

STRESZCZENIE W JĘZYKU ANGIELSKIM

New reactions of aryl and hetaryl thioketones with 1,3-dipolar compounds

Due to the growing importance of the sulfur containing heterocycles (medicinal and materials chemistry, crystal engineering) in the current organic chemistry and the progressive interest in reaction mechanisms, a series of [3+2]-cycloaddition reactions based on the exploration of aryl and hetaryl thioketones considered as so called 'superdipolarophilic' reagents, with diverse 1,3-dipoles were designed and performed.

Firstly, reactions of aryl and hetaryl thioketones with *N*-protected (*S*)-2-(diazocetyl)pyrrolidines were investigated. Selected *N*-protected (*S*)-2-(diazocetyl)pyrrolidines were tested in reactions with C=S dipolarophiles as chiral α -oxo diazocompounds. Depending on the structure of the starting thioketone, 1,3-oxathiole or ethylene derivatives were obtained as final products. It was found that the course of the reaction is governed by the structure of the intermediate α -oxo thiocarbonyl ylide, which can undergo either 1,5-electrocyclization to form 1,3-oxathiole derivatives or 1,3-electrocyclization leading to the corresponding thiiranes. Under the applied reaction conditions, latter compounds, underwent spontaneous desulfurization yielding ethylene derivatives which were isolated as pure compounds. In the present study, first applications of the enantiomerically pure diazocompounds in [3+2]-cycloaddition reactions with C=S dipolarophiles are reported.

Hetaryl thioketones were demonstrated to react smoothly with *in situ* generated thiocarbonyl *S*-methanides $R_2C=S=CH_2$. Products obtained in these reactions were identified as sterically crowded 4,4,5,5-tetrasubstituted-1,3-dithiolates, which were formed as the sole or main reaction products. For the investigated reactions, a step-wise mechanism in which the intermediacy of a delocalized diradical playing the key role, was proposed.

In a further study reactions of aryl and hetaryl thioketones with diazomethane derivatives, such as 2-diazopropane, diazoethane, and (trimethylsilyl)diazomethane, were examined. The obtained products were identified as mixtures of isomeric 4,4,5,5-tetrasubstituted-1,3-dithiolanes, thiiranes and/or ethylene. The obtained results allowed to formulate a hypothesis about the competition of concerted versus step-wise mechanisms of the studied [3+2]-cycloadditions.

In extension of the study, hetaryl thioketones were subjected to reactions with (trimethylsilyl)diazomethane TMS-CHN₂ and the initially obtained 2-trimethylsilyl-1,3-dithiolanes were desilylated by treatment with TBAF (tetrabutylammonium fluoride). Upon these conditions, tetraaryl-substituted ethylenes were obtained in high yields. Unexpected formation of these products was explained by the initial formation of the unstable C(2) carbanion, which after formal [3+2]-cycloreversion dissociates into ethylene derivative and dithioformate anion. In this way, a new method

for synthesis of tetraaryl ethylenes has been developed, which can be considered as a useful modification of the well known Barton-Kellogg's olefination reaction.

Finally, the last part of the work, was focused on new reactions of chlorinated thiocarbonyl *S*-imides $\text{Cl}_2\text{C}=\text{S}=\text{NAr}$, formally derived from thiophosgene. It is well known, that chlorinated sulfenamides Cl_3CSNHAr readily undergo dehydrochlorination under basic conditions to form chlorinated thiocarbonyl *S*-imides as reactive intermediates. The study showed that the type of products obtained in the absence of any trapping reagent strongly depends on the structure of the *N*-aryl substituent present in the starting sulfenamide. Thus, the *in situ* generated thiocarbonyl *S*-imide bearing *o*-methylaniline fragment undergo 'head-to-head' dimerization to form the corresponding 1,4,2,3-dithiadiazines with complete regioselectivity. In turn, sulfenamides bearing 2,6-dimethylaniline and 2,4,6-trimethylaniline residues are converted into sulfur *N,N*-diaryldiimides via a cascade of reactions with mesomerically less stabilized diradical species formed initially as a key intermediate.

Pauline Pipiet