

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>

Fast Isomerization of Sym-Monothiopyrophosphates in Pyridine Solutions

J. Michalski^a; W. Reimschuessel^a; R. Kamiński^b

^a Centre of Molecular and Macromolecular Studies, Polish Academy of Science, Lodz, Poland ^b Institute of Applied Radiation Chemistry, Technical University, Lodz, Poland

To cite this Article Michalski, J. , Reimschuessel, W. and Kamiński, R.(1990) 'Fast Isomerization of Sym-Monothiopyrophosphates in Pyridine Solutions', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 51: 1, 216

To link to this Article: DOI: 10.1080/10426509008040750

URL: <http://dx.doi.org/10.1080/10426509008040750>

PLEASE SCROLL DOWN FOR ARTICLE

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

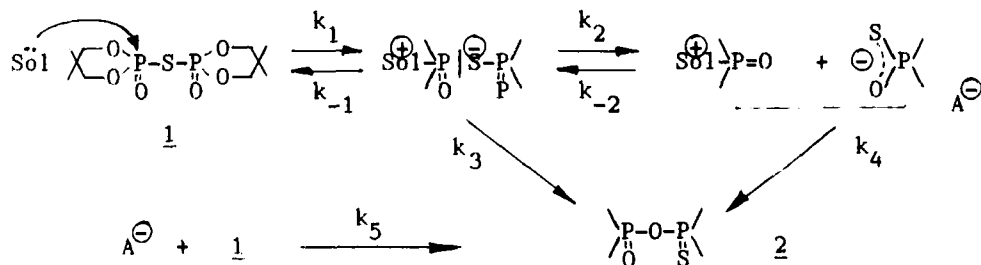
This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

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.

J. Michalski, W. Reimschuessel,^a R. Kamiński

Centre of Molecular and Macromolecular Studies,
Polish Academy of Science, Lodz, Poland
^aInstitute of Applied Radiation Chemistry,
Technical University, Lodz, Poland

Organic monopyrophosphates, structural analogues of biologically important diphosphates, undergo spontaneous thiolo-thiono isomerization $O=P(=O)(R)-S-P(=O)(R)_2 \longrightarrow S=P(=O)(R)-O-P(=O)(R)_2$ (1). On the basis of the detailed kinetic mechanistic studies of the isomerization of bis(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphorinane) 1 in 1-methylnaphthalene (MN), benzonitrile or propylene carbonate solutions the dissociative mechanism has been proposed (2):



To support this mechanism we have studied the kinetics of isomerization of 1 labelled with ^{35}S in pyridine (Py) solutions. As expected the reaction is very fast. The first-order reaction rate constant in Py at 25°C is about 10^7 times greater than the value obtained by extrapolation of the kinetic data for the reaction in MN. The reaction rate constant in Py solutions is almost not sensitive to triethylammonium salt of the acid AH. This demonstrates that the dissociative step (k_1) dominates in this case. The kinetics of isomerization of 1 in binary solvents containing Py will also be discussed in this communication.

- (1) J. Michalski, W. Reimschuessel, R. Kamiński,
Russ. Chem. Rev., 47, 814 (1978) and references therein.
- (2) J. Michalski, W. Reimschuessel, R. Kamiński, P. Paneth,
Phosphorus and Sulfur, 30, 257 (1987)