NITRO- AND AMINO-SUBSTITUTED 10,10-DIMETHYL-10-SILA-2-AZAANTHRONES

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Under conditions of the Mencke reaction, 10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene is nitrated on the benzene fragment of the molecule, but the corresponding ketone is nitrated on the pyridine fragment. Dihydrosilaazaanthrone is nitrated by nitrating mixture in positions 5, 7, and 8 of the benzene fragment of the molecule. The nitro-substituted dihydrosilazaanthrones have been reduced to the corresponding amino derivatives.

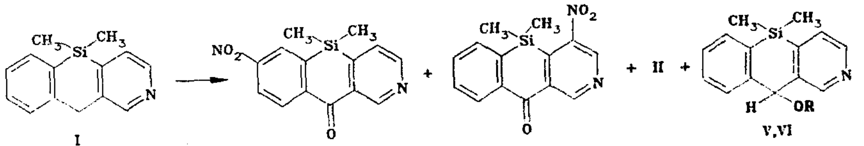
Nitro- and amino-substituted organosilicon compounds are of interest because they are the starting point in the synthesis of various derivatives with properties that are of practical value. The nitration of arylsilanes is a complex problem because of the instability of the $Si{-}C_{aryl}$ bond to the action of acids [1, 2]. The success in nitration depends on the selection of the nitrating agent and on the reaction conditions. The nitration of tricyclic condensed sila-containing heterocycles was first reported in [3].

We have studied the nitration of 10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (I) and the corresponding ketone (II). The synthesis of these compounds was first described in [4].

Compounds I and II differ in resistance to the action of 80% sulfuric acid at 20°. Whereas the dihydrosilaazaanthracene I exhibits quantitative cleavage of the $Si{-}C_{aryl}$ bond under these conditions, the dihydrosilazaanthrone II remains practically unchanged for 1-1.5 h. The high stability of the $Si{-}C_{aryl}$ bond in the silaazaanthrone II relative to the action of acids is apparently due to the electron-acceptor effect of the carbonyl group in the o-position, resulting in a decrease in electron density on the aromatic carbon atoms bonded to the silicon atom. The planar structure of the silaazaanthrone II favors maximum transmission of electronic effects of the carbonyl group.

These results governed our selection of the nitrating reagents used in the nitration of compounds I and II.

The nitration of the dihydrosilaazaanthracene I was accomplished by the use of copper, iron, or aluminum nitrate in mixtures with acetic anhydride. Under these conditions, we found that the nitration process is accompanied by oxidation of the nitration products and also the original I to the corresponding ketones. In all cases, we recovered from the reaction mixture as the main nitration product 6-nitro-10,10-dimethyl-10-sila-2-azaanthrone-9 (III) (15-17%), along with a small quantity (∿2%) of 4-nitro-10,10-dimethyl-10-sila-2-azaanthrone-9 (IV).



I III IV V,VI

V R=H; VI R=COCH$_3$

In addition to these compounds, we recovered the anthrone II (24-40%) and small amounts of 10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthrol (V) and its acetate (VI), products of the acetoxylation of the compound I.

In the nitration of the dihydrosilaazaanthrone II by copper nitrate in acetic anhydride, only the nitro derivative IV was formed, with a yield of about 1.5-2.5%. Thus, we can consider that compound III is formed as a result of oxidation of 6-nitro-10,10-dimethyl-9,10-

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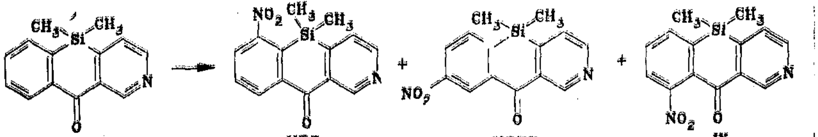
dihydro-10-sila-2-azaanthracene. The formation of this compound in the nitration of the silaazaanthracene I is due to predominance of the p-orienting effect of the methylene group, and the result is consistent with literature data on the nitration of silyl-substituted toluenes [5].

The nitration of the silaazaanthrone II by the nitrating mixture at 20° proceeds quantitatively and is confined to nitration at the phenylene fragment. This forms a mixture of 5- (VII), 7- (VIII), and 8-nitrosilaazanthrone (IX), with a predominance of the products of matched orientation of the carbonyl and dimethylsilyl groups — compounds VII and VIII.



II VII VIII IX

The formation of significant amounts of the 8-nitro derivative IX is apparently related to the low selectivity of the nitronium cation.

The different directions of nitration of the silaazaanthrone II under conditions of the Mencke reaction and in nitration by the nitrating mixture are due to differences in activity of both the nitrating agents and the pyridine and benzene fragments of the molecule. Nitration by the nitrating mixture is accompanied by protonation of the pyridine nitrogen, leading to a sharp deactivation of this fragment of the molecule with respect to electrophilic substitution. Under the conditions of the Mencke reaction, the quaternary salt is not formed. Here, the nitration, being accomplished by a weak electrophile, acetyl nitrate, should take place at the site of the highest electron density. Actually, calculation of the charges on the atoms in compound II by the CNDO/2 method shows that the greatest charge is concentrated on the atom in the $C_{(4)}$ position. The $C_{(5)}$ and $C_{(7)}$ atoms have high electron densities.

The nitro compounds III and VII-IX were reduced with hydrazine hydrate in the presence of Raney nickel to the corresponding 6- (X), 5- (XI), 7- (XII), and 8-amino-10,10-dimethyl-10-sila-2-azaanthrone-9 (XIII).

The positions of the nitro and amino groups in compounds III, IV, and VII-XIII were established by means of PMR spectrometry [6]. Relationships in the dissociative ionization of the nitro derivatives III, IV, and VII-IX under electron impact were examined in [7].

In the UV spectra of the nitro compounds III, IV, and VII-IX, bands are observed in the 374-384 nm region corresponding to the n-π* transition in the carbonyl group. However, in contrast to the silaazaanthrone II, where this band is very distinct, we find that for the nitro-substituted silaazaanthrones it is manifested in the form of a shoulder. This is due to overlapping of the bands of the π-π* and n-π transitions with the band of intramolecular charge transfer from the aromatic system to the nitro group.

EXPERIMENTAL

The UV spectra were taken in a Specord UV-Vis spectrophotometer in alcohol; the PMR spectra were taken in a Bruker WP 80 Fourier spectrometer (80 MHz) with TMS internal standard. The mass spectra were obtained in an MKh-1303 instrument. The column chromatography was performed on Al_2O_3 with Brockman standard activity II, and the thin-layer chromatography was performed on a fixed layer of silica gel, either Silufol UV-254 or L 100/160. Iodine vapor was used for development.

The characteristics of the compounds that were obtained are listed in Table 1.

6-Nitro- (III) and 4-Nitro-10,10-dimethyl-10-sila-2-azaanthrone-9 (IV). A. To a suspension of 8 g (21.3 mmoles) of $Al(NO_3)_2 \cdot 9H_2O$ in 100 ml of acetic anhydride at 20°, a solution of 3 g (13.3 mmoles) of the silaazaanthracene I in 30 ml of acetic anhydride was added. After 30 h, the reaction mass was poured onto ice and neutralized with ammonia. The reaction products were extracted with ether. The extract was dried with magnesium sulfate. The residue (3.0 g) after driving off the ether from the extract was chromatographed in a column (h = 50 cm, d = 2.5 cm) with aluminum oxide, elution with 5:1 heptane/ethyl acetate gave, successively, 0.07 g (1.9%) of the 4-nitro-substituted compound IV, 1.2 g (37.5%) of the dihydrosilaazanthrone II, and 0.35 g (9.3%) of the 6-nitro-substituted compound III. Then, using a 1:1 mixture of the same solvents, 0.02 g of the 9-acetoxydihydrosilaazaanthra-

TABLE 1. Characteristics of Nitro and Amino Derivatives of 10-Sila-2-azaanthrone-9

Comp.	mp, °C*	R_f † (Silufol)	M^+	UV spectrum, λ_{max}, nm (and log ε)	Found, %			Empirical formula	Calc., %			Yield (%)
					C	H	N		C	H	N	
III	204—206	0,62	284	208 (4,54); 280 (4,28); 380 (2,45)	59,4	9,4	4,4	$C_{14}H_{12}N_2O_3Si$	59,1	9,8	4,2	15
IV	194—196	0,6	284	206 (4,46); 236 (4,25); 273 (4,06); 384 (2,28)	59,3	9,6	4,3	$C_{14}H_{12}N_2O_3Si$	59,1	9,8	4,2	2
VII	215—217	0,7	284	206 (4,46); 250 (4,42); 380 (2,15)	59,2	9,6	4,4	$C_{14}H_{12}N_2O_3Si$	59,1	9,8	4,2	26
VIII	230—232	0,44	284	206 (4,26); 256 (4,34); 374 (2,12)	59,2	9,6	4,4	$C_{14}H_{12}N_2O_3Si$	59,1	9,8	4,2	17,3
IX	208—210	0,36	284	208 (4,46); 272 (4,04); 380 (2,46)	59,2	9,6	4,5	$C_{14}H_{12}N_2O_3Si$	59,1	9,8	4,2	25,7
X	168—170	0,31	254	—	66,2	5,7	10,8	$C_{14}H_{14}N_2OSi$	66,3	5,5	11,0	77
XI	220—222	0,46	254	—	66,3	5,5	11,0	$C_{14}H_{14}N_2OSi$	66,3	5,5	11,0	75
XII	208—210	0,52	254	—	66,1	5,2	10,9	$C_{14}H_{14}N_2OSi$	66,3	5,5	11,0	71
XIII	162—164	0,68	254	—	65,9	5,3	10,8	$C_{14}H_{14}N_2OSi$	66,3	5,5	11,0	62

*Compounds III, IV, IX, and XII were crystallized from ethyl acetate/heptane mixture; VII and VIII from ethyl acetate; XI and XIII from hexane/ether mixture.

†For compound IV, on aluminum oxide in ethyl acetate/heptane solvent system (1:2 ratio); for X, hexane/ethyl acetate solvent system (2:1); for other compounds, ether.

cene VI was eluted, mp 133-134° (from heptane). IR spectrum (KBr): 1745 cm^{-1} (C=O). PMR spectrum (in $CDCl_3$): 8.79 (1H, s, 1-H), 8.59 (1H, d, 3-H), 6.89 (1H, s, 9-H), 1.95 (3H, s, CH_3CO), 0.61 (3H, s, $Si{-}CH_3$), 0.56 ppm (3H, s, $Si{-}CH_3$). Mass spectrum: 283 (M^+, 14.9%); 268 [$(M{-}CH_3)^+$, 44.7%]; 241 [$(M{-}CH_2CO)^+$, 89.3%]; 240 [$(M{-}CH_3CO)^+$, 63.8%]; 224 [$(M{-}CH_3COO)^+$, 100%]. At the end of the chromatographic operation, ethanol was used to elute 0.3 g of the dihydrosilaazaanthrol V, mp 177-180° (from heptane/ethyl acetate mixture). Found: M^+ 241. $C_{14}H_{15}NOSi$. Calculated: M 241. A mixed sample with a standard material melted without any temperature depression.

B. To a mixture of 3.3 g (13.4 mmoles) of $Cu(NO_3)_2 \cdot 3H_2O$ and 20 ml of acetic anhydride, a solution of 1.5 g (6.6 mmoles) of the silaazaanthracene I in 10 ml of acetic anhydride was added. The mixture was heated to 70° and held at that temperature for 36 h. The reaction mass was worked up as described above. Obtained 0.01 g of compound IV, 0.4 g of the anthrone II, 0.33 g of compound III, and 0.1 g of the anthrol V.

4-Nitro-10,10-dimethyl-10-sila-2-azaanthrone-9 (IV). To a mixture of 2 g (8.12 mmoles) of $Cu(NO_3)_2 \cdot 3H_2O$ and 40 ml of acetic anhydride, at 60°, a solution of 0.6 g (2.5 mmoles) of the silaazaanthrone II in 10 ml of acetic anhydride was added over a period of 20 min. After holding for 40 h, the reaction mass was worked up in the same manner as shown for experiment A. By column chromatography with aluminum oxide, recovered 0.1 g (2%) of compound IV, mp 193-194° (from heptane/ethyl acetate mixture).

5- (VII), 7- (VIII), and 8-Nitro-10,10-dimethyl-10-sila-2-azaanthrone-9 (IX). To a solution of 3 g (12.5 mmoles) of the silaazaanthrone II in 25 ml of concentrated H_2SO_4, 17 ml of nitrating mixture was added while stirring vigorously over the course of 1 h (nitrating mixture 11 ml of concentrated H_2SO_4 and 6 ml of nitric acid, d = 1.5 g/cm^3). After 40 min, the reaction mass was poured onto ice and made alkaline with an aqueous ammonia solution. The reaction products were extracted with ether. The extract was dried with magnesium sulfate. The residue (3 g) after driving off the ether was chromatographed in a column with silica gel. The following products were eluted: with a 4:1 hexane/ethyl acetate mixture, 0.93 g (26%) of compound VII; then, with a 3:1 mixture of the same solvents, 0.36 g (10%) of compound VIII, 0.75 g (20%) of a mixture of compounds VIII and IX (a 1:2 mixture, according to PMR data), and finally, 0.41 g (12%) of compound IX.

6- (X), 5- (XI), 7- (XII), and 8-Amino-10,10-dimethyl-10-sila-2-azaanthrone-9 (XIII). To a solution of 2 mmoles of the corresponding nitro-substituted silaazaanthrone in 20 ml of alcohol, 3 ml of hydrazine hydrate and a catalytic quantity of Raney nickel were added. The reaction mass was held for 24-48 h at 20°. The course of the reduction was monitored by means of TLC. If necessary, addition amounts of the hydrazine hydrate and catalyst were added.

At the end of the reaction, the catalyst was filtered off, and the alcohol was evaporated under vacuum. A 10-ml quantity of water was added to the residue, and the reaction products were extracted with ether. The residue after driving off the ether from the extract was crystallized. In the IR spectra of the amines (in KBr), bands of stretching vibrations of the bound NH_2 group were observed in the 3200-3450 cm^{-1} region.

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DETERMINATION AND PROOF OF STRUCTURE OF MONOSUBSTITUTED DIHYDROSILAAZANTHRONES ON THE BASIS OF PMR SPECTRA

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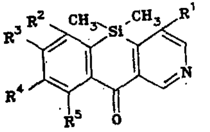
PMR spectra have been used in establishing the structure of ten bromo-, nitro-, and amino-substituted 10,10-dimethyl-10-sila-2-azaanthrones. Anomalous effects of NO_2 and NH_2 groups adjacent to the carbonyl carbon have been observed and explained; these effects are related to the specific geometry of these molecules.

One of the areas in studying silaazaanthrones that we have synthesized [1] is the determination of relationships in their substitution. The geometry of the planar molecules, which is determined by the substantially different lengths of the C–C and C–Si bonds [2] (Fig. 1), may influence the orientation of substituent entry and the chemical properties of the resulting compounds.



I–XII

I, III–VI, VIII–XII R^1=H; II R^1=NO_2; VII R^1=Br; I, II, IV–VII, IX, XI, XII R^2=H; III R^2=NO_2; VIII R^2=Br; X R^2=NH_2; I–III, V–XII R^3=H; IV R^3=NO_2; I–IV, VI–VIII, X, XII R^4=H; V R^4=NO_2; IX R^4=Br; XI R^4=NH_2; I–V, VII–XI R^5=H: VI R^5=NO_2; XII R^5=NH_2

Upon nitration of 10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene and the corresponding silaazanthrone I in our laboratory, we obtained 10,10-dimethyl-4- (II), -5- (III), -6- (IV), -7- (V), and -8- (VI) -nitro-10-sila-2-azaanthrone. We isolated as the bromine derivatives 10,10-dimethyl-4- (VII), -5- (VIII), and -7- (IX) -bromo-10-sila-2-azaanthrone. The nitro derivatives III, V, and VI were reduced to the corresponding amino derivatives X, XI, and XII.

The position of the substituents in compounds II-XII was determined from an analysis of PMR spectra (Tables 1-3). Any ambiguity in such structural analysis was eliminated by performing a comparative investigation of increments in chemical shift and SSCC in relation

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