SYNTHESIS OF 2-METHYL-9,9-DIPHENYL-9,10-DIHYDRO-9-SILA-3-AZAANTHRACENE

N. S. Prostakov, A. V. Varlamov,
and V. P. Zvolinskii

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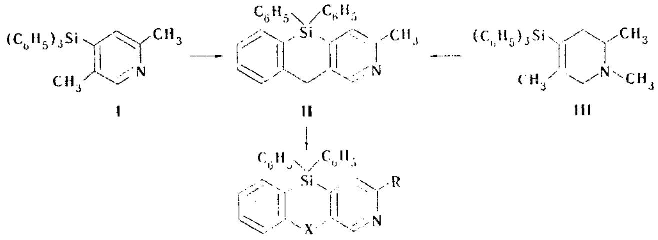
2-Methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthracene (II) has been obtained for the first time in 14% yield by dehydrocyclization of 2,5-dimethyl-4-triphenylsilylpyridine (I) [1] on a K-16 catalyst at 510-520°C. Under the same conditions, II is formed in 2% yield from 1,2,5-trimethyl-4-triphenylsilylpiperideine (III).

trans-Stilbazole IV was obtained by condensation of II with benzaldehyde, while ketone V was isolated from the oxidation of II.



IV $R = CH{=}CH{-}C_6H_5$, $X = CH_2$; V $R = CH_3$, $X = CO$

EXPERIMENTAL

2-Methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthracene (II). A solution of 4 g (10.9 mmole) of I in 30 ml of benzene was passed at a constant rate over K-16 catalyst (10 ml) at 510-520° in the course of 2 h in a flow system. A total of 200 ml of gas (758 mm, 23°; 93.5% H_2, 6.5% CH_4) was collected. The benzene was removed from the catalyzate by distillation, and the residue (2.46 g) was heated with 40 ml of hexane. The hexane solution yielded 1.26 g of bases, which were converted to the picrates. A total of 0.99 g of the picrate of II with mp 226-228° (from acetone–alcohol) was obtained. Found,%: N 9.4. $C_{25}H_{21}NSi \cdot C_6H_3N_3O_7$. Calculated,%: N 9.5. The free base was isolated from the picrate with a column filled with activity II aluminum oxide with elution with chloroform to give 0.56 g of II with mp 173.5-174.5° (from hexane). Found,%: C 82.2; H 6.2; N 3.7. $C_{25}H_{21}NSi$. Calculated,%: C 82.6; H 5.8; N 3.9. UV spectrum, λ_{max}, nm ($\log \varepsilon$): 263 (3.52), 268 (3.57), 274 (3.6), 280 (3.58). PMR spectrum: δ 2.78 (CH_3), 4.16 ppm (CH_2).

2-Styryl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthracene (IV). A mixture of 1.4 g (3.8 mmole) of II and 10 ml of benzaldehyde was refluxed for 16.5 h. The benzaldehyde was removed by distillation, and the residue was dissolved in ether and treated with 2.5 ml of a 4 M solution of hydrogen chloride in dioxane to give 0.75 g (29%) of the hydrochloride of IV as pale-yellow crystals with mp 287-291° (dec., from acetone–methanol). Found,%: Cl 6.8; N 2.8. $C_{32}H_{25}NSi \cdot HCl$. Calculated,%: Cl 7.3; N 2.9. A 0.52-g sample of the hydrochloride of IV was passed through a column filled with activity II aluminum oxide with elution by chloroform to give 0.44 g of IV with mp 199-201° (from heptane–benzene). Found,%: C 85.2; H 5.7; N 2.8.

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$C_{32}H_{25}NSi$. Calculated,%: C 85.1; H 5.5; N 3.1. UV spectrum, λ_{max}, nm (log ε): 282 (4.35), 333 (4.37). IR spectrum: 1638 ($\nu_{C=C}$), 978 cm^{-1} ($\delta_{out\text{-}of\text{-}plane}$ trans-CH). PMR spectrum: δ 4.16 (CH_2), 7.16 ppm (CH = CH, doublet with J = 16 Hz; the second doublet is overlapped with the signals of the aromatic protons).

2-Methyl-9,9-diphenyl-9,10-dihydro-9-sila-3-azaanthrone (V). A 0.37-g (1 mmole) sample of II was oxidized with 0.22 g (1.4 mmole) of potassium permanganate at 20° in acetone. The manganese dioxide was removed by filtration, and the filtrate was worked up to give 0.15 g (39%) of V with mp 218-219.5° (from ligroin–alcohol). Found,%: C 79.5; H 5.2; N 3.9. $C_{15}H_{19}NOSi$. Calculated,%: C 79.8; H 5.9; N 3.7. UV spectrum, λ_{max}, nm (log ε): 273 (4.16), 362 (2.38). IR spectrum: 1665 cm^{-1} ($\nu_{C=O}$). PMR spectrum: δ 3.0 ppm (CH_3).

The UV spectra of alcohol solutions were obtained with an SF-4a spectrophotometer. The IR spectra of KBr pellets were recorded with a UR-20 spectrometer. The PMR spectra of CF_3COOH solutions were obtained with an HA-100D spectrometer with tetramethylsilane as the standard.

LITERATURE CITED

1. N. S. Prostakov and A. V. Varlamov, Khim. Geterotsikl. Soedin., 1637 (1970).