7. Summary

In this work it was shown that the use of Evans auxiliaries in aldol addition reactions is limited by ringopening reactions. The structures of the ringopening products were proved by X-ray analysis.

Imidazolidinone **1** (and it's hydrogenated variation **3**) was found to be an auxiliary that combines the useful characteristics of Evans auxiliaries with greater stability especially against nucleophilic attack at the carbonyl group. The hydrogenated auxiliary **3** showed excellent selectivity in the aldol addition reaction at 4-*t*butylcyclohexanone but not in the case of the carbacyclin precursor. However it has the disadvantages of lower yields, difficult removal of auxiliary and higher price.

Using the new auxiliary **1** and following way I chiral olefin **8** was prepared from 4-*t*butylcyclohexanone in very good yield. Contrary to expectation the optical purity of **8** was only 82 % ee. Racemization of aldol addition product **5A** under the basic conditions of auxiliary cleavage appeared to be the reason. The usage of other techniques of cleavage (lower temperature, LiOOH instead of LiOH, $Ti(OEt)_4$ etc.) could probably prevent racemization.

Application of the olefination sequence to a carbacyclin precursor was very successful. The optical purity of olefin **13A** reached 97.6 % de. Due to this result almost no racemization occured during auxiliary removal.

Extension of the sequence was very promising until the auxiliary removal step (good yields, only one diastereomer). But even with only the ethyl group instead of methyl it is impossible to remove the auxiliary (usually retroaldol is observed). The most probable reason for this behaviour seems to be steric hindrance. The possibility to adapt this sequence to larger substituents should be a good reason for further studies on the auxiliary removal. In addition it could be examined whether larger substituents are possible with other molecules like for example the carbacyclin precursor.

Also starting from 4-*t*butylcyclohexanone a synthesis of endocyclic olefins **37A** and **37B** was developed. It leads to an isocarbacyclin precursor in good yield. The elimination reaction produces more (Z)-olefin than (E)-olefin but this can be changed by using the auxiliary's enantiomer.

Though for carbacyclins as well as for isocarbacyclins Gais and coworkers recently published some good syntheses[104] with high yields and high optical purities (up to 98% de).

As a solution to the problems observed on way I (racemization, larger substituents) the alternative way II was examined. Because of the different structure racemisation is almost

[104] H.-J. Gais, G. Schmiedl, R.K.L. Ossenkamp, Liebigs Ann. **1997**, 2419-2431; R.K.L. Ossenkamp, H.-J. Gais, Liebigs Ann. **1997**, 2433-2441; I. Vaulont, H.-J. Gais, N. Reuter, E. Schmitz, R.K.L. Ossenkamp, Eur. J. Org. Chem. **1998**, 1, 805-827; J. Bund, H.-J. Gais, E. Schmitz, I. Erdelmeier, G. Raabe, Eur. J. Org. Chem. **1998**, 1, 1319-1335.

impossible and the synthesis of larger substituents seems to be possible. Following way II axial chiral olefin **(R)-8** was produced in very high optical purity (98 % ee) for the first time. A synthesis of the (S)-enantiomer with the same optical purity would be possible in the same way using auxiliary **1**'s enantiomer.

No racemization and the probable possibility to introduce larger substituents are the main arguments for using way II in a synthesis of carbacyclin precursors.