

This article was downloaded by:

On: 28 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>

The First Example of 1,1- σ -Complexes of Phosphorus Nucleophiles

Peter P. Onys'ko^a; Tatyana V. Kolodka^a

^a Institute of Organic Chemistry, National Academy of Sciences, Kiev, Ukraine

To cite this Article Onys'ko, Peter P. and Kolodka, Tatyana V.(1996) 'The First Example of 1,1- σ -Complexes of Phosphorus Nucleophiles', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 111: 1, 152

To link to this Article: DOI: 10.1080/10426509608054781

URL: <http://dx.doi.org/10.1080/10426509608054781>

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.

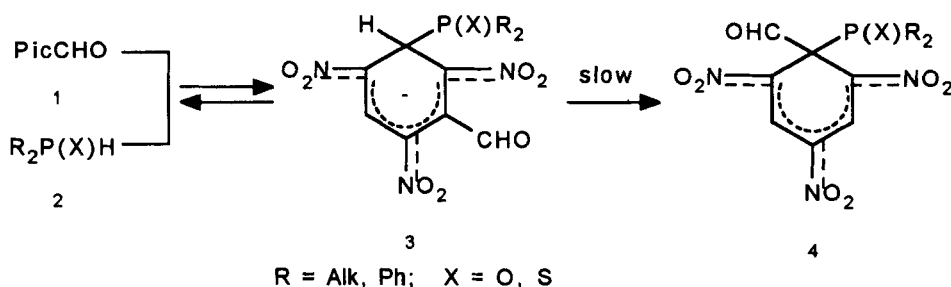
The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any 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.

THE FIRST EXAMPLE OF 1,1- σ -COMPLEXES OF PHOSPHORUS NUCLEOPHILES.

PETER P. ONYS'KO* AND TATYANA V. KOLODKA

Institute of Organic Chemistry, National Academy of Sciences,
 Kiev 252660, 5 Murmanskaya St., Ukraine

We report on the first phosphorus 1,1- σ -complexes, relatively stable in DMSO. Adducts of this type are important as possible intermediates in nucleophilic aromatic substitution reactions but for phosphorus nucleophiles 1,1- σ -complexes were never detected [1]. We have found that interaction of **1** with **2** in DMSO leads initially to 1,3- σ -complexes **3** which slowly rearrange to 1,1- σ -complexes **4**.



The effect of R and X on the σ -complexation and mechanism of 1,3-phosphorotropic rearrangement **3**→**4** will be discussed. The results obtained show that nucleophilic phosphorylation of electron-deficient aromatics can, in principle, proceed by addition-elimination S_NAr mechanism. The capability of phosphorus atom to change its coordination number provides new pathways (in particular, those involving five-coordinated intermediates) of aromatic substitution for phosphorus nucleophiles.

REFERENCES

1. Yu. G. Gololobov and P. P. Onys'ko, *Sov. Sci. Revs. B. Chem. Revs.*, **6**, 313, (1984).