

Reactivity Comparison of D-Glucose-Derived Dienophiles. Analysis of the Conformational and Electronic Properties

S. C. Pellegrinet¹, M. T. Baumgartner² and R.A. Spanevello¹

¹Instituto de Química Orgánica de Síntesis (IQUIOS)- CONICET; Facultad de Ciencias Bioquímicas y Farmacéuticas-U.N.R. Suipacha 531, Rosario (2000), Argentina

E-mail: iquiosra@citynet.net.ar

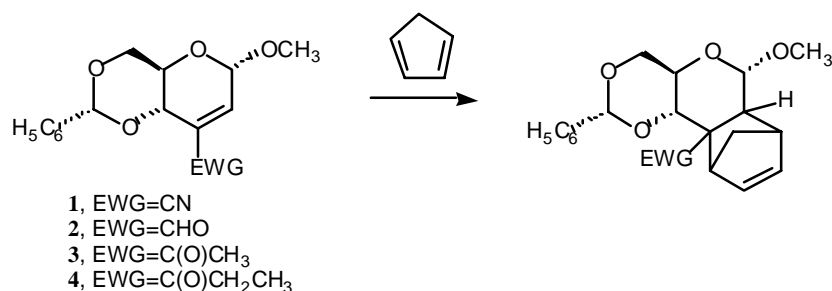
²INFIQC - Departamento de Química Orgánica, Fac. Ciencias Químicas- U.N.C. Ciudad Universitaria, (5000) Córdoba, Argentina

E-mail: tere@dqo.fcq.unc.edu.ar

Abstract: Semiempirical calculations were performed to carry out a conformational analysis for carbohydrate-derived dienophiles **1-4**. For α,β -unsaturated carbonylic compounds **2-4**, a good correlation between Diels-Alder reactivity with calculated values for LUMO energies was observed.

Introduction

As part of our studies on the Diels-Alder reactions of D-glucose-derived dienophiles with cyclopentadiene,[1,2] we undertook a theoretical investigation on the conformational and electronic properties of the dienophilic structures **1-4**.



The application of the frontier molecular orbital theory could be of interest since the reactivity of the dienophiles in normal Diels-Alder reaction could be correlated with their LUMO energies. This kind of theoretical treatment has been used to make important qualitative studies on the reactivity and outcome of cycloaddition reactions in different dienophilic systems, including some sugar-derived dienophiles.[3]

Experimental

The search for the minimum on the potential energy surface for the dienophiles **1-4** and cyclopentadiene were carried out using the semiempirical program AMPAC version 2.1. The calculations were performed at the Restricted Hartree–Fock (RHF) AM1 level of theory. The stationary points were obtained through adequate algorithms and characterized through a hessian matrix calculation. Finally, the relative stability and the LUMO values of the different conformers corresponding to each dienophile were analyzed.

Results and Discussion

The comparison of the energy differences between HOMO_{diene}-LUMO_{dienophile} versus HOMO_{dienophile}-LUMO_{diene} demonstrated that the frontier molecular orbitals for the processes under study were the HOMO of the diene and the LUMO of the dienophile. These results confirmed that the Diels–Alder reactions were normal ones. A comparative analysis of the LUMO energies for the series of α,β -unsaturated carbonylic dienophiles showed that longer side chain favored the existence of non coplanar structures, and this effect is in concordance with the spectroscopic data recorded from these compounds. Furthermore it was observed an increased of the LUMO energies, thus, diminishing the reaction rate. This fact is sustained by the experimental results which indicated that longer side chains correspond to lower dienophile reactivity.

Acknowledgements: CONICET, International Foundation for Science, Universidad Nacional de Rosario, Agencia Nacional de Promoción Científica y Tecnológica, CONICOR y SECyT-U.N.C.

References and Notes

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