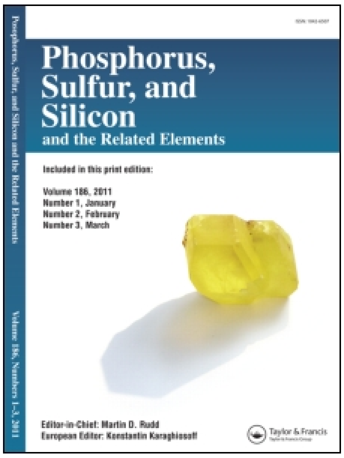


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Chiral Ketene Equivalents for Use in Asymmetric Synthesis

Varinder K. Aggarwal[ab]; Mark Lightowler[a]
[a] School of Chemistry, University of Bath, Bath, UK [b] Department of Chemistry, University of Sheffield, Sheffield, U.K.

To cite this Article Aggarwal, Varinder K. and Lightowler, Mark(1993) 'Chiral Ketene Equivalents for Use in Asymmetric Synthesis', Phosphorus, Sulfur, and Silicon and the Related Elements, 74: 1, 407 — 408
To link to this Article: DOI: 10.1080/10426509308038138
URL: http://dx.doi.org/10.1080/10426509308038138

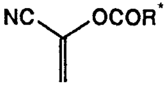
Phosphorus, Sulfur, and Silicon, 1993, Vol. 74, pp. 407–408

CHIRAL KETENE EQUIVALENTS FOR USE IN ASYMMETRIC SYNTHESIS

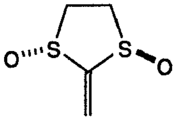
VARINDER K. AGGARWAL,† MARK LIGHTOWLER
School of Chemistry, University of Bath, Bath BA2 7AY, UK

Abstract Trans-1,3-dithiolane-1,3-dioxide is a more reactive and more selective chiral ketene equivalent than trans-1,3-dithiane-1,3-dioxide.

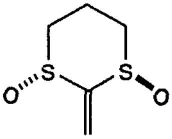
Chiral ketene equivalents that undergo 4+2 Diels Alder reactions are useful synthons in asymmetric synthesis. However, ketene equivalents based on the condensation between chiral acid chlorides and pyruvonitrile **1**, only show low levels of diastereocontrol in their reactions with dienes.[1] Ketene equivalents based on simple vinyl[2] or acetylenic[3] sulfoxides show low dienophilicity, low levels of diastereocontrol or give rise to complex mixtures of diastereoisomers limiting their synthetic use. We have turned to ketene equivalents, but based on novel cyclic, alkenyl sulfoxides **2** and **3** since we believed they might offer several advantages: (a) the low steric bulk together with the presence of two activating groups at the same carbon should result in high Diels Alder reactivity (b) C_2 symmetry reduces the number of different approaches of the diene and should enhance the selectivity.



(1)

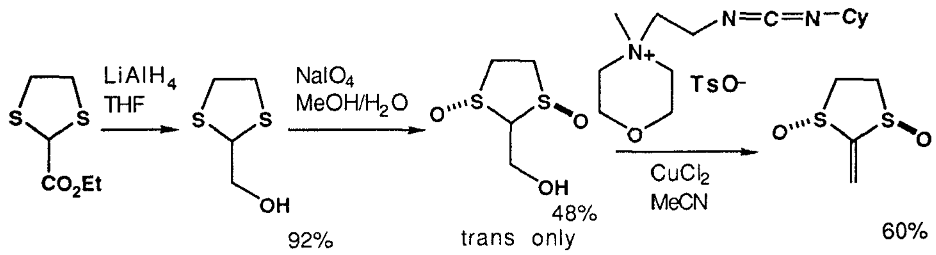


(2)

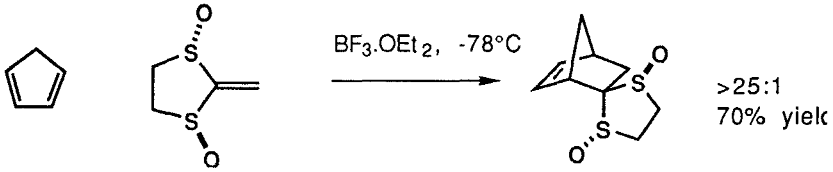


(3)

The dienophile **2** was prepared in three short high yielding steps from 2-carboethoxy 1,3-dithiolane and dienophile **3** was prepared in a similar manner.[4]



Both dienophiles reacted with cyclopentadiene at -78°C under BF_3OEt_2 conditions to give adducts as single diastereoisomers. Reactions with acyclic dienes (1-methoxybutadiene, Danishefsky's diene) also occurred readily furnishing single diastereomeric adducts in the absence of Lewis acids but only with the 5 membered ring dienophile **2**. The dithiane based dienophile **3** failed to react with these acyclic dienes under the same reaction conditions. In contrast to the stereoselective Diels Alder reactions described above, furan gave a mixture of adducts (5:1) with dienophile **2** whilst dienophile **3** reacted less selectively (1.8:1).



These results show that the 5 membered ring dienophile **2** is a more reactive and more selective dienophile than the dithiane based system **3**. The origin of the enhanced reactivity is thought to be due to ring strain in the 5 membered ring and the higher selectivity of **2** over **3** is thought to be due to conformational effects.

References

† Current address: Department of Chemistry, University of Sheffield, Sheffield S3 7HF, U.K..

1 Vogel, P.; Fattori, D.; Gasparini, F.; Le Drian, C. *Synlett*, **1990**, 173.
2 Maignan, C.; Raphael, R.A.; *Tetrahedron*, **1983**, 3245.
3 Maignan, C.; Brelkasmioui, F. *Tetrahedron Lett.*, **1988**, *29*, 2823.
4 Aggarwal, V.K.; Lightowler, M.; Lindell, S.D. *Synlett*, submitted for publication.