Abstract

Within the scope of the present thesis miscellaneous reactions of 1,3-dithiane-derivatives were investigated. During the master's thesis a methodology for the hydrolysis of 1,3-dithianes to their parent carbonyl compounds via their corresponding monosulfoxides in acidic acetonitrile was developed. In continuation of this work, we initiated an investigation of the acid catalyzed cleavage of α-hydroxy-1,3-dithianes, which are important substrates in organic synthesis. In addition, rearrangement reactions of α-hydroxy-1,3-dithianes under acidic conditions and a possible one-carbon-homologation reaction of aldehydes to carboxylic acids via keten dithioacetal sulfoxides as intermediates was studied. A smaller part of this thesis dealt with the isolation and structure elucidation of natural products from plants and endophytic fungi.

The investigated rearrangement reactions gave in some cases surprising results. Secondary benzylic or aliphatic α-hydroxydithianes rearrange to α-thioketones **30** - **32** when treated with acid. Related tertiary alcohols eliminated to the corresponding ketene dithioacetals (**4** and **7**) and in some cases gave the open-chained vinyl sulfides (**34** and **35**). Allylic α-hydroxydithianes formed the thioesters and two tertiary alcohols (**10** and **11**) underwent deoxygenation to the respective dithianes **39** and **40**.

With the developed cleavage methodology, α-hydroxy-1,3-dithianes with a tertiary hydroxy group gave the desired α-hydroxyaldehydes in good yields (**65**, **66** and **68**). The cleavage of two other tertiary alcohols resulted in the formation of hydroxy acetone derivative **63** and aldehyde hydrate **67**, which suggested the intial formation of the corresponding α-hydroxyaldehydes. The method failed in cleaving secondary alcohols. Surprisingly, the rearrangement products **30** - **32** were obtained, which could be arisen from a deoxygenation of the sulfoxide unit and subsequent rearrangement reaction.

Aldehydes and ketones were converted into the corresponding homologous carboxylic acids in two steps by treatment with 2-(trimethylsilyl)-1,3-dithiane-1-oxide. A modified Peterson olefination of the carbonyl compounds gave the ketene dithioacetal sulfoxides

that were readily cleaved in acidic acetonitrile to give the required carboxylic acids **52** - **61**. Notably, no further purification step (e. g. column chromatography) is necessary during the work up procedure of the carboxylic acids.

The investigations of the plant *Zanthoxylum rhetsa* and the fungus 8908 (*Aureobasidium* sp.) resulted in addtition to the structure elucidation of the known bioactive compounds 6-acetonyldihydrochelerythrine, 1-methoxy-7,8-dehydrorutaecarpine, Arnottianamide, Skimmianine, indole-3-carboxylic acid, *p*-hydroxy benzoic acid and *p*-hydroxy mandelic acid in the disovery of the new compound 5,12-dihydro-12-oxoindolo[2,1-b]quinazoline-6-carboxylic acid.