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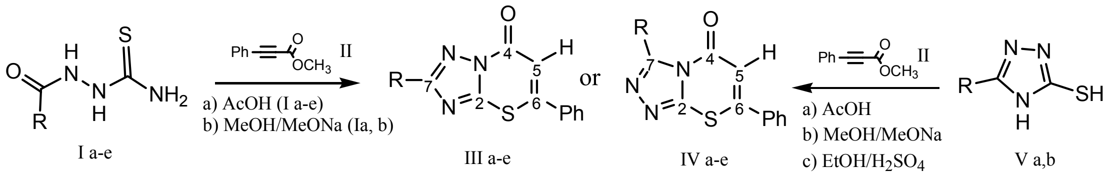
Poster Presentation

Triazolothiazines from Thiosemicarbazides

Natalia A. Danilkina, Leonid E. Mikhailov, Boris. A. Ivin

Academy of Chemisry & Pharmacy,
Prof. Popov street, 14, 197022,St.-Petersburg, Russia
e-mail: himi383@mail.ru

Reaction of acetylenecarboxylic acid derivatives with N,S-dinucleophiles provides the general approach for construction of 1,3-thiazolidine and 1,3-thiazine systems which are of greate interest [1]. Thus, using derivatives of propynonic acid without electonwithdrawing groups at β-position, the exclusively formation of 1,3-thiazine ring occurs [2]. The aim of present work was to investigated reaction of methyl(phenyl)propynoate with cyclic and acyclic thiosemicarbazide derivatives.



R = H (a), CH_3 (b), C_2H_5 (c), Ph (d), 4-C_5H_4N (e)

We've found out that the reaction of 1-acylthiosemycarbazides (I a, b) with ester (II) in acetic acid under reflux and in boiling methanolic sodium methylate leads to triazolothiazines (III a, b or IV a, b). The latter compounds were also synthesized by condensation of mercaptortiazoles (V a, b) with the ester (II) under the same conditions and in refluxing ethanol with a few drops of sulphuric acid. On the basis of the usual IR, NMR ^{1}H and ^{13}C and mass spectra it couldn't be determined which of the isomers (III or IV) was obtained. The structure elucidation of this type of compounds has been a problem for a long time. In present work the structure of isomer (IV a) was excluded by analysis of LSPD NMR ^{13}C spectra. Thus the main evidence for the triazolothiazines (III a) was the absence of J [C^4-H(C^7)] coupling, while geminal ^2J [C^4-H(C^5)] (1 Hz) and vicinal ^3J [C^2-H(C^5)] (8.2 Hz) coupling do occur. It should be noted that the choice between isomers (III a) and (IV a) couldn't be extended for other derivatives (III or IV b-e) because of additional bonds between C^4 and hydrogen atoms adjacent to substituent at C^7. However the isomers (III b-e) are more preferable, since chemical shifts of carbon atoms (C^2, C^4, C^6, C^7) and signals sequence in the NMR ^{13}C spectra of triasolothiazines (III b-e) and triasolothiazine (III a) are similar. It should be noted that spectral data of compounds (III b) and (IV b) (the latest was synthesized by condensation of thiosemicarbazide (I b) and ester (II) in acidificated ethanol) are quite different.

[1] Yu.I. Roabukhin, O.B. Korzhavina, K.S. Suzdalev, *Adv. Het. Chem*. 1996, **66,** 131
[2] S. Coen, B. Ragonnet, C. Vieillescazen, J.-P. Roggero, *Heterocycles,* 1985, **23**, 1225