# INTERACTION OF FERVENULIN-4-OXIDE WITH 1-PHENYL-3-METHYLPYRAZOL-5-ONE IN THE ABSENCE OF BASES

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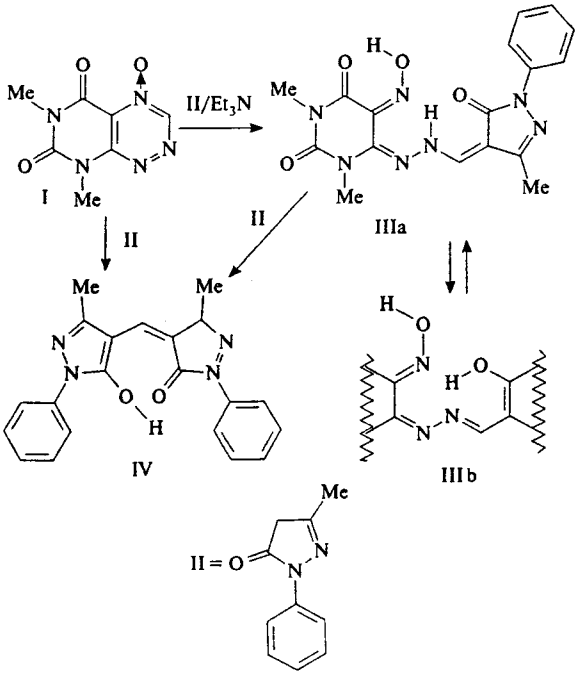
As is known, 6,8-dimethyl-5,7-dioxo-5,6,7,8-tetrahydropyrimido-[5,4-e][1,2,4]-triazine-4-oxide, or fervenulin-4-oxide (I), exhibits cleavage on heating in aqueous ethanol in the presence of hydrochloric acid with the formation of 1,3-dimethyl-5-nitroso-6-hydrazinouracil [1]. Heating compound I under similar conditions with 2-methylindole leads to 1,2,3,4-tetrahydro-1,3-dimethyl-5-nitroso-6-(2-methyl-3-indolylmethylenehydtrazino)pyrimidine-2,4-dione [2]. A number of 5-nitroso-6-hydrazino derivatives were obtained by interaction of compound I with some other CH-acids in the presence of bases. According to the $^1$H NMR data, compounds of this type exist in chloroform solutions in the form of enhydrazine tautomers [3]. It should be noted that the core of these molecules exhibits a small deviation from planar configuration, which is probably caused by significant conjugation in the chain C(1)=N(2)–N(3)–C(4)=C(5)–C(6) confirmed by values of the corresponding bond lengths determined using the x-ray diffraction data [4].

Previously we have reported on a compound (III) obtained by interaction of fervenulin-4-oxide with 1-phenyl-3-methylpyrazol-5-one (II) in the presence of triethylamine [3].

In this work, we heated fervenulin-4-oxide with 1-phenyl-3-methylpyrazol-5-one in boiling butanol in the absence of triethanolamine. This interaction led with a yield of 37% to a new compound (IV), which has proved to be identical (according to the IR absorption spectrum) to a dipyrazolylmethane derivative studied by x-ray diffraction in [5].

The same product IV was obtained by interaction of pyrazolone II with hydrazino derivative III in boiling butanol.

The formation of dipyrazolylmethane IV can be represented as a sequence of reaction steps: (1) nucleophilic attachment of pyrazolone at the C(3) site of fervenulin-4-oxide, (2) cleavage of the triazine cycle with the formation of hydrazino derivative III, and (3) nucleophilic attack of the azomethine bond of III by the second molecule of pyrazolone II.




This reaction is apparently the first example of transformation in 1,2,4-triazine-4-oxides under the action of C-nucleophilic agents without activation of the reactants by acids or bases. A deeper conversion of fervenulin-4-oxide observed on heating in butanol is probably caused by the highly electrophilic character of the azomethine carbon atom. This character is explained by the considerable degree of conjugation in molecules of compound III. In the presence of bases, hydrazino derivative III is likely to form a salt that is passive with respect to the nucleophilic attack. As a result, the interaction between I and II suspends at the stage of formation of compound III.

## EXPERIMENTAL PART

The synthesis and properties of compounds III and IV were described elsewhere [3, 5]. The IR spectra were measured on a UR-20 spectrophotometer (Germany) using sam-

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ples prepared as nujol mulls. The compounds were identified by comparing their spectra with those of the samples obtained by known methods.

**Reaction of fervenulin-4-oxide (I) with 1-phenyl-3-methylpyrazol-5-one (II).** A mixture of 1.0 mmole fervenulin-4-oxide with 2.0 mmole 1-phenyl-3-methylpyrazol-5-one in 5 ml of butanol was boiled for 5 h. Then the reaction mass was cooled to room temperature and the precipitate was separated by filtration and recrystallization from DMF. Yield of compound IV, 37%.

**Reaction of hydrazino derivative III with 1-phenyl-3-methylpyrazol-5-one (II).** A mixture of 0.5 mmole hydrazino derivative III with 0.5 mmole 1-phenyl-3-methylpyrazol-5-one in 3 ml of butanol was boiled for 5 h. Then the reaction mass was cooled to room temperature and the precipitate was separated by filtration. Yield of compound IV, 45 – 50%.

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