

A B S T R A C T

Investigations embodied in this thesis entitled 'SYNTHETIC STUDIES ON INTRAMOLECULAR ALDER ENE REACTION, INTRAMOLECULAR DIELS-ALDER REACTION AND HERZ-FAVORSKII REARRANGEMENT' have been carried out, in part, with a view to developing new and efficient carbocyclizations with special emphasis on stereoselectivity in the ring forming processes. The relatively dormant Herz-Favorskii rearrangement has been studied and utility of the known end products of this rearrangement has been documented by efficient transformation into advanced intermediates for a few selected biologically active complex natural products. The content of the dissertation is divided into three chapters. Chapter I entitled 'Synthetic Studies on Alder Ene Reactions' is subdivided into two parts. Part A incorporates a detailed study on the feasibility of carrying out Type-I intramolecular ene reaction of activated 1,6-dienes in the presence of Lewis acids leading to vicinally substituted cyclopentanes. In part B, a general and highly stereoselective route to *cis*-1,2-disubstituted cyclopentanoic allylsilanes based on thermal intramolecular ene reactions of suitably functionalized homoallylsilanes is presented. In addition, extension of this methodology to the synthesis of functionalized diquinanes as well as a key intermediate for a fungal metabolite, e.g. (+)-hirsutene has been documented. Chapter II presents some synthetic studies on intramolecular Diels-Alder (IMDA) reaction of functionalized 1,3-diketones. A new variant of IMDA reaction under FVP conditions using enolic 1,3-diketone as diene partner for rapid assembly of a variety of carbocyclic structures for eventual exploitation in natural products synthesis is described. Additionally attempts were made to carry out the above cycloaddition reaction under relatively milder conditions

using a silicon modified strategy. Chapter III deals with some synthetic studies on Herz-Favorskii rearrangement and consists of two parts. In part A, a highly stereocontrolled route to a densely functionalized diquinane intermediate for its further elaboration to targeted natural products, e.g. pentalenolactones (E & G) is described. Part B concerns a reinvestigation of Herz-Favorskii rearrangement of cyclopentadiene-benzoquinone epoxide in view of the wide discrepancy between the reported and observed physical data of a derivative of the rearrangement product. In addition, this section also incorporates the preliminary work on the transformation of a selected Herz-Favorskii rearrangement product into a bridged lactam, a key intermediate in a projected synthesis of an alkaloid e.g. pumiliotoxin-C, and a novel one - carbon degradation of this lactam during an attempted ozonolysis experiment.

Key words : ene, stereoselectivity, allylsilane, carbocyclisation, rearrangement, diquinane, cyclopentane.