TESIS DOCTORAL

The *N*-Cyclopropylimine-1-pyrroline Rearrangement

Alberto Soldevilla Armas

ABSTRACT

In this work, it has been studied the rearrangement of *N*-cyclopropylimines to 1-pyrrolines which involves a type of aza(vinylcyclopropane-cyclopentene) rearrangement. It has been explored in its photochemical fashion, which constitutes a new reaction not described up to date, as well as the thermal rearrangement, which has been previously explored only in a very limited extent. As a result, it has been synthesized a number of 1-pyrrolines in a quite simple way, with synthetically useful yields, exploring different patterns of substitution on the *N*-cyclopropylimine template.

Also, it has been studied the mechanism of the photoprocess, using a classical approach (products study, kinetics, solvent effect, selectivity, etc.) and from a theoretical point of view, to calculate energies of excited states, potential energy surfaces and conical intersections.

As a result of this combined study, it can be concluded a whole mechanistic proposal for the photorearrangement: a non-concerted direct process without reaction intermediates (thus, an ultrarrapid process in the time scale of picoseconds), but with diradical character in the calculated structures in the potential energy surface of the S1 state. From that state, the structure of the conical intersection between S1 and S0 determines the efficiency of the reaction and the product distribution (deactivation of the excited state, isomerization of the cyclopropane, rearrangement to the pyrroline and the selectivity of the latter process).

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