

Abstract

Our project, the development of a new strategy for the synthesis of ten membered lactones, led us to study, in a first time, the cycloaddition of cyclic enol ethers and enoxysilanes with electrodefficient 1-oxabutadienes. Two complementary catalytic conditions [Eu(fod)₃ and SnCl₄] were successfully used, and the particular structure of the bicyclic adducts obtained allowed us to propose a reaction mechanism for each catalytic mode. Using the right heterodiene and dienophile, we've reached high yields and stereoselectivities.

The potential of these hetero Diels-Alder reaction products was next illustrated by the six steps synthesis of a model 9-decanolide. Starting from a diastereomerically pure adduct, coming from the cycloaddition of 1-methoxycyclohexene with methyl *tert*-butoxymethylenepyruvate, we managed, after some transformations and the radical oxidation of a bicyclic lactol under UV irradiation and in the presence of iodine, to prepare an iodo-9-decanolide.

Then, we've attempted to carry out the synthesis of two natural macrolactones (decarestrictines J and H) according to the same strategy. In order to succeed in this project, a new dienophile (1,5-dimethoxycyclohexa-1,4-diene) has been engaged. This led us to search for the best protecting group for the carbonyl group of the decarestrictines J and H. Finally, we succeeded to prepare a precursor very close to our goal using a protection as a dithiane for this group.

Key words :

Hetero cycloaddition

1-Oxabutadiene

Diels-Alder

Mukaiyama-Michael

Enoxysilanes

Decarestrictines

Enol ethers

9-Decanolide

Eu(fod)₃

SnCl₄