ABSTRACT

Recently, the use of organosilicon compounds as reagents and synthons directed toward the construction of natural products has become a powerful strategy in organic synthesis. Among all the silicon-based carbon nucleophiles now in use, allylsilanes occupy a premier place in terms of their numerous applications in this arena. These species are endowed with highly nucleophilic π-systems and are yet stable toward a wide range of reagents and most of the common functional group manipulations, such as saponification, reduction, oxidation, etc. On the other hand, they can be readily activated by so-called initiators (electrophiles), which are generated in situ by addition of a Lewis acid. Besides allylation reaction of allylsilanes can also be carried out under nucleophilic conditions usually in the presence of a fluoride ion.

In this laboratory, a comprehensive programme was initiated a few years ago to develop new and efficient methods for the preparation of functionalized allylsilanes and demonstrate their utility in the synthesis of structurally intriguing and/or biologically significant natural products. The thesis entitled **"Use of Allylsilanes in the Synthesis of Natural Products: Synthetic Efforts Toward Hydroxylated Pyrrolizidine Alkaloids and a Novel 5-8 Fused Sesquiterpene, Asteriscanolide"** is an effort in this direction and is divided into two parts, part-I and part-II. Both part-I and part-II are subdivided into two sections.

Part I:

Section A: This section deals with a short review summarizing various approaches to the synthesis of asteriscanolide, a novel 5-8 fused sesquiterpene of enormous contemporary interest.

Section B: In this section, a short synthesis of (7*RS*,10*RS*,11*RS*)-8,8-dimethyl-7-(*tert*butyldiphenyl)silyloxybicyclo[6.3.0]undec-5-en-2-one, an advanced intermediate for asteriscanolide is presented. This work entails a series of highly diastereoselective reactions including a 5-(3,4) ene cyclization, an allylsilane induced lactone formation and a [3,3] sigmatropic rearrangement in the key steps of the synthesis.

Part II:

Section A: This section deals with a brief review on recent advances in the synthesis of hydroxylated pyrrolizidine alkaloids.

Section B: This section describes development of an aza-ene based route to two 5-membered heterocycles, namely N-carbomethoxyamino-5-[*E*-3-(trimethyl silyl)-1-propenyl] –2-pyrrolidinone and 5-[*E*-3-(trimehtylsilyl)-1-propenyl]-2-pyrrolidinone, each of which has a built-in allylsilane terminator. The former heterocycle was used in a model study to probe the level of diastereoselectivity of an allylsilane mediated ring forming reaction leading to a fused tetrahydropyrazole. This work paved the way for use of the second heterocycle in a synthesis of (1*SR*,2*SR*,7a*SR*)-1-ethenyl-2-hydroxy-5-oxo-hexahydro-1*H*-pyrrolizine, an advanced intermediate for a number of pyrrolizidine alkaloids, e.g. trachelanthamidine and macronecine.