PREFACE

Organocatalysis can be defined as the acceleration of chemical reactions by the addition of a substoichiometric quantity of organic compound which does not contain an inorganic element. Organocatalysis has several advantages over transition metal catalysis and enzymatic transformations. Presently organocatalysis is an area of great interest in synthetic organic chemistry. The catalysts are usually robust, inexpensive and readily available small organic molecules. In this scenario, \(N\)-heterocyclic carbenes (NHCs) have been studied for their ability to catalyze organic reactions. In recent years NHCs have assumed importance due to the progress made in umpolung reactivity of aldehydes and especially in generating homoenolates, a species containing anionic carbon \(\beta\)- to a carbonyl group. Several research groups including our own have employed this three carbon synthon in the synthesis of various carbon– and heterocycles.

In the context of our continuing interest in the chemistry of NHCs, we have carried out a detailed and systematic investigation of the reactivity of the homoenololate, generated in situ from enals and NHCs, towards various electrophiles. The results of our studies in this direction constitute the subject matter of the thesis entitled “Exploration of Novel Organic Reactions Catalyzed by Nucleophilic Heterocyclic Carbenes (NHCs)”.

The thesis is composed of five chapters which are presented as independent units and therefore the structure formulae, schemes, figures and references are numbered chapterwise.

Exploration of the reactivity of NHC-bound homoenolate towards various electrophiles for the construction of novel carbon-carbon and carbon-heteroatom bonds was selected as the general theme of this thesis. To put things in perspective, an overview of the chemistry of NHCs and homoenolates is provided in the first chapter of the thesis and the definition of the present research problem is also provided in this chapter.

The second chapter presents the results of our investigations of the reaction of homoenololate, generated from enal by NHC, with various substituted
nitrostyrenes. General information on the experimental procedures is given in this chapter.

The reaction of NHC with chromene-3-carboxaldehyde, which revealed a novel reactivity pattern, constitutes the subject matter of the third chapter of the thesis. Our original objective was to extend the homoenolate generation to endocyclic systems, but the reaction took an unexpected path leading to an efficient synthesis of 3-alkylcoumarins.

The results of our investigations on the intramolecular reaction of NHC-homoenoalte with α,β-unsaturated esters, leading to the facile synthesis of 4-alkylcoumarin derivatives are disclosed in the fourth chapter.

The final chapter describes an unexpected transformation of 1,6-disubstituted hexa-1,5-diene-3,4-diones (Cinnamils) catalyzed by NHCs to vinylfulvenes and terphenyls.

A summary of the work is given towards the end of the thesis.