ABSTRACT

Investigations embodied in this dissertation entitled "**Studies on Alder-Ene Reactions And σ-Allylmetallics of Silicon : Total Synthesis of Cyclopentanoid Natural Products**" have been carried out mainly with a view to developing new and efficient carbocyclization processes with special emphasis on diastereoselectivity and diastereofacial selectivity in the ring forming step. The content of the thesis is divided into two parts of which part I is further subdivided into three chapters.

Chapter 1 describes an intramolecular ene approach to stereochemical control over contiguous stereogenic centres, where three centres are created with very high level of both diastereofacial selectivity and diastereoselectivity by the influence of an oxygen substituent as a stereodirecting resident group in the ene component. In addition, this chapter also incorporates the preliminary work on the transformation of an ene adduct into a diquinane, a key intermediate in a projected synthesis of a cyclopentanoid natural product, e.g., coriolin.

Chapter 2 describes an application of the foregoing ene cyclization methodology for the stereocontrolled synthesis of (±)-methyl cucurbate, a plant growth regulator and (±)-methyl epijasmonate, the odoriferous component of jasmine oil.

A spin-off from this work is a brief study on the possibility of using homoallylic silanes as activated ene donors and this is discussed in Chapter 3.

Part II describes a new and only methodology for transforming an acyclic β-silyl ketones into allylic silanes. This protocol has taken advantage of the ability of TMS group to direct Bamford-Stevens reaction in β-trimethylsilyl N-aziridinylimines in presence or absence of rhodium acetate as a catalyst. The nearly total elimination of homoallylsilanes (and other TMS-containing by-products) in favour of allylsilanes in the Rh^{II}-catalysed decomposition of β-silylated N-aziridinylimines has been discovered. Incidentally, this methodology was needed to carry out a specific transformation in a projected synthesis of a novel cyclopentanoid natural product, e.g., oreodaphnenol.

Key Words : *Ene, diastereofacial selectivity, diastereoselectivity, allylsilane, carbocyclization, diquinane, carbenes, homoallylsilanes, rhodium carbenoids.*