

1. STRESZCZENIE W JEZYKU ANGIELSKIM (ABSTRACT IN ENGLISH)

Development of methods for synthesis of ferrocenyl thioketones and studies on their reactivity

Due to continuing increase of interest in ferrocenyl functionalized compounds on one hand, and the growing importance of thiocarbonyl compounds in organic synthesis on the other one, a study aimed at the exploration of ferrocenyl thioketones as useful substrates for the preparation of more complex sulfur-containing or sulfur-free compounds has been performed.

At the beginning, the performed work was focused on the development of efficient methods for the preparation of ferrocenyl thioketones. To achieve this goal, an efficient procedure for the preparation of ferrocenyl substituted ketones was elaborated. It comprised a modified Friedel-Crafts reaction, in which the *in situ* generated mixed anhydrides of trifluoroacetic acid were used as acetylating agents. Then, the ferrocenyl functionalized ketones were converted into thioketones via oxygen/sulfur exchange by treatment with Lawesson's reagent under standard conditions or with support of the microwave irradiation.

Next, a series of experiments were designed to investigate reactivity and applicability of ferrocenyl thioketones as practically useful building blocks in the organic synthesis aimed at the elaboration of new methods for the preparation of diverse, ferrocenyl functionalized compounds.

Reactions of ferrocenyl thioketones with diaryl diazo compounds and α -diazo ketones, demonstrated that ferrocenyl substituted thioketones, similarly to aromatic analogues, readily undergo the [3+2]-cycloaddition reactions as reactive dipolarophiles. It has been found that the reactions of ferrocenyl thioketones with diazomethane derivatives lead to the corresponding 1,3,4-thiadiazolines, which easily undergo [3+2]-cycloelimination reactions and after elimination of nitrogen, generate reactive thiocarbonyl ylides (thiocarbonyl *S*-methanides). The latter intermediates convert into ferrocenyl substituted thiiranes after spontaneous 1,3-dipolar electrocyclization. Depending on the type of substituents, thiiranes can be isolated or undergo spontaneous desulfurization yielding the corresponding tetrasubstituted ethylene.

Another project comprised the studies on the reactions of the ferrocenyl substituted thioketones with the *in situ* generated cycloaliphatic and aromatic thiocarbonyl *S*-metanides

(‘sulfur centered’ 1,3-dipoles). The main or exclusive product of these transformations were sterically hindered 4,4,5,5-tetrasubstituted 1,3-dithiolanes. Basing on the observed regioselectivity, a non-concerted reaction mechanism with delocalized 1,5-diradical as a key intermediate was formulated.

In extension of the study, ferrocenyl thioketones were reacted with silylated thiocarbonyl *S*-metanides, which were generated via the initial reaction of TMS-diazomethane with the corresponding aromatic thioketones followed by subsequent [3+2]-cycloelimination of nitrogen from the intermediate 1,3,4-thiadiazolines. Reactions of the *in situ* generated, silylated thiocarbonyl ylides with ferrocenyl thioketones led to sterically crowded 2-TMS-1,3-dithiolanes, which upon desilylation by treatment with the fluoride anion underwent [3+2]-cycloelimination yielding tetrasubstituted ethylenes. These reactions occurred with elimination of the dithioformate anion as a side product. Mechanism of this new olefination reaction combines elements of the known Barton-Kellogg and Corey-Winter reactions and it should be considered as one of the most significant achievements of the presented dissertation.

Finally, the known, multi-step Barton-Kellogg olefination, starting with bis(4-methoxyphenyl)diazomethane and an alkyl ferrocenyl thioketone was used to develop an efficient method of synthesis of the known anti-cancer ‘ferrocifenes’ via a ‘sulfur approach’. In addition, new ferrocenyl functionalized dibenzofulvenes were obtained in reactions of ferrocenyl thioketones with aromatic diazo compounds such as diphenyldiazomethane, diazofluorene, and diazo(dibenzo)cycloheptane derivatives. The approach described in the presented dissertation, is based on the application of alkyl ferrocenyl thioketones as basic substrates for the synthesis of diverse mono-ferrocenyl ethylenes is an attractive alternative to the commonly used McMurry coupling reaction.