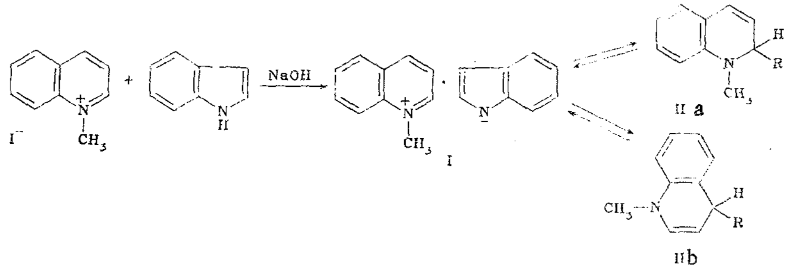
IONIC STRUCTURE OF 1-METHYL-2-(3-INDOLYL)-1,2-DIHYDROQUINOLINE

T. N. Nezdiiminoga, T. S. Chmilenko,
and A. K. Sheinkman

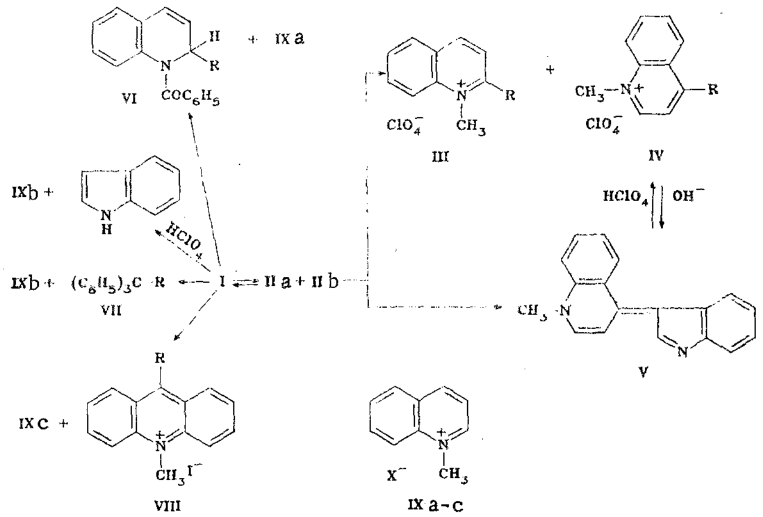
UDC 547.751'831.1:543.422.4

2-(3-Indolyl)quinolinium methiodide is formed in the case of prolonged refluxing of quinolinium methiodide with indole in methanol in the presence of sodium methoxide [1]; an intermediate product of nucleophilic addition of indole to the N-alkylquinolinium cation could not be isolated. We have obtained this compound in the crystalline state (mp 140-142°C) and identified it as ion pair I:



Here and subsequently, R = 3-indolyl

The IR spectrum of I (KBr pellet) does not contain a band of indole νNH stretching vibrations. Compound I also exists in the form of an ion pair in polar solvents, and its IR spectrum in solution is similar to the spectrum of a crystalline sample. The UV spectrum contains characteristics bands of an N-methylquinolinium cation (312 and 233 nm). These bands vanish in the UV spectra of solutions in nonpolar solvents (toluene, heptane, and ether), but an indole νNH band appears in the IR spectrum at 3400-3450 cm^{-1}; this constitutes evidence for an equilibrium between adduct I and covalent forms IIa, b. The existence of the I $\rightleftarrows$ II equilibrium in solutions was confirmed by several reactions. Thus we obtained N-methylquinolinium salts with the corresponding anions and indole or substituted indoles by the action of mineral acids, triphenylmethyl perchlorate, N-methylacridinium perchlorate, N-benzoylquinolinium salts, and other reagents. Isomers IIa, b react with 1-oxo-2,2,6,6-tetramethylpiperidinium perchlorate to give (3-indolyl)quinolinium salts III and IV, and p-nitrosodimethylaniline converts adduct I to anhydro base V, from which salt IV is formed by the action of $HClO_4$:



IXa X=Cl; b X=ClO₄; c X=I

Dnepropetrovsk Construction-Engineering Institute, Dnepropetrovsk 320631. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 418-419, March, 1984. Original article submitted June 9, 1983.

0009-3122/84/2003-0341$08.50

Compound I has satisfactory analytical characteristics. The structures of III-VIII obtained from adduct I were proved by comparison with genuine samples.

The instance of the extreme facile heterolysis of the C—C bond in 1-methyl-2-(3-indolyl)-1,2-dihydroquinoline evidently also explains the previously observed participation of N-acyl derivatives of 2-substituted 1,2-dihydroheteroaromatic compounds as donors of nucleophilic particles in nucleophilic alkylation [2] and transhetarylation [3] reactions.

LITERATURE CITED

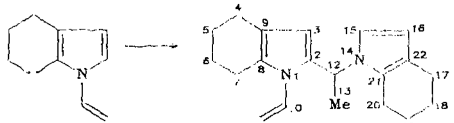
1. H. Dobeneck and W. Goltzsche, Chem. Ber., 95, 1484 (1962).
2. A. K. Sheinkman, Z. M. Skorobogatova, T. S. Chmilenko, and T. M. Baranova, Dokl. Akad. Nauk SSSR, 267, 405 (1982).
3. A. K. Sheinkman and A. K. Tokarev, Zh. Org. Khim., 7, 855 (1971).

DIMERIZATION OF 1-VINYL-4,5,6,7-TETRAHYDROINDOLE UNDER THE INFLUENCE OF THE $NaOH—CHCl_3—C_6H_5CH_2N^+(C_2H_5)_3Cl^-$ SYSTEM

M. G. Voronkov, V. G. Kozyrev, M. V. Sigalov,
B. A. Trofimov, and A. I. Mikhaleva

UDC 547.754.758.1.07

Instead of the expected dichlorocarbenylation product [1], dimer II, which was previously obtained from indole I only under electrophilic conditions [2], is formed by treatment of 1-vinyl-4,5,6,7-tetrahydroindole (I) with the $NaOH—CHCl_3$—triethylbenzylammonium chloride (TEBA) system.



I II

Dimer II is not formed when $CHCl_3$ or TEBA is excluded from the indicated system.

Thus 8 ml of $CHCl_3$ dissolved in 10 ml of CH_2Cl_2 was added with vigorous stirring at 10°C in the course of 30 min to a mixture of 7.35 g of I, 0.23 g of TEBA, 10 ml of CH_2Cl_2, and 20 ml of 50% aqueous NaOH solution, after which the mixture was stirred at 10°C for 2 h and worked up in the usual way to give 2.57 g (35%) of 1-vinyl-2-[1-(1,4,5,6,7-tetrahydroindolyl)ethyl]-4,5,6,7-tetrahydroindole (II) with mp 114°C (from hexane). The results of elementary analysis were in agreement with the formula. Mass spectrum (m/z): 294 (M^+) and 174 (splitting out of a 4,5,6,7-tetrahydroindolyl radical). ^{13}C NMR spectrum (in $CDCl_3$, with an FX-90Q spectrometer): 130.72 [$C_{(2)}$], 130.13 [$C_{(10)}$], 128.72 [$C_{(21)}$], 126.33 [$C_{(8)}$], 117.88 [$C_{(9)}$], 117.45 [$C_{(22)}$], 116.31 [$C_{(15)}$], 107.97 [$C_{(16)}$], 106.24 [$C_{(3)}$], 105.75 [$C_{(11)}$], 47.40 [$C_{(12)}$], 21.67 [$C_{(13)}$], and 22.11-23.90 ppm [$C_{(4-7,17-20)}$]. The PMR and IR spectra were identical to the spectra previously described for II [2].

LITERATURE CITED

1. M. Makosha, Usp. Khim., 46, 2174 (1977).
2. B. A. Trofimov, A. I. Mikhaleva, L. V. Morozova, A. N. Vasil'ev, and M. V. Sigalov, Khim. Geterotsikl. Soedin., No. 2, 269 (1983).

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, p. 420, March, 1984. Original article submitted July 19, 1983.

0009-3122/84/2003- 0342$08.50