STUDIES OF THE REACTION OF N^3 -SUBSTITUTED AMIDRAZONES WITH PYRIDINE 2,3-DICARBOXYLIC ANHYDRID

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Abstract

The studies of the course of reaction of N^3-substituted amidrazones with pyridine 2,3-dicarboxylic anhydrid demonstrated the influence of amidrazone substituents on the direction of the reaction.

Introduction

The amidrazones can be regarded as the reaction products of acidic thioamides with hydrazine and its derivatives. These compounds have basic character, which is attributed to the amide nitrogen atom [1]. Nitrogen atoms of amidrazone group are the potential site attack of the electrophilic agents.

In case of N^3-substituted amidrazones, N^1 and then N^3 nitrogen atoms are most susceptible for attack of electrophilic agents. At the same time carbon-nitrogen bonds are polarized and makes amidrazone carbon atom low electron density center. Such configuration enables those atoms for the reactions with nucleophilic agents.

Hindered synthesis, apparent in low yields and side reactions, is the major limitation of amidrazone use [2].

Most frequently amidrazones are used as substrates to synthesis of heterocyclic systems derivatives: five-membered [3, 4], six-membered [4, 5], seven-membered [6], and condensed systems [7].

Reactions carried out on N^3-substituted amidrazones as free bases with: ammonium isothiocyanate [8], aliphatic and aromatic isothiocyanates [9, 10], N-arylsulfonyl- and iminodithiocarbonate acid dimethyl esters [11], acethylen dicarboxylic acid dimethyl ester [12], acids and chlorides [13] lead to formation of 1,2,4-triazole system derivatives. In those researches, the authors demonstrated the formation of by products from amidrazone decomposition. This decomposition depends on both reaction conditions and substituents on N^1 and N^3 nitrogen atoms. In reaction of amidrazone and ammonium isothiocyanate e.g., there was proved the influence of amidrazone substituents on direction of the reaction:

- phenyl substituents – lead to formation thiosemicarbazide system, which cyclizated in butanol to 1,2,4-triazole-5-thiol derivatives;
- substituent of basic character – the reaction occurred with 3,5-di-(2-pyridyl)-4-phenyl-1,2,4-triazole formation (which was formed from amidrazone decomposition).

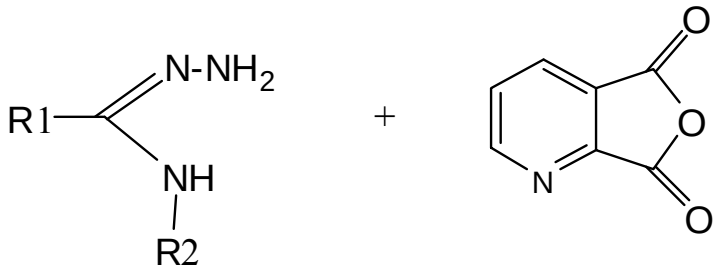
There were noted also the reactions of amidrazones with organic acids, where the influence of the environment on their course was remarkable. In the presence of acetic acid the reaction occurred in two directions. Aside from 3-(2-pyridyl)-4-phenyl-5-methyl-1,2,4-triazole, 2,3,5,6-tetrazine derivative was obtained as a product of amidrazone decomposition.
The reaction of amidrazones with maleic anhydride lead to formation of Z 3-(2,4-diaryl-1,2,4-triazolo) propenoic acid [14]. The reaction occurred in one direction, in anhydrous diethyl

ether, in room temperature. The influence of amidrazone substituents was not observed.

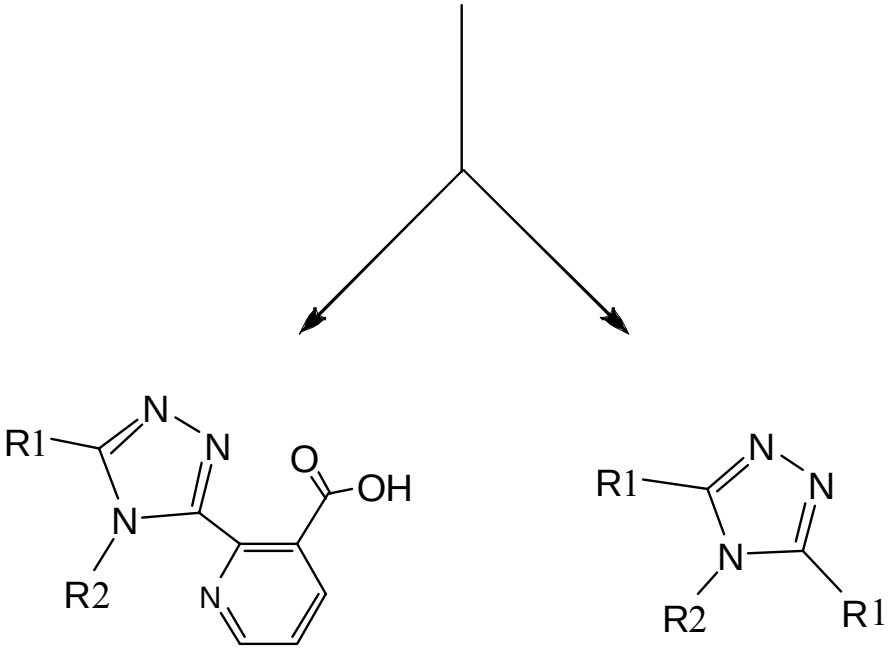
The paper presents the reaction of N^3-phenyl-(2-picolin)-amidrazone **1** and N^3-(2-pyridil)-2-picolin amidrazone **2** with pyridine 2,3-dicarboxylic anhydride **3**. The reaction was carried out in anhydrous ether at the room temperature.

The structures of obtained compounds were confirmed by elementary and spectral analysis. In the IR spectra of compound **4** characteristic absorption bands for the C=O group in the range 1703 cm^{-1} were observed.

In the ^1H NMR spectrum for compound **4** occurs wide signal of the protons of carboxyl group in the range 13.1 ppm. The signals in the range 7.0-8.8 ppm were attributed to aromatic protons.



1,2 3



4 5

	R1	R2
1,4	2-C_5H_4N	C_6H_5
2,5	2-C_5H_4N	2-C_5H_4N

Experimental part.

Melting points were measured on a Boetius apparatus and are given uncorrected in Table 1. ^{1}H NMR spectra were recorded on a Tesla BS 567A (300 MHz) apparatus in D_6-DMSO with TMS as an external standard. IR spectra were recorded on a Specord IR- 75 spectrometer. Results of elemental analysis for C, H, N by microanalysis method were in accordance with the calculated values: ±0.7% for C, 0.75% for N and 0.9% for H.

Synthesis of 3,4-diaryl-5-(3-carboxy-2-pyridyl)-1,2,4triazole **4**.

Amidrazone **1** (0,01 mole) was dissolved in 30cm^3 anhydrous diethyl ether. 0,01mole of pyridine 2,3-dicarboxylic anhydride **3** was added. The mixture was then left in room temperature for one week. The precipitated solid was then filtered and washed with diethyl ether and purified by crystallization from methanoI. The product **4,** with melting point at 250-252°C, was obtained with 48% yield (1,6g).

Spectral analysis:
IR (KBr, cm^{-1}): 2970 arom, 1703 C=O
^{1}H NMR (D_6-DMSO -, δ ppm): 13.1 (s, lH, COOH), 7.0-8.8 (m, 12H, ar)

Filtrate after separation of **4** was evaporated under pressure and solid residue was then extracted with absolute ethanol. After concentration of extract pyridine 2,4-dicarboxylic acid (of melting point at 174°C) precipitated

Synthesis of 3,4,5-triarylo-1 ,2,4-triazole **5**.

Amidrazone **2** (0,01 mole) was dissolved in 30cm^3 anhydrous diethyl ether. 0,01 mole of pyridine-2,3-dicarboxylic anhydride **3** was added. The mixture was left in room temperature for one week. The precipitated solid was then filtered, washed with diethyl ether and mixed with 10cm^3 of 10% water solution of potassium hydrocarbonate. Solid, insoluble in solution of potassium hydrocarbonate, was filtered.
The product compound **5**, with melting point at 198-200°C, was obtained with 49% yield (1,5g).

Spectral analysis:
IR (KBr, cm^{-1}): 3054 arom, 1616 C=N
^{1}H NMR (D_6-DMSO, δ ppm): 7.2-9.2(m, 12H, ar)

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