

Ph.D. thesis topic: **Functionalization of selected quinoline derivatives based on aromatic electrophilic substitution reaction**

The aim of the study was the investigation of the substitution direction preferences in the aromatic electrophilic substitution reactions for compounds based on the quinoline skeleton, mainly 8-hydroxyquinoline derivatives. The performed reactions were as follows: deuteration, nitration, nitrosation, Friedel-Crafts acylation, Vilsmeier-Haack, Reimer-Tiemann, Kolbe-Schmitt reaction and coupling with diazonium salts.

As a result of the study over 70 compounds were synthesized, including 13 that have been characterized by X-ray analysis. To the best of our knowledge, the majority of compounds have not been previously described in the chemical literature.

Direction of the substitution depends mainly on the type of reaction and thus on the type of electrophile used. The H/D isotope conversion and nitration reaction revealed that substitution occurs simultaneously in both *C5* and *C7* positions of the quinoline skeleton leading to the disubstituted product.

The reaction of nitrosation, Friedel-Crafts acylation and coupling with diazonium salts demonstrate that the substitution occurs primarily in the *C5* position of the quinoline skeleton which results in a monosubstituted product.

Formylation reaction of quinoline derivatives have shown that the Vilsmeier-Haack method is more selective than the Reimer-Tiemann, but it has a lot of synthetic restrictions preventing the production of the quinoline aldehyde derivatives. On the other hand, the Reimer-Tiemann reaction due to the high reactivity of carbenes, is non-selective and leads to the formation of two regioisomeric products with a newly formed aldehyde group at the *C5* or *C7* position.

The direction of substitution in the carboxylation reaction using the Kolbe-Schmitt method is completely different. It leads to substitution in the *C7* position of the quinoline skeleton.

During the research, it was indicated that the presence of additional functional groups in both quinoline skeleton and the electrophiles used in the reaction affect significantly the yield of the isolated reaction products. These are related to: electron and steric effects, the formation of the hydrogen bonds and the affinity of functional groups to solvents.

Moreover, it was proven that the derivatives of 8-hydroxyquinolin-7-carboxylic acids are characterized by very good luminescent properties, enabling them to use in modern technologies such as optoelectronics. Consequently, the obtained azo compounds based on the 8-hydroxyquinoline skeleton can be applied as dyes for fibers which can be used as sorption materials, i.e. for adsorption of heavy metal ions in aqueous solutions.

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