Streszczenie w języku angielskim (abstract in English)

Applications of trifluoroacetonitrile imines in the synthesis of nitrogen- and sulfur-containing heterocycles via (3+2)-cycloaddition reactions

During last decades a large number of organofluorine compounds have been demonstrated as an attractive products for practical applications e.g. in the field of pharmaceutical and materials industry. For this reason, a wide range of synthetic methodologies have been developed to access manifold classes of target fluoroorganics. In this context, (3+2)-cycloaddition reactions (so-called Huisgen reactions) of appropriate fluorinated components (i.e. 1,3-dipoles and/or dipolarophiles) are considered extremely useful strategy towards five-membered, polyfunctionalized heterocyclic systems.

In the submitted PhD thesis, special attention was paid to the chemistry of trifluoroacetonitrile imines recognized as readily available class of fluorinated 1,3-dipoles, typically generated *in situ* starting with the appropriate hydrazonoyl bromides. The title nitrile imines were tested in (3+2)-cycloaddition reactions with such dipolarophiles as thioketones, enol ethers and alkoxyallenes, to afford the expected trifluoromethylated heterocycles including thiadiazoline, pyrazole and pyrazoline derivatives, respectively. Thus, a series of selected (het)aryl and (cyclo)aliphatic thioketones (C=S superdipolarophiles) was demonstrated to smoothly undergo fully regioselective (3+2)-cycloaddition reactions with fluorinated nitrile imines leading to a new class of CF_3-functionalized 2,3-dihydro-1,3,4-thiadiazole derivatives. In both cases, a stepwise reaction pathway of the studied cycloaddition was proposed, and the structure-property relationships were examined for the series. As always, the structure of new compounds was confirmed on the basis of spectroscopic methods supplemented by X-ray measurements.

In continuation, electron-rich enol ethers were demonstrated as highly useful synthetic acetylene equivalents in the reactions with fluorinated nitrile imines to give desired 3-trifluoromethylated pyrazoles, including well-known antitumor agent *SC-560*. Noteworthy, the electronically biased nature of the aforementioned class of dipolarophiles assured complete regioselectivity of the studied 1,3-dipolar cycloaddition. Selected transformations of hydroxy-functionalized products *via* (a) selective C(5)-deprotonation followed by nucleophilic substitution/addition, (b) Suzuki-Miyaura and Sonogashira cross-coupling reactions and (c) intramolecular CH-arylations, opened up straightforward access to more complex fluorinated pyrazole-based systems including polycyclic derivatives.

Finally, a general protocol for the preparation of bistrifluoromethylated spirobipyrazolines was developed by using title 1,3-dipoles and alkoxyallenes (bearing both enol ether and ethylene dipolarophilic centres) as reaction partners. The final products were isolated as single *anti*-configured diastereoisomers formed through a highly regio- and stereoselective formal double (3+2)-cycloaddition. Based on the observed reaction outcome and taking into account unusual electronic properties of the substrates (inverse electron demand), a step-wise mechanism *via* allylic-like intermediate zwitterion was postulated.

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