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9-IMINO(AMINO)-10-SILA-2-AZAANTHRACENES

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9-Imino derivatives of dihydrosilaazaanthracenes were obtained from 10,10-diorganosila-2-azaanthrones. It was shown by PMR spectroscopy that they exist in the form of Z and E isomers. The azomethines were reduced to secondary amines, from which the N-acyl derivatives were obtained.

The previously undescribed azomethines 10,10-dimethyl- and 3-methyl-10,10-diphenyl-9phenylimino-10-sila-2-azaanthracenes (III, IV) and also 10,10-dimethyl-9-(2,4-dinitrophenylhydrazono)-10-sila-2-azaanthracene (V) were obtained by the condensation of the corresponding 10-sila-2-azaanthrones (I) and (II) [1, 2] with aniline or 2,4-dinitrophenylhydrazine in the presence of boron trifluoride etherate or anhydrous zinc chloride, where the latter proved more effective.



I, III, V R=CH₃, R¹=H; II, IV R=C₆H₅, R¹=CH₃; III, IV R²=C₆H₅; V R²= =NH--C₆H₃(NO₂)₂-2,4

In view of the analogy between the carbonyl and imino groups [3] we investigated the reaction of (III) with organometallic compounds. The azomethine (III) does not react with phenylmagnesium bromide on account, evidently, of steric hindrances. The action of phenyllithium leads to phenylation of the pyridine fragment of the azomethine molecule at position 1. 10,10-Dimethyl-1-phenyl-9-phenylimino-10-sila-2-azaanthracene (VI) and 10,10-dimethyl-9-phenylamino-10-sila-2-azaanthracene (VII) were isolated from the reaction mixture with identical yields (30%). The secondary amine is evidently formed as a result of reduction of the azomethine bond by the lithium hydride produced during nucleophilic substitution of another azomethine molecule at position 1. The data from the PMR spectrum of (VI) confirm its structure (Table 1) (see scheme below).

At room temperature, according to the data from PMR spectroscopy, the azomethines (III, IV) and the dinitrophenylhydrazone (V) represent mixtures of the Z and E isomers (Table 1). The latter were identified on the basis of the effect of the magnetic anisotropy of the ben-

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	3-CH ₃	2,44	
U-U)	N—C ₆ H ₅	$\begin{array}{c} 6,90\ldots 7,20\\ 6,90\ldots 7,20\\ 7,40\ldots 7,54\\ 7,40\ldots 7,54\\ 7,40\ldots 7,54\\ 6,80\ldots 7,10\\ 7,00\ldots 7,40\end{array}$	
MHZ, 2	SiCII ₃	0,19 0,19 0,17 0,17 0,17 0,19 0,17	
noc) md	8-11	8,37 7,09 7,18 7,46 8,33 7,46 7,50	_
(T), 0, P	11-2	7,32 6,71 7,68 7,68 7,04	
-TTT) sat	6-H	7,19 6,90 7,40. 7,40. 7,24 7,24 7,24	
AZOMETUTI	5-H	6,87 6,87 6,51 6,57 6,57 7,29 6,73	_
III LUE	4-H	$\begin{array}{c} 7,40 \\ 7,40 \\ 7,68 \\ 7,40 \\ 7,68 \\ 6,96 \\ 6,94 \\ 7,70 \end{array}$	_
Frolons	3-11	8,530 8,51 8,83 8,49 8,67	
or rue	H·I	8,62 9,82 8,17 9,24 9,31	_
STILL THE	Z, E ratio	1:1 4:3 5:1	
ormano	Isomer	NEN E NENE	
TADLE 1.	Compound	111 117 118**	

nnm (360 MHz 20°C) 4 Chemical Shifts of the Protons in the Azomethines (III-VI) TARLE 1 *The spectra of compounds (III, V, VI) were recorded in hexadeuterobenzene, and that of (IV) in deuterochloroform.

The spectra were recorded at 250 MHz. Protons of dinitrophenyl radical in the Z isomer: $3^{-}H$ 8.64, 5'-H 7.73, 6'-H 7.56 ppm; E isomer: $3^{-}H$ 8.64, 5'-H 7.71, 6'-H 7.49 ppm; NH 11.88 and 11.78 ppm, respectively. *The signals for the protons of the phenyl at $C_{(1)}$ in the Z isomer lie at 6.2-6.8 ppm, while those in the E isomer are at 6.0-7.1 ppm.

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TABLE 2.	ization

Com- pound	Solvent	^r c, K*	∆G [≠] Tc (Z→E), kJ/mole	$\Delta G \stackrel{\neq}{T_{\mathbf{C}}} (E \rightarrow Z),$ kJ/mole
	C ₆ D ₆	343	64,4	64,4
	CDCl ₃	322	66,6	67,7
	ДМСО-D ₆	341	75,2	71,1

 ${}^{\star}\mathrm{T}_{\mathrm{C}}$ is the coalescence temperature.



VII $R = CH_3$, $R^1 = H$; VIII $R = C_6H_5$, $R^1 = CH_3$

zene ring of the phenylimine fragment on the chemical shifts of the 1-H and 8-H protons, as in the azomethines of the azafluorene series [4].

Unlike the azomethines (III, IV) the individual Z and E isomers of the dinitrophenylhydrazone (V) were isolated by chromatography. This was due to the high barrier to isomerization about the C=N bond in the hydrazones.

The energy barriers for the $Z \Leftrightarrow E$ isomerization process were determined on the basis of the temperature dependence of the PMR spectra of the azomethines (III, IV, VI) by the method in [5]. The indicator groups for the observation of the dynamic spectra were the signals of the 1-H [in the azomethine (III)], 3-CH₃ [in the azomethine (IV)], and 3-H [in the azomethine (VI)] protons. The sizes of the energy barriers (Table 2) indicate that the $Z \Leftrightarrow E$ isomerization in the investigated compounds (III, IV, VI) takes place predominantly by a mechanism of inversion at the imine nitrogen atom [6].

The azomethines (III, IV) were reduced with hydrazine hydrate in the presence of Raney nickel to the secondary amines (VII, VIII), respectively. The latter are readily acylated by propionic anhydride and chloroacetyl chloride and condensed with phenyl isocyanate with the formation of the corresponding derivatives (IX-XII).



IX--XI R=CH₃, R¹=H; XII R=C₆H₅, R¹=CH₅; IX, XII R²=COC₂H₅; X R²=COCH₂Cl; XI R²=CONHC₆H₅

EXPERIMENTAL

The IR spectra were obtained in tablets with potassium bromide on a UR-20 instrument. The mass spectra were measured on MX-1303 and Hitachi M-80-A mass spectrometers. The PMR spectra (of solutions in deuterochloroform and hexadeuterobenzene) were obtained on Bruker WP-80 and WH-360 spectrometers with TMS as internal standard. Column chromatography and thin-layer chromatography were conducted on silica gel L 100/160 μ and Silufol UV-254. The elemental analyses for C, H, and N corresponded to the calculated composition.

<u>10,10-Dimethyl-9-phenylimino-10-sila-2-azaanthracene (III, $C_{20}H_{18}N_2Si$).</u> A solution of 2.6 g (11 mmoles) of silaazaanthrone (I) in 30 ml of aniline with 5 g (40 mmoles) of anhydrous zinc chloride was boiled for 7 h, cooled, treated with aqueous ammonia, and extracted with ether. The extract was dried with magnesium sulfate, and the residue (3 g) after distillation of the ether was crystallized from hexane. We obtained 2.6 g (76%) of the azomethine (III) in the form of light-yellow crystals; mp 132-133°C, R_f 0.45 (3:1 hexane-ethyl acetate). IR spectrum: 1630 cm⁻¹ (C=N). M⁺ 314.

<u>3-Methyl-10,10-diphenyl-9-phenylimino-10-sila-2-azaanthracene (IV, $C_{1,3}H_{2,4}N_2Si$).</u> The compound was obtained similarly from 0.6 g (1.6 mmoles) of the silaazaanthrone (II) and 2 g (14.8 mmoles) of anhydrous zinc chloride in 15 ml of aniline. The yield was 0.36 g (50%), and the product formed light-yellow crystals; mp 152-153°C (from heptane), $R_{\rm f}$ 0.28 (3:1 hexane-ethyl acetate). IR spectrum: 1625 cm⁻¹ (C=N). M⁺ 452.

<u>10,10-Dimethyl-9-(2',4'-dinitrophenylhydrazino)-10-sila-2-azaanthracene (V, $C_{20}H_{17}N_5O_4Si$).</u> A mixture of 1 g (4.2 mmoles) of the silaazaanthrone (I), 1 g (5.1 mmoles) of 2,4-dinitrophenylhydrazine, and 0.5 ml of boron trifluoride etherate in 50 ml of ethanol was boiled for 6 h. The residue (2 g) after distillation of the alcohol was chromatographed on a column of silica gel with a 5:1 mixture of hexane and ethyl acetate as eluant. We first eluted 0.3 g (17%) of the E isomer of (V) in the form of dark-red crystals; mp 230-231°C (from hexane), R_f 0.72 (1:1 hexane-ethyl acetate). M⁺ 419. We then eluted 0.3 g (17%) of the Z isomer of (V) in the form of orange crystals; mp 225-226°C (from hexane), R_f 0.44 (1:1 hexane-ethyl acetate). M⁺ 419.

<u>10,10-Dimethyl-1-phenyl-9-phenylimino-10-sila-2-azaanthracene (VI, $C_{26}H_{24}N_2Si$).</u> To phenyllithium, obtained from 0.25 g (36 mmoles) of lithium and 3 g (19 mmoles) of bromobenzene in 50 ml of absolute ether, we added dropwise a solution of 0.8 g (2.5 mmoles) of the azomethine (III) in 10 ml of absolute ether. The mixture was boiled for 2 h, diluted with 100 ml of water, and extracted with ether. The extract was dried with magnesium sulfate, and the residue (0.9 g) after distillation of the ether was chromatographed with a 5:1 mixture of hexane and ethyl acetate as eluant. We first eluted 0.3 g (30%) of the azomethine (VI) in the form of light-yellow crystals; mp 127-128°C (from hexane), $R_{\rm f}$ 0.35 (3:1 hexane-ethyl acetate). M⁺ 390.

We then eluted 0.25 g (30%) of the amine (VII) in the form of colorless crystals; mp 135-136 °C (from hexane). A mixed melting test with a standard sample melted without depression.

 $\frac{10,10-\text{Dimethyl-9-phenylamino-9,10-dihydro-10-sila-2-azaanthracene (VII, C_{20}H_{20}N_2Si)}{\text{To a solution of 0.3 g (1 mmole) of the azomethine (III) in 30 ml of ethanol we added 0.1 g of Raney nickel and 1 ml of hydrazine hydrate. The mixture was stirred for 20 h. The catalyst was filtered off, and the residue after distillation of the ethanol was crystal-lized from hexane. We obtained 0.25 g (83%) of the amine (VII) in the form of colorless crystals; mp 136-137°C, Rf 0.28 (3:1 hexane-ethyl acetate). IR spectrum: 3400 (v_{NH}), 1520 (<math>\delta_{\text{NH}}$), 1260, and 815 cm⁻¹ [Si(CH₃)₂]. PMR spectrum (deuterochloroform: 8.80 (1H, s, 1-H); 8.50 (1H, d, 3-H), 7.66 (1H, d, 8-H), 7.58 (1H, d, 5-H), 7.51 (1H, d, 4-H), 7.42-7.31 (2H, m, 6-H, 7-H), 7.14 (2H, m, m-H N-C₆H₅), 6.71 (3H, m, o- and p-H N-C₆H₅), 5.49 (1H, d, 9-H), 3.97 (1H, b.s, NH), 0.65 (3H, s, SiCH₃), 0.55 ppm (3H, s, SiCH₃). M⁺ 316.

<u>3-Methyl-10,10-diphenyl-9-phenylamino-9,10-dihydro-10-sila-2-azaanthracene (VIII, C₃₁H₂₆N₂Si).</u> The compound was obtained similarly from 0.45 g (1 mmole) of the azomethine (IV), 0.15 g of Raney nickel, and 2 ml of hydrazine hydrate in 30 ml of ethanol with a yield of 0.37 g (80%). The product formed colorless crystals; mp 174-175°C (from hexane), R_f 0.16 (3:1 hexane-ethyl acetate). IR spectrum: 3320 ($\nu_{\rm NH}$), 1510 ($\delta_{\rm NH}$), 1435, and 1120 cm⁻¹ [Si(C₆H₅)₂]. M⁺ 454.

<u>10,10-Dimethyl-9-(phenylpropionylamino)-9,10-dihydro-10-sila-2-azaanthracene (IX, C₂₃H₂₄N₂OSi). A solution of 0.5 g (1.5 mmoles) of the amine (VII) in 5 ml of propionic anhydride was boiled for 1 h. The residue after distillation of the anhydride was crystallized from hexane. We obtained 0.43 g (82%) of (IX) in the form of colorless crystals; mp 154-155°C, R_f 0.3 (1:1 hexane-ethyl acetate).</u>

 $\frac{10,10-\text{Dimethyl-9-(phenylchloroacetylamino)-9,10-dihydro-10-sila-2-azaanthracene (X, C_{22}H_{21}ClN_2OSi).$ To a solution of 1 g (3.2 mmoles) of the amine (VII) in 30 ml of absolute benzene we added a solution of 0.5 g (4.4 mmoles) of chloroacetyl chloride in 10 ml of absolute benzene. After 7 h the mixture was diluted with 20 ml of a saturated aqueous solution of sodium carbonate and extracted with benzene. The extract was dried with magnesium sulfate. The residue (1.3 g) after distillation of the benzene was crystallized from benzine. We obtained 0.44 g (35%) of (X) in the form of colorless crystals; mp 206-207°C (decomp.), Rf 0.42 (1:1 hexane-ethyl acetate).

<u>10,10-Dimethyl-9-(N,N-diphenylureido)-9,10-dihydro-10-sila-2-azaanthracene (XI, C₂₇H₂₅N₃OSi).</u> To a solution of 1.1 g (3.5 mmoles) of the amine (VII) and 0.3 ml of triethylamine in 30 ml of absolute benzene, heated to boiling, we added a solution of 0.6 g (5 mmoles) of phenyl isocyanate in 10 ml of absolute benzene. The mixture was boiled for 5 h, the benzene was distilled, and the residue (1.5 g) was crystallized from heptane. We obtained 1.2 g (80%) of (XI) in the form of colorless crystals; mp 152-153°C, R_f 0.13 (3:1 hexane-ethyl acetate). M⁺ 435.

 $\frac{3-\text{Methyl-10,10-diphenyl-9-(phenylpropionylamino)-9,10-dihydroxy-10-sila-2-azaanthracene}{(XII, C_{34}H_{30}N_2OSi)}$. The compound was obtained similarly to (IX) from 0.45 g (1 mmole) of the amine (VIII) and 5 ml of propionic anhydride with a yield of 0.4 g (80%). The product formed colorless crystals; mp 198-199°C (from hexane), R_f 0.34 (1:1 hexane-ethyl acetate). M⁺ 510.

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