

2,4,6-Trimethyl-1-cyclohexylindole (III), mp. 53-55°C. PMR spectrum (acetone-D₆): 1.55 (m, 10H, CH₂), 2.31 (s, 9H, 2-, 4- and 6-CH₃), 4.18 (m, 1H, NCH), 6.05 (s, 1H, 3-H), 6.40 (s, 1H, 5-H), 7.17 ppm (s, 1H, 7-H). The data of the elemental analysis of indole III for C and H correspond to the calculated ones.

1,2,4,6-Tetramethylindole (IV) was identical to the compound obtained from salt II and imine V.

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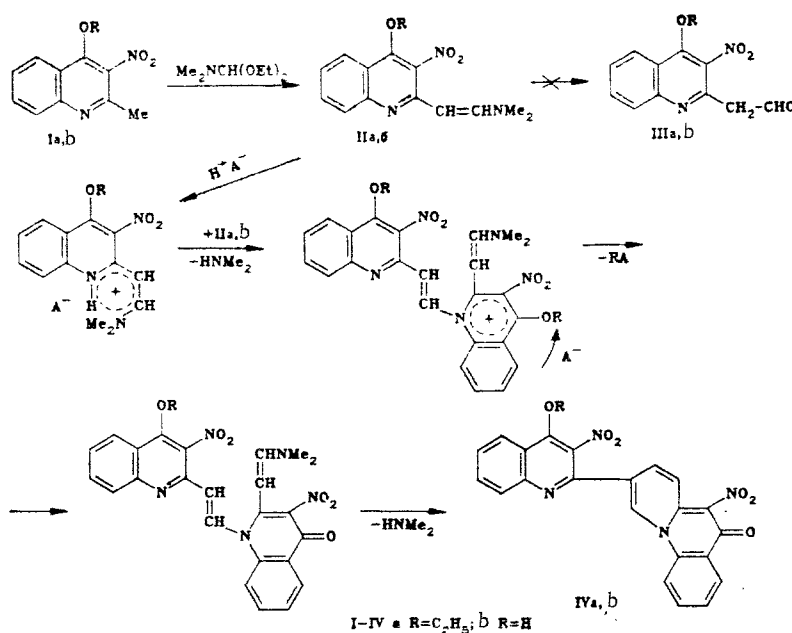
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HYDROLYTIC DIMERIZATION OF SUBSTITUTED 2-(2-DIMETHYLAMINOVINYL)QUINOLINES

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UDC 547.831.6'832.1.07

In the course of studies of the quinoline series and their condensed derivatives, 4-substituted 3-nitro-2-methylquinolines (Ia, b) were synthesized, from which by reaction with DMFA diethyl acetal, enamines (IIa, b) were obtained. In the investigation of the hydrolysis of the latter by aqueous solutions of formic and acetic acids, instead of the expected carbonyl compounds IIIa, b [1, 2], compounds were isolated which, according to elemental analysis data and spectral characteristics, are dimerization products of the starting enamines IIa, b (IVa, b). According to ¹H and ¹³C NMR spectra, a structure of pyridine[1,2-a]quinoline derivatives was proposed for compounds IVa, b. Compound IV exists in the crystalline state in the oxo form (ν_{NH} 3260 cm⁻¹).



In the ¹H NMR spectra of compounds IVa, b, signals of only 11 aromatic protons are observed. For compound IVa there are also signals of the ethyl group. The position of the

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singlets at 9.62 (IVa) and 9.85 ppm (IVb) in the spectra is not dependent on the temperature of exposure of the samples. These signals do not belong to the aldehyde group protons since, in the ^{13}C spectrum NMR spectrum, the signal of the formyl group carbon atom is absent. The weak-field singlet observed in the ^1H NMR spectra can be ascribed to the 1-H proton (the signal is broadened due to long range spin-spin coupling with the 3-H proton, $^4J = 1.4$ Hz).

Compound IVa, yield 30%, mp $>300^\circ\text{C}$. IR spectrum (mineral oil), ν : 3110 (C-H), 1620, 1605, 1585, 1520 (C=N, C=O, CH=CH, NO_2), 1305 cm^{-1} (NO_2). UV spectrum (CHCl_3), λ_{max} ($\log \epsilon$): 250 (4.27), 340 nm (3.85). Mass spectrum, m/z: 456 (M^+), 426 [$\text{M} - \text{NO}$] $^+$, 398 [$\text{M} - \text{CO}$] $^+$. ^1H NMR spectrum, (DMSO- D_6): 1.48 (t, 3H, CH_3), 4.51 (quart., 2H, CH_2), 7.72-8.14 (m, 6H), 8.26 (d, 1H), 8.37 (d, 1H), 8.49 (d, 1H), 8.63 (d, 1H), 9.62 ppm (s, 1H).

Compound IVb, yield 40%, mp $>350^\circ\text{C}$ (from DMFA). IR spectrum (mineral oil), ν : 3260 (N-H), 3090 (C-H), 1640, 1595, 1510 (C=N, C=O, CH=CH, NO_2), 1335 cm^{-1} (NO_2). ^1H NMR spectrum (DMSO- D_6): 7.58 (t, 1H), 7.73-7.91 (m, 5H), 7.95 (t, 1H), 8.29 (d, 1H), 8.50 (d, 1H), 8.75 (d, 1H), 9.85 ppm (s, 1H). ^{13}C NMR spectrum (DMSO- D_6), δ : 167.4, 163.8, 142.5, 139.9, 138.8, 136.1, 134.7, 133.0, 131.5, 129.9, 128.4, 127.8, 126.4, 126.1, 125.2, 125.1, 119.4, 117.7, 117.6 ppm.

These data of the elemental analysis of compounds IVa, b correspond to the calculated ones.

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REARRANGEMENT OF 2-DIMETHYLSILYLTETRAHYDROPYRAN INTO 2,2-DIMETHYL-1-OXA-2-SILACYCLOHEPTANE

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UDC 547.245'517.07

It has previously been shown [1] that under the conditions of liquid-phase catalytic hydrogenation (1 atm H_2 , 25°C , 0.1 mole/liter solution in hexane, 5% Pd/ Al_2O_3 or Pd/C, $[\text{I}]:[\text{Pd}] = 100:1$), 2-dimethylsilyl-4,5-dihydrofuran (I) undergoes several successive transformations: It is hydrogenated into 2-dimethylsilyltetrahydrofuran (II), and after the complete conversion of the initial dihydrofuran I, the tetrahydro-derivative II readily and quantitatively (15 min) rearranges into the six-membered 2,2-dimethyl-1-oxa-2-silacyclohexane (III) with the silicon atom entering the ring. The II \rightarrow III transformation also proceeds in the absence of hydrogen, when silane II is contacted with a supported palladium catalyst [1].

To clarify the influence of the ring size on the possible occurrence of such a rearrangement, we studied the catalytic transformations of 2-dimethylsilyl-5,6-dihydro-4H-pyran (IV), obtained by treating 2-lithium-5,6-dihydro-4H-pyran with dimethylchlorosilane at -50°C in a 1:1 tetrahydrofuran-hexane solvent mixture.

Under conditions similar to those for compound I, silane IV readily (60 min, yield 95%, according to GLC) hydrogenates into 2-dimethylsilyltetrahydropyran (V), which then rearranges into a seven membered 2,2-dimethyl-1-oxa-2-silylcycloheptane (VI):

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Translated from Khimiya Geterotsiklicheskikh Soedinienii, No. 1, pp. 136-137, January, 1987.
Original article submitted July 9, 1986.