CONDENSATION OF N-(p-NITROBENZYL)-10,10-DIMETHYL-9,10-DIHYDRO-10-SILA-2-AZAANTHRACENE BROMIDE AND ITS 9-OXO DERIVATIVE WITH ACETYLENEDICARBOXYLIC ESTER

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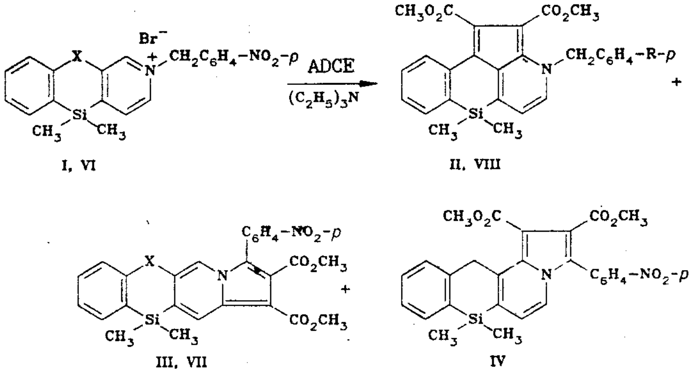
Carbanions derived from N-(p-nitrobenzyl)-dihydrosilaazaanthracene condense with acetylenedicarboxylic ester to form substituted silanaphthoindolizines and silaazaaceanthrenes. The analogous salt of the 9-oxo derivative gave the oxo substituted silanaphthoindolizine. The compounds obtained were subjected to reduction, hydrolysis, and opening of the sila-ring.

Base induced deprotonation of quaternary salts of dihydrosilaazaanthracene (in which the N-radical linkage occurs via a methylene group) can occur both at this methylene and at position C-9. It has previously been shown that the course of deprotonation and the structure of the product (obtained by condensation of the carbanion so formed with acetylene dicarboxylic ester (ADCE)) depends on the CH-acidity of both methylene groups and on the stability of the carbanions. From the bromides of N-phenacyldihydrosilaazaanthracene there were obtained the ring isomers dihydrosilanaphtho[2,3-g] and [3,2-f]indolizines [1, 2] and from the halides of N-benzyl and also N-methyldihydrosilaazaanthracene the dihydrosilaazaaceanthrenes (heterocycles with the 1-H pyrindine fragment) [2-4]. It can be proposed that the presence of electron acceptor substituents of medium strength at the N-CH_2 group will lead to deprotonation of both methylene groups and thus to a mixture of dihydrosilanaphthoindolizines and dihydrosilaazaaceanthrene. As a test we have studied the condensation of N-p-nitrophenyl-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene I with ADCE in the presence of triethylamine.

In this case it is found that a mixture of 3H,6H-6,6-dimethyl-3-p-nitrobenzyl-1,2-dicarbomethoxy-6-sila-3-azaaceanthrene (II), 5,5-dimethyl-1-p-nitrophenyl-2,3-dicarcomethoxy-5,10-dihydro-5-sila-naphtho [3,2-f]indolizine (III), and 6,6-dimethyl-3-nitrophenyl-1,2-dicarbomethoxy-6,11-dihydro-6-silanaphtho[3,2-g]indolizine (IV) is formed.



I, III X=CH_2; VI, VII X=C=O; II R=NO_2; VIII R=NH_2

Compounds II and III were separated chromatographically. Formation of the angular dihydrosilanaphthoindolizine was shown using PMR spectra by the presence at low field of a 5-H doublet (6.63 ppm) with $^3J_{4,5}$ = 6.7 Hz. Compound III was characterized by the presence of two singlet PMR spectral signals for the non-coupled 4-H and 11-H protons at 7.75 and 8.25 ppm, respectively. In addition to II-IV the reaction mixture yielded a small amount (∿ 0.5%) of 3H,6H-3,6,6-trimethyl-1,2-dicarbomethoxy-6-sila-3-azaaceanthrene (V), with

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TABLE 1. PMR and UV Spectra of Synthesized Compounds

Compound	PMR spectrum δ, ppm ($CDCl_3$)	UV spectrum, λ_{max}, nm (log ε)
II	8,07 (2H, d, o-protons p-$NO_2C_6H_4$; $J=9$ Hz); 7,69 (1H, d, 4-H, $J_{4,5}=5,9$ Hz); 7,50 (2H, d, m-protons p-$NO_2C_6H_4$); 7,12 (1H, d, 5-H); 6,45 (2H, s, CH_2N); 4,00 (3H, s, CH_3O); 3,72 (3H, s, CH_3O); 0,57 (6H, s, $SiCH_3$)	203 (4,93), 230 (4,93), 2,60 (4,75), 300 (4,94), 312 (4,90), 500 (3,52)
III	8,25 (1H, s, 11-H); 8,01 (2H, d, o-protons p-$NO_2C_6H_4$, $J=9$ Hz); 7,75 (1H, s, 4-H); 7,50 (2H, d, m-protons -$NO_2C_6H_4$); 3,82 (5H, s, CH_2 and CH_3O); 3,75 (3H, s, CH_3O); 0,55 (6H, s, $SiCH_3$)	260 (4.54), 304 (4,12), 364 (4,22), 408 sh (4,06)
IV*	8,20 (2H, d, o-protons -$NO_2C_6H_4$, $J=9,1$ Hz); 7,50 (2H, d, m-protons -$NO_2C_6H_4$); 6,63 (1H, d, 5-H, $J_{4,5}=6,7$ Hz); 4,32 (2H, s, CH_2); 4,0 (3H, s, CH_3O); 3,68 (3H, s, CH_3O); 0,42 (6H, s $SiCH_3$)	
VII	8,48 (1H, s, 11-H); 8,35 (1H, s, 4-H); 7,90 (2H, d, o-protons, p-$NO_2C_6H_4$, $J=9$ Hz); 6,85 (2H, d, m-protons, p-$NO_2C_6H_4$); 4,07 (3H, s, CH_3O); 3,75 (3H, s, CH_3O); 0,50 (6H, s, $SiCH_3$)	206 (4,62), 274 (4,52), 304 (4.18), 3,86 (3,82), 420 sh (3,70)
VIII	7,67 (1H, d, 10-H, $J_{9,10}=8$ Hz); 7,65 (1H, d, 4-H, $J_{4,5}=6$ Hz); 7,54 (1H, m, 7-H); 7,34 (1H, t, 9-H); 7,15 (1H, t, 8-H); 6,98 (2H, d, m-protons-$NH_2C_5H_4$); 6,59 (2H, d, o-protons p-$NH_2C_6H_4$); 6,09 (1H, s, CH_2); 4,03 (3H, s, CH_3O); 3,80 (3H, s, CH_3O); 3,69 (2H, s, NH_2); 0,43 (6H, s, $SiCH_3$)	206 (4,62), 246 (4,40), 296 (4,44), 314 (4,50), 496 (3,36)
X	7,96 (1H, d, 2-H, $J_{2,3}=6,8$ Hz); 7,66 (1H, d, 4-H, $J_{3,4}=6,4$ Hz); 7,50 (1H, dd 6'-H, $J_{5',6'}=7,2$, $J_{6',3'}=1,6$ Hz); 6,56 (1H, dd, 3-H); 6,06 (2H, s, CH_2); 0,17 (6H, s, $SiCH_3$)	245 (4,12), 282 (4,30), 334 (3,54), 445 (2,76)
XII	8,38 (1H, d, 10-H, $J_{9,10}=8$ Hz); 8,06 (1H, d 4-H, $J_{4,5}=6$ Hz); 5,63 (2H, s, CH_2); 0,53 (6H, s, $SiCH_3$)	208 (4,60), 258 (4,15), 336 (4,15), 529 (3,20)

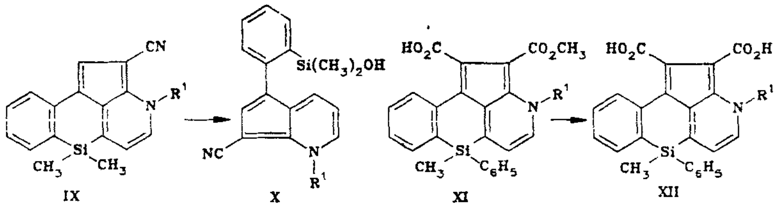
*PMR spectral analysis of a mixture of III and IV.

analogous physico-chemical and spectral properties to those described in [2]. Exchange of N-benzyl for N-methyl during condensation of N-benzyldihydrosilaazaanthracene halides with acrylonitrile in DMF has been reported by us previously [2].

Condensation of N-p-nitrobenzyl-9-oxo-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene bromide (VI) with ADCE occurs at C-3. A 9% yield of 10-oxo-5,5-dimethyl-1-p-nitrophenyl-2,3-dicarbomethoxy-5-silanaphtho[3,2-f]indolizine (VII) was obtained.

Information about the reduction of 1H-pyrindines and their reaction with nucleophilic reagents is very limited [5]. We have shown that the nitro group in the nitrobenzyl radical of the aceanthrene II is reduced to amino by hydrazine hdyrate in the presence of Raney nickel. The amino compound VIII, in which the starting heterocycle is preserved, was obtained in 63% yield.

3H,6H-6,6-Dimethyl-3-benzyl-2-cyano-6-sila-3-azaaceanthrene (IX), obtained by us before [2], proved to be inert towards hydrogenation. It was not reduced in the presence of Raney heptasulfide in benzene at 240°C with a hydrogen pressure of 130 atm. The nitrile group in this compound is also stable to basic hydrolysis. It is also preserved when the Si–$C_{pyridyl}$ bond is broken to form 1H-1-benzyl-5-(2-dimethylhydroxysilyl)phenyl-7-cyanocyclopentadieno[e]pyridine (X).



IX X XI XII

$R^1=CH_2C_6H_5$

3H,6H-6-Methyl-6-phenyl-3-benzyl-1,2-dicarbomethoxy-6-sila-3-azaaceanthrene (XI) [2] was hydrolyzed by 10% alcoholic base to the dicarboxylic acid (XII).

The high stability of the nitrile group in IX, as in the case of 1-cyanoazulene [6], may be explained by a significnat contribution of a polar structure with localized negative charge on the nitrile nitrogen atom.

In the PMR spectrum of pseudoazulene X there were observed signals at 7.96, 7.66, and 6.5 ppm due to the coupling nuclei 2-H, 4-H, and 3-H respectively. The position and J values for these protons agree with those for 1H-1-methylpyrindine [7]. The UV spectra of X and XII showed long wavelength bands characteristic of S^0—S^1 transfer in pseudoazulene systems [8]. A hypsochromic shift (54 nm) for X compared with IX points to a disturbance of the coplanarity of the phenyl and azulene fragments in the molecule. In contrast, a bathochromic shift for the long wavelength maximum is observed in the UV spectrum of the di-acid XII because of the formation of hydrogen bonds between the carboxyl groups which increases their coplanarity with the azulene fragment.

EXPERIMENTAL

PMR spectra were recorded on a Bruker WP-80 (80 MHz) with acetone-d_6 and $CDCl_3$ solvents and TMS internal standard. Mass spectra were obtained on an MX-1303 and IR spectra on a UR-20 spectrophotometer for KBr pellets. UV spectra were taken in ethanol solvent on a Specord UV-vis. Column and thin layer chromatography were performed on silica gel A 100/160 and visualized with iodine. PMR and UV data are given in Table 1.

Bromides on N-p-Nitrobenzyl-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (I) and N-p-Nitrobenzyl-9-oxo-10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene (VI). A solution of 10,10-dimethyl-9,10-dihydro-10-sila-2-azaanthracene or the corresponding silaazaanthrone (0.54 mmole) and p-nitrobenzylbromide (9 mmole) in methanol (40 ml) was refluxed for 10 h. Methanol was removed by distillation and the residue was crystallized by trituration with ether. Both salts were obtained in 90% yield. Salt 1: mp 220-222°C (from acetone). Found: C 57.2; H 5.0; Br 17.9; N 6.0%. $C_{14}H_{15}NSi \cdot C_7H_6BrNO_2$. Calculated: C 57.1; H 4.7; Br 18.1; N 6.3%. Salt VI: mp 217-219°C (alcohol). Found: C 54.8; H 3.9; Br 17.6; N 6.1%. $C_{14}H_{13}NOSi \cdot C_7H_6BrNO_2$. Calculated: C 55.2; H 4.1; Br 17.6; N 6.1%.

3H, 6H-6,6-Dimethyl-3-p-nitrobenzyl-1,2-dicarbomethoxy-6-sila-3-azaaceanthrene (II); 5,5-Dimethyl-1-p-nitrophenyl-2,3-dicarbomethoxy-5,10-dihydro-5-silanaphtho-[3,2-f]indolizine (III); 6,6-Dimethyl-3-p-nitrophenyl-1,2-dicarbomethoxy-6,11-dihydro-6-silanaphtho-[2,3-g]indolizine (IV). Triethylamine (0.2 g, 2 mmole) and a solution of ADCE (0.5 g, 3.6 mmole) in DMF (15 ml) were added to quaternary salt I (0.9 g, 2 mmole) in DMF (5 ml). After stirring for 8 h, water (15 ml) was added, the organic layer separated and the reaction products extracted from the aqueous layer with chloroform. The combined extracts were dried ($MgSO_4$), solvent distilled off and the residue (1 g) chromatographed on silica gel (h = 40 cm, d = 2.5 cm). Initial elution with heptane and ethyl acetate (5:1) gave III (0.06 g, 6%), mp 197-199°C (from a mixture of ethyl acetate/hexane). Found: N 5.8%; M^+ 500. $C_{27}H_{24}N_2O_6Si$. Calculated: N 5.4%; M 500. A 3:1 mixture of the same solvents then removed a mixture of III and IV (0.14 g, 14%). According to NMR spectral data the ratio of components was 1:2.7. Further elution gave the aceanthrene V (0.01 g, mp 207-208°C, M^+ 397 [2]). A mixture of heptane/ethyl acetate (2:1) finally removed the aceanthrene II (0.12 g, 12% mp 250-252°C) (from a mixture of ethyl of ethyl acetate/heptane). Found: C 64.8; H 4.8; N 5.6%; M^+ 500. $C_{27}H_{24}N_2O_6Si$. Calculated: C 65.1; H 5.2; N 5.4%; M 500.

11-Oxo-6,6-dimethyl-3-p-nitrophenyl-1,2-dicarbomethoxy-6,11-dihydro-6-silanaphtho-[2,3-g]indolizine (VII). An analogous preparation from quaternary salt VI (1.5 g, 3 mmole) and ADCE (0.85 g, 6.2 mmole) with triethylamine (0.34 g, 3 mmole) in methylene chloride (30 ml) gave a residue (2.4 g) after distillation of solvent. Chromatography on Al_2O_3 (h = 40 cm, d = 3.5 cm, eluant-ethyl acetate/heptane 1:5) gave VII (0.15 g, 9%) with mp 248-250°C (from alcohol). Found: C 63.2; H 4.4; N 4.9%; M^+ 514. $C_{27}H_{22}N_2O_7Si$. Calculated: C 63.0; H 4.2; N 5.4%; M 514.

3H, 6H-6,6-Dimethyl-3-p-aminobenzyl-1,2-dicarbomethoxy-6-sila-3-azaaceanthrene (VIII). To a solution of II (0.25 g, 0.5 mmole) in alcohol (20 ml) there were added hydrazine hydrate (5 ml) and freshly prepared Raney nickel (on the end of a spatula). A fresh portion of catalyst was added after 24 h and, after a further 24 h, the catalyst was filtered off. After removal of solvent, water was added and extracted with ether. Drying ($MgSO_4$) and removal of solvent gave a residue (0.2 g) which was chromatographed on silica gel (h = 27 cm, d = 1 cm, eluant ether). First removed was the starting aceanthrene II followed by VIII (0.145 g, 63%) with mp 173-175°C (heptane). Found: C 69.0; H 5.6; N 5.4%; M^+ 470. $C_{27}H_{26}N_2O_4Si$. Calculated: C 68.9; H 5.5; N 5.9%. M 470.

Hydrogenation of 3H,6H-6,6-Dimethyl-3-benzyl-2-cyano-6-sila-3-azaaceanthrene (IX). A glass ampul containing a solution of aceanthrene IX (0.13 g, 0.3 mmole) in absolute benzene (15 ml) and Raney heptasulfide (0.02 g) were placed in an autoclave (V = 0.15 liter) and heated for 4 h at 240°C under a hydrogen pressure of 130 atm. Following cooling, the catalyst was filtered off and the residue (0.13 g) after removal of benzene by distillation, was crystallized from methanol to give recovered starting material IX (0.12 g, mp 221-222°C, according to [2] mp = 221-222°C).

1H-1-Benzyl-5-(2-dimethylhydroxysilyl)phenyl-7-cyanocyclopentadieno[e]pyridine (X). A solution of aceanthrene IX, (0.1 g, 0.2 mmole) in 20% alcoholic KOH solution (20 ml) was refluxed for 4 h. It was cooled, water (50 ml) added, the precipitate filtered off, and recrystallized from methanol to give X (0.06 g, 55%) with mp 163-165°C. Found: N 7.5%; M^+ 382. $C_{24}H_{22}N_2OSi$. Calculated: N 7.9%; M 382.

3H,6H-6-Methyl-6-phenyl-3-benzyl-1,2-dicarboxy-6-sila-3-azaaceanthrene (XII). A solution of aceanthrene XI (0.1 g, 0.2 mmole) in 10% alcoholic KOH (20 ml) was refluxed for 4 h, water (50 ml) added, the product extracted with chloroform and solvent removed by distillation. The residue was dissolved in alcohol (2 ml) and neutralized with HCl. Solvent was removed and the residue crystallized from methanol to give the dicarboxylic acid XII (0.03 g, 33%) with mp 100-103°C. Found: C 73.4; H 4.6; N 2.8%. $C_{30}H_{23}NO_4Si$. Calculated: C 73.6; H 4.7; N 2.9%.

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