Abstract

The [3+2] cycloaddition reactions of allylsilanes occupy a very special position in the chemistry of organosilicon compounds. Various types of electrophiles, such as electron-deficient C=C π-bonds, activated C=N π-bonds, C=O π-bonds, etc. have been studied extensively in this process but, N=N π-bonds somehow failed to gain the attention of organic chemists. This dissertation "**On the [3+2] Annulation of Allylsilanes with *N*-Phenyltriazolinedione: Enantio- and Diastereoselective Synthesis of Urazoles and *cis*-1,3-Diaminocyclitols**" is a documentation of the systematic efforts to fill this void. The thesis is divided into three chapters. Chapter 1 is a brief overview on the [3+2] annulation of allylsilanes. In Chapter 2, the [3+2] annulation reactions of acyclic allysilanes with 4-phenyltriazolinedione (PTAD), which remained dormant for almost one and half decades, is reinvestigated. We have shown that only one alkyl group in the allylic position of the allylsilanes is required to trigger the [3+2] annulation pathway which gives rapid access to variously substituted urazoles in a highly enantio- and diastereoselective manner. Chapter 3 describes an extension of this chemistry using cyclic allylsilanes. We have shown that both 4- and 5-membered cyclic *β*-hydroxy allysilanes are good substrates for the [3+2] annulation process with PTAD. The [3+2] adducts produced thereof were tailored into various 4- and 5-membered enantioenriched aminocyclitols with full stereochemical control of up to four contiguous stereogenic centres. We, however, faced tremendous difficulty during this process; oxidation of the C-Si bond of the cycloadducts (Tamao-Fleming oxidation) turned out to be a tough task and we were forced to modify the whole strategy taking *o*-methoxyphenyl group on silicon in the place of phenyl group.

Keywords: Allylsilane, [3+2] cycloaddition, PTAD, urazoles, aminocyclitols, Tamao-Fleming oxidation