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THE KNOEVENAGEL REACTION OF MALONONITRILE WITH SOME CYCLIC β-KETO ACIDS ANILIDES

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As continuation of previous work on Knoevenagel's condensation of some cyclic β-keto acids anilides with compounds containing active methylene group the reaction of cyclopentan-2-one-1-carboxylic acid anilide (1) and cyclopentan-2-one-1,3-dicarboxylic acid dianilide (5) with malononitrile was investigated.

It was stated that the reaction of cyclopentan-2-one-1-carboxylic acid anilide (1) with malononitrile in presence of acetic acid in boiling benzene solution yielded 2-dicyanomethylene cyclopentane-1-carboxylic acid anilide (2).

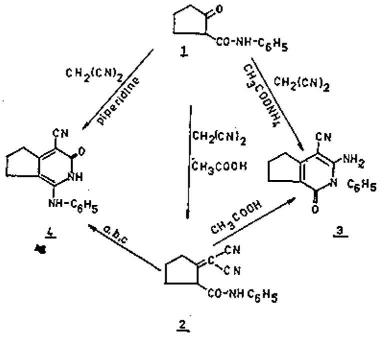
The condensation of anilide 1 with malononitrile in boiling toluene with acetic and ammonium acetate as catalyst yielded compound 3 isomeric with compound 2. The structure of compound 3 was determined on the basis of spectral data and of its chemical properties as 1-cyano-2-amino-3-phenyl-4-oxo-3,4,6,7-tetrahydro-5-H-cyclopenta(c)-pyridine.

A different course of the reaction of anilide 1 with malononitrile has been observed when the reaction was carried out in presence of base catalyst. The reaction performed in boiling toluene solution with piperidine and pyridine afforded compound 4, which has found to be isomeric with previously described compounds 2 and 3. Compound 4 was also obtained by conversion of compound 2:

a) in methanolic solution in presence of pipiridine and pyridine

b in boiling solution of sodium hydroxide

c) by prolonged boiling with water



On the basis of spectral data and chemical properties the structure 1-cyano-2-oxo-4-anilino-2,3,6,7-tetrahydro-5H-cyclopenta(c)-pyridine was assigned to compound 4.

The condensation of cyclopentan-2-one-1,3-dicarboxylic acid dianilide (5) with malononitrile in boiling toluene solution with piperidine and pyridine or ammonium acetate and acetic acid afforded the same product: 2-dicyanomethylene cyclopentane-1,3-dicarboxylic acid dianilide (6).

All the proposed structures were supported by IR, ^{1}H-NMR and MS spectral data

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ALKYLATION OF 2-CYANAMINOBENZIMIDAZOLE AND ITS ALKYLATED DERIVATIVES

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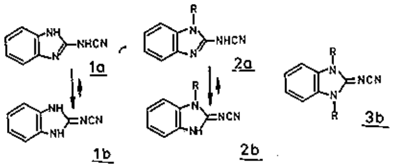
Alkylation of 2-cyanaminobenzimidazole 1 under various conditions led to mono and disubstituted products 2 and 3.

IR and UV spectra revealed that compounds 3 possess a symmetrical structure of 1,3-dialkyl-2-benzimidazolidenocyanamide 3b (IR: CN band at 2170 — 2200 cm^{-1}, shifted toward lower frequencies in consequence of coupling between cyano and imino group $\rangle C = N - C \equiv N$. UV: maxima at 240, 290 and 295 nm).



Analogous tautomeric form is also predominant in the case of the parent compound 1b and its monosubstituted derivatives 2b, position of the alkyl group in the latter being unequivocally established on chemical way.

An evidence of participation of tautomeric forms 1a and 2a in the structure of compounds 1 and 2 was provided by the synthesis of tricyclic derivative 4:

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THE OXIDATION-REDUCTION REACTION OF QUINOXALINE-2- AND 1,5-NAPHTHYRIDINE-2-ALDEHYDE N-OXIDES AND THEIR HYDRATES

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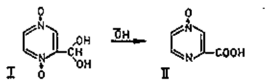
It was shown previously that pyrazine di-N-oxide, replaced by a dihydroxymethyl group at the carbon next to the oxidised nitrogen of the cycle (hydrate of pyrazine-2-aldehyde di-N-oxide, I) undergoes oxidation of its dihydroxymethyl group to carboxy group and deoxidation of the neighbouring nitrogen to form pyrazine-2-carboxylic acid 4-N-oxide (II) under the attack of strong or weak nucleophiles (reaction A)[1].



In order to develop investigations in this direction, the oxidation-reduction reactions of the hydrates of quinoxaline-2- and 1,5-naphthyridine-2-aldehydes di-N-oxides (III and IV respectively) have been studied.

It was found that in contrast to I, compounds III and IV, under the action of nucleophilic reagents (NaHCO$_3$ or NaOH solutions) undergo two types of reactions depending on pH: re-