Abstract

In this thesis, the synthesis of new azolium salts as precursors for carbenes is presented. They all have in common the structural motive of two *N*-aryl substituents which at their *ortho*-positions bear sterically demanding residues like alkylgroups or bromine and in one case a nitro group. With the last being an exception, they in addition fulfill the criterium of being a Dispersion Energy Donor (DED). Thus, the carbenes are best suited for the Umpolung of α,β-unsaturated aldehydes to homoenolates. In the case of bromine, this is combined with its electron withdrawing property. In some of the other salts, additional nitro groups provide a combination of the effects. Now, as an equivalent to the carbene precursors with electron poor substituents which have proved themselves in classical Umpolung reactions like the benzoin condensation and Stetter reaction, also such are available, which are tailored for homoenolate chemistry. In addition, two azolium salts with chiral versions of the *N*-aryl groups with aliphatic substituents only, which are well established in homoenolate chemistry, have been synthesized. The carbene precursors have been provided to other members of the research group for testing in catalytic reactions and to some extent their catalytic activity has been examined within this thesis in redox esterification and the synthesis of nepetalactone. An emphasis of the research in catalysis however was put on the acyloin condensation of 2-ethylhexanal. It was found that not only the known factor of steric crowding in the transition state, but also the tautomerization of the Breslow intermediate, which has been observed with SIPr, is a reason for this reaction being for a long time and being still an unsolved problem in the field of Umpolung catalysis. As a supplement the reactivity of carbenes towards methanol and benzaldehyde, the possibility of isolating a Breslow intermediate transition metal complex and the feasibility of a cyclovoltametric and UV/VIS spectroscopic study of Breslow intermediates has been investigated.