LITERATURE CITED

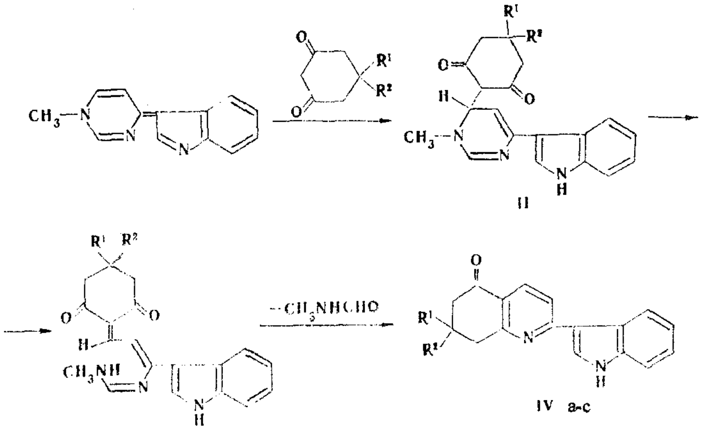
1. E. P. Fokin and V. Ya. Denisov, USSR Inventor's Certificate No. 480702; Ref. Zh. Khim., 14N210 (1977).
2. R. Elderfield, in: Heterocyclic Compounds, Vol. 6, Wiley.
3. A. C. Hazy and J. V. Karabinos, J. Org. Chem., 33, 2557 (1968).
4. Polaroid Corp., US Patent No. 3131061; Ref. Zh. Khim., 16N393 (1965).
5. Polaroid Corp., US Patent No. 3135606; Ref. Zh. Khim., 7N635 (1967).
6. Polaroid Corp., US Patent No. 3288778; Ref. Zh. Khim., 17N396 (1975).
7. J. D. Wool and A. F. Peters, J. Chem. Soc., No. 10, 3373 (1962).
8. E. P. Fokin and I. V. Fomicheva, Zh. Org. Khim., 6, 1282 (1970).

NEW SYNTHESIS OF 5,6,7,8-TETRAHYDROQUINOLINES WITH THE PARTICIPATION OF THE 4-(3-INDOLYL)PYRIMIDINE ANHYDRO BASE

T. V. Stupnikova, T. V. Nuzhnaya,
and A. N. Vdovichenko

UDC 547.759.2'831.3.8'855.7

Whereas 1,2,3,4-tetrahydroquinolines are extremely accessible and are obtained in one step by the reduction of quinoline and its derivatives, the corresponding 5,6,7,8-tetrahydroquinolines are much less well known, and their synthesis is fraught with a number of difficulties [1]. We have found a new method for the synthesis of such structures in the recyclization of the 4-(3-indolyl)pyrimidine anhydro base (I) under the influence of 1,3-cyclohexanedione and its analogs in dry acetonitrile.



IV a $R^1=R^2=CH_3$; b $R^1=H$, $R^2=2$-furyl c $R^1=R^2=H$

Inasmuch as they have an extremely acidic methylene proton, 1,3-cyclohexanediones attack the electron-deficient $C_{(6)}$ atom of the pyrimidine ring to give adduct II, which then undergoes ring opening to give intermediate III. Open form III undergoes recyclization with the participation of the electron-surplus nitrogen atom of the starting substance and the carbonyl group of the reagent to give 5,6,7,8-tetrahydroquinoline derivatives IVa-c in 10-14% yields. Compound IVa had mp 195-196°C (from methanol). PMR spectrum: 0.86 (s, 6H, CH_3), 2.4 (s, 2H, 8-H), 2.94 (s, 2H, 6-H), 7.84 (d, 1H, 3-H), 8.39 (d, 1H, J_{34} = 9.0 Hz, 4-H), 7.99 (d, 1H, $J_{1'2'}$ = 3.0 Hz, 2'-H), and 6.86-7.66 ppm (m, 4'-, 5'-, 6'-, and 7'-H).

Donetsk State University, Donetsk 340055. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 555-556, April, 1983. Original article submitted June 29, 1982.

0009-3122/83/1904-0459$07.50

Compound IVb had mp 194-195°C (from butanol). PMR spectrum: 7.89 (d, 1H, 3-H), 8.14 (d, J_{34} = 8 Hz, 4-H), 8.34 (s, 1H, 2'-H), 7.44 (m, 4'-, 5'-, 6'-, and 7'-H), and 6.26 ppm (m, furyl ring protons). Compound IVc had mp 218-219°C (from methanol). PMR spectrum: 8.17 (d, 1H, 3-H), 8.80 (d, 1H, J_{34} = 9 Hz, 4-H), 3.70 (t, 2H, J_{67} = 5 Hz, 6-H), 2.9 (t, 2H, J_{78} = 5 Hz, 8-H), 2.4 (m, 2H, 7-H), 8.37 (d, 1H, $J_{1'2'}$ = 4 Hz, 2'-H), and 7.17-8.03 ppm (m, 4'-, 5'-, 6'-, and 7'-H). The results of elementary analysis were in agreement with the calculated values.

LITERATURE CITED

1. R. Elderfield (editor), Heterocyclic Compounds, Vol. 4, Wiley.

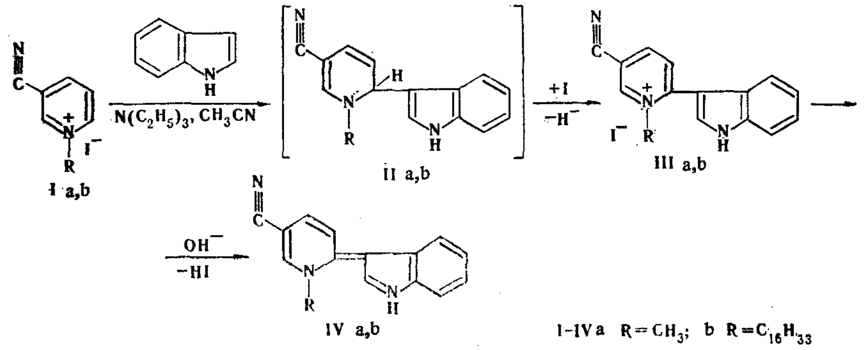
NEW SYNTHESIS OF PYRIDYLINDOLES

T. V. Stupnikova and V. V. Petrenko

UDC 547.821.3'828'759:543.422

Despite the large number of studies devoted to the synthesis of pyridylindoles, which display diverse physiological activity, these bisheterocycles with all possible modes of fusion of the pyridine and indole rings remain difficult to obtain. All of the methods for their synthesis reduce, as a rule, to Fischer cyclization of the arylhydrazones of a number of ketones of the pyridine series [1, 2], which are also difficult to obtain. However, cases involving the production of pyridylindoles by the direct reaction of pyridine and indole derivatives are extremely rare and are limited to only a few examples [3-5].

In a study of the reactions of quaternary 3-cyanopyridinium salts with nucleophiles we found a fundamentally new direct method for the synthesis of 3-(2-pyridyl)indole derivatives. We found that 1-alkyl-3-cyanopyridinium iodides I in acetonitrile in the presence of triethylamine readily react with indole to give 1-alkyl-3-cyano-6-(3-indolyl)pyridinium iodides (IIIa,b):



The reaction evidently proceeds through a step involving the intermediate formation of dihydro structure II, which then under the influence of excess salt I splits out a hydride ion to give final substance III. Salts III are readily deprotonated under the influence of alcoholic KOH solution to give stable anhydro bases IV. Intense absorption bands at 1650-1670 and 2190-2200 cm^{-1}, which correspond to the stretching vibrations of the $C{=}N$ and $C{\equiv}N$ bonds in the molecules, are observed in the IR spectra of III and IV. An intense maximum at 3485-3490 cm^{-1}, which is related to the absorption of the NH group of the indole fragment, is also present in the spectra of salts III. The following signals are observed in the PMR spectrum of one of the compounds (IVa): 3.70 (s, 3H, $N{-}CH_3$), 7.73 (s, 2H, pyridine 4-H and 5-H), 7.90 (d, 1H, indole 2-H, J_{12} = 3.0 Hz), and 6.5-7.4 ppm (indole aromatic protons).

Donetsk State University, Donetsk 340055. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 556-557, April, 1983. Original article submitted July 2, 1982; revision submitted October 10, 1982.

0009-3122/83/1904-0460$07.50