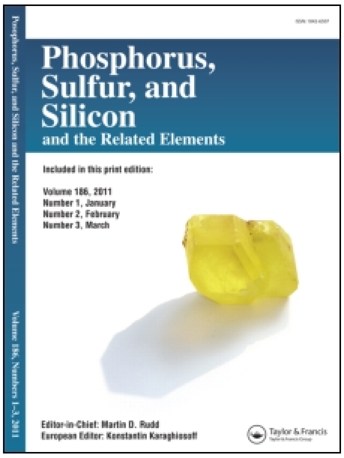
This article was downloaded by:
On: *30 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

A HIGHLY DIASTEREOSELECTIVE OXIDATION OF A CROWDED *GEM*-DISULPHIDE

M. Poje[a]; K. Balenović[a]
[a] Department of Organic Chemistry, University of Zagreb, Zagreb, Croatia, Yugoslavia

To cite this Article Poje, M. and Balenović, K.(1979) 'A HIGHLY DIASTEREOSELECTIVE OXIDATION OF A CROWDED *GEM*-DISULPHIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 6: 1, 245

To link to this Article: DOI: 10.1080/03086647908080396

URL: http://dx.doi.org/10.1080/03086647908080396

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus and Sulfur
1979, Vol. 6, p. 245

© Gordon and Breach Science Publishers Ltd., 1979
Printed in Great Britain

A HIGHLY DIASTEREOSELECTIVE OXIDATION OF A CROWDED *GEM*-DISULPHIDE

M. Poje and K. Balenović

Department of Organic Chemistry, University of Zagreb,
Strossmayerov trg 14, 41000 Zagreb, Croatia, Yugoslavia

Downloaded At: 13:16 30 January 2011

In all of the kinetically controlled oxidations to *gem*-disulphoxides, the *meso*-epimer predominated. Spontaneous interconversion of epimeric $(PhCH_2SO)_2CPh_2$ is made possible by the lower C—S bond energies in disulphoxide, permitting a room temperature homolytic dissociation-recombination mechanism to operate, being an example of kinetic and equilibrium control *(C. Y. Meyers, L. L. Ho, A. Ohno and M. Kagami, Tetrahedron Letters 1974, 729).*

We have now found an unexpected diastereoselective oxidation of another crowded *gem*-disulphide $(PhCH_2)_2C(SCH_3)_2$ (1) which afforded the *gem*-disulphoxide 2 as sole product. The NMR studies of 2 and its constitutional isomer, the monosulphone 3, showed amazing shielding features which suggested an intramolecular interaction. *Syn*-elimination reactions gave Z-olefins as sole products. When 2 is treated in boiling chloroform, fragmentation takes place and the corresponding Z-methylsulphinyl-alkene 4 is formed. Thermolysis of 2 in presence of BF_3 proceeded partly through bimolecular disproportionation (giving the corresponding monosulphoxide and sulphonyl-sulphoxide), followed by elimination of sulphenic acid and affording Z-methylsulphinyl-alkene 4, Z-methylsulphonyl-alkene 5, and a mixture of E- and Z-methylthio-alkenes 6a,b. All these reactions were highly stereospecific and gave 80% and higher yields of pure diastereoisomers. A detailed investigation of these unexpected selectivities is in progress.