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SYNTHESIS OF SPIRO[9,10-DIHYDRO-10-SILA-2-AZAANTHRACENE-9,1'-CYCLOPROPANES

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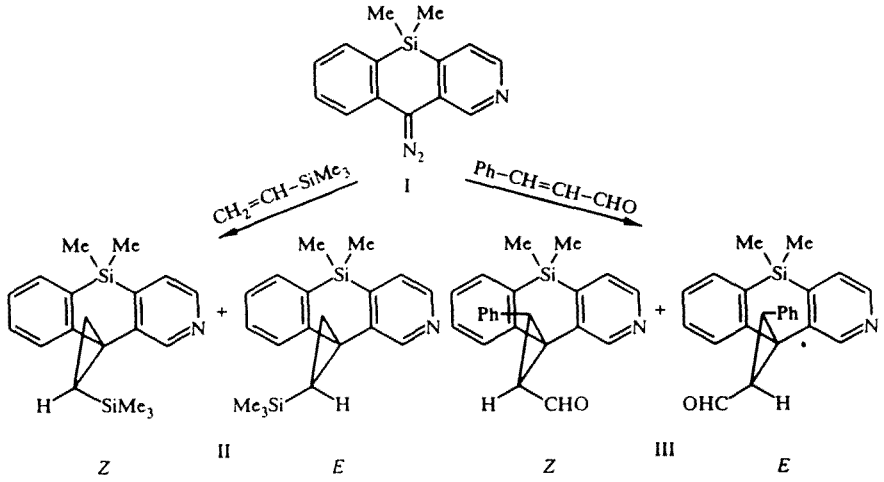
The Z- and E-isomers of 9,10-dihydro-10,10-dimethyl-2'-trimethylsilyl(2'-phenyl-3'-formyl)spiro[10-sila-2-aza-anthracene-9,1'-cyclopropane] have been obtained by heating 9-diazo-9,10-dihydro-10,10-dimethyl-10-sila-2-azaanthracene with trimethylvinylsilane and with cinnamaldehyde.

The reaction of diazo compounds with alkenes and alkynes is widely used for the synthesis of compounds of the cyclopropane, pyrazoline and pyrazole series [1-3]. A different direction for the reaction was established in the reaction of 9-diazo-9,10-dihydro-9,9-dimethyl-9-silaanthracene with *cis*-pseudobutylene and with α-β-dichloroethene under photolytic conditions [4]. The corresponding spirocompounds containing dihydrosilanthracene and cyclopropane (pyrazoline) units were not formed under these conditions. The reaction products were 10-butenyl-substituted-9-silaanthracenes and also 10-(2,2-dichloroethylidene)-9-silaanthracene, the product of the rearrangement of the biradical formed by the addition of the corresponding carbene to the double bond of dichloroethene. Bis(9,10-dihydro-9,9-dimethyl-9-silaanthracen-10-yl) was also isolated.

We have synthesised 9-diazo-9,10-dihydro-10,10-dimethyl-10-sila-2-aza-anthracene (I) [5], an analog of the dihydrosilaanthracene discussed above. In this paper the results of a study of the reactions of (I) with trimethylvinylsilane and cinnimaldehyde on heating with excess of the alkenes is reported. The corresponding 9,10-dihydro-10,10-dimethyl-2'-trimethylsilylspiro[10-sila-2-aza-anthracene-9,1'-cyclopropane] (II) and 9,10-dihydro-10,10-dimethyl-2'-phenyl-3'-formyl-spiro[10-sila-2-aza-anthracene-9,1'-cyclopropane] (III) were obtained in about 50% yield. It was established that the reaction of the diazo compound (I) with cinnamaldehyde was accompanied by the formation of 10,10-dimethyl-10-sila-2-azaanthrone.



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According to TLC and ^{1}H NMR spectroscopic data, spirocompounds II and III are formed as a mixture of geometric isomers with respect to the position of the substituents on the cyclopropane ring relative to the nitrogen containing ring of the dihydrosilaazaanthracene fragment. The signals of the 1-H and 8-H protons in the ^{1}H NMR spectra appear as two signals. The chemical shifts of these hydrogens are the most sensitive to the effects of substituents on the cyclopropane ring.

The individual isomers of the spirocompound III were isolated by chromatography. The coupling constants $^3J_{H2'H3'}$ = 7.5 Hz showed that the *trans* position was retained as in the cinnimaldehyde starting material. The proton of the formyl group in both isomers appeared as a doublet at 8.82 ppm ($^3J_{H3'CHO}$ = 6.4 Hz). The configuration of the isolated isomers of compound III and the isomeric mixture of compound II were assigned based on a previous study to establish the configuration of the *Z*- and *E*-isomers of spiro[4-azafluoren-9,1'-cyclopropanes]. The chromatographically less mobile isomer (R_f 0.12) of compound III, which the signal of proton 1-H at higher field, was assigned the *E*-configuration, while the *Z*-configuration was assigned to the more mobile isomer (R_f 0.18) which has the 1-H signal at lower field.

The mass spectra of compounds II and III are characterized by intense molecular peaks at *m/z* 323 and 355 which correspond to the molecular formulas. Fragmentations of the isomers of III are analogous. The main direction of fragmentation of the parent ions M^+ is associated with loss of the substituent on the cyclopropane ring, accompanied by opening of this ring with transfer of a hydrogen atom to the dihydrosilaazaanthracene unit, leading to the formation of an ion with *m/z* 224. Fragmentation of the M^+ ion of II is dominated by loss of a hydrogen from the cyclopropane ring. Loss of CO and CHO was observed in the fragmentation of both II and III. Fission of the dihydrosilaazaanthracene unit was demonstrated by the appearance of the $[M-Si(CH_3)_2]^+$ ion.

The difference in the reactions of diazocompound I and 10-diazo-9,10-dihydro-9,9-dimethyl-9-silaanthracene [4] with alkenes is apparently a result of differences in the structures of the intermediate carbenes. It is possible that the thermal reaction of compound I with alkenes occurs via the intermediate formation of adducts — spiro[dihydrosilaazaanthracen-9,3'-(1-pyrazolines)] which rearrange to compounds II and III with loss of nitrogen.

EXPERIMENTAL

^{1}H NMR Spectra of $CDCl_3$ solutions with TMS as internal standard were recorded on WP-80 and WH-400 instruments. IR spectra of KBr disks were measured on a UR-20 machine. Mass spectra were obtained with a Kratos MS 25RF mass spectrometer. Column and thin layer chromatography used silica gel L 40/100 and Silufol UV-254 respectively.

Elemental analysis results for the newly synthesised compounds agreed with calculated values.

9,10-Dihydro-10,10-dimethyl-2'-trimethylsilylspiro[10-sila-2-azaanthracene-9,1'-cyclopropane] (II). Diazocompound I (0.15 g, 0.6 mmol) and trimethylvinylsilane (1 cm^3) were heated for 1.5 h at 70-80°C with TLC monitoring. The excess trimethylvinylsilane was removed in vacuum and the residue was chromatographed on a 45 × 1.5 cm column with 1:3 ether–hexane to give a mixture of the isomers of compound II as a yellow oil (0.09 g, 46%), R_f 0.12 and 0.07 (Silufol, 1:3 ether–hexane). ^{1}H NMR Spectrum (*E*-isomer): 0.38 (9 H, s, $Si(CH_3)_3$), 0.48 (3 H, s, $Si-CH_3$) 0.58 (3 H, s, $Si-CH_3$), 1.80 (1 H, m, 3'-H, $^3J_{3'2'}$ = 5.2 and 8.3 Hz), 2.28 (1 H, m, 2-H), 7.12-7.52 (5 H, m, 4-, 5-, 6-, 7-, and 8-H), 8.36 (1 H, d, 3-H, $^3J_{3,4}$ = 4.9 Hz), 8.50 ppm (1 H, s, 1-H). (*Z*-isomer): 0.36 (9 H, s, $Si(CH_3)_3$), 0.50 (3 H, s, $SiCH_3$), 0.52 (3 H, s, $SiCH_3$), 1.62 (1 H, m, 3'-H, $^3J_{3'2'}$ = 5.2 and 8.5 Hz), 2.21 (1 H, m, 2'-H), 7.12-7.52 (5 H, m, 4-, 5-, 6-, 7-, 8-H), 8.36 (1 H, d, 3-H, $^3J_{3,4}$ = 4.9 Hz); 8.52 ppm (1 H, s, 1-H). Mass spectrum, *m/z* (I_{rel}, %): M^+ 323 (50), $[M-H]^+$ 322(52), $[M-CH_3]^+$ 308(7), $[M-Si(CH_3)_2]^+$ 265(3), $[M-Si(CH_3)_3]^+$ 250(8), $[M-C_2H_2Si(CH_3)_3]^+$ 224(60), $[Si(CH_3)_3)]^+$ 73(100). Found, %: C 67.1, H 7.5, N 4.0. Calc. for $C_{18}H_{25}NSi_2$, %: C 66.9, H 7.7, N 4.3.

9,10-Dihydro-10,10-dimethyl-2'-phenyl-3'formylspiro[10-sila-2-azaanthracene-9,1'-cyclopropane] (III, $C_{22}H_{21}NSi$). A mixture of the diaza compound I (0.63 g, 2.5 mmol) and cinnamaldehyde (1.2 g, 8.1 mmole) was heated for 4h at 130°C with TLC monitoring. The neutral reaction products were extracted with ether (2 × 20 cm^3). The water layer was basified to pH 9-10 with sodium carbonate solution, extracted with ether (3 × 25 cm^3), and the extract was dried with magnesium sulphate. The residue (0.59 g) after removal of ether was chromatographed on a 35 × 1.5 cm column with 5:1 petroleum ether–ethyl acetate as eluent. 9,10-Dihydro-10,10-dimethyl-10-sila-2-azaanthrone-9 (0.23 g, mp 148-150°C) eluted first. A mixed melting point with a known sample caused no depression. The Z-isomer of compound III (a yellow oil, 0.12 g, 13%) eluted next, R_f 0.18 (Silufol, ethyl acetate–heptane 1:3). IR spectrum: 1722 cm^{-1} (C=O). ^{1}H NMR spectrum: 0.53 (3 H, s, $SiCH_3$), 0.54 (3 H, s, $SiCH_3$), 2.90 (1 H, t, 2'-H, $^3J_{2',3'}$ = 7.5 Hz, $^3J_{2',CHO}$ = 6.4 Hz), 4.08 (1 H, d, 3'-H), 6.68 (1 H,

dd, 8-H, $^3J_{7,8}$ = 7.8, $^4J_{6,8}$ = 0.9 Hz), 6.95 (1 H, td, 6-H, $^3J_{5,6}$ = 7.4 Hz), 7.17 (1 H, td, 7-H, $^3J_{6,7}$ = 7.5 Hz), 7.27-7.40 (5 H, m, C_6H_5), 7.47 (1 H, d, 3-H, $^3J_{3,4}$ = 4.7 Hz), 7.53 (1 H, dd, 5-H, $^3J_{5,6}$ = 1.4 Hz), 8.52 (1 H, d, 4-H), 8.82 (1 H, d, CHO) 8.90 ppm (1 h, s, 1-H). Mass spectrum, *m/z* (I_{rel}, %): M^+ 355 (41), $[M-CH_3]^+$ 340(7), $[M-CO]^+$ 327(43), $[M-CHO]^+$ 326(100), $[M-C_6H_5\}^+$ 278(8), 224(81), 131(25), 103(66), 77(37). Found, %: C 74,5, H 5.8, N 3.8. Calc. for $C_{22}H_{21}NSi$, %: C 74.4, H 5.9, N 3.9.

The *E*-isomer of the spiro compound III eluted as a yellow oil (0.11 g, 12%) at the end of the chromatography, R_f 0.12 (Silufol, ethyl acetate–heptane 1:3). IR spectrum: 1720 cm^{-1} (C=O). ^1H NMR Spectrum: 0.53 (6 H, s, $Si(CH_3)_2$), 2.92 (1 H, t, 2'-H, $^3J_{2',3'}$ = 7.5, $^3J_{2',CHO}$ = 6.4 Hz), 4.10 (1 H, d, 3'-H), 7.10-7.40 (10 H, m, C_6H_5, 4-, 5-, 6-, 7-, and 8-H), 8.48 (1 H, d, 3-H, $^3J_{3,4}$ = 4.8 Hz), 8.32 (1 H, s 1-H), 8.85 ppm (1 H, d, CHO). Mass spectrum, *m/z* (I_{rel}, %): M^+ 355 (28), $[M-H]^+$ 354(18), $[M-CH_3]^+$ 340(7), $[M-CO]^+$ 327(42), $[M-CHO]^+$ 326(81), $[M-C_6H_5]^+$ 278(8), 224(100), 131(38), 103(55), 77(45). Found, %: C 74.0, H 6.1, N 3.7. Calc. for $C_{22}H_{21}NSi$, %: C 74.4, H 5.9, N 3.9.

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