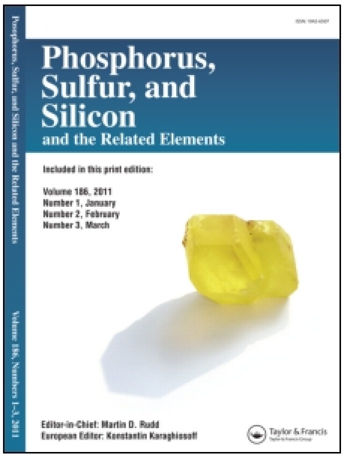
This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Kinetic Resolution of Cyclic Sulfoxides by Enzyme Promoted Hydrolysis of 2-Alkoxycarbonyl-3,6-Dihydro-*2H*-Thiapyran-1-Oxides

P. Kiełbasiński[a]; M. Mikołajczyk[a]; B. Zwanenburg[b]; R. C. De Laet[b]
[a] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź, Poland [b] Department of Organic Chemistry, University of Nijmegen, ED Nijmegen, The Netherlands

To cite this Article Kiełbasiński, P. , Mikołajczyk, M. , Zwanenburg, B. and De Laet, R. C.(1994) 'Kinetic Resolution of Cyclic Sulfoxides by Enzyme Promoted Hydrolysis of 2-Alkoxycarbonyl-3,6-Dihydro-*2H*-Thiapyran-1-Oxides', Phosphorus, Sulfur, and Silicon and the Related Elements, 95: 1, 495 — 496

To link to this Article: DOI: 10.1080/10426509408034290

URL: http://dx.doi.org/10.1080/10426509408034290

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.

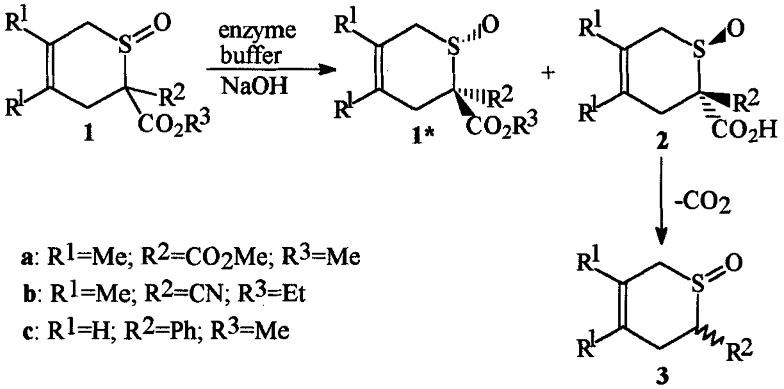
Phosphorus, Sulfur, and Silicon, 1994, Vol. 95–96, pp. 495–496
Reprints available directly from the publisher
Photocopying permitted by license only

KINETIC RESOLUTION OF CYCLIC SULFOXIDES BY ENZYME PROMOTED HYDROLYSIS OF 2-ALKOXYCARBONYL-3,6-DIHYDRO-2*H*-THIAPYRAN-1-OXIDES.

P.Kiełbasiński[a], M.Mikołajczyk[a], B.Zwanenburg[b] and R.C. de Laet[b]

[a]Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland [b]Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

Among many methods of preparation of optically active sulfoxides, those applying enzymes are becoming more and more popular[1]. In continuation of our recent investigations on the enzyme promoted hydrolysis of sulfinyldicarboxylates[2] we turned our attention to cyclic six-membered sulfoxides **1**. These compounds are easily available by the cycloaddition reaction of butadienes with appropriate sulfines obtained *in situ* from the corresponding esters (or their O-silyl enolethers) with thionyl chloride in the presence of a base[3]. Three compounds shown in the scheme were chosen for our investigations. It should be noted that compounds **1b** and **1c** are obtained as single diastereoisomers.



a: R^1=Me; R^2=CO_2Me; R^3=Me
b: R^1=Me; R^2=CN; R^3=Et
c: R^1=H; R^2=Ph; R^3=Me

Hydrolysis was performed in buffer solutions employing several readily available enzymes (see Table). The reactions proceeded smoothly in the case of the substrates **1a** and **1b** and optically active unreacted esters **1*** were isolated, using a standard workup procedure. However, the acidic products **2** underwent spontaneous decarboxylation to **3** isolated as epimeric mixtures. It is interesting to note that the use of different enzymes enabled us to obtain both enantiomerically enriched forms of **1b**. In contrast to **1a** and **1b**, **1c** appeared to be completely unreactive under similar conditions although several enzymes and different co-solvents were applied.

Enzyme	pH	Recovered ester			
			Yield [%]	$[\alpha]_D$	ee [%]
PLE	7.2	**1a**	47	-2.05	8.0
PLE	7.2	**1b**	35	+33.6	12.1
PLE	6.45	**1b**	34	+21.2	7.6
Cand.Cyl.	7.2	**1b**	27	-1.1	
α-CT	7.3	**1b**	65.8	-55.5	20.0
α-CT	7.3	**1b**	30	-132.5	48.4
PPL	7.3	**1b**	10	-180.0	65.0

Since it was suspected that a different configuration of **1b** and **1c** might be responsible for the observed differences in reactivity, an X-ray analysis of both substrates was performed. It was found that both compounds have the *trans* configuration, but in the solid state they adopt different conformations: in **1b** the ester group and the sulfinyl oxygen occupy equatorial positions while in **1c** - apical positions. Further studies are in progress to shed more light on the conformational effect on enzymatic hydrolysis of sulfinyl carboxylates.

Acknowledgment: The project is in part financially supported by the State Committee of Scientific Research, Poland (Grant no 206189101). The Authors thank Dr M.W.Wieczorek for X-ray structural determinations which will be published in a full paper.

REFERENCES

1. a) H.Holland, *Chem.Rev.* **88**, 473 (1988); b) K.Burgess, I.Henderson, K.-K.Ho, *J.Org.Chem.* **57**, 1290 (1992); c) S.Allenmark, A.C.Andersson, *Tetrahedron: Asymmetry* **4**, 2371 (1993).
2. M.Mikołajczyk, P.Kiełbasiński, R.Żurawiński, M.W.Wieczorek, J.Błaszczyk, *Synlett* 127 (1994).
3. B.G.Lenz, H.Regeling, H.L.M.van Rozendaal, B.Zwanenburg, *J.Org.Chem.* **50**, 2930 (1985); J.Rewinkel, Ph.D. Thesis, University of Nijmegen, NL, 1989.