DIPYRAZOLO[4",3":5,6][4',3'-*e*]PYRIDO[3,2-*c*]PYRIDAZINE - A NEW HETEROAROMATIC TETRACYCLIC SYSTEM

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ABSTRACT: An intramolecular diazo-coupling reaction of an aminopyrazolylpyrazolo[3,4-*b*]pyridine was employed to give the title ring system.
(keywords: Pyrazolo[3,4-*b*]pyridines; Diazo-coupling; Friedlander reaction).

INTRODUCTION

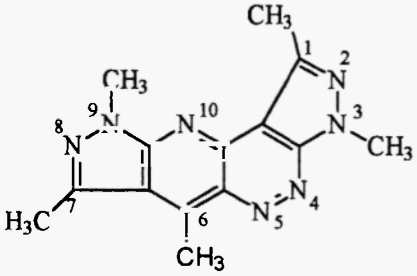
Synthesis and study of the pyrazolo[3,4-*b*]pyridines have been of interest for their potencial biological and pharmacological activities properties[1-7] . Antiviral activity[8] has also been investigated for several compounds of this system.

During our investigation on the chemistry of pyrazolo[3,4-*b*]pyridine ring systems, we were able to prepared their derivatives which enabled us to build-up some new tri and tetracyclic heteroaromatic system based on pyrazolo[3,4-*b*]pyridine[9,10].

RESULTS AND DISCUSSION

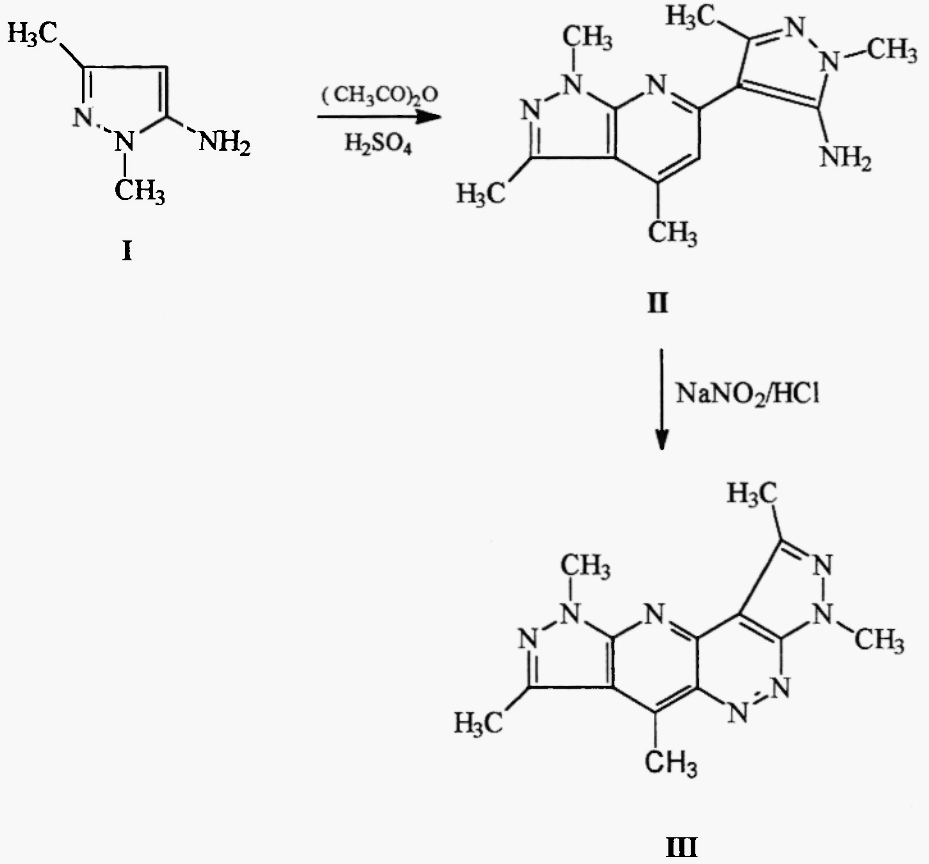
During our synthetic programme of pyrazolo[3,4-*b*]pyridines employing diverse reaction pathways[1,7,8,9,10], we had isolated 1,3,4-trimethyl-6-(5'-amino-1',3'-dimethylpyrazol-4'-yl)pyrazolo[3,4-*b*]pyridine (II) from an attemped acylation of 5-amino-1,3-dimethylpyrazole with acetic anhydrid[11]. The intermediate I has potential for preparation of diverse derivatives through manipulation of the amino group.

We would now like is reported the synthesis of a new tetracyclic system which was obtained from a diazotation of (I). The product it was isolated a yellow precipitate characterized as a derivative of the title ring system a 1,3,6,7,9-pentamethyldipyrazolo[4",3":5,6][4',3'-*e*]pyrido[3,4-*c*]pyridazine (III) (scheme 1).



III

Scheme: 1



EXPERIMENTAL.

The ^{1}H nuclear magnetic resonance spectra were obtained on a Varian model Unity Plus spectrometer operating at 300 MHz and Brucker AM-500 spectrometer (TMS as internal standard). Fourier transform infrared (FT IR) absorption spectra were recorded on a Perkin-Elmer mode 727 spectrophotometer. The solid samples were measured as potassium bromide pellets. Elemental analysis were determined on a Perkin- Elmer 240 and are in full agreement with the calculated values. Melting points (m.p) were determined with a Fisher-Johns apparatus and are uncorrected. The product 1,3,4-trimethyl-6-(5'-amino-1',3'-dimethylpyrazol-4'-yl)pyrazolo[3,4-*b*]pyridine (II), was prepared according to literature method[11].

1,3,6,7,9-pentamethyl-dypirazolo[4",3":5,6][4',3'-e]pyrido[3,4-c]pyridazine (II)

0.0014 mol de **I** dissolved in 10mL of hydrochloric acid was diazotized at 0-5°C by a solution of 0.0087 mol of sodium nitrite in 6mL of water for an hour and then at room temperature (25-28°) for further two hours period. There results a yellow precipitate which was filtered and dried to give product characterized as a derivative of the title ring system a 1,3,6,7,9-pentamethyldypirazolo[4",3":5,6][4',3'-*e*]pyrido[3,4-*c*]pyridazine (III). purified by colum chromatografy on silica gel (chloroform as eluting solvent) followed by crystallization from benzene, mp. 179-80°C, yield 0,4g; 77%.
Elemental analysis: $C_{14}H_{15}N_7$ requeries: C, 59.77; H. 5.37; N, 34.85% found: C, 60.01; H, 5.57; N, 34.81%.
^{1}H NMR ($CDCl_3$) δ (ppm): 2.84(s); 2.98(s); 3.44(s); 4.08(s); 4.;42(s); (15H-5CH_3);

^{13}C NMR ($CDCl_3$): 14.25(CH_3–1), 33.05(CH_3-2), 34.56(CH_3-7), 13.78(CH_3-9), 15.72(CH_3-10);
IR (KBr): absence of NH_2 absorption bands.
EIMS *m/z* (%): 281 M^+/(100); 266(37); 252(11); 238(41); 225(5); 212(13); 197(22); 182(6); 170(7); 156(5); 141(55); 129(6); 115(10); 102(6); 91(11); 88(6); 76(7); 75(7); 64(10); 5(7); 48(51).

CONCLUSIONS

The new ring system III is formed by an intramolecular diazo-coupling forming a pyridazine ring. Such cyclization have also been reported in similar reaction[12].

ACKNOWLEDGMENT

We would like to thank Conselho Nacional de Desenvolvimento Cientifico e Tecnologico (CNPQ) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for the continnous financial support.

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Received on March 5, 2003