LETTERS TO THE EDITOR

SYNTHESIS OF INDOLES FROM PYRIDINIUM SALTS.

3.* ORIGIN OF NITROGEN IN THE INDOLE MOLECULE IN SYNTHESIS FROM 3-NITROPYRIDINIUM SALT

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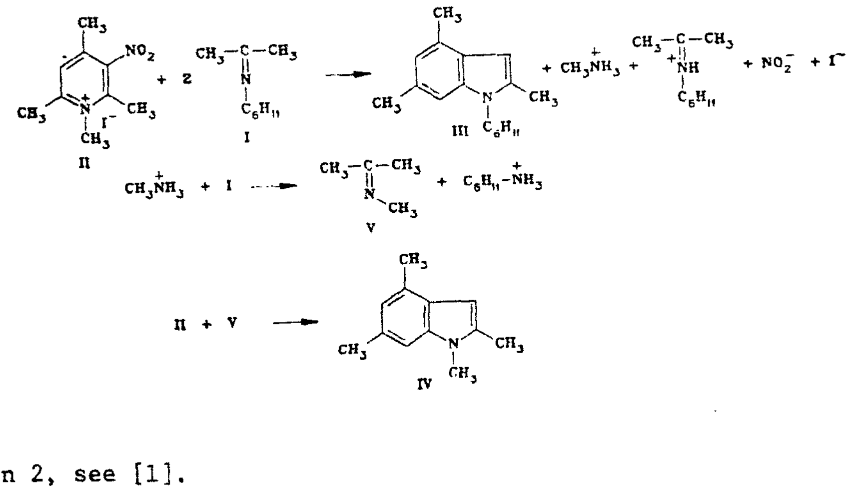
It has previously been shown [2] in the synthesis of alkylindoles from 3-nitropyridinium salts that when ketones and primary aliphatic amines with a radical different from the N-substituent of the pyridinium salt are used, the process proceeds with the formation of a mixture of indoles having both N-alkyl substituents. It was assumed that this course of the process is due to a complete or partial transamination at the open intermediate stage.

However, another explanation for this phenomenon is also possible. Since reaction of an amine and ketone leads to a ketimine, it can be assumed that this imine is the source of the nitrogen in the indole molecule formed, while the N-substituent of the pyridinium salt is eliminated in the form of the corresponding amine.

To verify this supposition, we used N-cyclohexylacetone-imine (I) in reaction with 1,2,4,6-tetramethyl-3-nitropyridinium iodide (II) in DMSO as solvent. This imine was selected because of the substantial difference in the R_f values of the corresponding N-cyclohexyl- (III) and N-methylindole (IV), which facilitates the control of the course of the reaction and separation of the mixture. Thus, in the reaction of 5 mmoles of salt II with 2.5 mmoles of imine I in 10 ml of DMSO at 25°C, first (TLC) only indole III is formed, and only after its accumulation, the indole IV begins to form. After 10 min, the yield of the mixture of indoles is 25% with a ratio III:IV = 13.5; after 20 min, 29% and III:IV = 8.7; and after 24 h, the yield reaches 52%, and the ratio is 4.2. The decrease in the III:IV ratio with time is possibly explained by the fact that imine I first forms the corresponding indole III with the elimination of the methylimine salt which, in turn, is capable [3] of transaminating the unreacted imine I to form N-methylacetone-imine V. The latter, similarly to imine I, reacts with salt II to form indole IV.

To confirm the possibility of transamination, a mixture of equimolar amounts of imine I and methylamine hydrochloride in DMSO was allowed to stand for 20 min, and then salt II was added at the same ratio of components as before. In contrast to the previous result, the main reaction product was indole IV (20 min after the addition of salt II, the yield of the mixture of indoles was 50% and the ratio III:IV = 0.11).



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*For Communication 2, see [1].

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2,4,6-Trimethyl-1-cyclohexylindole (III), mp 53-55°C. PMR spectrum (acetone-D_6): 1.55 (m, 10H, CH_2), 2.31 (s, 9H, 2-, 4- and 6-CH_2), 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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HYDROLYTIC DIMERIZATION OF SUBSTITUTED 2-(2-DIMETHYLAMINOVINYL)QUINOLINES

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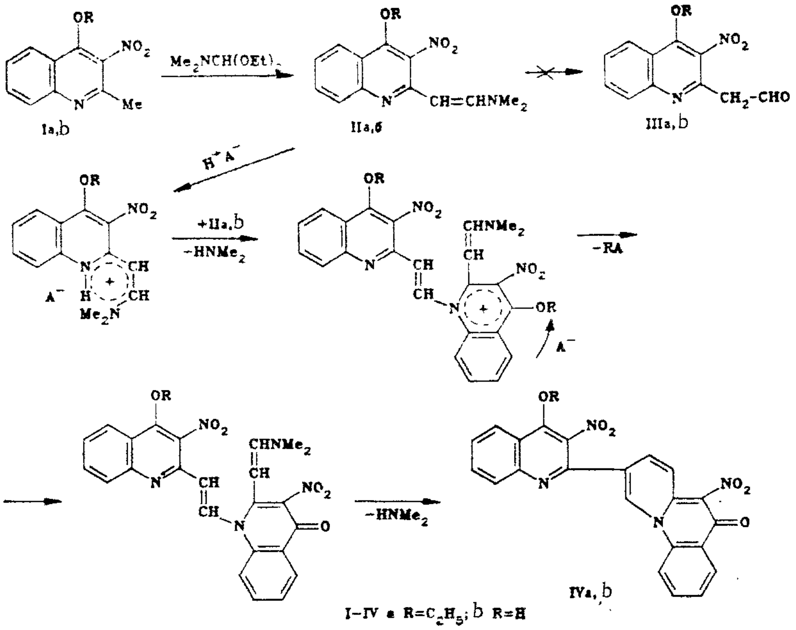
In the course of studies of the quinoline series and their condensed derivatives, 4-substituted 3-nitro-2-methylquinolines (Ia, b) were synthesized, from which by reaction with DMFA diethyl acetal, enamines (IIa, b) were obtained. In the investigation of the hydrolysis of the latter by aqueous solutions 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 ^{13}C 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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