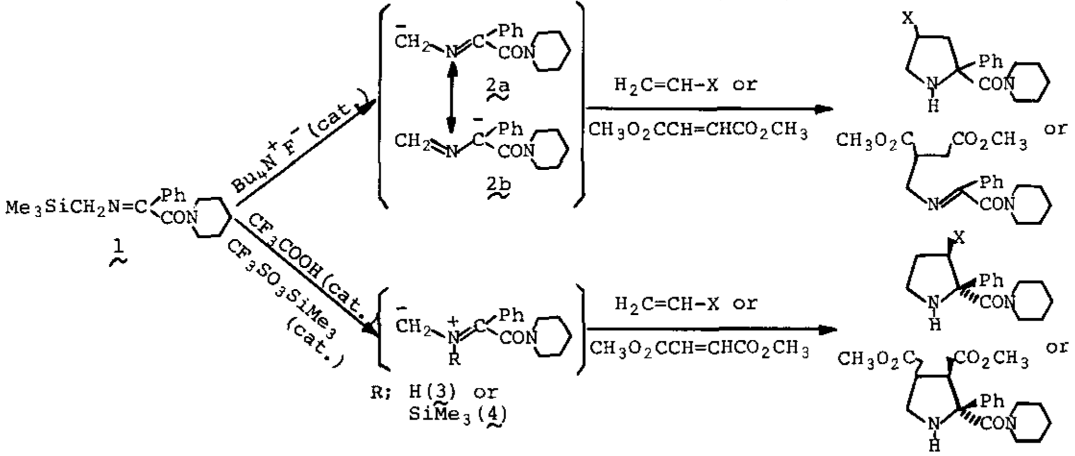
[3+2]CYCLOADDITION UTILIZING THE CHARACTARISTICS OF ORGANIC SILICON COMPOUNDS—— STUDY ON REGIO- AND STEREOSELECTIVITY OF PYRROLIDINE RING FORMATION

Nobuyuki Imai, Hiromi Kotaki, Yoshiyasu Terao, and Kazuo Achiwa
Shizuoka College of Pharmacy, 2-2-1 Oshika, Shizuoka 422, Japan

As an application of our studies on the 1,3-dipolar cycloadditions leading to formation of pyrrolidine and 2,5-dihydropyrrole nuclei, their regio- and stereoselectivities were examined in connection with erythrinane alkaloids and azaprostacyclines syntheses.

[A] 1,3-Cycloaddition of N-[α-(piperidinocarbonyl)benzylidene]trimethylsilylmethylamine (1) with Olefinic and Acetylenic Dipolarophiles.

Reaction of 1 with olefinic and acetylenic dipolarophiles in the presence of catalytic amount of tetrabutylammonium fluoride gave the products derived from the intermediary iminomethylene carbanions (2a or 2b) depending on the structure of used reagents. On the other hand, the reaction catalyzed by trifluoroacetic acid or trimethylsilyl triflate yielded regiospecifically the corresponding products derived from the intermediary methyleneiminium ylides (3 or 4) as shown bellow.



[B] 1,3-Dipolar Cycloaddition of N-benzyl-N-(methoxymethyl)trimethylsilylmethylamine (5) with Olefinic and Acetylenic Dipolarophiles.

This reaction proceeded smoothly to give 3,4- or 3-substituted pyrrolidines and 2,5-dihydropyrroles with retention of the olefin-stereochemistry.