

Study of the structure of reaction products of acetyl-containing furancarboxylates with hydrazine hydrate by 1D and 2D NMR spectroscopy

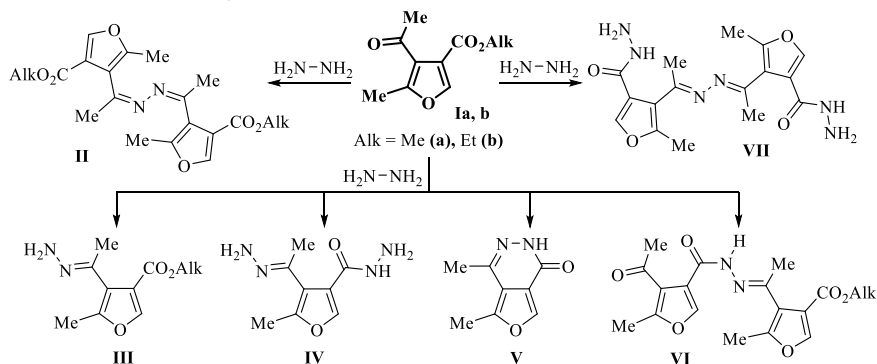
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Alkyl 4-acetyl-5-methylfuran-3-carboxylates **Ia, b** [1], containing two electrophilic centers, are interesting objects for studying the direction of their interaction with hydrazine, a representative of polynitrogen nucleophiles. Theoretically, this reaction can end with the formation of various **II-VII** structures.



The aim of this work was to study the structure of the reaction products of furan-3-carboxylates **1, 2** with hydrazine using ^1H and ^{13}C NMR spectroscopy, including experiments: $^1\text{H}-^{13}\text{C}$ HMQC and $^1\text{H}-^{13}\text{C}$ HMBC.

In the structures of the intended proposed products, the following features can be distinguished:

- there is an ester fragment (CO_2Alk) in molecules **II, III, VI**;
- NH or NH_2 group – in molecules **III, IV, V** and **VII**;
- molecules **II** and **VII** have internal symmetry.

The implementation of the studied reaction using the ratio of reagents 1:1 led to obtain the crystalline products.

The ^1H NMR spectrum of a representative of the synthesized compounds contains signals of the alkyl substituent of the ester fragment (δCH_3 1.22 ppm, t, ^3J 7.1 Hz and δCH_2 4.18 ppm, q, ^3J 7.1 Hz), which confirms the preparation of structures **II, III** or **VI** (Fig. 1).

According to the results of studying this molecule by the experiment of the $^1\text{H}-^{13}\text{C}$ HMQC it turned out that the broadened proton signal at 11.45 ppm (1H) does not correlate with carbon atom signals and therefore belongs to the NH group. This result is consistent only with the structure **VI** of the previously selected (Fig. 2).

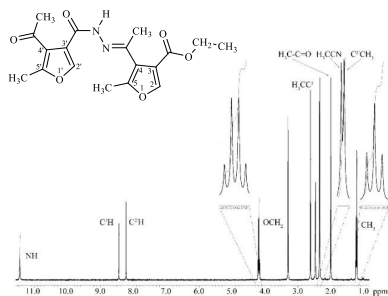


Figure 1. ^1H NMR spectrum of compound **VIb** (DMSO- d_6)

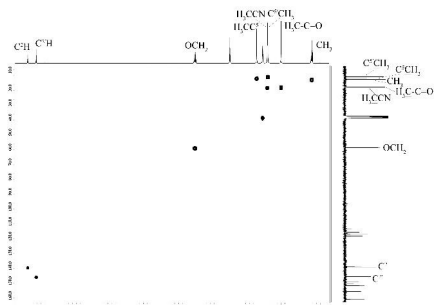


Figure 2. ^1H - ^{13}C HMQC spectrum of compound **VIb** (DMSO- d_6)

Indeed, the ^{13}C - $\{^1\text{H}\}$ NMR spectrum of the molecule **VI** contain signals of the following structural fragments: 140.52 ppm. (C=N), 153.60 ppm (C=O) and 162.72 ppm. (CO₂Alk) (Fig. 3). The assignment of these carbon signals is confirmed by the results of the ^1H - ^{13}C HMBC experiment (Fig. 4).

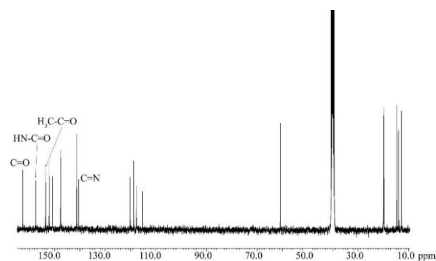


Figure 3. ^{13}C NMR spectrum of compound **VIb** (DMSO- d_6)

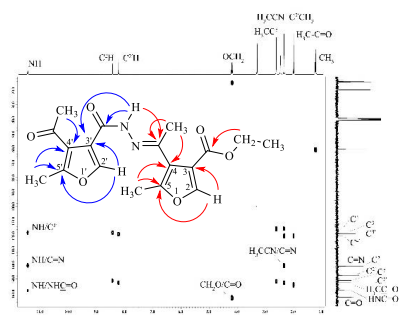


Figure 4. ^1H - ^{13}C HMBC spectrum of compound **VIb** (DMSO- d_6)

Thus, based on the obtained data of homo- and heterocorrelation experiments of NMR spectroscopy, it was found that the interaction of furan-3-carboxylates **Ia, b** with hydrazine leads to the formation of alkyl 4-(1-{2-[(4-acetyl-5-methylfuran-3-yl)carbonyl]hydrazinylidene}ethyl)-5-methylfuran-3-carboxylates **VIa, b**.

Acknowledgments

The studies were carried out at the Central Collective Use Center at the Faculty of Chemistry of the Herzen State Pedagogical University of Russia on the Jeol ECX-400A spectrometer (Royal probe) with an operating frequency of 399.78 (^1H), 100.53 (^{13}C) MHz at standard experimental settings, using the solvent signal as an internal standard.

References

- Gomonov, K.A., Pelipko, V.V., Litvinov, I.A., Baichurin, R.I., Makarenko, S.V. Mendeleev Commun. 2023, 33, 11-13.