

UDC 547.638 + 547.821.2

**PYRIDINE-2-DIAZONIUM SALTS IN ANIONARYLATION  
REACTIONS OF UNSATURATED CARBOXYLIC  
ACIDS AMIDES**

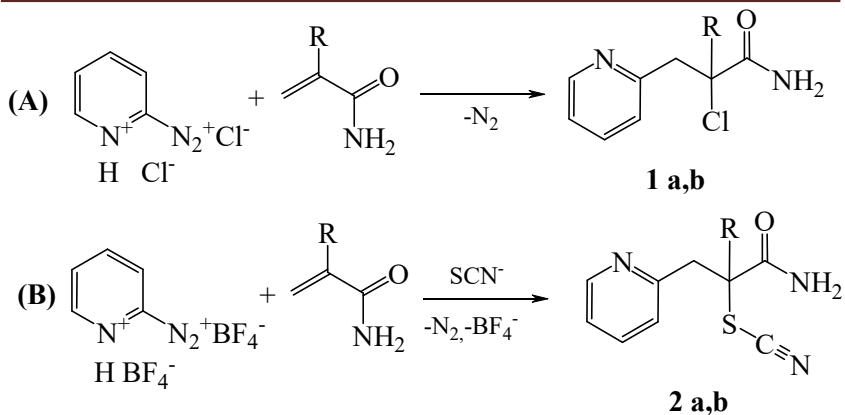
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Continuing our research in the direction of studying  $\alpha,\beta$ -unsaturated carboxylic acids derivatives [1, 2] we used diazonium salts based on heterocyclic amines in the reactions of chloro- and thiocyanatoarylation of unsaturated amides.

Taking into account the extremely high reactivity of pyridine-2-diazonium salts [3], especially in diazo group substitution reactions, we used the sequential diazotization-anionhetarylation method. A similar method proposed by Allen and Thirtle is used for the synthesis of 2-halogenosubstituted pyridines [4] and is the main preparative method for obtaining such derivatives [5].

It was established that pyridine-2-diazonium chloride interacts with acrylic and methacrylic acids amides in the presence of copper (II) chloride with the formation of chlorohetarylation products – (2-methyl)-3-(pyridin-2-yl)-2-chloropropanamides **1 a,b** (reaction A), and pyridine-2-diazonium tetrafluoroborate in the presence of rhodanide anions forms thiocyanatohetarylation products – (2-methyl)-3-(pyridin-2-yl)-2-thiocyanatopropanamides **2a,b** (reaction B). These reactions occur according to the following scheme:



The yields of chloro- and thiocyanatohetarylation products are 29-48% and are much lower than in the anionarylation reactions of unsaturated acids amides. It should be noted that the formation of arylation products in both cases was not recorded. Instead, there is a partial conversion of the pyridine-2-diazonium salt with the formation of 2-chloro(thiocyanato)pyridines, the yields of which are up to 30-35% based on the arylating reagent.

Increasing the reaction temperature and introducing excess pyridine-2-diazonium salt and anionoid reagent (potassium rhodanide) does not contribute to increasing the yields of the target products. It was established that with increasing temperature, the proportion of resinous substances of unknown structure increases. Most likely, these substances are products of telomerization and polymerization of the studied unsaturated amides. At the same time, at temperatures above 5<sup>0</sup>C, azo-combination processes are significantly accelerated, which can be visually observed judging by the color of the extracts. Dediazonization of the pyridine-2-diazonium salt does not occur at lower temperatures.

Chloro- and thiocyanatohetarylation products of acrylamide and methacrylamide – (2-methyl)-3-(pyridin-2-yl)-2-chloro(thiocyanato)propanamides 1, 2 are colorless or light yellow crystalline substances with melting points of 76-103<sup>0</sup>C, which crystallize well from methanol or ethanol. The structure of the synthesized compounds was confirmed by IR and 1H NMR spectra

data.

The obtained experimental data on the chloro- and thiocyanatohetarylation of acrylic and methacrylic acids amides confirms that these processes occur analogously to the anionarylation of  $\alpha,\beta$ -unsaturated carboxylic acids derivatives. The high reactivity of the arylating reagent does not contribute to increasing the yields of target products, which is primarily determined by kinetic factors and the stability of intermediates. In the case of pyridine-2-diazonium salts, the proximity of the diazo group to the heteroatom (ortho-position) reduces their stability due to the partial delocalization of the positive charge of this group on the cyclic nitrogen atom. Although strengthening the covalency of the diazonium component stimulates its dediazonization. In reactions with unsaturated compounds catalyzed by copper salts, this process largely occurs along the route of the Gattermann-Sandmeyer reaction.

Thus, the combination of the high reactivity of the diazonium component and the inactivation of the catalytic process due to the multi-ligand coordination of copper ions lead to a change in the regiodirection of pyridine-2-diazonium salts reactions with unsaturated amides and increase the share of processes competing for anionhetarylation.

#### References

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**UDC 547.638 + 547.789**

**2-S-IMINOTHIOCARBONATO-3-ARYLPROPANAMIDES AS BIFUNCTIONAL SYNTHONS FOR THE PREPARATION OF THIAZOLE DERIVATIVES**

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It is known that  $\alpha$ -functionalized thiocyanates are available and convenient bicenter reagents for various cyclizations. The thiocyanate group is hydrolyzed to the thiocarbamate group in an acidic solutions and the presence of additional functional group in the molecular structure allows to obtaining heterocyclic compounds during the hydrolysis process [1]. An example of such cyclizations is the direct cyclization of 3-aryl-2-thiocyanatopropanamides, which occurs with the formation of 5-arylsubstituted 2-aminothiazol-4(5*H*)-ones. These thiazole derivatives are converted into acetamide derivatives when boiled in acetic anhydride medium [2, 3].

The previously synthesized 2-S-iminothiocarbonato-3-arylpropanoic acids derivatives [4] can also be used as bifunctional synthons for the construction of the thiazole cycle. In order to confirm this conclusion, we investigated the cyclization of 2-(S-iminothiocarbonato)-(2-methyl)-3-arylpropanoic acid amides **1-3** with the formation of 2-aminothiazol-4(5*H*)-one derivatives **4-6**.