

ABSTRACT

Investigations embodied in the thesis entitled "SYNTHETIC STUDIES ON ALLYLIC SILANES" have been carried out with a view to developing new and efficient methods for the preparation of functionalized and stereo-defined allylsilanes which enjoy widespread utility as reagents and intermediates in organic synthesis. The content of this dissertation is divided into FIVE chapters. In Chapter I a brief overview of the chemistry of stereohomogeneous allylsilanes has been presented. Chapter II concerns a thorough study of the scope and limitations of a recently developed protocol in this laboratory for the synthesis of terminal E-allylsilanes. In particular, the method has been applied with some success to the synthesis of the difficultly accessible stereohomogeneous unsymmetrically substituted allylic silanes. During the course of this work some unusual observations were made which have been fully highlighted in the text. Chapter III explores the possibilities of a direct synthesis of allylsilanes from β -seleno- γ -silyl alcohols obtainable from interaction of aldehydes and ketones with 1-lithio-2-(trimethylsilyl)ethyl phenyl selenide, the latter being available from 1-selenophenyl-2-(trimethylsilyl)ethyl phenyl selenide by Se/Li exchange with n-BuLi. In this section the successful preparation of 1-lithio-2-(trimethylsilyl)ethyl phenyl selenide, its reactions with carbonyl compounds and the unprecedented 1,1- and 1,2-elimination reactions which precluded the synthesis of its tin analog has been discussed. Chapter IV consists of two parts. In Part A, a general and highly stereoselective route

to cis-1,2-disubstituted cyclopentanoid allylsilanes based on thermal intramolecular ene reactions of suitably functionalized homoallylsilanes is presented. In addition, application of cyclopentanoid allylsilanes to the synthesis of some functionalized diquinanes has also been documented. Part B deals with the results of a preliminary investigation on the successful preparation of a heterocyclic allylic silane based on aza-ene cyclization of a transient acylazacarboxylate with a built-in homoallylsilane unit as the ene donor. Finally, the last chapter, i.e. Chapter V, concerns a preliminary investigation on the development of a new approach to stereoselective synthesis of acyclic 1,2- and 1,3-diols via allylic silanes.

Key Words : ene, stereoselectivity, allylsilane, carbocyclization, diquinane, cyclopentane.
