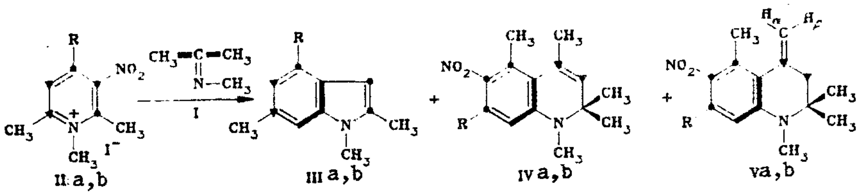
# FORMATION OF 6-NITRODIHYDRO- AND 6-NITROTETRAHYDROQUINOLINES. ANOTHER REACTION OF 3-NITROPYRIDINIUM SALTS WITH N-METHYLACETONIMINE

M. A. Yurovskaya, A. Z. Afanas'ev,
V. A. Chertkov, and Yu. G. Bundel'

UDC 547.753:831.6'822.7

The main route of reaction of alkyl-3-nitropyridinium salts with N-methylacetonimine (I) is to give the indoles [1]. Examining the reaction of 4-alkyl-2,6-dimethyl-3-nitropyridinium iodides (IIa, b) with (I) in DMF [2], we observed that in addition to the indoles (IIIa, b) dihydroquinolines (IVa, b) and tetrahydroquinolines (Va, b) were formed (according to the $^{13}C$ NMR spectra).



II–V a R=$CH_3$; b R=$CH_2C(CH_3)_3$

The principal difference between this reaction and those previously reported [1, 2] is the participation of two ketonic fragments in the construction of the quinoline skeleton, with rupture of the $C_{(4)}-C_{(5)}$ bond in the starting salt. This reaction imposes specific structural requirements on both starting materials. For example, the formation of quinolines such as (IV) and (V) occurs only in the absence of an alkyl substituent in the 5-position in the salt, and only with acetonimine. The presence of a 4-alkyl substituent is essential, this apparently influencing the ease of rupture of the $C_{(4)}-C_{(5)}$ bond.

Chromatographic separation of the products of the reactions of salts (IIa, b) with the imine (I) gave the following quinolines (compound, yield (%), mp, °C (from hexane), and $R_f$ (benzene–hexane, 1:3)): (IVa), 4, 110-111, 0.18; (Va), 2, 165-167, 0.22; (IVb), 18, 94-96, 0.29; (Vb), 6, 99-100, 0.37. The $^{13}C$ NMR spectra ($CDCl_3$) of the dihydroquinolines (IVa, b) showed signals for the 4-$CH_3$ groups (2.11 and 2.12 ppm, d, J = 1.46 and 1.15 Hz, respectively) and the 3-H vinyl protons (5.46 and 5.53 ppm, q), and in the spectra of the 4-methylenetetrahydroquinolines (Va, b), signals for the 4-methylene protons (5.13, $J_{gem}$ = 1.3 Hz and 5.23 for (Va); 5.15, $J_{gem}$ = 1.6 Hz and 5.24 ppm for (Vb)). The allyl coupling constant $J_{\alpha 3}$ = 0.9 Hz was seen only in the case of (Vb). The signals for the protons of the ring $CH_2$ groups in (Va, b) are seen at 2.32 and 2.34 ppm (d, J = 0.9 Hz) respectively. The signals for the remaining protons are located in good agreement with the proposed structures. The elemental analyses are in accordance with the calculated values.

The overall yield of quinolines (IVb) and (Vb) was 24%, whereas for (IVa) and (Va) it was 6% (the yields of indoles (IIIa) and (IIIb) being nearly the same, namely 62 and 64%, respectively). This decrease in the overall yield is probably due to side reactions involving condensation of the γ-$CH_3$ group of the starting salt (IIa) (see, for example [2]).

## LITERATURE CITED

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M. V. Lomonosov State University, Moscow 119899. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, p. 854, June, 1988. Original article submitted October 19, 1987.

0009-3127/88/2406-0704$12.50