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Synthesis and spectral properties of heterocycles as 2*H*-2-chromenone derivatives

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Abstract: 3-Aryl-2*H*-2-chromenehydrazones react with isothiocyanates to form 3-aryl-2*H*-2-chromene thiosemicarbazones, which exist in tautomeric equilibrium in DMSO-*d*₆ solution. 3-R \blacklozenge -2-(3-aryl-2*H*-2-chromenylideneazo)-4-thiazolidinones were obtained by cyclocondensation of 3-aryl-2*H*-2-chromene thiosemicarbazones with ester of bromoacetic acid in the presence of sodium acetate. 1-(2*H*-2-Oxochromen-6-yl)-4-phenyl thiosemicarbazide was obtained in the same manner from 2*H*-2-oxochromen-6-yl hydrazine. The interaction of C-4-nitrophenyl-N-3-nitrophenylnitron with 1-(2-oxo-2*H*-1-benzopyran-6-yl)-1*H*-pyrrole-2,5-dione leads to [3+2] cycloaddition products as mixture of stereoisomers.

Key words: 2*H*-2-chromene, cyclocondensation, heterocycles, thiosemicarbazones, thiazolidinones, ester of bromoacetic acid, stereoisomers.

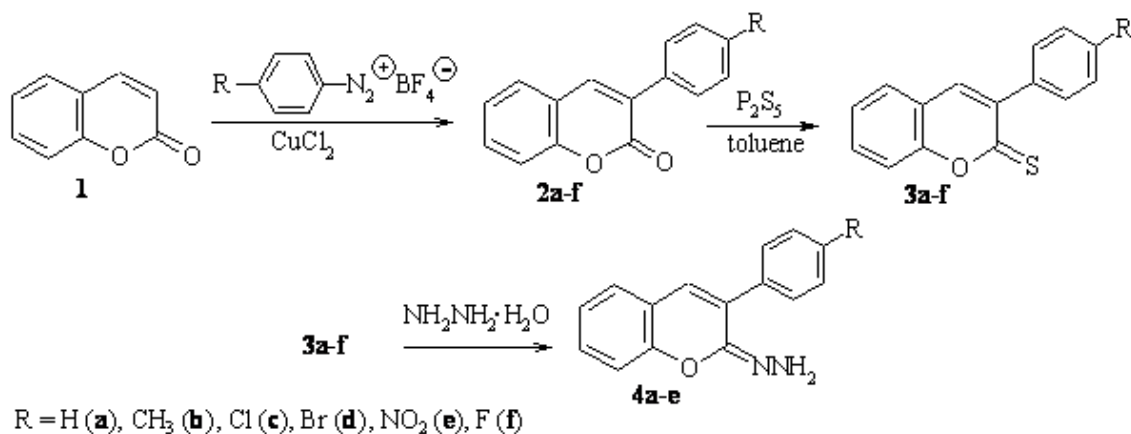
2*H*-2-Chromenone derivatives are widely used for production of highly effective fluorescent dyes for synthetic fibres and daylight fluorescent pigments [1-6]. They also play a vital role in electrophotographic and electroluminiscent devices [7-9]. Synthesis and investigation of new heterocycles based on 2*H*-2-cromenone ring make possible new ways for scientific and technical usage. 2*H*-2-Chromenone (or coumarin) and its derivatives are known as bioactive compounds, many of them possess antibacterial and antifungal properties [10]. Coumarins are also of considerable biological and medical interest. Many derivatives of these products show significant physiological effects: weakly toxic, anticarcinogenic, anticoagulant and antibiotic activities [11-12].

Previously we carried out investigation of the influence of the electronic character of the substituent and its position of substitution on the UV/visible spectral properties of the coumarin compounds [13].

Synthesis of new 2*H*-2- chromenone derivatives with additional chromophore system \blacklozenge 4-thiazolidinone \blacklozenge was performed.

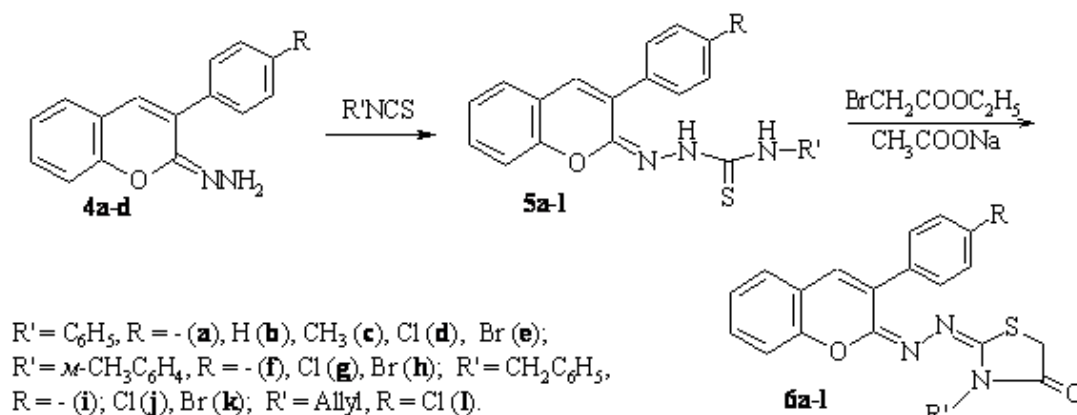
3-Aryl-2*H*-2-chromenones **2a-f** have been synthesized by arylation of 2*H*-2-chromenone **1** with arendiazonium salts and later were transformed into 3-aryl-2*H*-2-chromenethiones **3a-f** via action of phosphorus pentasulfide. Reaction of **3a-f** with hydrazine hydrate leads to 3-aryl-2*H*-2-chromene

hydrazones **4a-e** (Scheme 1).



Scheme 1

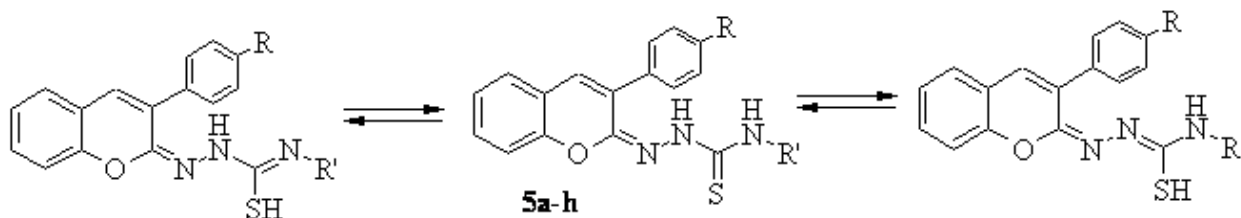
Interaction of 3-aryl-2*H*-2-chromene hydrazones **4a-e** with allyl-, aryl-, aralkylisothiocyanates resulted in formation of thiosemicarbazones **5a-l** (Scheme 2).



Scheme 2

The next stage is reaction of substances **5a-l** with ester of bromoacetic acid in the presence of sodium acetate with formation of 3-R-2-(3-aryl-2*H*-2-chromenylideneazo)-4-thiazolidinones **6a-l**.

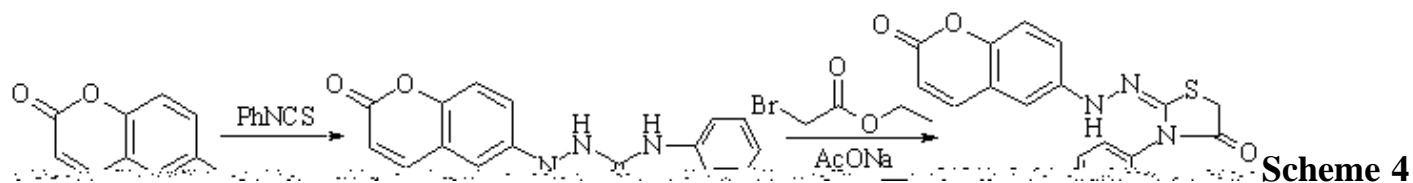
It was established that 3-aryl-2*H*-2-chromene thiosemicarbazones **5a-h** exist in tautomeric equilibrium in DMSO-*d*₆ solution (Scheme 3), just thion-thiol rearrangement take place, that absent in CDCl₃ solution.



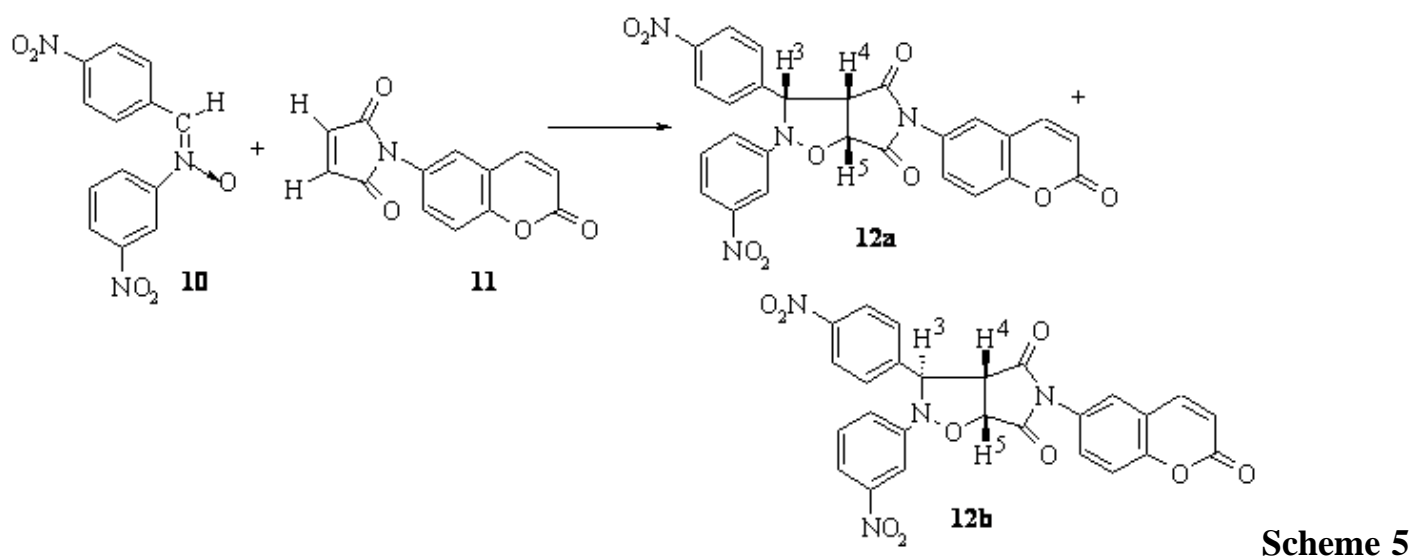
Scheme 3

1-(2*H*-2-Oxochromen-6-yl)-4-phenyl thiosemicarbazide **8** was obtained in the same manner from 2*H*-2-oxochromen-6-yl hydrazine **7** by reaction with phenylisothiocyanate and the next cyclocondensation of compound **8** with bromoacetic acid ester in ring closure product **9** was

transformed (Scheme 4).



The interesting interaction of C-4-nitrophenyl-N-3-nitrophenylnitron **10** with 1-(2-oxo-2H-1-benzopyran-6-yl)-1H-pyrrole-2,5-dione **11** leads to [3+2] cycloaddition products 2-(3-nitrophenyl)-3-(4-nitrophenyl)-5-(2-oxo-2H-1-benzopyran-6-yl)-perhydropyrrolo[3,4-d]isoxazole-4,6-diones (*cis*-**12a** and *trans*-**12b**) as mixture of stereoisomers (Scheme 5). The product was separated into two stereoisomers, *cis*- and *trans*- isoxazolidines with respect H³ and H⁴, which were identified by NMR ¹H spectra.



The UV-VIS-, ¹H-NMR spectra of synthesized dyes were investigated. The quantitative relationship between structure and their spectral properties were established.

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