# 10-SILA-2-AZAANTHRACENES HYDROGENATED IN THE PYRIDINE FRAGMENT

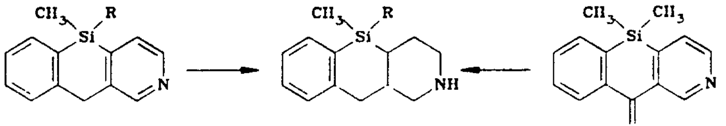
N. A. Prostakov, A. V. Varlamov, M. A. Ryashentseva,
A. A. Fomichev, V. A. Rezakov, Kossuo Kozm,
V. M. Polosin, Nazrul Islam, and V. K. Shevtsov

UDC 547.828'672.1.04:542.942:
541.634:542.51'422

*The corresponding 1,2,3,4,4a,9,9a,10-octahydro derivatives were obtained in the catalytic hydrogenation of 10,10-dimethyl- and 10-methyl-10-phenyl-9,10-dihydro-10-sila-2-azaanthracenes. The hydrogenation of 10,10-dimethyl-10-sila-2-azaanthrone also leads to a substituted octahydrosilaazaanthracene. Isomeric (with respect to the position of the double bond in the nitrogen-containing ring) hexahydrosilaaza-9-anthrols were isolated as a result of the reduction of the methiodide of this silaazaanthrone with sodium borohydride.*

Rhenium heptasulfide is a catalyst for the selective hydrogenation of polynuclear heterocyclic compounds containing a pyridine ring [1, 2]. Hydrogenation of only the nitrogen-containing ring occurs under relatively severe conditions (250-300°C, 120-150 atm).

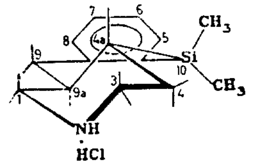
10,10-Dimethyl- and 10-methyl-10-phenyl-1,2,3,4,4*a*,9,9*a*,10-octahydro-10sila-2-azaanthracenes III and IV were obtained in 55-60% yields in the hydrogenation of 10,10-dimethyl- and 10-methyl-10-phenyl-9,10-dihydro-10-sila-2-azaanthracenes I and II [3] in the presence of rhenium heptasulfide. Like the hydrogenation of azafluorenones [1], the hydrogenation of 10,10-dimethyl-10-sila-2-azaanthrone (V) under similar conditions is accompanied by complete reduction of the carbonyl group to give octahydro compound III.



I, II    III, IV    V

I. III R=$CH_3$; II, IV R=$C_6H_5$

The structure of III was confirmed by analysis of the PMR spectrum of its hydrochloride (Table 1). The vicinal spin-spin coupling constants (SSCC) of the aliphatic protons ($J_{aa}$ = 11.5-12.0, $J_{ae}$ = 3.0-3.8, and $J_{ee}$ = 3 Hz) show that the piperidine fragment of III has a fixed chair conformation, while the tetrahydrosilanaphthalene fragment has the half-chair conformation that is usual for cyclohexenes and tetrahydronaphthalenes [4]. These rings are trans-diequatorially fused.



The substantial shift to weak field of the 1-$H_e$ and 3-$H_e$ protons of the α-methylene groups of the piperidine ring (3.47 and 3.52 ppm) and the large (in absolute value) geminal SSCC (–16 Hz) of the $C_{(9)}$ protons in the vicinity of the π-electron system of the benzene ring are also characteristic. The decrease in the geminal SSCC (–11.5 Hz) for the protons of the α-methylene groups is due to the effect of the electronegative nitrogen atom.

Molecular-ion peaks with m/z 231 (100)* and m/z 293 (100) are observed in the mass spectra of octahydrosilaazaanthracenes III and IV. The principal pathway of fragmentation of the $M^+$ ions is detachment of the radicals bonded to the sili-

---

*The relative intensities of the ion peaks are presented in parentheses.

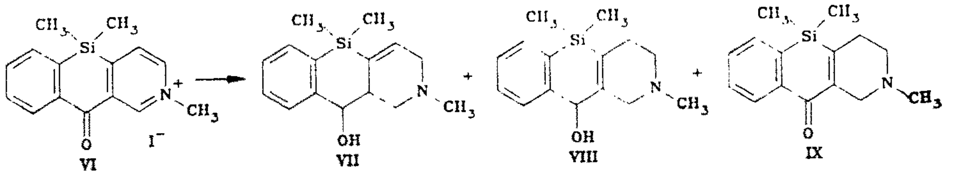
Patrice Lumumba Peoples' Friendship University, Moscow 117923. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1279-1284, September, 1990. Original article submitted July 14, 1988.

0009-3122/90/2609-1068 $12.50 ©1991 Plenum Publishing Corporation

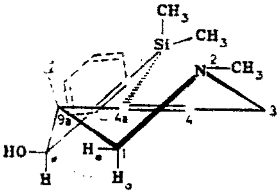
con atom, which is accompanied by the formation of $[M - CH_3]^+$ fragment ions with m/z 216 (47) for III and of $[M - C_6H_5]^+$ fragment ions with m/z 216 (21) and $[M - CH_3]^+$ fragment ions with m/z 278 (14) for IV. In contrast to the fragmentation of dihydrosilaazaanthracene II [5], in which the maximally intense peak is the peak corresponding to detachment of a molecule of benzene from the $M^+$ ion, this fragmentation pathway is not realized in the fragmentation of octahydro derivative IV. The reason for this is evidently replacement of the boat conformation of the central silicon-containing ring (II) by a half-chair conformation (III and IV), which leads to an increase in the distance between the phenyl radical attached to the silicon atom and the methylene group in the 9 position.

To obtain partially hydrogenated (in the nitrogen-containing ring) silaazaanthracenes – subjects for a study of the physiological activity – we reduced 10,10-dimethyl-10-sila-2-azaanthrone methiodide (VI) with sodium borohydride. The reduction products were isolated from the resulting mixture by chromatography, and their structures were established by spectral methods.

1,2,3,9,9*a*,10-Hexahydro-10-sila-2-aza-9-anthrol VII predominated (40% yield) in the mixture; the isomeric (with respect to the position of the double bond in the nitrogen-containing ring) 1,2,3,4,9,10-hexahydro-10-sila-2-aza-9-anthrol VIII was isolated in 9% yield. In addition to VII and VIII, 1,2,3,4-tetrahydro-10-sila-2-azaanthrone IX is formed in very low yield (3%).



The IR spectra of VII-IX at 2780-2800 $cm^{-1}$ contain bands of stretching vibrations of an $N–CH_3$ group. A band of stretching vibrations of the C=C bond in VII and VIII is observed at 1635-1640 $cm^{-1}$, while this band is observed at 1610 $cm^{-1}$ in the case of IX as a consequence of its conjugation with the carbonyl group [6]. Bands of an associated hydroxy group are located at 3165 and 3150 $cm^{-1}$ in the spectra of alcohols VII and VIII, respectively. The band of the carbonyl group of IX is located at 1640 $cm^{-1}$. The structures of VII and VIII were established unequivocally by means of PMR spectroscopy (Table 1). Signals of one olefin proton (6.02 ppm), two isolated (from one another) pairs of methylene protons, and a 9*a*-H methylidyne proton are observed in the spectrum of VII. The large negative $^2J_{3-H_a,3-H_e}$ value (–16 Hz) can be explained by the effect of the π orbital of the adjacent $C_{(4)}–C_{(4a)}$ double bond vis-à-vis small torsion angles in the allyl fragment [7]. In the aggregate, this unambiguously determines the position of the 4–4*a* double bond. It is natural to assume that in this case the tetrahydropyridine ring, just like the central ring, will have a half-chair conformation.



However, vicinal constants of spin-spin coupling of the methylene protons attached to the $C_{(1)}$ atom with the 9*a*-H proton ($^3J_{cis}$ = 5.0 Hz and $^3J_{trans}$ = 7.9 Hz, Table 1) that differ little can be obtained only by averaging in the case of $1\text{-}H_a \rightleftarrows 1\text{-}H_e$ proton exchange, which is possible in the case of bending of the tetrahydropyridine ring along the $C_{(1)}–C_{(3)}$ line. Thus, the designation of axial and equatorial orientations adopted here is extremely arbitrary and can be ascribed only to a slightly more populated conformation. This conformational lability can be explained by the additional strain in the tetrahydropyridine ring because of the adjacency of the double bond and the "rigid" bridge $C_{(9a)}$ atom. The large value of the vicinal constant of spin-spin coupling of the 9*a*-H and 9-H protons (10.8 Hz) can be due only to a trans-diaxial interaction, which determines the fixed equatorial orientation of the hydroxy group in VII. The special spatial orientation of the 9*a*-H proton is reflected in the spin-spin coupling of this proton with all of the protons of the unsaturated bicyclic system (those attached to the $C_{(9)}$, $C_{(1)}$, $C_{(3)}$, and $C_{(4)}$ atoms; see Table 1). Exceptionally large long-range homoallyl constants of spin-spin coupling ($^5J_{HH}$) of the 9*a* proton with the protons attached to the $C_{(3)}$ atom (3 and 2.5 Hz, Table 1) are extremely characteristic for the monoene six-membered ring. Similar values of these SSCC have already been observed in substituted 3-piperidines [8].

According to the PMR data (Table 1), a boat conformation can be assumed for the central silicon-containing ring of VIII, while a half-chair conformation can be assumed for the tetrahydropyridine ring. The large difference in the chemical shifts of

TABLE 1. Spectral Characteristics of III, VII, and VIII

| Compound | Chemical shifts, δ, pp (250 MHz, $CDCl_3$) | | | | | | | | | | | | | | | | | $I_{rel}$, *% | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $1\text{-}H_a$ | $1\text{-}H_e$ | $3\text{-}H_a$ | $3\text{-}H_e$ | $4\text{-}H_a$ | $4\text{-}H_e$ | 4a-H | 9a-H | $9\text{-}H_a$ | $9\text{-}H_e$ | 5-H | 6-H | 7-H | 8-H | $Si{-}CH_3$ | N—R | OH | M⁺ | $(M-H)^+$ | $(M-H_2O)^+$ | $[M-Si(CH_3)_2]^+$ | $[M-CH_2{=}NHCH_3]^+$ | $(M-H_2O-H)^+$ | $(M-H_2O-C_2H_4)^+$ |
| III*2 | 2,55 | 3,47 | 2,82 | 3,52 | 2,01 | 1,88 | 0,85 | 2,35 | 2,52 | 2,64 | 7,40 | 7,22. 7,25 | | 7,06 | 0,21; 0,23 | 7,36 ($NH_2$) | — | — | — | — | — | — | — | — |
| VII*3 | 2,10 | 3,02 | 2,78 | 3,07 | 6,13 | | — | 2,70 | 4,39 | — | 7,42 | 7,23 | 7,38 | 7,72 | 0,21; 0,27 | 2,23 ($N{-}CH_3$) | 2,7 | 100 | — | 32 | 35 | 35 | 59 | — |
| VIII*4 | 2,83 | 3,44 | 2,30 . . . 2,60 | | | | — | — | 4,83 | — | 7,40 | 7,22 | 7,31 | 7,48 | 0,23; 0,30 | 2,16 ($N{-}CH_3$) | 3,15 | 60 | 22 | 100 | — | — | 18 | 20 |

---

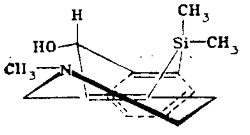
*For VII and VIII, $I_{rel}$ for the $[M-H_2O-Si(CH_3)_2]^+$ ion is 35%, while $I_{rel}$ for the $[M-H_2O-CH_3]^+$ ion is 15%.

*2Spectrum of the hydrochloride: $J_{1a1e} = J_{3a3e} = -11.5$; $J_{4a4e} = -13.0$, $J_{9a9e} = 16.00$, $J_{1a9a} = 11.5$, $J_{1e9a} = J_{9a9c} = J_{4a3e} = J_{4a3e} = 3.0$, $J_{9a9a} = -11.5$, $J_{4a9a} = J_{4a3a} = 12.0$, $J_{4a4e} = 3.8$, $J_{4e3a} = 3.5$ Hz.

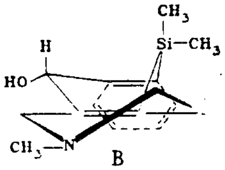
*3$J_{1a1e} = -11.6$, $J_{3a3e} = 16.9$, $J_{1a9a} = 7.9$, $J_{1e9a} = 5.0$, $J_{9a9a} = 10.8$, $J_{3a4} = 2.5$, $J_{3e4} = 3.5$, $J_{9a4} = 2.4$, $J_{9a3a} = 2.5$, $J_{9a3e} = 3.0$ Hz.

*4$J_{1a1e} = -16$, $J_{1a4a} \sim J_{1e4a} \sim J_{1a4e} \sim J_{1e4e} \sim 2.0$ Hz.

the protons attached to the $C_{(1)}$ atom constitutes evidence in favor of conformational homogeneity or substantial predominance of one of the conformers (**A** or **B**).



A



B

Peaks of molecular ions corresponding to their empirical formulas are observed in the mass spectra of VII-IX. The peculiarities of the fragmentation of isomers VII and VIII (Table 1) due to different locations of the double bond in the tetrahydropyridine fragment can be used for the structural analysis of similar systems.

The elimination of water and the formation of an $[M - H_2O]^+$ ion are characteristic for the fragmentation of the molecular ions of isomeric alcohols VII and VIII. Water is split out from the $M^+$ ion of VII in one step; this is due to the presence of a 9*a*–H proton. Splitting out of water from the $M^+$ ion of isomer VIII is a stepwise process: hydrogen is initially split out, and this is followed by splitting out of a hydroxy group. The existence of the indicated processes is confirmed by the corresponding metastable ions. In contrast to VIII, where stepwise splitting out of water is the only pathway of fragmentation of the $M^+$ ion, splitting out of $Si(CH_3)_2$ and $CH_2{=}\overset{+}{N}H{-}CH_3$ particles is characteristic for the dissociative ionization of the $M^+$ ion of isomer VII. The formation of an $[M - NC_2H_6]^+$ ion with m/z 215 is characteristic for the fragmentation of VII. The ejection of hydrogen and dimethylsilyl and methyl groups from the $[M - H_2O]^+$ ion is observed in the second stage of fragmentation for both isomers. A different structure of the $[M - H_2O]^+$ ions is responsible for the development in the case of the fragmentation of VIII of a characteristic ion with m/z 213, which is formed as a result of splitting out of a $C_2H_4$ particle. This fragmentation pathway is confirmed by the corresponding metastable ion.

10,10-Dimethyl-2-(p-nitrobenzyl)-1,2,3,3,9*a*,10-hexahydro-10-sila-2-aza-9-anthrol (XI), the structure of which was proved by means of PMR (Table 1) and IR (see Experimental) spectroscopy, was obtained in ~40% yield in the reduction of 10,10-dimethyl-2-(p-nitrobenzyl)-9-oxo-10-sila-2-azoniaanthracene bromide (X) with sodium borohydride.

## EXPERIMENTAL

The PMR spectra of the compounds were recorded with WP-80-SY, WM-250, and WM-400 spectrometers with tetramethylsilane (TMS) as the internal standard. The IR spectra of KBr pellets of the compounds were obtained with a UR-20 spectrometer. The mass spectra were measured with MKh-1303 and CN-8 mass spectrometers with a system for the direct introduction of samples into the ion source at an ionizing voltage of 70 V.

Thin-layer chromatography (TLC) was carried out on a loose layer of Brockman activity II $Al_2O_3$ and on Silufol UV-254 plates. Column chromatography was carried out on L100/160μ silica gel and on activity II $Al_2O_3$.

**10,10-Dimethyl-1,2,3,4,4*a*,9,9*a*,10-octahydro-10-sila-2-azaanthracene (III, $C_{14}H_{19}NSi$). A.** An autoclave was charged with 1 g (4.4 mmoles) of dihydrosilaazaanthracene I [3], 15 ml of benzene, and 0.1 g of rhenium heptasulfide, and hydrogenation was carried out for 3 h at 260°C and a hydrogen pressure of 130 atm. The mixture was then cooled, and the catalyst was removed by filtration. The benzene was removed by distillation, and the residue was treated with 5 ml of hydrochloric acid (1:1). The neutral reaction products were extracted with ether (two 20-ml portions). The aqueous solution was made alkaline to pH ~10 with ammonia, and the nitrogen bases were extracted with ether (three 50-ml portions). The extract was dried with magnesium sulfate, and the ether was removed by distillation to give 0.65 g (63%) of silaazaanthracene III in the form of colorless crystals with mp 99-100°C (from hexane) and $R_f$ 0.43 [Silufol, ethanol–chloroform (1:1)]. IR spectrum: 815 and 1260 ($Si{-}CH_3$), 3450 $cm^{-1}$ (NH).

**B.** A 0.6-g (62%) sample of III, with mp 98-99°C (from hexane), was obtained from 1 g (4.2 mmoles) if silaazaanthrone V [3] and 0.1 g of rhenium heptasulfide by hydrogenation in benzene via the method described above. No melting-point depression was observed for a mixture of samples of the compounds obtained by methods A and B.

**10-Methyl-10-phenyl-1,2,3,4,4*a*,9,9*a*,10-octahydro-10-sila-2-azaanthracene (IV, $C_{19}H_{23}NSi$).** This compound was similarly obtained from 1 g (3.5 mmoles) of dihydrosilaazaanthracene II [3] and 0.1 g of rhenium heptasulfide in 15 ml of benzene. This procedure gave 0.56 g (55%) of colorless crystals with mp 110-111°C (from heptane) and $R_f$ 0.62 [Silufol, ethanol–chloroform (1:1)]. IR spectrum: 815 and 1263 ($Si{-}CH_3$), 1109 and 1435 ($Si{-}C_6H_5$), 3430 $cm^{-1}$ (NH).

**10,10-Dimethyl-9,10-dihydro-10-sila-2-azaanthrone Methiodide (VI, $C_{15}H_{16}INOSi$).** A 7.0 g (29 mmoles) sample of silaazaanthrone V and 2.24 g (29 mmoles) of methyl iodide were refluxed in 200 ml of benzene for 5 h with the addition of another 2.24 g of methyl iodide twice during this period. The precipitate was removed by filtration and recrystallized from methanol to give 9.6 g (86%) of salt VI in the form of orange acicular crystals with mp 207-208°C.

**2,10,10-Trimethyl-1,2,3,9,9*a*,10- and -1,2,3,4,9,10-hexahydro-10-sila-2-aza-9-anthrols (VII and VIII, $C_{15}H_{21}NOSi$) and 2,10,10-Trimethyl-9-oxo-1,2,3,4-tetrahydro-10-sila-2-azaanthracene (IX, $C_{15}H_{19}NOSi$).** An 8.5-g (0.22 mmole) sample of sodium borohydride was added in the course of 1.5 h at 20°C to a solution of 8 g (21 mmoles) of salt VI in 300 ml of methanol, after which the mixture was heated for 20 min at 40°C. It was then cooled and poured into 700 ml of water. The reaction products were extracted with ether (five 100-ml portions), and the extract was dried with magnesium sulfate. The ether was removed by distillation, and the residue (4.1 g) was chromatographed on aluminum oxide (70 × 2 cm column). Elution with ether initially gave 0.1 g (3%) of ketone IX in the form of colorless crystals with mp 175-176°C (heptane–ethyl acetate) and $R_f$ 0.8 [$Al_2O_3$, ethyl acetate–alcohol (10:1)]. PMR spectrum: 0.34 (6H, s, Si–$CH_3$), 2.42 (3H, s, N–$CH_3$), 2.50-2.80 (4H, m, 3-H, 4-H), 3.40 (2H, m, 1-H), 7.25-7.60 (3H, m, 5-H–7-H), 8.30 ppm (1H, d, 8-H). Subsequent elution gave 2.17 g (40%) of hexahydrosilaazaanthrol VII in the form of colorless crystals with mp 115-116°C (hexane–ethyl acetate) and $R_f$ 0.6 [$Al_2O_3$, ethyl acetate–alcohol (10:1)]. Final elution with ethyl acetate–hexane (2:1) gave 0.49 g (9%) of hexahydrosilaazaanthrol VIII in the form of colorless crystals with mp 155-156°C (heptane–ethyl acetate) and $R_f$ 0.42 [$Al_2O_3$, ethyl acetate–alcohol (10:1)].

**10,10-Dimethyl-2-(p-nitrobenzyl)-9-oxo-10-sila-2-azoniaanthracene Bromide (X, $C_{21}H_{19}BrN_2O_3Si$).** A mixture of 1.3 g (5 mmoles) of V and 1.87 g (9 mmoles) of p-nitrobenzyl bromide was refluxed for 10 h in 40 ml of methanol. The methanol was removed by distillation, and the residue was triturated repeatedly with ether to give 2.5 g (90%) of salt X in the form of white crystals with mp 217-219°C (from alcohol).

**10,10-Dimethyl-2-(p-nitrobenzyl)-1,2,3,9,9*a*,10-hexahydro-10-sila-2-aza-9-anthrol (XI, $C_{21}H_{24}N_2O_3Si$).** A 1-g (26 mmoles) sample of sodium borohydride was added to a solution of 1 g (2.2 mmoles) of salt X in a mixture of 40 ml of alcohol and 5 ml of water. After 10 h, the reaction mass was poured into 100 ml of water, and the reaction products were extracted with chloroform. The extract was dried with magnesium sulfate, the chloroform was removed by distillation, and the residue was chromatographed with a column (40 × 2 cm) packed with aluminum oxide by elution with ethyl acetate–heptane (1:5). Elution gave 0.35 g (38%) of XI in the form of colorless crystals with mp 136-138°C (ethyl acetate-heptane) and $R_f$ 0.43 [$Al_2O_3$, ethyl acetate–heptane (1:1)]. IR spectrum: 1355 and 1530 ($NO_2$), 1630 (C=C), 3450 $cm^{-1}$ (OH). PMR spectrum: 0.23 (3H, s, $SiCH_3$), 0.30 (3H, s, $SiCH_3$), 2.70-3.20 (5H, m, 1-H, 2-H, 9*a*-H), 3.70 (2H, s, $CH_2N$), 4.56 (1H, m, 9-H), 6.08 (1H, m, 4-H), 7.40 (2H, d, o-H of the nitrophenyl radical), 8.08 ppm (2H, d, m-H of the nitrophenyl radical).

## LITERATURE CITED

1. N. S. Prostakov, G. Alvorado-Urbina, M. A. Ryashentseva, and L. A. Gaivoronskaya, *Khim. Geterotsikl. Soedin.*, No. 10, 1379 (1973).
2. N. S. Prostakov, V. I. Kuznetsov, M. A. Ryashentseva, and L. M. Kirillova, *Khim. Geterotsikl. Soedin.*, No. 4, 517 (1979).
3. N. S. Prostakov, N. Saksena, A. V. Varlamov, and A. M. Klochkov, *Khim. Geterotsikl. Soedin.*, No. 2, 240 (1981).
4. F. R. Jensen and C. H. Bushweller, *Adv. Alicyclic Chem.*, 3, 139 (1971).
5. N. S. Prostakov, N. Saxena, P. I. Zakharov, and A. V. Varlamov, *J. Organomet. Chem.*, **184**, 167 (1980).
6. L. Bellamy, *Infrared Spectra of Complex Molecules*, Methuen, London (1958).
7. V. F. Bystrov, *Usp. Khim.*, 41, 512 (1972).
8. V. A. Rezakov, S. K. Das, A. A. Fomichev, and N. S. Prostakov, *Khim. Geterotsikl. Soedin.*, No. 10, 1367 (1986).