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Synthesis of Fused Heterocyclic Systems Based on 4-Chloromethylcoumarins

Svitlana P. Bondarenko[1], Mykhaylo S. Frasinyuk[2]

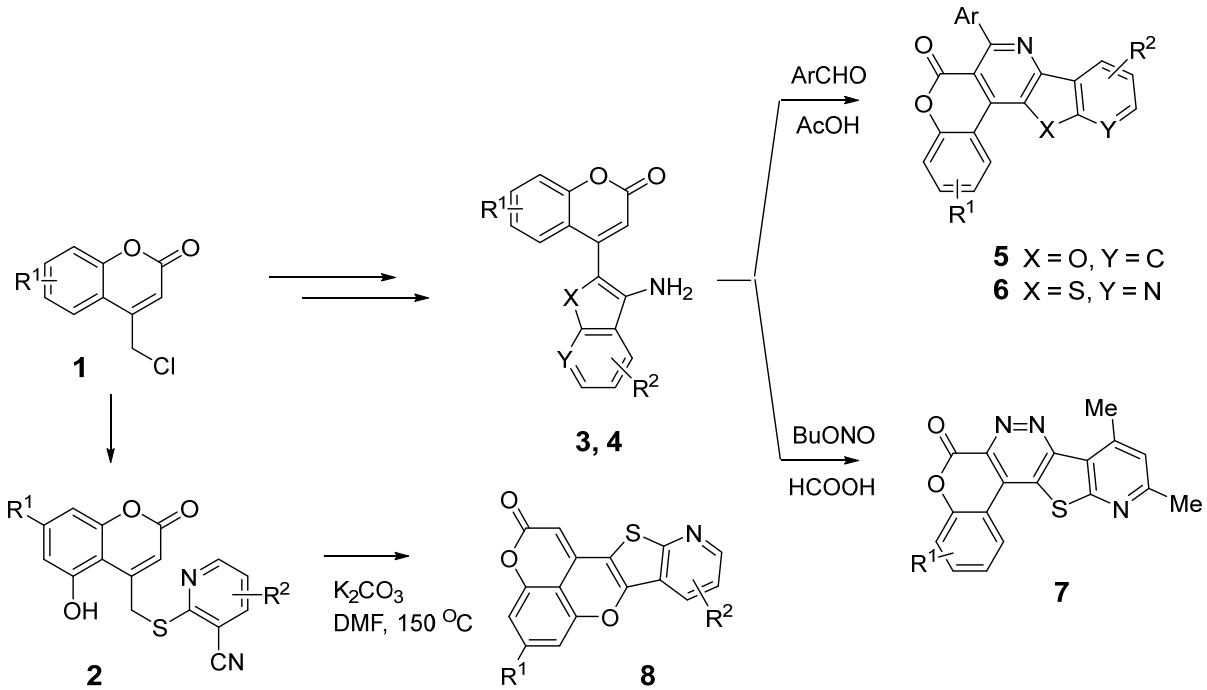
[1]*National University of Food Technologies, Kyiv, 01601, Ukraine*
[2]*Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine, Kyiv 02094, Ukraine*
e-mail: svitlana.bondarenko@ukr.net

Nitrogen-containing coumarins have important role in development of drugs. Some pyridino[3,4-*c*]coumarins were isolated from *Schumanniophyton problematicum* and referred to alkaloids. Development of new ways of synthesis of novel alkaloid-like compounds based on fused coumarins is topical problem.

We developed new methods for the synthesis of various fused coumarins using 4-chloromethylcoumarins as versatile starting compounds. Alkylation of 2-cyanophenol with 4-chloromethylcoumarins **1** led to one-pot formation of 4-(3-aminobenzofuran-2-yl)coumarins **3**. The similar reaction involving 2-mercapto-3-cyanopyridines affords S-alkylpyridines **2**. 4-(3-Aminothieno[2,3-*b*]pyridin-2-yl)-2*H*-chromen-2-ones **4** were synthesized by subsequent intramolecular condensation of the methylene and cyano groups.

Unusual condensation of compounds **3, 4** with aldehydes led to formation of fused pyridino[3,4-*c*]coumarins **5, 6** which is results of formation of the Shiff's bases, intramolecular [5+1] cycloaddition and oxidation of dihydropyridino[3,4-*c*]coumarins.

Interaction of compounds **4** with BuONO in formic acid led to synthesis of diazo compounds with further intramolecular ring-closure reaction and formation of 6*H*-chromeno[3,4-*c*]pyrido[3',2':4,5]thieno[2,3-*e*]pyridazin-6-ones **7**.



In case of applying 4-chloromethyl-5-hydroxycoumarins **1** alkylated 2-mecapro-3-cyanopyridines **2** undergoes tandem intramolecular cyclizations with formation of 2*H*-pyrano[4'',3'',2'':4',5']chromeno[2',3':4,5]thieno[2,3-*b*]pyridin-2-ones **8**.