A 1-g sample of the base obtained was taken for chromatography on activity II Al₂O₃ [h = 50 cm, d = 2.3 cm, elution with hexane—ethyl acetate (5:1)]. Initially, 0.34 g (34%) of the δ isomer was eluted in the form of a viscous colorless liquid with R_f 0.6 [activity II Al₂O₃, elution with ethyl acetate—hexane (1:2)]. At the end of the chromatographic process we iso-lated 0.6 g (53%) of the γ isomer as a viscous yellowish liquid with R_f 0.3 (the same system). Found: C 76.9; H 10.4; N 12.5%; M⁺ 218. C₁₄H₂₂N₂. Calculated: C 77.1; H 10.1; N 12.8%; M 218.

A 1-g sample of the mixture of isomers was dissolved in 30 ml of ethanol. A solvate (0.2 g) of the δ isomer with one molecule of alcohol precipitated at room temperature in the form of colorless crystals with mp 73-82°C. Found: C 73.4; H 10.6; N 10.5%; M⁺ 218. C₁₄H₂₂N₂· C₂H₅OH... Calculated: 73.7; H 10.6; N 10.6%.

LITERATURE CITED

- 1. I. N. Nazarov, N. S. Prostakov, and N. I. Shvetsov, Zh. Obshch. Khim., 26, 2798 (1956).
- 2. T. F. Vlasova and Yu. N. Sheinker, Zh. Struk. Khim., 11, No. 4, 640 (1970).
- 3. I. N. Nazarov, N. S. Prostakov, N. N. Mikheeva, and V. N. Dobrynin, Izv. Vyssh. Uchebn. Zaved SSSR, Khim. Khim. Tekhnol., No. 2, 726 (1959).
- 4. A. F. Casy and K. M. J. McErlane, J. Chem. Soc., Perkin Trans. I, 726 (1972).
- 5. A. F. Jones, C. P. Beeman, A. F. Casy, and K. M. J. McErlane, Can. J. Chem., <u>51</u>, 1790 (1973).
- 6. D. M. Grant and B. V. Cheney, J. Am. Chem. Soc., 89, 5315 (1967).

AMINO DERIVATIVES OF 9,9-DIORGANO-9,10-DIHYDRO-9-SILA-3-AZAANTHRACENE

N. S. Prostakov, A. M. Klochkov, and A. V. Varlamov UDC 546.287:547.833.5.7.9.07:543.422

Derivatives of 9,9-disubstituted 9,10-dihydro-9-sila-3-azaanthracene (compounds with possible biological activity) were synthesized by means of two methods. 10- β -Cyanoethyl derivatives were obtained by condensation of dihydrosilaazaanthracenes with acrylonitrole in the presence of Triton B. One of these products was reduced with lithium aluminum hydride to 9,9-dimethyl-10-(γ -aminopropyl)-9,10-di-hydro-9-sila-3-azaanthracene. The second method involves conversion of dihydro-silaazaanthrones (obtained by oxidation of dihydrosilaazaanthracenes) to oximes followed by reduction of the latter with hydrazine hydrate in the presence of Raney nickel to give 10-amino derivatives. The latter were subjected to acylation.

We have previously described the synthesis of 9,10-dihydro-9-sila-3-azaanthracene derivatives [1, 2]. It seems of interest to study their properties in order to search for physiologically active substances. Considering the fact that many biologically active compounds contain an amine function, we addressed ourselves to the synthesis of amino derivatives of dihydrosilaazaanthracenes, which were obtained by two methods, viz., by reduction of $10-\beta$ -cyanoethyl dihydrosilaazaanthracenes and also by reduction of oximes of silaazaanthrones.

The starting compounds in the cyanoethylation reactions were 2-methyl-9,9-diphenyl(I)and 9,9-dimethyl(II)[9-methyl-9-phenyl(III)]-9,10-dihydro-9-sila-3-azaanthracenes. The reactions were carried out in the presence of Triton B. The principal products of the Michael reaction were products of monocyanoethylation at C_{10} , viz., IV-VI, the yields of which varied in the order V > VI > IV this is evidently due to the different degree of shielding of the methyl group by the substituents attached to the silicon atom of the starting dihydrosilaazaanthracenes.

Patrice Lumumba People's Friendship University, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1516-1520, November, 1982. Original article submitted January 18, 1982.



I, IV $R = CH_3$, $R' = R'' = C_6H_5$; II, V R = H, $R' = R'' = CH_3$; III, VI R = H, $R' = CH_3$, $R'' = C_6H_5$

In addition to the cyanoethylation products, we also isolated small amounts of ($\sim 5\%$) of the corresponding dihydrosilaazaanthrones, which are formed as a result of oxidation of the starting dihydrosilaazaanthracenes I-III by air oxygen [3]. Dihydrosilaazaanthrones are not formed when the reaction is carried out in a nitrogen atmosphere.

9,9-Dimethyl-10-(β -cyanoethyl)-9,10-dihydro-9-sila-3-azaanthracene (V) was reduced with lithium aluminum hydride to 9,9-dimethyl-10-(γ -aminopropyl)-9,10-dihydro-9-sila-3-azaanthracene (VII).

For the synthesis of the second group of amino derivatives of silaazaanthracenes we used 2-methyl-9,9-diphenyl(VIII)-, 9,9-dimethyl(IX)-, and 9-methyl-9-phenyl(X)-9,10-dihydro-9-sila-3-azaanthrones [1, 2]. They were converted to oximes XI-XIII, respectively, which are colorless high-melting crystalline substances that form solvents with ethanol. According to the data from the PMR spectra, oximes XI-XIII are mixtures (in a ratio of 2:1) of the Z and E isomers. This conclusion was drawn on the basis of a comparison of the integral intensities of the signals of the 4-H protons of the two isomers. It must be noted that the band of the stretching vibrations of the exocyclic C=N bond in the IR spectra of these oximes is of low intensity. However, all of the spectra contain a high-intensity band at 1000 cm⁻¹, which is evidently characteristic for oximes of polycyclic ketones. This band is absent in the spectra of the products of reduction of the oximes.

Oximes XI and XII were subjected to reduction with hydrazine hydrate in the presence of Raney nickel. 10-Amino-2-methyl-9,9-diphenyl(XIV)- and 9,9-dimethyl(XV)-9,10-dihydro-9-sila-3-azaanthracenes were obtained in higher than 70% yields in the form of colorless crystalline substances that were quite soluble in polar solvents.



VIII, XI, XIV $R = CH_3$, $R' = R'' = C_6H_5$; IX, XII, XV R = H, $R' = R'' = CH_3$; X, XIII R = H, $R' = CH_3$, $R'' = C_6H_3$

In the reduction of oxime XI with lithium aluminum hydride in refluxing tetrahydrofuran (THF), in addition to amine XIV, we isolated silaazaanthrone VIII and a compound, which, according to the spectral and analytical data, is benzopyridosilaazepino-5H-3-methyl-5,5-diphenyl-2,10(11)-diaza-10,11-dihydro-5-silabenzo[b]pyrido[4,5-e]azepine. Examples of the formation of secondary amines in the reduction of oximes with lithium aluminum hydride have been described [4, 5].

2-Methyl-9,9-diphenyl-10-acetamido-9,10-dihydro-9-sila-3-azaanthracene (XVII) was obtained by acylation of amine XIV. We also carried out the acylation of amine XV with γ -chlorobutyric and δ -chlorovaleric acid chlorides to give amides XVIII and XIX, respectively.



EXPERIMENTAL

The PMR spectra of solutions of the compounds in CDCl₃ were recorded with a BS-487 spectrometer with tetramethylsilane as the internal standard. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The mass spectra were obtained with a Varian MAT CH8 spectrometer. Activity II aluminum oxide was used for thin-layer chromatogTABLE 1. Physicochemical and Spectral Characteristics of 10-Substituted 9-Sila-9.10-dihydro-3-azaanthracenes

Yield,		35	70	20	37,6	87	70	55	59	80	10	001	54	60
	z	6,7	10,1	8,2	6,6	7,2	11,0	8,9	7,4	6,0	7,4	6,7	8,1	7,8
c., %	н	6,8	6,5	5,9	7,8	5,1	5,5	5,0	5,6	5,8	5,8	5,5	5,1	6,4
Cal	υ	80,3	73,4	77,6	72,3	76,6	66,6	70,2	80,0	53,7	79,4	77,2	62,7	63,6
Empirical formula		C ₂₈ H ₂₄ N ₂ Si	C ₁₇ H ₁₈ N ₂ Si	C ₂₂ H ₂₀ N ₂ Si	C ₁₇ H ₂₂ N ₂ Si	C25H20N2OSi	C ₁₄ H ₁₄ N ₂ OSi	C ₁₉ H ₁₆ N ₂ OSi	C ₂₅ H ₂₂ N ₂ Si	C ₁₄ H ₁₈ Cl ₂ N ₂ Si ^e	C25H22N2Si	C ₂₇ H ₂₄ N ₂ OSi	C ₁₈ H ₂₁ CIN ₂ OSi f	C ₁₉ H ₂₃ CIN ₂ OSi ^B
%	z	6,7	10,2	8,1	9,8	7,0	10,8	8,8	7,1	8,6	7,5	6,5	8,1	7,7
ound,	н	6,8	6,4	6,0		5,1	5,6	5,3	5,6	6,0	6,2	5,6	2,3	6,0
Ъ	υ	80,1	73,6	77,4		76,6	66.5	70,2	9,67	53,7	7,67	77,4	62,5	63,9
	PMR spectrum, ppm	8,53, s, 1H (4,H); 4,16, t, 1H (10-H); 2,43, s, 3H (CH ₃); 2,07–1,5, m, 4H (CH ₂)	8,55, s, 1H (4,H); 8,50, d, 1-H (2-H); 4,15, t, 1H (10-H); 2,29-1,86, m 4H (CH ₂); 0,59, s, 3H (CH ₃); 0,49, s, 3H	(CH ₃) 8,66, s, 1H (4-H); 8,44, d, 1H (2-H); 4,26, t, 1-H (10-H); 2,361,96, m 4H (CH ₂); 0,82, s, 3H (CH ₃)	8,55, s, 1H (4-H), 8,52, d, 1H (2-H); 4,20, t, 1H (10-H), 0,60, s, 3H (CH ₃); 0,52, s, 3H (CH ₃)	11,1, s, 1H (OH); 9,29, s; (4H Z iso- mer); 8,80, \$ (4H E isomer); 2,42, \$, 3H (CH ₃)	11,13, s, 1H (OH); 9,26, s, (4H Z iso- mer); 8,83, s, (4H E isomer); 0,47, s, 3H (CH ₃)	11,07, s, 1H (OH); 9,90, s, (4H Z iso- mer); 8,45, d, (4H E isomer); 0,76, s, 3H (CH ₃)	8.55, s, 1H (4-H): 5,0, s, 1H (10-H); 2,40, s, 3H (CH ₃); 1.65, s, 2H (NH ₃)	8,56, s, 11H (4-H); 8,44, d, 11H (2-H); 5,13, s, 11H (10-H); 1,63, s, 21H (NH ₂); 0,59, s, 3H (CH ₃); 0,53, s, 3H (CH ₃)	7.78, s, 1H (4-H); 6.83, s, 1H (1-H); 4,44, 1H (NH); 4,22, s, 2H (CH ₂); 2,22, s, 3H	(CH3)	8,63, s 1H (4-H); 8,34, d, 1H (2-H); 6,25, d, 1H (10-H); 6,03, d, 1H (NH); 3,46, t, 2H (CH ₂ CI); 2,42-1,96, m, 4H (CH ₂ CH ₂); 0,53, d, 6H (CH ₃)	$ \begin{array}{c} 8,69,\ s,\ 1H,\ (4-H),\ 8,38,\ d,\ 1H,\ (2-H);\ 6,25, \\ d,\ 1H,\ (10-H);\ 6,0,\ d,\ 1H,\ (NH);\ 3,44,\ t, \\ 24,\ (CH_2CI);\ 2,25-1,63,\ m \ 6H,\ [(CH_2)_3]; \\ 0.53,\ d \ 6H,\ (CH_3) \end{array} $
	IR spectrum, cm ⁻¹	2252 (CN); 1425, 1108 (SiPh)	2250 (CN); 1260, 818 [Si(CH ₃) ₂]	2250 (CN); 1120, 1429 (SiPh); 1260, 830 [Si(CH ₃)]		2470 (OH); 1640 (C=N); 1113, 1430 (SiPh); 1000	2830 (OH); 1630 (C=N); 1250; 845 [Si(CH ₃) ₂]; 1000	2560 (OH): 1645 (C=N); 810, 1260 (SiMet); 1120, 1440 (SiPh); 1000	3370 (NH); 1650 (NH); 1110, 1426 (SiPh)	1260, 820 [Si(CH3)2]	3270 (NH); 1333 (CN); 1428, 1104 (SiPh)		3200 (NH), 1680 (C=O); 1260, 820 [SI(CH ₃) ₂]	3220 (NH), 3180 (NH); 1680 (C=O); 1260, 820 [Si(CH ₃) ₂]
	+W	416	278	340	282	392	254	316	378	1	378	ļ	344	358
	mp, °C	185,5186 ^a	9191,5ª	163—164 ^b	127,5—129 ^a	235—235,5 c	215°	210-211 ^C	185,5-186,5ª	116,5117d	194—195d	195,5—196°	130—130,5a	134,5—135ª
Com-	punod	IV	>	VI	ΝII	IX	IIX	IIIX	VIX	XV	IVX	IIVX	XVIII	XIX

Calculated: Cl 10.3% Spound: Cl "From heptane with ethyl acetate. "From methano1. From ethano1. ide. Found: Cl 22.7%. Calculated: Cl 22.7%. fround: Cl 10.7%. 0.7%. Calculated: Cl 9.9%. gaphy (GLC). The characteristics of the synthesized compounds are presented in Table 1.

<u>2-Methyl-9,9-diphenyl-l0-(β -cyanoethyl)-9,10-dihydro-9-sila-3-azaanthracene (IV).</u> A 1.5-g (28.3 mmole) sample of acrylonitrile was added in the course of 20 min at 40°C to a solution of 1 g (2.75 mmole) of dihydrosilaazaanthracene I in 20 ml of absolute benzene and 0.2 ml of a 50% alcohol solution of Triton B, and the reaction mixture was maintained at 60°C for 3.5 h. It was then decomposed with 50 ml of water, and the benzene solution was dried with magnesium sulfate. The residue (1.3 g) after removal of the benzene by distillation was chromatographed (h = 50 cm, d = 2.5 cm) by elution with heptane—ethyl acetate (30:1). Initially, 0.15 g of the starting dihydrosilaazaanthracene was eluted, after which we obtained 0.05 g (5%) of dihydrosilaazaanthrone X with mp 128-219.5°C (from ethyl acetate—hexane). At the end of the chromatographic process we obtained 0.4 g of silaazaanthracene IV in the form of colorless crystals. Compounds V and VI were similarly obtained from dihydrosolaazaanthracenes II and III.

<u>9,9-Dimethyl-10-(γ -aminopropyl)-9,10-dihydro-9-sila-3-azaanthracene (VII).</u> A 0.5-g (13.2 mmole) sample of lithium aluminum hydride was added to a solution of 1 g (3.25 mmole) of V in 30 ml of absolute ether, and the mixture was stirred for 2 h. It was then treated with 1 ml of ethyl acetate and 15 ml of a 20% sodium hydroxide solution, and the organic layer was separated and dried with magnesium sulfate. The ether was removed, and the residue was crystallized from heptane-ethyl acetate to give 0.38 g of colorless crystals of VII.

2-Methyl-9,9-diphenyl-10-oximino-9,10-dihydro-9-sila-3-azaanthracene (XI). A 1.32-g (3.5 mmole) sample of dihydrosilaazanthrone VIII and 1.3 g (18.7 mmole) of hydroxylamine hydrochloride were refluxed in 10 ml of pyridine for 3 h, after which the mixture was poured into 100 ml of cold water, and the precipitate was crystallized from alcohol to give 1.2 g of white crystals of oxime XII. Oximes XII and XIII were obtained from silaazaanthrones IX and X.

<u>10-Amino-2-methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthracene (XIV)</u>. A) A 0.1-g sample of Raney nickel was added to a solution of 1.73 g (4.41 mmole) of oxime XI and 2.4 ml of hydrazine hydrate in 100 ml of alcohol, and the mixture was stirred at 20°C for 10 h. Another 2 ml of hydrazine hydrate and 0.15 g of Raney nickel were then added, and the mixture was allowed to stand for 5 h. The catalyst was removed by filtration, and the filtrate was poured into water. The precipitate was crystallized from heptane—ethyl acetate to give 0.98 g of stable white crystals of amine XIV. Amine XV was similarly obtained by reduction of oxime XII.

B) A 1.15-g (30.3 mmole) sample of lithium aluminum hydride was added to a solution of 1.2 g (3.06 mmole) of oxime XII in 50 ml of absolute THF, and the mixture was refluxed for 5 h. It was then cooled and treated successively with 5 ml of ethyl acetate and 30 ml of 20% aqueous sodium hydroxide solution. The residue (1 g) remaining after removal of the THF from the organic layer by distillation was chromatographed (h = 60 cm, d = 2 cm, elution with ethyl acetate hexane). Elution with an eluent containing 5% ethyl acetate gave successively 0.29 g of dihydrosilaazaanthrone VIII, with mp 215-217°C, and 0.12 g (10%) of colorless crystals of benzopyridosilaazepine XVI. Elution with an eluent containing 10% ethyl acetate then gave 0.12 g (10%) of amine XIV with mp 185.5-186.5°C. No melting-point depression was observed for a mixture with a standard sample.

10-Acetamido-2-methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthracene (XVII). A 0.1-g (0.56 mmole) sample of amine XIV was refluxed in 2 ml of acetic anhydride for 3 h, after which the mixture was poured into water, and the precipitate was crystallized from alcohol to give 0.11 g of amide XVII.

 $\frac{10-(\gamma-\text{Chlorobutyrylamino})-9,9-\text{dimethyl}-9,10-\text{dihydro}-9-\text{sila}-3-\text{azaanthracene} (XVIII). A solution of 0.3 g (2.12 mmole) of <math>\gamma$ -chlorobutyryl chloride in 10 ml of absolute ether was added in the course of 30 min to a solution of 0.5 g (2.08 mmole) of amine XV and 0.3 g (2.9 mmole) of triethylamine in 25 ml of absolute ether, and the mixture was refluxed for 4 h. The precipitated triethylamine hydrochloride was removed by filtration, the ether was removed from the filtrate by distillation, and the residue was crystallized from heptane-ethyl acet-ate to give 0.39 g of XVIII. Compound XIX was similarly obtained from amine XV and δ -chlorovaleryl chloride.

LITERATURE CITED

1. N. S. Prostakov, A. V. Varlamov, and V. P. Zvolinskii, Khim. Geterotsikl. Soedin., No. 11, 1578 (1972).

- N. S. Prostakov, Saksena Navin, A. V. Varlamov, and A. M. Klochkov, Khim. Geterotsikl. Soedin., No. 2, 240 (1981).
- 3. J. Sprinzak, J. Am. Chem. Soc., <u>80</u>, 5449 (1958).
- 4. R. E. Lyle and H. J. Troscianee, J. Org. Chem., 20, 1757 (1955).

5. D. R. Smith, M. Maienthan, and J. Tipton, J. Org. Chem., 17, 294 (1952).

REACTION OF 2-PICOLYLLITHIUM AND 6-METHYL-2-PICOLYLLITHIUM WITH

VINYL(tert-BUTYL)ACETYLENE

L. N. Cherkasov

UDC 547.821.4 315.1.07:543.422.4

The possibility of obtaining pyridylallene hydrocarbons with normal structure with a branched grouping in the side chain on the basis of vinyl(alkyl)acetylene hydrocarbons with iso structures and, respectively, 2-picolyl- and 2,6-lutidyllithium is demonstrated.

The reaction of 2-picolyllithium with vinyl(alkyl acetylene hydrocarbons with normal structures may serve as a convenient method for preparation of pyridylallene hydrocarbons [1-3].

In order to extend the possibility of the utilization of this reaction in the synthesis of pyridine, furan, and thiophene derivatives and also to study the effect of groupings with iso structures attached to the triple bond of vinyl(alkyl)acetylenes on the direction of addition of heterocyclic lithium compounds to them we studied the reaction of 2-picolyl-, 2,6-lutidyl-, 2-pyridyl-, 2-furyl-, and 2-thienyllithium with vinyl(tert-butyl)acetylene. Our experiments showed that of all of the above-indicated heterocyclic lithium compounds, only 2-picolyllithium and 2,6-lutidyllithium add to the multiple bonds of vinyl(tert-butyl)acetylene in a ratio of 1:1 to give adducts, the demetallation of which with water in a stream of argon gives, respectively, 2-(6,6-dimethylhepta-3,4-dienyl)pyridine and 6-methyl-2-(6,6-dimethyl-hepta-3,4-dienyl)pyridine.

R = H CH. R = H CH. R = H CH. R = H CH.

The IR spectra of the compounds obtained in this research contain intense absorption bands of unsummetrical stretching vibrations of the CH=C=CH grouping at 1965-1970 cm⁻¹, but absorption bands of the stretching vibrations of an acetylenic bond $(2100-2300 \text{ cm}^{-1})$ and a 1,3-diene grouping (1610-1760 cm⁻¹) are completely absent; this excludes the formation in these reactions of acetylenic and 1,3-diene isomers (products of 1,2 and 3,4 addition). Characteristic absorption bands of stretching vibrations of a puridine ring at 1589-1600 cm^{-1} are also observed in the IR spectra. We established the site of fixation of the groupings in 2-(6,6-dimethylhepta-3,4-dienyl)pyridine on the basis of data on its ozonization; in this case we isolated only 3-(2-pyridyl) propionic and trimethylacetic acids, and the copious liberation of carbon dioxide was observed in the decomposition of the ozonide, which additionally confirmed the presence of an allene system of bonds in the compound obtained. Taking into account the monotypical character of the indicated reactions, a similar conclusion regarding the site of fixation of the grouping can also be extended to 6-methyl-2-(6,6-dimethylhepta-3,4-dienyl)pyridine. 2-Pyridyl-, 2-furyl-, and 2-thienellithium do not add under similar conditions to the multiple bonds of both vinyl(tert-butyl)acetylene and vinyl(alkyl)acetylenic hydrocarbons with normal structures [vinyl(methyl) - and vinyl(ethyl)acetylene] in the same way as w-styryl- and phenylacetylenyllithium [4]. Thus the direction of addition of 2-picolyllithium to vinyl(tert-butyl)acetylene does not differ from the direction of its addition to

S. O. Makarov Leningrad Higher Engineering Nautical School, Leningrad. Translated from Khimiya Geterotsiklicheskikh Soedinenni, No. 11, pp. 1521-1522, November, 1982. Original article submitted December 28, 1981.