 cm^{-1} (NH). Mass spectrum: 308 (M^+, 22), 293 $[M - CH_3]^+$ (6), 239 $[M - CH_2{=}C(CH_3)CO]^+$ (100), 224 $[M - CH_2{=}C(CH_3)CONH]^+$ (59).

9-(3-Bromo-3-methyl-2-oxo-1-azetidinyl)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (III, $C_{18}H_{19}BrN_2OSi$). A. A solution of 0.25 g (1.56 mmole) of bromine in 10 ml of absolute benzene was added dropwise in the course of 0.5 h in a stream of helium at 20°C to a solution of 0.45 g (1.46 mmole) of amide I in 80 ml of absolute benzene. After 2 h (monitoring by TLC), 10 ml of absolute DMF and 0.2 g (8.3 mmole) of sodium hydride were added, and the mixture was heated for 3 h at 80°C (monitoring by TLC). It was then cooled and treated with 50 ml of water. The benzene layer was separated, the aqueous layer was extracted with benzene (two 40-ml portions), and the combined extract was dried with magnesium sulfate. The residue (0.6 g) that remained after removal of the benzene by distillation was chromatographed with a column (45 by 2 cm) in heptane–ethyl acetate (5:1) to successively elute 0.25 g (72%) of 10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthrone and 0.17 g (30%) of light-yellow crystals of III with mp 109-110°C (heptane–ethyl acetate) and R_f 0.25 [hexane–ethyl acetate (1:1)].

B. A 1-g (3.2 mmole) sample of amide I in 80 ml of absolute benzene was brominated with 0.6 g (3.7 mmole) of bromine as described above. At the end of the reaction 4 ml of an alcohol solution of Triton B was added to the reaction mixture, and the resulting mixture was heated for 3 h at 80°C. It was then worked up as described above.

TABLE 2. ^{13}C NMR Spectra of Diastereomers IVA,B

Diastereomer	Chemical shifts, ppm													
	$C_{(1)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(7)}$	$C_{(8)}$	$C_{(9)}$	10-CH_3	$C_{(2')}$	$C_{(3')}$	3'-CH_3	$C_{(4')}$	$C_{(4a)}$, $C_{(8a)}$, $C_{(9a)}$, $C_{(10a)}$
IVA	147,65	150,70	127,61	133,51	127,21	130,59	130,01	55,22	−2,35; −0,68	169,86	43,91	13,36	44,30	139,94 ... 144,65
IVB	147,65	150,83	127,61	133,51	127,21	130,58	130,17	55,22	−2,35; −0,68	170,40	43,82	13,20	44,30	139,94 ... 144,65

The residue (1.4 g) was chromatographed rapidly with a column (80 by 1.5 cm) under nitrogen pressure in heptane—ethyl acetate (1:1) to successively elute 0.3 g (25%) of III [mp 108-109°C (no melting-point depression was observed for a mixture of this product with a sample obtained by method A)] and 0.15 g (15%) of amide I (colorless crystals, mp 152-153°C).

9-(3-Methyl-2-oxo-1-azetidinyl)-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (IV, $C_{18}H_{20}N_2OSi$). A 0.25-g (0.64 mmole) sample of III was refluxed for 8 h with 0.2 g (3.23 mmole) of activated zinc dust in 50 ml of alcohol. The filtrate was made alkaline to pH 10 and extracted with ether (three 50-ml portions), and the extract with dried with magnesium sulfate. The residue (0.24 g) remaining after removal of the ether by distillation was chromatographed with a column (30 by 1.5 cm) in heptane—ethyl acetate (5:1) to give, initially, 20 mg (8%) of starting III, with mp 108-109°C, and then 0.18 g (90%) of colorless crystals of IV with mp 103-104°C (hexane—ethyl acetate) and R_f 0.29 (ethyl acetate).

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