9th International Electronic Conference on Synthetic Organic Chemistry. ECSOC-9
1-30 November 2005. http://www.usc.es/congresos/ecsoc/9/ECSOC9.HTM & http://www.mdpi.net/ecsoc/

[A013]

Arylation of unsaturated compounds by 6-coumarinyldiazonium salt

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Abstract: Interactions of 6-coumarinyldiazonium chloride with styrene, acrylonitrile, metylmetacrylate were investigated. The products of chloroarylation with acrylonitrile – 2-chloro-3-(2-oxo-2*H*-6-chromenyl)propanenitrile, metylmetacrylate – methyl 2-chloro-2-methyl-3-(2-oxo-2*H*-6-chromenyl)propanoate and 6-(2-phenyl-1-ethenyl)-2*H*-2-chromenone with styrene in catalytic conditions by copper (II) salts were obtained.

Key words: 6-aminocoumarin, 6-diazocoumarinyldiazonium chloride, chloroarylation.

Introduction

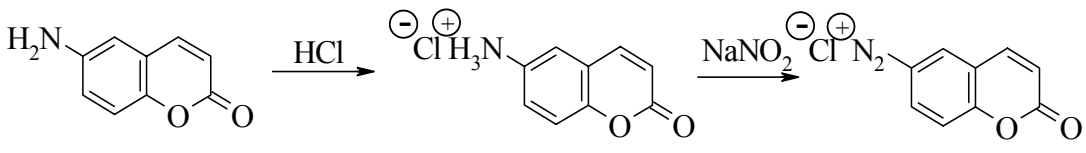
2*H*-2-Chromenone (coumarin) derivatives are widely used for production of highly effective fluorescent dyes for synthetic fibres and daylight fluorescent pigments [1-6]. They also play a vital role in electrophotographic and electroluminiscent devices [7-9]. Synthesis and investigation of new substituted 2*H*-2-cromenone derivatives make possible new ways for scientific and technical usage. Coumarin derivatives are known as bioactive compounds with weakly toxic, anticarcinogenic, anticoagulant and antibiotic activities [10-12].

Results and discussion

6-Coumarinyldiazonium salts in catalitic reactions practically were not investigated. Formation of triazines by interaction of 6-coumarinyldiazonium salts with anilines and azocoupling reactions were described [13, 14]. The purpose of our research was investigation of interaction of 6-coumarinyldiazonium chloride with unsaturated compounds at the presence of copper(II) salt as catalyst.

As unsaturated compounds styrene, acrylonitrile, metylmetacrylate were used.

6-Coumarinyldiazonium chloride **2** was obtained from 6-aminocoumarin **1** by general method (Scheme 1) [15].

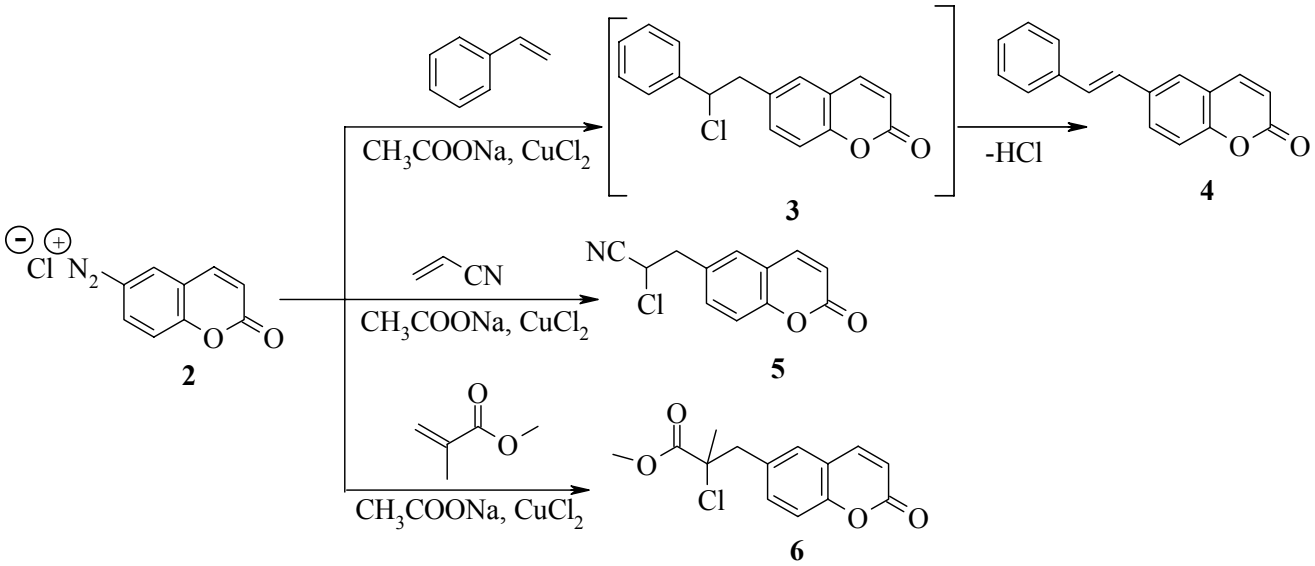


1 **2**

Scheme 1

Interactions of styrene, acrylonitrile, metylmetacrylate with 6-coumarinyldiazonium chloride **2** were carried out in water-acetone medium in the presence of sodium acetate and copper(II) chloride as catalyst.

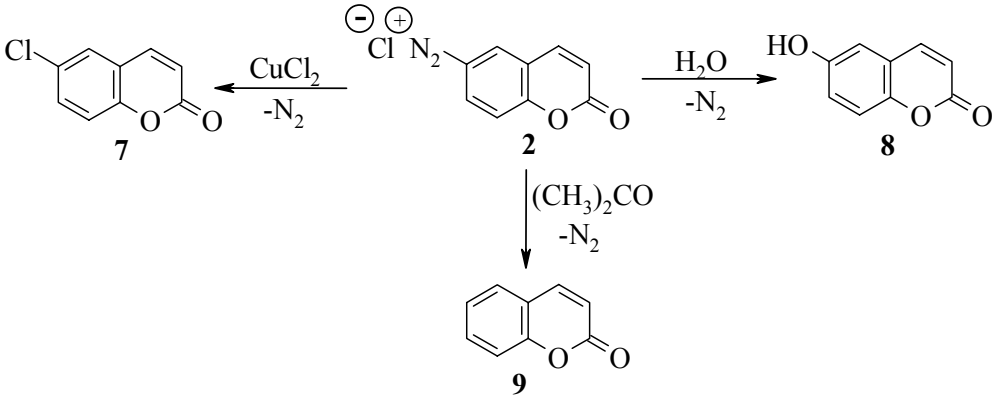
Products of reaction were separated by chromatography on silica gel. The basic compounds of reactions are 6-(2-phenyl-1-ethenyl)-2*H*-2-chromenone **4**, 2-chloro-3-(2-oxo-2*H*-6-chromenyl)propanenitrile **5**, methyl 2-chloro-2-methyl-3-(2-oxo-2*H*-6-chromenyl)propanoate **6** resrectively. Formation of these products may be explaned by addition of chlorine and 6-coumarinyl radicals to double bond C=C. In the case of styrene we supposed that the dehydrochlorination process from original adduct **3** with formation of the conjugate system in compound **4** take place.



Scheme 2

The structure of compounds **5**, **6** and direction of addition to double bond C=C were proved by presence of multiplet signals of methylene groups in α-position to coumarin cycle in ^{1}H NMR spectra.

Along with products **4-6** 6-chlorocoumarin **7**, 6-hydroxycoumarin **8**, and also unsubstituted coumarin **9** have been separated and identified from reaction mictures. Formation of such substances was by-process, that causes a low yield of the basic reaction products.



Scheme 3

The UV-VIS-, ^{1}H-NMR spectra of synthesized compounds were investigated. The quantitative relationship between structure and their spectral propeties were established.

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