XX REUNIÓN NACIONAL DE ESPECTROSCOPÍA

IV CONGRESO IBÉRICO DE ESPECTROSCOPÍA

LIBRO DE RESÚMENES

Ciudad Real, 10 – 14 de Septiembre de 2006

NMR in the epoxidation of (*E*,*E*)-cinnamylideneacetophenones

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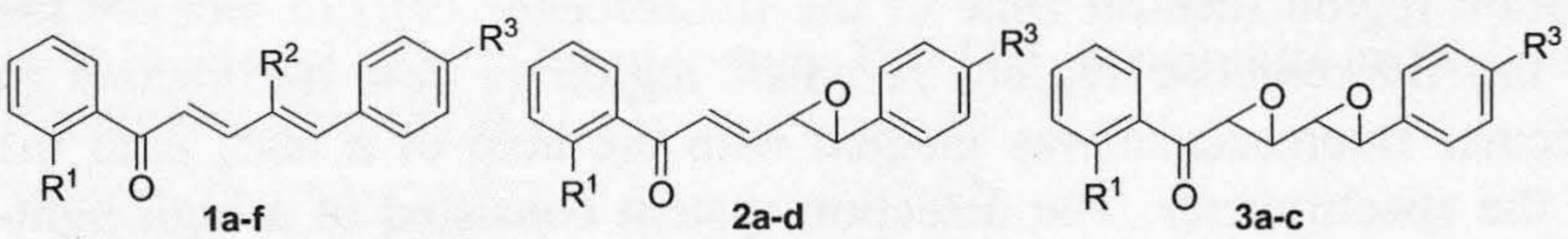
The epoxidation of cinnamylideneacetophenones have been already performed with hydrogen peroxide as oxidant in Julia's method [1] and with dimethyldioxirane [2], however no studies were performed using salen Mn(III) complexes as catalysts. On these basis, we developed a study on the epoxidation of cinnamylideneacetophenones **1**, catalyzed by commercially available Jacobsen's catalyst [salen Mn(III)] and using iodosylbenzene and hydrogen peroxide as oxidants. The structure of the epoxidation products **2-5**, their stereochemistry and the regiochemistry of the monoepoxides **2** formation were established by 1D and 2D NMR spectroscopy. These studies will be presented and discussed.



Scheme

Acknowledgements: Thanks are due to the University of Aveiro, FCT and FEDER for funding the Organic Chemistry Research Unit and the project POCTI/QUI/38394/2001. One of us (C.M.M. Santos) is also grateful to PRODEP 5.3 for financial support.

[1] M. E. Lasterra Sanchez, U. Felper, P. Mayon, S. M. Roberts, A. R. Thornton, C. J. Todd, *J. Chem. Soc., Perkin Trans. I*, **1996**, 343.
[2] A. Lévai, A. M. S. Silva, J. A. S. Cavaleiro, T. Patonay, V. L. M. Silva, *Eur. J. Org. Chem.*, **2001**, 3213.

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CERTIFICATE

BARTOLOMÉ M. SIMONET SUAU, Secretary of the Organizing Committee of the Conference "**XX RNE – IV CIE**"

CERTIFY

that **Clementina M. M. Santos** has attended this Conference and has presented the oral communication with the title:

"NMR in the epoxidation of (*E*,*E*)-cinnamylideneacetophenones"

Ciudad Real, September 14, 2006

Dr. Bartolomé M. Simonet Suau
Secretary of the Organizing Committee
Sociedad de Espectroscopía Aplicada
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Introduction

The epoxidation of cinnamylideneacetophenones have been already performed with hydrogen peroxide as oxidant in Julia's method [1] and with dimethyldioxirane [2], however no studies were performed using salen Mn(III) complexes as catalysts.

On this basis, we developed a study on the epoxidation of cinnamylideneacetophenones **1**, catalyzed by commercially available Jacobsen's catalyst [salen Mn(III)] and using iodosylbenzene and hydrogen peroxide as oxidants.

The structure of the epoxidation products **2-5**, their stereochemistry and the regiochemistry of the monoepoxides **2** formation were established by 1D and 2D NMR spectroscopy. These studies are presented and discussed.

Epoxidation of (*E,E*)-cinnamylideneacetophenones

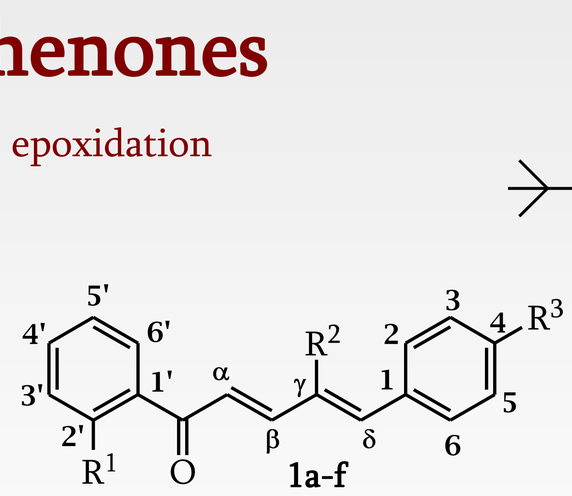
Salen Mn(III) complexes are efficient catalysts for the epoxidation of α,β-unsaturated carbonyl compounds.

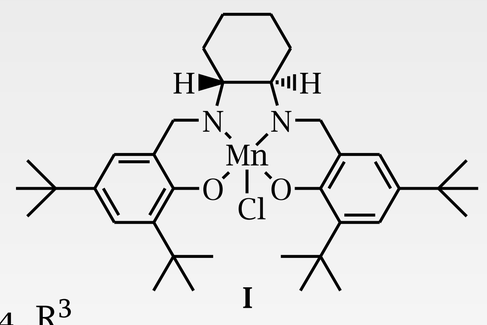
We developed a new study on the epoxidation of cinnamylideneacetophenones **1a-f,** catalysed by commercially available Jacobsen's catalyst **I** and using hydrogen peroxide (H_2O_2) and iodosylbenzene (PhIO) as oxidants.

The optimized conditions in the epoxidation of **1a-f** are described in **A** and **B**.

A: 0.05 eq. Catalyst **I**, 0.7 eq. 1-MeIm, 10 eq. H_2O_2, CH_3OH/CH_2Cl_2 (1:1), 40 ºC, 4h

B: 0.05 eq. Catalyst **I**, 0.5 eq. PyNO, 2 eq. PhIO, CH_3CN, r.t., 4h

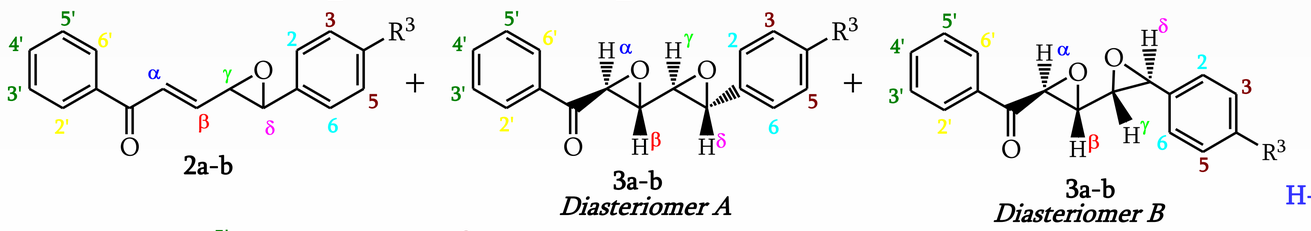




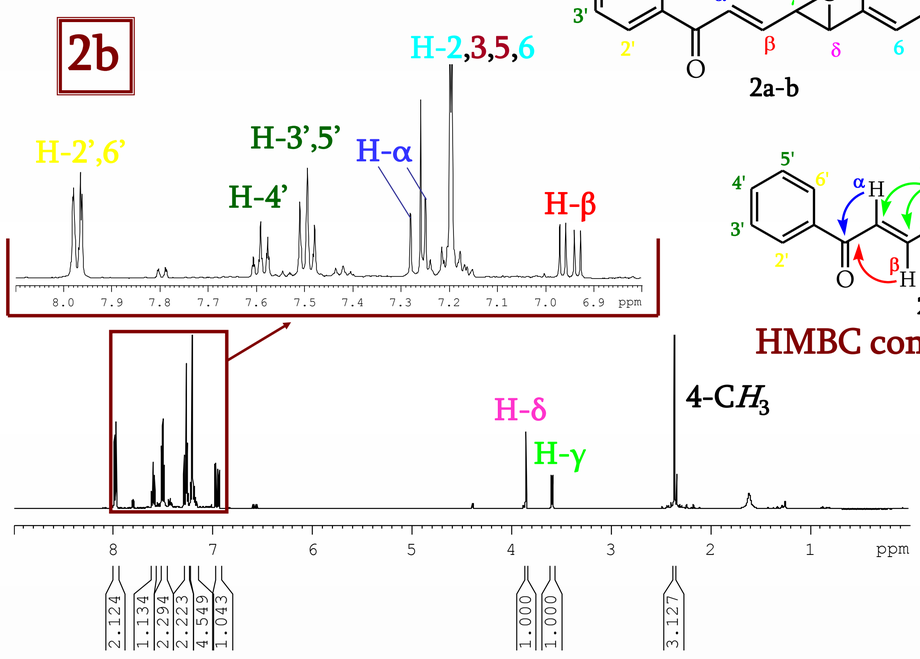
Jacobsen's catalyst

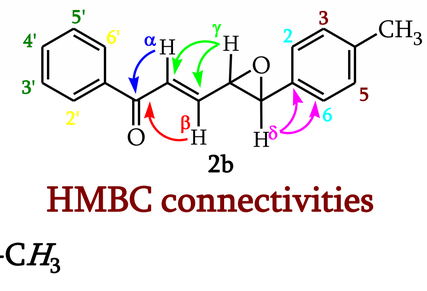
a) $R^1 = R^2 = R^3 = H$
b) $R^1 = R^2 = H$, $R^3 = Me$
c) $R^1 = R^2 = H$, $R^3 = NO_2$
d) $R^1 = OH$, $R^2 = R^3 = H$
e) $R^1 = R^3 = H$, $R^2 = Me$
f) $R^1 = OH$, $R^2 = Me$, $R^3 = H$

For the derivatives **a)** and **b)**, the epoxidation products are:

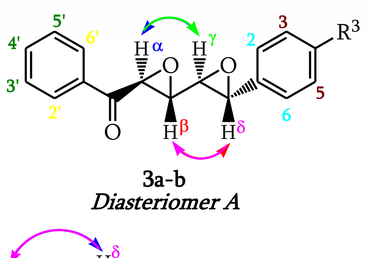


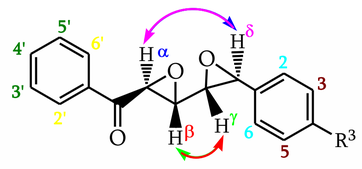
2b





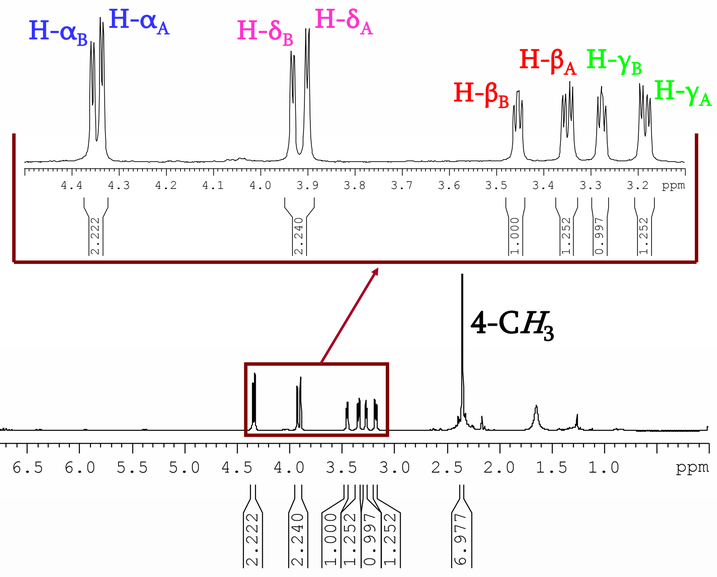
HMBC connectivities



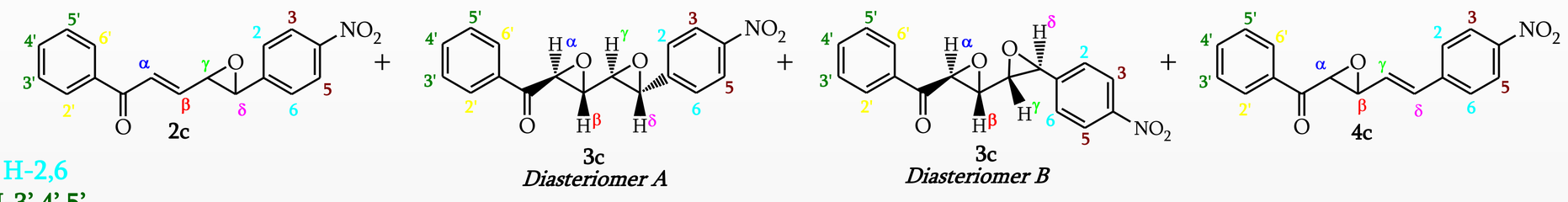


NOE effects

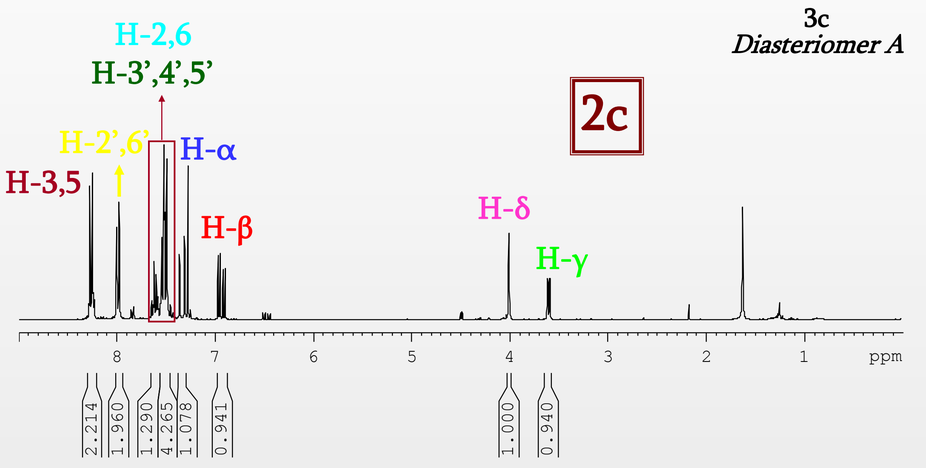
3b



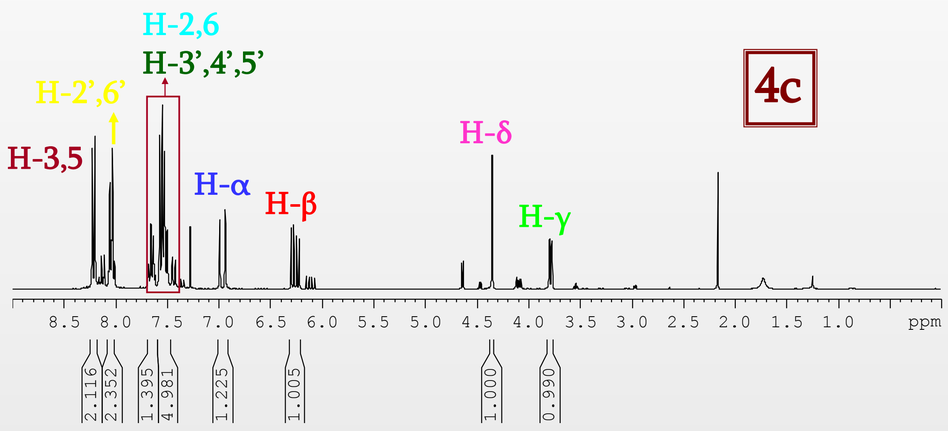
For the derivatives **c)**, the epoxidation products are:

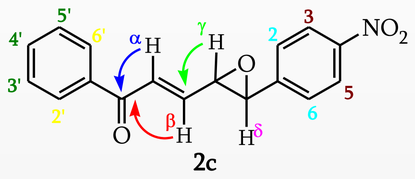


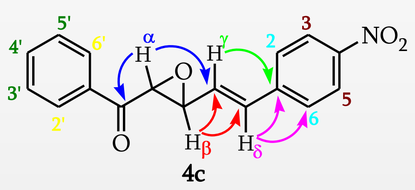
2c



4c

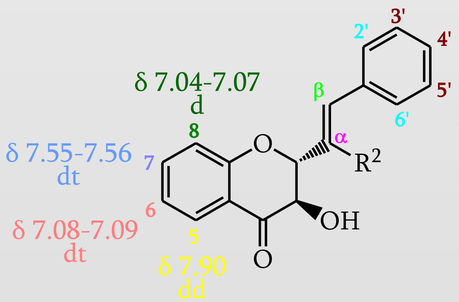






HMBC connectivities

For the derivatives **d)**, **e)** and **f)**, the epoxidation products are:

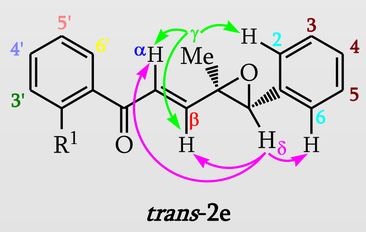


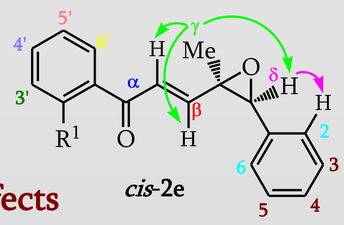
5d) $J_{\alpha\text{-}\beta}$ = 16 Hz

E configuration

$J_{H2\text{-}H3}$ = 12 Hz

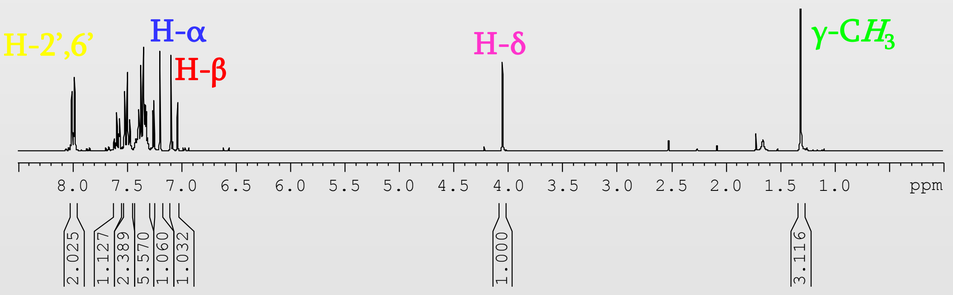
trans-diaxial configuration



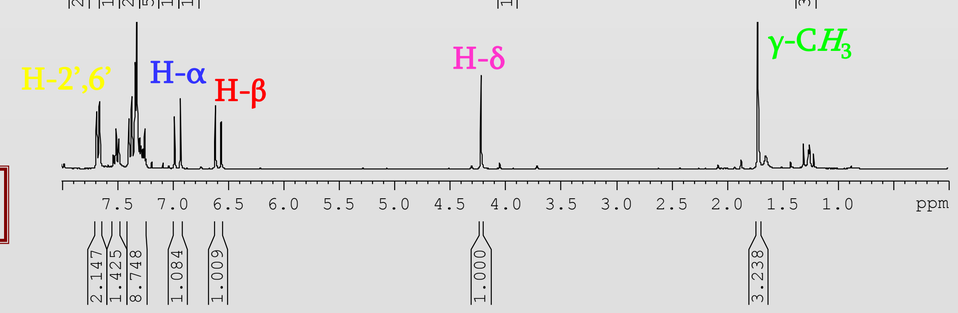


NOE effects

***trans*-2e**



***cis*-2e**



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