

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

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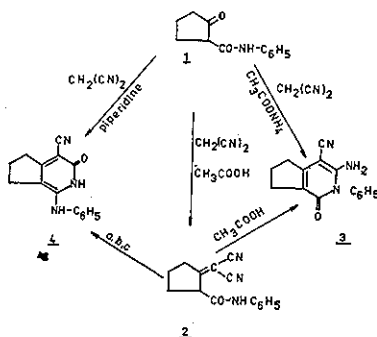
As continuation of previous work on Knoevenagel's condensation of some cyclic β -keto acids anilides with compounds containing active methylene group the reaction of cyclopentan-2-one-1-carboxylic acid anilide (1) and cyclopentan-2-one-1,3-dicarboxylic acid dianilide (5) with malononitrile was investigated.

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-5H-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 piperidine 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, $^1\text{H-NMR}$ and MS spectral data

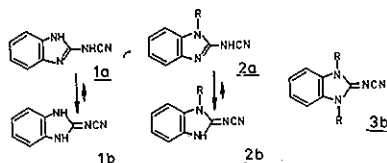
ALKYLATION OF 2-CYANAMINOBENZIMIDAZOLE AND ITS ALKYLATED DERIVATIVES

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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 $2170-2200\text{ cm}^{-1}$, shifted toward lower frequencies in consequence of coupling between cyano and imino group) $\text{C}=\text{N}-\text{C}\equiv\text{N}$. 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:

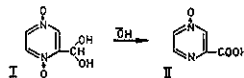


THE OXIDATION-REDUCTION REACTION OF QUINOXALINE-2- AND 1,5-NAPHTHYRIDINE-2-ALDEHYDE N-OXIDES AND THEIR HYDRATES

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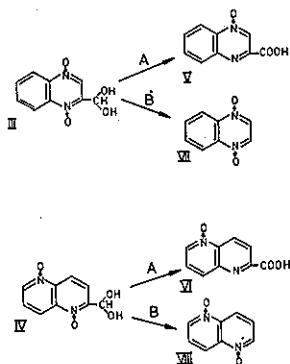
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It was shown previously that pyrazine di-N-oxide, replaced by a dihydroxymethyl group at the carbon next to the oxidized nitrogen of the cycle (hydrate of pyrazine-2-aldehyde di-N-oxide, I) undergoes oxidation of its dihydroxymethyl group to carboxy 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-



action A to form 2-carboxyquinoxaline 4-N-oxide (V) or 2-carboxy-1,5-naphthyridine 5-N-oxide (VI) respectively and reaction B to form di-N-oxides of unsubstituted quinoxaline or 1,5-naphthyridine (VII and VIII).

Quinoxaline-2-aldehyde isolated in the form of a carbonyl compound mainly undergoes reaction B changing to quinoxaline-di-N-oxide.

The optimum pH ranges for reactions A and B were investigated and a possibility of these reactions proceeding simultaneously shown.

The differences in the behavior of quinoxaline and 1,5-naphthyridine di-N-oxides derivatives were revealed.

The transformations of diethylacetal quinoxaline-2-aldehyde di-N-oxide proceeding in the presence of alkaline reagents were studied.

REFERENCES

- 1) A. S. Elina, I. S. Musatova, G. P. Syrova "Chemistry of the Heterocyclic Compounds", 1972, 9, 1275-1280.

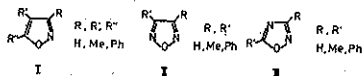
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POLAROGRAPHIC REDUCTION OF ISOXAZOLES AND THEIR AZAANALOGS IN ANHYDROUS DIMETHYLFORMAMIDE

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The polarographic behavior of substituted isoxazoles (I) and their azaanalogs (II, III)



was studied in anhydrous dimethylformamide against the background of quaternary ammonium salts. It was shown that the phenyl substituted compounds I possess polarographic activity and the first irreversible two-electron wave corresponds to N-O-bond rupture to form the dianion which is capable of being reduced only in a more negative potential range. In an accessible potential range, four-electron reduction of the derivatives I is likely, with the $E_{1/2}$ value of the second wave depending on the cation nature of the background. Complete saturation of multiple bonds after N-O-bond rupture requiring six electrons can be realized in excess proton donors (benzoic acid).

While reducing the derivatives II and III the first stage also involves two-electron irreversible rupture of N-O-bond. Isoxazole analogs are reduced substantially easier in all cases. The reduction depth of oxadiazoles studied is determined by their structure and protonation rate of intervening particles formed. In the accessible potential region oxadiazole III ($R = R' = Me$) is capable of accepting two electrons, oxadiazole II ($R = R' = Me$), III ($R = R' = Ph$), III ($R = Ph, R' = Me$) and III ($R = Me, R' = Ph$) — four electrons. Complete molecular reduction involving eight electrons takes place only in the case of oxadiazole II ($R = R' = Ph$).

In the series of isoxazole I and oxadiazole II and III derivatives greater conjugation of the phenyl ring in the fifth position facilitates the reduction as compared to the corresponding 3-substituted compounds. The replacement of methyl substituents by phenyl ones in disubstituted oxadiazoles III leads to facilitating the reduction $\Delta E_{1/2}$ of the first waves — 970 mV whereas the analogous effect for oxadiazoles II is 540 mV which is determined by partially broken conjugation due to space interaction of benzene rings in case of 3,4-diphenyl-1,2,5-oxadiazole.

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SYNTHESIS AND REACTIONS OF ARYLOXYFURAN DERIVATIVES

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A general method of preparing aryloxyfuran derivatives has been developed.

The aryloxyfuran formulation according to the method of Vilsmeier yields 5-aryloxyfurfurals, which were further transformed to 5-aryloxy-2-methylfurans by the Kishner-Wolff reduction.

The corresponding amides were obtained on the basis of the aryl esters of 5-aryloxyfurfurals with the reduction with $LiAlH_4$.

The aryl esters of aryloxyfurfurals acids reacted with hydrazine-hydrate to give aryloxyfurfuric hydrazides, which formed isopropylidene derivatives by the reaction with acetone.

The hermetic activity of the compounds synthesized has been investigated

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THE REACTION OF ARYL- AND ARYLOXYFURANS WITH DIMETHYL ACETYLENEDICARBOXYLATE

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The diene synthesis of aryl- and aryloxyfurans with dimethyl acetylenedicarboxylate has been studied.

The interaction of arylfurans with acetylenedicarboxylic ester yields adducts, which undergo aromatization leading to the esters of hydroxybiphenyldicarboxylic acids.

