

Stereochemical and ^{13}C NMR study in order to characterize intermediates obtained by cyclisation of diisoxazoledilactone

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INTRODUCTION

A ring-expansion synthesis from bicyclic enol-ethers can lead to surprises. From a standard procedure to synthesize (\pm)-pirenophorin,¹ a unique molecule has been found, a diisoxazoledilactone (Figure 1).

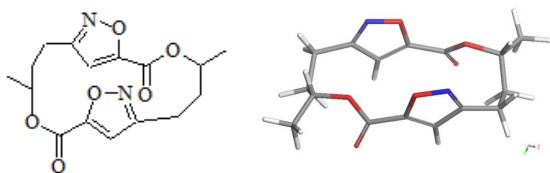


Figure 1. Diisoxazoledilactone and its 3D view

Racemic mixtures as dioximedilactones, diketodialactones and diisoxazoledilactone were observed on intermediate steps. Its components were characterized by chromatographic and spectrometric methods.

In order to explain the formation of the oxazolinic rings, molecular dynamics (MD), Austin Model 1 (AM1)², density functional theory (DFT) and AM1 ^{13}C NMR simulations were performed⁴ in order to characterize stereochemistry of the intermediates and to verify if it is possible to predict isomerism from the chemical shifts variations by AM1.

RESULTS AND DISCUSSION

Its chemical precursors are the stereoisomers of dioximedilactone (Figure 2), a molecule with four assimetric centers, which complicates the elucidation of the precise mechanism of the intramolecular cyclisation.

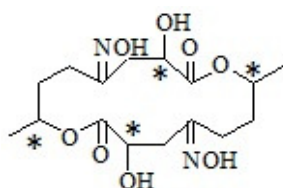


Figure 2. Dioximedilactone

The isomers of the raw material and products were simulated first by molecular dynamics at 650 K to reorganize their molecular structures, then by the AM1 semi-empirical Hamiltonian program to prepare for the ab initio method, PW91 with DNP basis set (DFT).³ ^{13}C NMR calculations were performed using AM1.

CONCLUSION

The adopted methodology was useful not only to elucidate the mechanism of oxazolinic rings' formation, but to demonstrate the compatibility of the simulated ^{13}C NMR chemical shifts with the experimental data.

The possibility to use this method to verify the stereochemistry of components of racemic mixtures can lead to significant progress on the determination of regiochemistry and stereochemistry of different chemical reactions.

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REFERENCES

- Costa, M. B. Tese de Doutorado em Química Orgânica - Universidade de Brasília. **2006**
- Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. J Am Chem Soc. **1985**, 107, 3902.
- Delley, B. In Density Functional Methods in Chemistry; Labanowski, J. K.; Andzelm, J. W., Eds.; Springer: Berlin, 1991; p 101.
- Materials Studio S/W. Acelrys, Inc., 10188 Telesis Court, Suite 100, San Diego, CA 92121, USA.