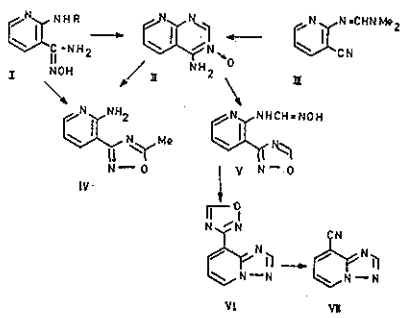

The structures of compounds follow from analytical, spectroscopic and X-ray data. Some other transformations, such as reduction, deoxygenation and cyclizations will be presented.

LE II 12

VILSMEIER-HAACK REACTION OF 5-AMINO-PYRAZOLE DERIVATIVES

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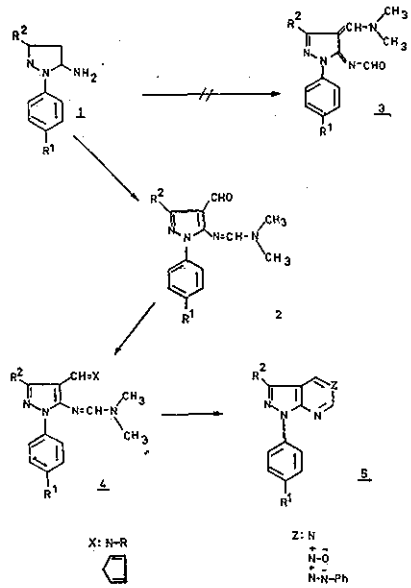
Vilsmeier-Haack reaction of some 1-substituted 5-amino-pyrazoles (1) has been reported by several groups of authors. The products of the reaction have been characterised either by structure 2 (1,2) or 3 (3).

In order to elucidate the above mentioned structural problem we reinvestigated the reactions of 1-substituted and 1,3-disubstituted 5-amino-pyrazoles with dimethyl-formamide — phosphoryl-chloride reagent.

We have found that reactions of 1 and DMF-$POCl_3$ result in the formation of compounds 2 only, independently of the character of R_1 and R_2 substituents. No protection of the 5-amino group could be achieved by acylation. Vilsmeier-Haack reaction of 5-acylaminopyrazoles is accompanied by acyl-splitting and also in these cases compounds 2 are obtained.



Structure 2 was proved by the spectral and chemical properties of the products. The formyl group of 2 could be selectively condensed with nitrogen bases (i. e. phenyl-hydrazine etc.) and CH- acid compounds, leading to pyrazole derivatives 4. Certain representatives of compounds 4 (X = NR) could be cyclized and pyrazolo[3,4-d]pyrimidines (5) were obtained. In some cases spontaneous second-step cyclisation was observed.

The mechanism of the reactions mentioned above will also be discussed.

REFERENCES

1) US Patents 3,544,585; 3,686,171; C. A. 74 76414 (1971); 77 140058 (1972)
2) Ger. Patent 2,008,677; C. A. 76 3850 (1972)
3) Kvitko, I. J., Loginova, T. M.: Zh. Obshch. Khim. 10 1088 (1974)

LE II 13

SYNTHESIS OF PYRROLO[3,2-d]SELENAZOLE AND PYRROLO [3,2-d]THIAZOLE. TWO NOVEL HETEROCYCLES

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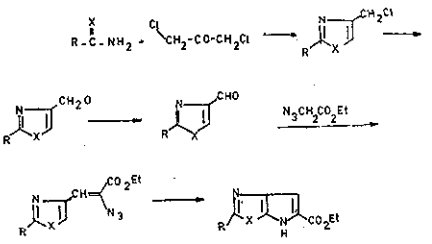
As a part of a program designed to expand the chemistry of fused pyrrole heterocycles, a method was developed for the synthesis of pyrrolo [3,2-d]selenazoles and pyrrolo [3,2-d]thiazoles as it is shown bellow.



R = H, CH_3, C_6H_5; X = S
R = C_6H_5, p-ClC_6H_4-, p-BrC_6H_4-, p-MeC_6H_4-, p-$CH_3OC_6H_4$-, C_4H_3S-; X = Se

The chemistry and structure elucidation of these new heterocycles will be discussed.

LE II 14

THE SYNTHESIS OF 3-SUBSTITUTED AND 3,5-DISUBSTITUTED DERIVATIVES OF 1,2,4-TRIAZOLE

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Thermal condensation of thioamides I with acylhydrazides II affords N^1-acylamidrazones III which cyclize to triazoles IV on heating above their melting point. The reaction can be carried out in one step, without the isolation of the intermediate III.