Journal of Organometallic Chemistry, 218 (1981) 17—26
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SYNTHESIS OF DIHYDROSILANAPHTHOINDOLIZINES AND DIHYDROSILAAZAACEANTHRELENES

N.S. PROSTAKOV *, N. SAXENA, A.V. VARLAMOV and A.A. FOMICHOV

Patrice Lumumba People's Friendship University, 117923 Moscow B 302 (U.S.S.R.)

(Received March 17th, 1981)

Summary

New heterocyclic systems, dihydrosilanaphthoindolizines and dihydrosilaazaaceanthrelenes, have been synthesized starting from 9,10-dihydro-9-sila-3-azaanthracenes. Substituted 6,11-dihydro-6-silanaphtho[2,3-*g*]indolizines were obtained as a result of 1,3-dipolar cycloaddition reaction of dimethylacetylenedicarboxylate with the quaternary salts of dihydrosilaazaanthracenes having a *N*-phenacyl group. In a similar manner, substituted 3*H*,6*H*-6-sila-3-azaaceanthrelenes, a new pseudoazulene system, have been synthesized from *N*-benzyl (methyl) quaternary salts. Dihydrosilanaphthoindolizine, having a linear linkage of the dihydrosilanaphtholene and the indolizine cycles has been synthesized from the corresponding dihydrosilaazaanthracene quaternary salt using the Tschitschibabin method.

Introduction

Dihydrosilaazaanthracenes, tricyclic condensed heterocyclic systems containing a nitrogen atom in the side ring and a silicon atom in the *meso*-position, were first reported by us in our earlier papers [1,2]. These compounds were obtained by the catalytic dehydrocyclisation of the pyridine bases, having a methyl group in the β-position and an alkylaryl group in the γ-position.

The availability of such pyridines [3], and the relatively simple method for their conversion into dihydrosilaazaanthracenes and their isolation, made it possible to start a detailed study of the properties of this new heterocyclic system.

Dihydrosilaanthracenes, analogs of dihydrosilaazaanthracenes without a nitrogen atom, have been studied thoroughly [4—9]. Their oxidation [5,7,9], metallation [4—7], halogenation [5] and conversions of the functiona' groups at the silicon atom [4,5,7,9] have been published. The physiological properties of the derivatives of dihydrosilaanthracenes have also been reported [5].

In comparison to dihydrosilaanthracenes, the dihydrosilaazaanthracenes under-

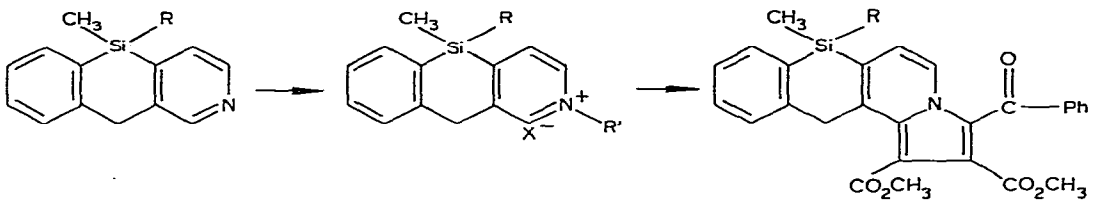
0022-328X/82/0000—0000/$02.50

go various chemical conversions due to the presence of the pyridine cycle in their framework. One of these conversions of dihydrosilaazaanthracenes, investigated in this paper, leads to the synthesis of new condensed heterocycles: dihydrosilaazaaceanthrelenes and dihydrosilanaphthoindolizines.

Results and discussion

9,9-Dimethyl- and 9-methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthracenes (I and II, respectively) were the starting compounds in the following synthesis. The interaction with an excess of the corresponding halogen derivative in methanol gave their quaternary salts: *N*-phenacyl-*N*-benzyl- and *N*-methyl-9,9-dimethyl-9,10-dihydro-9-sila-3-azaanthracenium halides (III—V) and also the bromides *N*-phenacyl- and *N*-benzyl-9-methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthracenium (VI, VII).

For the synthesis of dihydrosilanaphthoindolizines, the *N*-phenacyl salts III and VI were put into reaction with dimethyl acetylenedicarboxylate. The reaction was conducted in the presence of triethylamine. Under these conditions, as in the case of the salts of pyridine and azafluorenes, salts III and VI form the corresponding benzoylmethylides which undergo further 1,3-dipolar cycloaddition with dimethylacetylene dicarboxylate. Such an addition may take place along both of the α-positions relative to the nitrogen atom, leading to the linear dihydrosilanaphthoindolizines 5,5-dimethyl(5-methyl-5-phenyl)-5,10-dihydro-5-silanaphtho[3,2-*f*]indolizines, as well as analogous compounds of angular structure: 6,6-dimethyl- and 6-methyl-6-phenyl-3-benzoyl-1,2-dicarbomethoxy-6,11-dihydro-6-silanaphtho[2,3-*g*]indolizines (VII, IX).

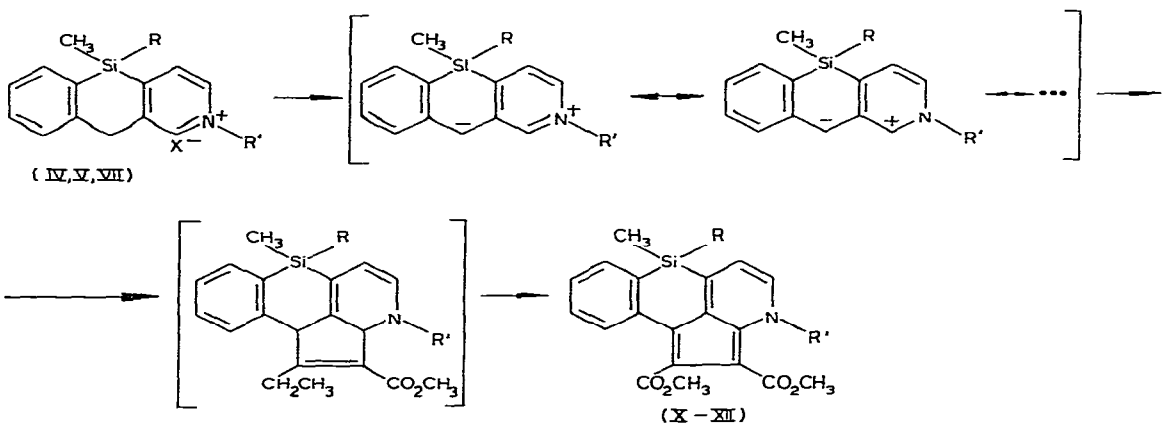


(I, II) (III–VII) (VIII, IX)

I, III–V, VIII, R = CH_3; II, VI, VII, IX R = C_6H_5; III, VI R' = $CH_2COC_6H_5$; IV, VII R' = $CH_2C_6H_5$; V R' = CH_3; III, IV, VI, VII X = Br; V X = I)

NMR data show the presence of both the dihydrosilanaphthoindolizine isomers (angular and linear) in the reaction mixture. Experimentally, only the angular isomers VIII and IX could be isolated as individual compounds. These are yellow, stable crystals. The signals of H(4) and H(5) protons in compound VIII have chemical shifts of 9.3 and 7.1 ppm ($J_{4,5}$ = 7 Hz), whereas these occur at 9.25 and 7.03 ppm for compound IX. The NMR spectra of the chromatographic fraction obtained after the isolation of the individual angular isomer IX shows the presence of two singlet signals with δ 8.28 and 9.36 ppm, corresponding to the H(4) and H(11) protons of the linear isomer. The low-field shift of the H(4) protons in the ^{1}H NMR spectra of compounds VIII and IX and also H(11) in the spectra of 5,10-dihydro-5-silanaphtho[3,2-*f*]indolizine is due to the influence of the benzoyl group.

A separate class of heterocyclic compounds is formed as a result of the interaction of the quaternary salts IV, V and VII with dimethylacetylene dicarboxylate in the presence of triethylamine. In the case of these salts, the methylene group at the C(10) position is more active during deprotonation, than the methylene group attached to the nitrogen atom. Such a zwitterion with the anionic centre at the C(10) atom is formed in the first stage of the reaction. Further, as is also the case of the formation of the indolizine cycle [12], as a result of 1,3-dipolar cycloaddition of dimethylacetylene dicarboxylate to the mesomeric zwitterion with a cation centre at the C(4) atom, followed by the deprotonation of the adduct by a second dimethylacetylene dicarboxylate molecule the dihydrosilaazaacenthrelenes are formed. As such starting from the salts IV, VII and V the 3*H*,6*H*-6,6-dimethyl- and 3*H*,6*H*-6-methyl-6-phenyl-3-benzyl-1,2-dicarbomethoxy-6-sila-3-azaaceanthrelenes (X, XII) and 3*H*,6*H*-3,6,6-trimethyl-1,2-dicarbomethoxy-6-sila-3-azaaceanthrelene (XI) were obtained.

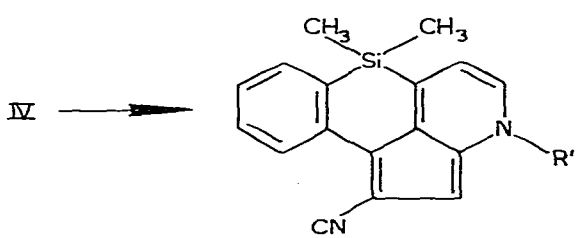


(IV, V, VII)

(X – XII)

X, XI, R = CH_3 ; XII, R = C_6H_5 ; XI, R' = CH_3; X, XIII, R' = $CH_2C_6H_5$.

3*H*,6*H*-6,6-dimethyl-3-benzyl-1-cyano-6-sila-3-azaaceanthrelene (XIII) was isolated as the main reaction product from the condensation of the quaternary salt IV with acrylonitrile. In the same experiment, in extremely low yield, the analogous silaazaaceanthrelene XIV, with a methyl group at the nitrogen atom, has been identified. Most probably it is formed due to an exchange reaction between the *N*-benzyl group of the initial quaternary salt IV or compound XIII with dimethylformamide [13]. The position of the nitrile group in the five-membered ring in the light of NMR data and its computer analysis has been previously discussed [14].



(XIII, R' = $CH_2C_6H_5$; XIV, R' = CH_3)

TABLE 1

SPECTRAL DATA OF DIHYDROSILAAZAACEANTHRELENES X–XVI

Cmpd.	^{1}H NMR spectra (acetone-d_6) (δ, ppm)							UV spectra (ethanol)
	Si–CH_3	$COOCH_3$	N–CH_3	N–CH_2	H(5)	H(4)	$J_{4,5}$	λ_{max} (nm) (lg ε)
X	0.49, s	3.64, s 3.90, s	—	6.12, q	7.38	8.18	5.9	210(4.72), 218(4.72), 252(4.4) 312(4.74), 490(3.42)
XI	0.52, s	3.76, s 3.86, s	4.38, s	—	7.27	7.99	5.9	206(4.54), 218(4.56), 254(4.2) 300(4.54), 312(4.6), 480(3.26)
XII	0.78, s	3.78, s 4.06, s	—	6.31, q	7.07	7.66	—	206(4.6), 220(4.54), 260(4.25) 310(4.48), 496(3.22)
XIII	0.50, s	—	—	6.04, q	7.36	8.13	5.8	220(4.6), 238(4.33), 244(4.33) 287(4.43), 312(4.32), 498(3.2)
XIV	0.46, s	—	4.44, s	—	7.87	7.95	5.7	206(4.6), 238(4.3), 254(4.1), 285(4.3), 310(4.15), 490(3.1)
XV [a]	0.30, s 0.36, s	3.53, s 3.66, s 3.75, s 3.87, s	—	6.33, q	—	8.05	—	210(4.74), 254(4.3), 304(4.47) 313(4.5), 500(2.87)
XVI	—	—	—	—	—	—	—	210(4.76), 260(4.3), 305(4.4), 314(4.4), 502(2.99)

[a] ^{1}H NMR spectra registered in $CDCl_3$.

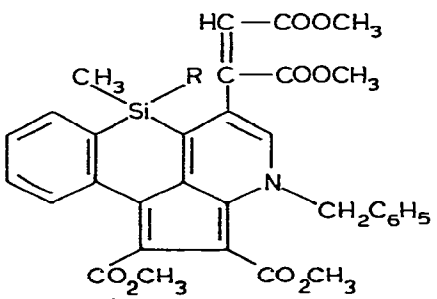
The molecules of dihydrosilaazaaceanthrelenes X—XIV contain a 1*H*-pyridinium (azalene) fragment. The UV spectra (see Table 1) show an absorption band in the region of 480—498 nm, which is characteristic of the pseudo-azulene system [15]. This band is the result of a charge transfer from the six-membered ring on to the five-membered one.

Dihydrosilaazaaceanthrelenes X—XIV are deep crimson-red-coloured crystals. The solution of these pseudoazulenes in $CDCl_3$ lose their colour on acidification with CF_3COOH and on the subsequent treatment with water, gain their colour once again. These changes are initiated by the conversions of the 1*H*-pyridinum fragment in azaindene.

Most probably, the stability of the carbanion which is formed during the dehydrohalogenation of the salts III—VII determines the reaction path. In the case of the *N*-phenacyl salts III and VI the charge in the carbanion so formed is delocalised on the benzoyl radical [16,17]. Whereas, in case of *N*-benzyl and *N*-methyl salts IV, VII and V the carbanion with the anion centred at the C(10) position is probably more stable, due to the delocalisation of the negative charge along the π-orbitals of the phenylene and pyridine cycles [17,18], than the carbanion formed had the deprotonation taken place from the methylene or methyl groups attached to the nitrogen atom.

On the basis of NMR data it was concluded that the dehydrohalogenation of salts IV, V and VII takes place with the participation of the methylene group at the C(10) position. The zwitterions with the anion centre at C(10) formed as a result of the dehydrohalogenation of salts IV, V and VII have a 14-π electron system, satisfying the Huckel aromatic rule. In analogy with the anions of 9,10-dihydro-9-silaanthracene [6] the above-mentioned anions can also be given an aromatic structure with a pentavalent silicon atom.

As a result of the interaction of the quaternary salts IV and VII with dimethylacetylene dicarboxylate, in addition to the main products (dihydrosilaazaaceanthrelenes X and XII), compounds XV and XVI were isolated with 1.5% yield. According to analytical data, compounds XV and XVI are the addition products of two molecules of dimethylacetylene dicarboxylate to the salts. On the basis of the facts discussed below we assign to them the following structure: 3*H*,6*H*-6,6-dimethyl- and 3*H*,6*H*-6-methyl-6-phenyl-3-benzyl-5-(1,2-dicarbomethoxyvinyl)-1,2-dicarbomethoxy-6-sila-3-azaaceanthrelenes (XV and XVI, respectively).



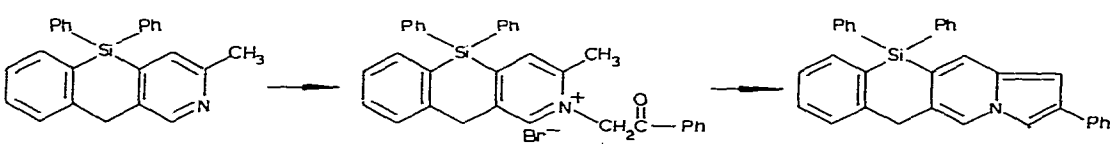
(XV , R = CH_3 ; XVI , R = C_6H_5)

The UV spectra of compounds XV and XVI (see Table 1) are analogous to

the spectra of compounds X and XII, the molecules of which contain a 1 H-indenopyridine fragment. As a result of the increase in the conjugation chain a bathochromic shift is observed for the long wavelength: 10 nm for compound XV and 6 nm for compound XVI. The mass spectra of compound XV show a molecular ion peak with *m/e* 579 (100%). The peak with *m/e* 455 (5%) corresponds to the loss of a dimethylacetylene dicarboxylate molecule from the molecular ion. The further fragmentation of the ion so formed is similar to the fragmentation of the compound X. In the mass spectra of compound XVI the molecular ion peak is observed at *m/e* 659 (27%), and the peak *m/e* 517 (7.5%) corresponds to the loss of a dimethylacetylene dicarboxylate molecule. The intensity of the molecular ion peak in the mass spectra of compounds XV and XVI show that these compounds are not the products of a diene condensation (Diels-Alder reaction) of the dihydrosilaazaaceanthrelenes X and XII with dimethylacetylene dicarboxylate. In the ^{1}H NMR spectra of compound XV the H(4) proton comes out as a singlet at 8.05 ppm which proves that the addition of the second molecule of dimethylacetylene dicarboxylate takes place at the C(5) position. The non-equivalence of the two methyl groups at the silicon atom (δ 0.30 and 0.36 ppm) shows that the dicarbomethoxyvinyl group does not lie in the plane of the azulene fragment. The four carbomethoxy groups appear at δ 3.53, 3.66, 3.75 and 3.87 ppm.

The quantitative ratio of compounds X and XV depends on the reaction conditions (temperature, solvent). In a mixture of methylene chloride with chloroform at 50°C, compounds X and XV are formed in 14 and 1.5% yield, respectively. In the same solvent mixture at 20°C the yield of compound X constitutes 29% whereas compound XV is almost absent. If a solvent mixture of dimethylformamide with chloroform at 50°C is used, then only compound X is isolated with 30% yield.

One of the first representatives of dihydrosilanaphthoindolizines with a linear combination of the dihydrosilanaphthalene and the indolizine cycles was obtained using the Tschitschibabin method [19]. *N*-Phenacyl-2-methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthraceniumbromide (XVIII) was obtained by the reaction of 2-methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthracene (XVII) with ω-bromoacetophenone. The salt XVIII was converted into 2,2,5-triphenyl-5,10-dihydro-5-silanaphtho[3,2-*f*]indolizine (XIX).



(XVII) (XVIII) (XIX)

The structure of compound XIX was confirmed by elemental and spectral analysis. In the ^{1}H NMR spectra of compound XIX the methylene protons appear as a singlet at δ 3.67 ppm; at δ 6.46 and 7.72 ppm the protons H(1) and H(3) are found [20].

Experimental

Dihydrosilaazaanthracenes were synthesized according to the known method [3]. The IR spectra were recorded on an UR-20 spectrometer (in KBr). ^{1}H NMR spectra were obtained on a Bruker WP-80 instrument: compounds III, IV, VIII, IX and XIX in $CDCl_3$, compounds X—XVI in acetone-d_6, internal standard TMS. Chromatography was conducted using aluminium oxide (Reanal, Hungary), silufol UV-254 (Kavalier, Czechoslovakia) and silica gel L 100/160 (Lachema, Czechoslovakia).

Quaternary salts of 9,9-dimethyl- and 9-methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthracenes

a) N-Phenacyl-9,9-dimethyl-9,10-dihydro-9-sila-3-azaanthracenium bromide (III). A mixture of 1 g (0.0044 mol) silaazaanthracene I and 2.72 g (0.0136 mol) ω-bromoacetophenone was refluxed for 10 h in methanol (25 ml) (chromatographic control of the progress of the reaction). The methanol was distilled and the residue repeatedly worked up with dry ether. Recrystallisation from a mixture of ethyl acetate and acetone (15/5) gave 1.68 g (90%) of the quaternary salt III, m.p. 190—191°C. Anal. Found: C, 62.0; H, 5.4; N, 3.5; Br, 18.3. Calcd. for $C_{22}H_{22}NSiOBr$: C, 62.2; H, 5.1; N, 3.3; Br, 18.8%. ^{1}H NMR: δ 0.52 (s, Si—CH_3); 3.8 (s, CH_2); 7.0 ppm (s, N—CH_2).

b) N-Benzyl-9,9-dimethyl-9,10-dihydro-9-sila-3-azaanthracenium bromide (IV). Similarly, from 1 g (4.4 mmol) of the base I and 2.4 g (0.0136 mol) benzyl bromide, the bromobenzylate IV (1.56 g, 90%), m.p. 142—144°C was obtained. Anal. Found: C, 63.4; H, 5.5; N, 3.3; Br, 20.0. Calcd. for $C_{21}H_{22}NSiBr$: C, 63.6; H, 5.5; N, 3.5; Br, 20.2%. ^{1}H NMR: δ 0.54 (s, Si—CH_3), 3.98 (s, CH_2), 6.0 ppm (s, N—CH_2).

c) N-Methyl-9,9-dimethyl-9,10-dihydro-9-sila-3-azaanthracenium iodide (V). Similarly from 1 g (4.4 mmol) of base I and 6 g (4.4 mmol) methyl iodide, the iodide methylate V (1.2 g, 80%), m.p. 130—132°C, was obtained. Anal. Found: C, 49.8; H, 5.1; N, 3.6. Calcd. for $C_{15}H_{18}NSiI$: C, 50.0; H, 5.0; N, 3.8%.

d) N-Phenacyl-9-methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthracenium bromide (VII). 1.4 g (85%) of the phenacyl bromide VI was obtained from 1 g (3.5 mmol) silaazaanthracene II and 2.78 g (0.0137 mol) ω-bromoacetophenone according to the above method, m.p. 193—194°C. Anal. Found: C, 66.8; H, 4.8; N, 2.8; Br, 16.0%. Calcd. for $C_{27}H_{24}NSiOBr$: C, 66.6; H, 4.9; N, 2.8; Br, 16.4%.

e) N-Benzyl-9-methyl-9-phenyl-9,10-dihydro-9-sila-3-azaanthracenium bromide (VII). From silaazaanthracene I (1 g, 3.5 mmol) and benzyl bromide (2.4 g, 0.0136 mol), the bromobenzylate VII (1.3 g, 80%), m.p. 112—114°C, was obtained. Anal. Found: C, 66.8; H, 5.4; N, 2.8; Br, 17.4%. Calcd. for $C_{26}H_{25}NSiBr$: C, 68.1; H, 5.2; N, 3.0; Br, 17.4%.

6,6-Dimethyl-3-benzoyl-1,2-dicarbomethoxy-6,11-dihydro-6-sila-naptho[2,3-g]-indolizine (VIII)

To a solution of the quaternary salt III (1.34 g, 2.5 mmol) in 30 ml of chloroform, 0.8 g (5 mmol) of dimethylacetylene dicarboxylate, and 1.2 g (0.01 mol) of triethylamine was added, accompanied by vigorous stirring. The reaction mix-

ture developed a deep red colour. Stirring was continued for 5 h at 40°C and 15 ml of water were added. The organic layer was separated, and the water layer was extracted with chloroform. The chloroform layer was dried on magnesium sulphate. The resulting residue (2 g) is chromatographed on alumina (h = 40 cm, d = 8 cm, eluent: heptane/ethyl acetate 20/1). Silanaphthoindolizine VIII (0.16, 14% yield), m.p. 154—156°C (acetone/ethyl acetate, 1/5) was isolated. Anal. Found: C, 69.4; H, 5.4; N, 2.7; M 483. Calcd. for $C_{28}H_{25}No_5Si$: C, 69.6; H, 5.2; N, 2.9%; M 483. IR: 820, 1250 (Si—CH_3), 1632 (C=O), 1745 and 1715 cm^{-1} ($COOCH_3$). ^1H NMR: δ 0.44 (s, Si—CH_3), 3.2 (s, OCH_3), 3.98 (s, OCH_3), 4.23 (s, CH_2), 7.15 (d, $J_{4,5}$ = 7 Hz, H(5)), 9.3 ppm (d, $J_{4,5}$ = 7 Hz, H(4)).

6-Methyl-6-phenyl-3-benzoyl-1,2-dicarbomethoxy-6,11-dihydro-6-silanaphtho-[2,3-g]indolizine (IX)

By the above method, starting from salt VII (1.5 g, 3 mmol) and dimethylacetylene dicarboxylate (0.85 g, 6 mmol); the silanaphthoindolizine IX (0.15 g, 11%), m.p. 155—157°C (ethyl acetate/heptane, 2/1) was obtained. Anal. Found: C, 72.4; H, 5.1; N, 2.4%, M 545. Calcd. for $C_{32}H_{27}NO_5Si$: C, 72.7; H, 5.0; N, 2.6%, M, 545. IR: 1620 (C=O), 1720 and 1745 cm^{-1} ($COOCH_3$). ^1H NMR: δ 0.80 (s, Si—CH_3), 3.16 (s, OCH_3), 3.95 (s, OCH_3), 4.50 (s, CH_2), 7.03 (d, $J_{4,5}$ = 7 Hz, H(5)), 9.25 ppm (d, H(4)).

In addition to the initial compound IX; 0.16 g of a mixture of compound IX along with 5-methyl-5-phenyl-5,10-dihydro-5-silanaphtho[3,2-f]indolizine (ratio 1 ' 2), m.p. 90—95°C, was obtained. ^1H NMR: δ 0.8 and 0.96 (s, Si—CH_3), 3.16, 3.30, 3.64, 3.95 (s, OCH_3), 4.02 (s, CH_2), 7.03 (d, J = 7 Hz, H(4)), 8.28 (s, H(4)), 9.15 (d, J = 7 Hz), 9.36 ppm (s, H(11)).

3H,6H-6,6-Dimethyl-3-benzyl-1,2-dicarbomethoxy-6-sila-3-azaaceanthrelene (X)

a) A mixture of the salt IV (1.8 g, 4.5 mmol), dimethylacetylene dicarboxylate (1.14 g, 8 mmol) and triethylamine (1.6 g, 0.016 mol) in 30 ml of methylene chloride was stirred for 8 h. 15 ml of water was added. The reaction mixture was worked up as described earlier. The residue (2.5 g) was chromatographed. As a result, dihydrosilaazaaceanthrelene X (0.6 g, 29%), red-coloured crystals, m.p. 175.5—176°C (methanol), R_f 0.82 (ether), was obtained. Anal. Found: C, 71.5; H, 5.7; N, 3.2, M, 455. Calcd. for $C_{27}H_{25}NO_4Si$: C, 71.3; H, 5.5; N, 3.1%, M, 455. IR: 815 and 1255 (Si—CH_3); 1695 and 1733 cm^{-1} ($COOCH_3$).

b) Using the above method, in a solvent mixture of methylene chloride and chooroform at 50°C, 0.29 g (14%) of compound X and 0.04 g (1.5%) of dihydrosilaazaaceanthrelene XV, m.p. 70°C (methanol), R_f 0.69 (ether) were obtained. Anal. Found: M, 2.3; M 579. Calcd. for $C_{31}H_{33}NO_8Si$: N, 2.1%, M 579. IR: 815 and 1255 (Si—CH_3); 1725 and 1690 cm^{-1} ($COOCH_3$).

3H,6H-3,6,6-Trimethyl-1,2-dicarbomethoxy-6-sila-3-azaaceanthrelene (XI)

A mixture of the quaternary salt V (1.4 g, 3 mmol) and dimethylacetylene dicarboxylate (1.08 g, 7 mmol) in methylene chloride was refluxed for 4 h. The reaction mixture was worked up as described above. 0.3 g (21%) of compound XI, m.p. 208—209°C (methanol) R_f 0.75 (ether) was obtained. Anal. Found: C, 68.0; H, 5.5; N, 4.0, M, 379. Calcd. for $C_{21}H_{21}NO_4Si$: C, 68.1; H, 5.6; N, 3.7%, M, 379. IR: 815 and 1255 (Si—CH_3), 1695 and 1735 cm^{-1} ($COOCH_3$).

3H,6H-6-Methyl-6-phenyl-3-benzyl-1,2-dicarbomethoxy-6-sila-3-azaaceanthrelene (XII)

a) 2.6 g (5.6 mmol) of the quaternary salt VII, 1.6 g (0.011 mol) of dimethylacetylene dicarboxylate and 1.1 g (0.011 mol) of triethylamine in 30 ml of methylene chloride were stirred at room temperature for 4 h. The reaction mixture was worked up as described above. 0.6 g (21%) of compound XII, m.p. 149.5—150°C (methanol), R_f 0.93 (ether) was obtained. Anal. Found: C, 74.0; H, 5.4; N, 2.5, *M*, 517. Calcd. for $C_{32}H_{27}NO_4Si$: C, 74.3; H, 5.2; N, 2.7%, *M*, 517. IR: 810 and 1260 (Si—CH_3), 1115 and 1430 (Si—Ph), 1690 and 1725 cm^{-1} ($COOCH_3$).

b) Similarly from 1.34 g (0.0028 mol) of the salt VII, 0.85 g (0.006 mol) of dimethylacetylene dicarboxylate and 0.6 g (6 mmol) of triethylamine in 30 ml of boiling methylene chloride, 0.13 g (9%) of compound XII and 0.03 g (1.5%) of compound XVI, m.p. 80—82°C (methanol) R_f 0.4 (ether) were obtained. Anal. Found: N, 2.3%, *M*, 659. Calcd. for N, 2.1%, *M*, 659. IR: 794 and 1255 (Si—CH_3), 1105 and 1425 (Si—Ph), 1693 and 1725 cm^{-1} ($COOCH_3$).

3H,6H-6,6-Dimethyl-3-benzyl- and 3H,6H-6,6-dimethyl-3-methyl-1-cyano-6-sila-3-azaaceanthrelenes (XIII, XIV)

The quaternary salt IV (3.5 g, 9 mmol) was dissolved in 20 ml of dimethylformamide. Triethylamine (4.5 g, 0.045 mol) and acrylonitrile (2.4 g, 0.045 mol) were added and the reaction mixture was refluxed for 10 h under continuous stirring. After the necessary working up of the reaction mixture as described earlier, the residue (4 g) was chromatographed (h = 40 cm, d = 5 cm) using silica gel L 100/160, eluent: mixture of ethyl acetate and heptane, 1/5. Compound XIII (0.5 g, 16%), m.p. 221—222°C (methanol) R_f 0.92 (silufol UV-254, ethyl acetate/heptane, 1/1) was obtained. Anal. Found: C, 79.8; H, 5.2; N, 7.7%, M^+, 364. Calcd. for $C_{24}H_{20}N_2Si$: C, 80.0; H, 5.5; N, 7.7%, *M*, 364. IR: 845 and 1245 (Si—CH_3), 2188 cm^{-1} (CN).

Further, compound XIV (0.05 g, 2.5%) was isolated. These are red crystals, m.p. 71—72°C (methanol) R_f 0.83 (silufol, ethyl acetate/heptane I/I). Anal. Found: N, 9.6, *M*, 288.

2,5,5-Triphenyl-5,10-dihydro-5-silanaphtho[3,2-f]indolizine (XIX)

0.6 g (2 mmol) dihydrosilaazaanthracene XVII and 0.33 g (1.7 mmol) of ω-bromoacetophenone were refluxed in 30 ml of benzene for 6 h. The residue after the distillation of benzene was repeatedly worked up in dry ether. The salt XVIII was dissolved in 10 ml of chloroform and 2 ml of 40% solution of K_2CO_3. The mixture was refluxed for 1.5 h. The residue after the distillation of $CHCl_3$ was chromatographed (eluent : heptane). 0.07 g (9%) of the indolizine XIX, m.p. 195—196°C, R_f 0.61 (ethyl acetate/heptane 1/4) was obtained. Anal. Found: C, 85.3; H, 5.4; N, 3.3, *M*, 463. Calcd. for $C_{33}H_{25}NSi$: C, 85.5; H, 5.5; N, 3.0%, *M*, 463. IR: 1118 and 1430 cm^{-1} (Si—Ph).

References

1 N.S. Prostakov, A.V. Varlamov and V.P. Zvolinskii, Khim. Geterotsik. Soedin., (1972) 1579.
2 A.V. Varlamov, N.S. Prostakov, N. Saxena and A.M. Klochkov, Abstracts, VIth Symposium on chemistry of heterocyclic compounds, Brno, Czechoslovakia, 1978, p. 80.

3 N.S. Prostakov, N. Saxena, A.V. Varlamov and A.M. Klochkov, Khim. Geterotsik. Soedin, in press.
4 P. Jutzi, Z. Naturforsch., 248 (1969) 354.
5 J.Y. Corey, M.J. Dye, R.L. Farrell and M.V. Mitchell, J. Organometal. Chem., 153 (1978) 127.
6 P. Jutzi, J. Organometal. Chem., 22 (1970) 297.
7 P. Jutzi, Chem. Ber., 104 (1971) 1455.
8 P. Jutzi, Chem. Ber., 106 (1973) 3495.
9 I.I. Chernishov, N.G. Komalenkova, L.N. Shamshin and V.N. Bochkarov, J. Obsch. Khim., 42 (1972) 1373.
10 D.R. Bragg and D.J. Wibberley, J. Chem. Soc., (1963) 3277.
11 N.S. Prostakov, L.A. Gaivoronskaya, R.I. Anastami, S.M. Kamara, Maiga, A.A. Savina, L.A. Murugova and P.I. Zakharov, Khim. Geterotsik. Soedin, (1979) 1514.
12 F. Kronke and W. Zecher, Ber., 95 (1962) 1128; C.A. Henrik, E. Ritchie and W.C. Taylor, Austral. J. Chem., 20 (1967) 2467.
13 D. Aumann and L.W. Deady, J. Chem. Soc. Chem. Commun., (1973) 32.
14 A.A. Fomitchov, V.A. Svoren, N.F. Sipetov, A.V. Varlamov and N.S. Prostakov, in press.
15 H.J. Timpe, J. Mlochowski and Z. Szulc, Z. Chem., 19 (1979) 374.
16 C. Fabre, M. Hadj Ali Salem, J.P. Mazaleyram, A. Tchapala and Z. Welvart, J. Organometal. Chem., 87 (1975) 9.
17 P.W. Rabideau and E.G. Burkholder, J. Org. Chem., 43 (1979) 4283.
18 A.E. Tschitschibabin, Zh. Ruskovo. Khim. Obsh., 59 (1927) 477.
19 N.S. Prostakov, V.I. Kuznetsov, A.A. Savina, M.A. Ryashentsova and V.P. Zvolinskii, Khim. Geterotsik. Soedin., (1977) 646.