Abstract

(Numbered compounds are represented by their molecular formulas on pages 110 and 111. An abstract in German is found on pages 108 and 110)

The main part of this thesis deals with the preparation of a cyclic, optically active carbodiimide **6**, which should be suited for the use as a chiral auxiliary in peptide synthesis and other condensation reactions.

An additional important aspect is related to the allene-like structure of the carbodiimides:

If the barrier to inversion at nitrogen would be sufficiently high due to ring strain in the system diastereomers of **6** could be separated.

The preparation of the compound **6** was tried in different ways. The first approach, which was based on the dehydrosulfurization of the cyclic thiourea **27**, failed. It was neither possible to prepare the compound **27** by a cyclization of the diamin **26** with thiophosgene nor by a intramolecular biaryl-coupling of the acyclic thiourea **35b**.

On the other hand Ulrich's method to prepare cyclic carbodiimides proved to be successful. The eight-membered-ring of the amid-oxime **51** was synthesized from the seven-membered-ring cyclic ketone **42** via the eight-membered-ring lactam **45** and the corresponding lactim methyl ether **47**. Finally the carbodiimide **6** was available by conversion of the amidoxime **51** to the corres-ponding mesylate **52** and a subsequent Tiemann rearrangement.

While the infrared spectrum of the crude product showed the typical carbodiimide-bands, the purification yielded only the cyclic

urea **53**, which was very likely the product of the addition of water to the carbodiimide. This high reactivity and with that associated difficulty to isolate the carbodiimide **6** gave rise to stop the investigation of **6**.

Another method was used to prepare the 14-membered-ring cyclic bis-carbodiimide **67**. Indeed, this cyclic carbodiimide is not strained, but the two binaphthyl-units should bring about the optical activity. Thus, the bis-carbodiimide was obtained by the reaction of the bis-isothiocyanate with the corresponding bis-iminophosphoran via an Aza-Wittig-reaction.

Unfortunately, the bis-carbodiimide **67** was contaminated with triphenylphosphinsulfide, the by-product of the Aza-Wittig-reaction. Removal of this impurity was difficult. Moreover, this synthetic method allowed only the preparation of small quantities of the bis-carbodiimide. Therefore the search was abandoned for a useful application for these new carbodiimides.

Finally, an unexpected reaction between the strained cycloalkyne, the 3,3,6,6-tetramethyl-1-thia-4-cycloalkyne **85**, and methylisothiocyanate was observed. The resulting compounds of this reaction and an analogous with phenylisothiocyanate were the spiro-heterocycles **87** and **93**,res.. These 1:3 adducts of cycloalkyne and isothiocyanates are typical products of the reaction of nucleophilic singulett-carbenes with isothiocyanates. Thus, the formation of the compounds **87** and **93** is due to a [3+2]-cycloaddition of the alkyne and a isothiocyanate. Then the reaction proceeded with the trapping of the 1,3-thiazol-2-ylidene **98** by two further molecules of methylisothiocyanate to yield **87** and **93**, res.. Attempts to

accomplish an analogous [3+2]-cycloaddition with carbodiimides failed.

In conclusion, the preparation of two new cyclic carbodiimides **6** and **67** as well as the [3+2]-cycloaddition of a strained cycloalkyne and methylisothiocyanate to the nucleophilic carbene **98** succeeded for the first time.