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CONCERNING THE RECYCLIZATION OF PYRROLO[2,1-a]ISOQUINOLINES TO BENZ[g]INDOLES

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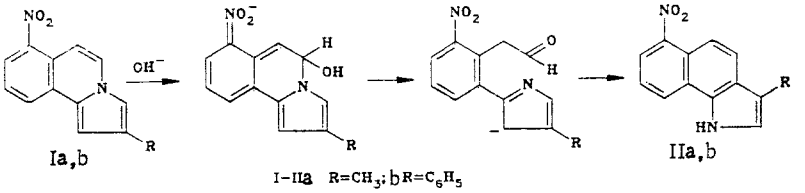
UDC 547.759.3'833.04

Indolizines containing a nitro group in the pyridine ring are capable of isomerizing upon treatment with base under mild conditions to give the corresponding nitroindoles [1]. An analogous rearrangement, although requiring harsher conditions, has also been demonstrated to occur for quaternary isoquinolinium salts containing a methyl or methylene group in the α-position relative to the heteroatom in the ring [2].

Based on these reactions, one would assume that a pyrrolo[2,1-a]isoquinoline molecule, which contains both an indolizine as well as an isoquinoline fragment, should also be capable of recyclization upon treatment with base. In order to answer this question, we have synthesized a series of pyrrolo[2,1-a]isoquinolines, among them some with a nitro group in the benzene portion of the molecule.

Our experiments have revealed that both the unsubstituted pyrroloisoquinoline, as well as pyrroloisoquinolines with methyl and phenyl substituents in the 2-position, exhibit high stability with respect to reactions with nucleophilic reagents.

Introduction of a nitro group to the benzene portion of the pyrroloisoquinoline would be expected to increase the sensitivity of the system to reactions with nucleophiles and thus confer more favorable conditions for recyclization. In fact, upon heating in aqueous ethanolic base solution, both 2-methyl-7-nitro- and 2-phenyl-7-nitropyrrolo[2,1-a]isoquinoline (Ia, b) isomerized in the absence of oxygen to give the corresponding benz[g]indoles (IIa, b) in high yields:



I-IIa R=CH3; b R=C6H5

3-Methyl-6-nitrobenz[g]indole (IIa). This was prepared by refluxing a mixture of 50 mg of compound Ia, 4 g KOH, 2 ml water, and 18 ml ethanol for 3 h in a inert gas stream. The resulting crystals of IIa were separated and washed with water. Yield 88%, mp 240-242°C (dec., from toluene). PMR spectrum ($CDCl_3$): 3.3 (s, 3H, CH_3), 4.7 (s, 1H, NH), 8.8-9.6 ppm (m, 6H, aromatic protons). IR spectrum: 3075-3150 (NH), 1360 ($\nu_{NO_2}^{S}$), 1515 cm^{-1} (ν_{NO}^{as}).

6-Nitro-3-phenylbenz[g]indole (IIb). This was prepared under analogous conditions by refluxing for 10 h. Yield 84%, mp 265-266°C (dec., from toluene). PMR spectrum ($CDCl_3$): 4.4 (s, 1H, NH), 8.9-9.8 ppm (m, 11H, aromatic protons). IR spectrum: 3080-3400 (NH), 1360 ($\nu_{NO_2}^{S}$), 1520 ($\nu_{NO_2}^{as}$), 3000-3100 cm^{-1} (C–H).

Elemental analyses of compounds IIa, b were consistent with calculated values.

Omsk State University, Omsk. M. V. Lomonosov Moscow State University, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 421-422, March, 1987. Original article submitted August 6, 1986.

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SYNTHESIS OF 1-(4-ALKANOYLPHENYL)-2-PYRAZOLINES BASED ON DITHIOLIUM SALTS

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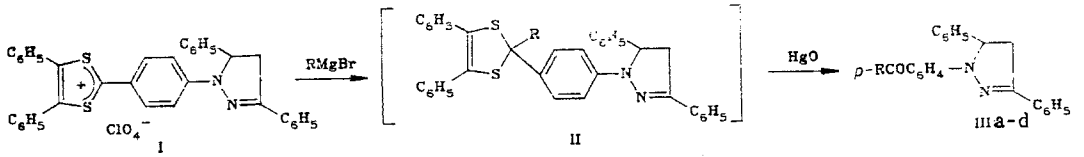
UDC 547.738'778.07

Dithiolium salts of 2-pyrazoline derivatives (I), which have been reported previously by us [1], may be regarded as convenient precursors for the preparation of 1-(4-alkanoylphenyl)-3,5-diphenyl-2-pyrazolines (IIIb-d), based on the known conversion reaction of 1,3-dithiols to ketones [2]. We have found that reaction of compound I with Grignard reagents, followed by hydrolysis of the intermediate dithiols II according to [2], leads to the formation of 1-(4-alkanoylphenyl)-2-pyrazolines, and have demonstrated that the pyrazoline ring is not disturbed under these conditions. Although the yields obtained are not very high (35-40%), the method described here is quite general in character and allows one to vary the nature of the substituent R significantly. The direction of the reaction was verified by an independent synthesis of pyrazolines IIIa and IIIb, based on the formylation and acetylation of 1,3,5-triphenyl-2-pyrazoline [3, 4]. As a result of side reactions, the aldehyde IIIa, which was separated chromatographically, was also formed in all cases in addition to ketones IIIb-d.



III a R=H, b R=CH_3, c R=C_4H_9, d R=$C_{10}H_{21}$

A suspension of 0.8 g (1.2 mmole) of salt I in 50 ml absolute ether was treated with 2 mmole of freshly prepared Grignard reagent and stirred at 30-35°C until the violet deposit of salt I had completely disappeared and a stable yellow color was observed. After workup of the reaction mixture with saturated NH_4Cl solution, the ether layer was washed with water and dried over $CaCl_2$, and the solvent was evaporated. The residue was hydrolyzed by dissolving in 3-5 ml tetrahydrofuran and adding it in one portion to a suspension of 0.9 g (4.2 mmole) of HgO in 2 ml of 35% HBF_4 in 10 ml tetrahydrofuran. After completion of the reaction (which was monitored by TLC with chloroform eluent for complete disappearance of compound II), the suspension was extracted with benzene, dried, and the solvent was evaporated. The residue was subjected to chromatography on a SiO_2 column (chloroform eluent) and crystallized from heptane.

Compound IIIa, mp 118-120°C (according to [3], mp 122-123°C), R_f 0.28, yield 60%; IIIb, mp 150-152°C (according to [4], mp 152°C, R_f 0.38, yield 40%; IIIc, mp 137-139°C, R_f 0.41, yield 50%; IIId, mp 108-109°C, R_f 0.42, yield 35%. Compounds IIIb-d exhibit identical electronic absorption spectra in toluene [λ_{max} 375 nm (ε $3\cdot10^4$)] and ethanol [λ_{max} ($\varepsilon\cdot10^{-3}$):

A. M. Gor'kii Khar'kov State University, Khar'kov. Khar'kov Scientific-Research Institute for Endocrinology and Hormone Chemistry, Khar'kov. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 3, pp. 422-423, March, 1987. Original article submitted June 18, 1986.

 0009-3122/87/2303-0358$12.50