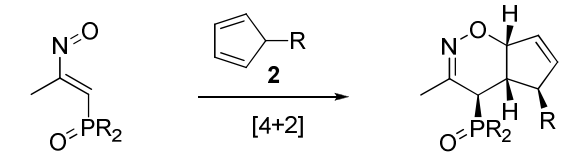
[P2.099]

Hetero-Diels-Alder Reaction of Phosphorus Substituted Nitroso Alkenes with Conjugate Cyclic Dienes

J. M. de los Santos*, G. Rubiales, R. Ignacio, D. Aparicio, F. Palacios
University of the Basque Country, Spain

The chemistry of nitroso compounds has been intensively studied in the past decades, especially due to their applications in the field of asymmetric synthesis and cycloaddition processes.[1] Otherwise, nitroso alkenes[2] are functionalized nitroso derivatives, and the presence of an adjacent double bond in conjugation with the nitroso moiety introduces new reactivity centres in these substrates and then increases the synthetic value of these compounds. Cycloaddition reactions in which nitroso alkenes participates as the 4π-electron component in hetero-Diels-Alder reactions[3] with dienophiles have been described for several years.

We have previously described the generation of phosphorus substituted nitroso alkenes **1** and the conjugate addition of some nitrogen nucleophiles for the preparation of α-amino phosphonate derivatives.[4] Recently, this phosphorated nitroso alkenes **1** have been used for the regioselective preparation of highly functionalized *N*-hydroxypyrroles with a phosphorus substituents at the 3-position, generated through treatment of phosphinyl and phosphonyl nitroso alkenes **1** with enamines.[5]



1 R = Ph, OEt

3

In this study, phosphorated nitroso alkenes **1** derived from phosphine oxides (R = Ph) and phosphonates (R = OEt) react with cyclic nucleophilic dienes **2** to afford highly functionalized 5,6-dihydro-4*H*-1,2-oxazines **3**. Depending on the R substitution, the nitroso alkene may participates as the 2π-electron component, through a nitroso-Diels–Alder cycloaddition, or as the heterodiene system through a hetero-Diels–Alder reaction.

Acknowledgements

Authors thank the Departamento de Educación, Universidades e Investigación del Gobierno Vasco (IT-422-10), Universidad del País Vasco (UPV/EHU) (GIU 09/57) and Dirección General de Investigación del Ministerio de Ciencia e Innovación (DGI, CTQ2009-12156 BQU) for financial support. We also thank SGIker technical support for computational resources, and NMR spectra (MCINN, GV/EJ, and European Social Found).

References

1. Gowenlock, B. G.; Richter-Addo, G. B. *Chem. Rev.* **2004**, *104*, 3315-3340.

2. For an excellent review see: Gilchrist, T. L. *Chem. Soc. Rev*. **1983**, *12*, 53-73.

3. Gilchrist, T. L.; Wood, J. E. *Comprehensive Heterocyclic Chemistry II*; Boulton, A. J., Ed.; Pergamon: Oxford, 1996; Vol. 6, pp 279-299.

4. de los Santos, J. M.; Ignacio, R.; Aparicio, D.; Palacios, F. *J. Org. Chem*. **2007**, *72*, 5202-5206.

5. de los Santos, J. M.; Ignacio, R.; Aparicio, D.; Palacios, F.; Ezpeleta, J. M. *J. Org. Chem*. **2009**, *74*, 3444-3448.