

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>

### Novel Rearrangements and Heterocyclisation of P-Imides

Y. Gololobov<sup>a</sup>; N. Gusar<sup>b</sup>; Y. Balitzky<sup>b</sup>; L. Nesterova<sup>b</sup>; M. Chaus<sup>b</sup>

<sup>a</sup> A. N. Nesmeyanov Institute of Element-Organic compounds of the USSR Academy of Sciences, Moscow <sup>b</sup> Institute of Organic Chemistry of the Academy of Sciences of the Ukrainian SSR, Kiev, USSR

**To cite this Article** Gololobov, Y. , Gusar, N. , Balitzky, Y. , Nesterova, L. and Chaus, M.(1983) 'Novel Rearrangements and Heterocyclisation of P-Imides', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 18: 1, 245 — 248

**To link to this Article:** DOI: 10.1080/03086648308076012

**URL:** <http://dx.doi.org/10.1080/03086648308076012>

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.

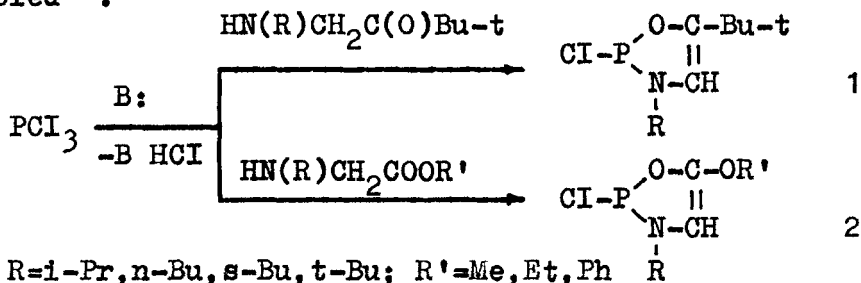
## NOVEL REARRANGEMENTS AND HETEROCYCLISATION OF P-IMIDES

Y. GOLOLOBOV

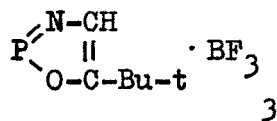
A.N. Nesmeyanov Institute of Element-Organic  
compounds of the USSR Academy of Sciences, Moscow

N. GUSAR, Y. BALITZKY, L. NESTEROVA, M. CHAUS  
Institute of Organic Chemistry of the Academy of  
Sciences of the Ukrainian SSR, Kiev, USSR

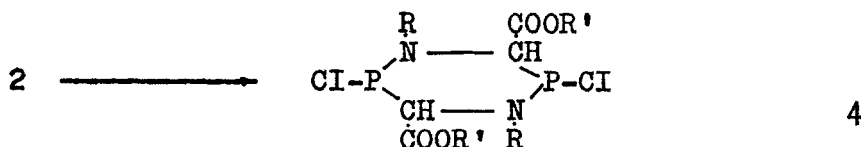
The preliminary introduction of electron accepting di-  
chlorophosphine group at nitrogen atom of N-monosub-  
stituted  $\alpha$ -aminoketones or  $\alpha$ -aminocarbon acid es-  
ters increases the mobility of the  $\alpha$ -carbon hydrogen  
atom so, that the intermolecular O-phosphorylation is  
enabled <sup>1</sup>.



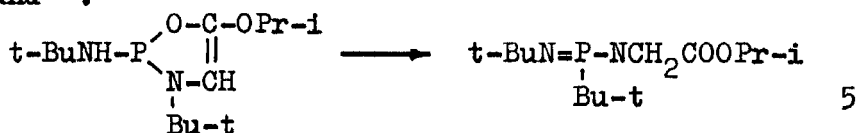
The extension of this method to the reaction between  
PCI<sub>3</sub> and unsubstituted aminoketone  
has led to new dicoordinated phos-  
phorus compound 3 with P-atom in-  
cluded into unknown -O-P=N- <sup>2</sup>.



On heating or storage phospholines 2 are transformed  
into P-C isomers with the double molecular weight 4.

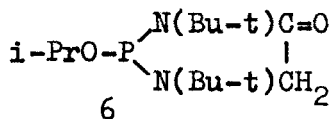


Mobile hydrogen atom being at the  $\alpha$ -position of an exocyclic substituent, the easy cleavage of the P-O bond provides 2 rearrangement into dicoordinated P-compound <sup>3</sup>.

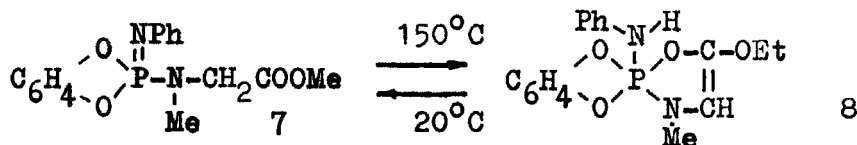


The advanced method of dicoordinated P-compounds synthesis via disruption ("opening") of the heterocycle is a new way in preparation ("construction") of dicoordinated phosphorus derivatives.

Compound 5 undergoes distillation in vacuum, but on storage it rearranges into diazaphospholanone 6.



Imides 7 with hyrocatehine cycle (or fluorine atoms) at phosphorus prepared by imination of N-phosphorylated aminoacetic acid isomerize into diazaphosphetidines (on storage), as well as they undergo reversible isomerization into NH-phosphoranes 8 (above 150°C) <sup>4</sup>.



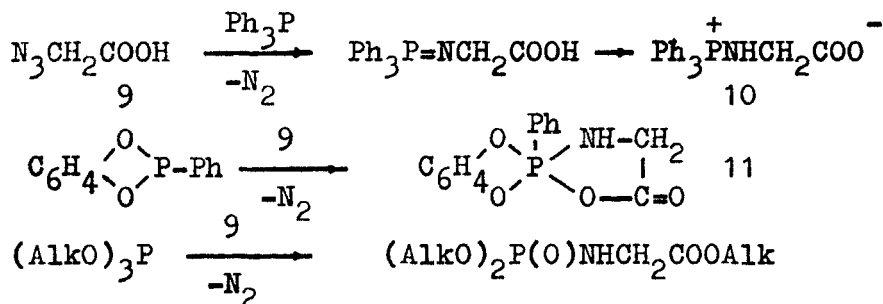
Probably these are the first examples of reversible isomerization of phosphorus acids imides into NH-phosphoranes (cf. <sup>5</sup>).

In literature <sup>6</sup> exist different mechanistic viewpoints on phosphorus acids imides cyclisation with proton transfer. Thus we consider novel prototropic isomerizations and cyclisation of the imides prepared from the corresponding azides according to Staudinger method <sup>7</sup>.

Three types of transformation depending on substituents at phosphorus are characteristic of imides obtained at

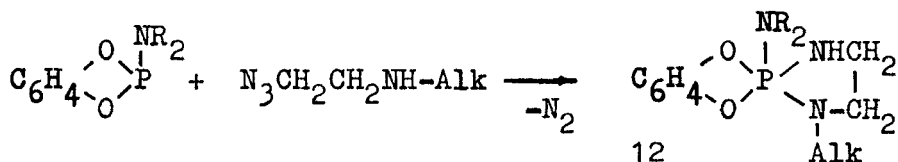
the first stage of reaction between azidoacetic acid and various P(III)-compounds.

The reaction of triphenylphosphine with azidoacetic acid leads <sup>8</sup> to betaine 10. But similar process with fivemember cyclic phosphorus compounds gives phosphoranes of the type 11 (cf.<sup>9</sup>). Alkylation of the carboxy-anion following the proton transfer is brought about by alkyloxy groups at phosphorus.



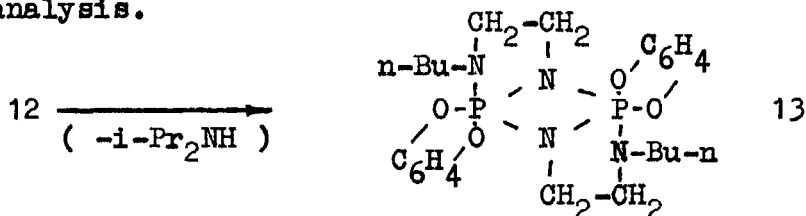
Thus in all the studied processes the limiting stage is transfer of the acidic hydrogen atom to nitrogen of the imino group.

On the other hand, cyclisation proceeds without acidic hydrogen atom as well, provided the secondary highly basic nitrogen atom is present. The nucleophilic attack of the amino group on phosphorus accounts for the possibility of phosphoranes 12 formation.

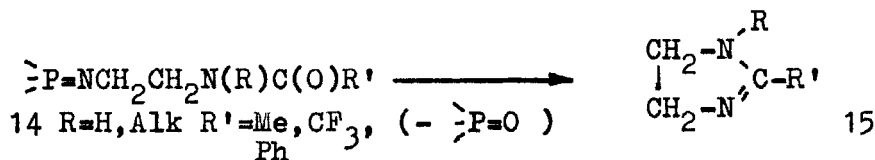


Hydrogen atom is evidently transferred either synchronous or at the final stage. Thus being attributed to various reaction series, both viewpoints <sup>6</sup> are correct. On heating elimination of a molecule of secondary amine from phosphorane 12 leads to the imine, followed by

dimerization of the latter into polycycle 13. Phosphoranes 12 ( $R=Pr-i.$ ,  $Alk=Me$ ) and 13 are formed in good crystalline structures that are strictly confirmed by X-ray analysis.



Hydrogen atoms at amide nitrogen of imides 14 are not enough acidic to transfer to imide nitrogen atom. But in several cases imides 14 form imidazolines 15.



## REFERENCES

1. Y. Gololobov and L. Nesterova, Zh. Org. Khim., **14**, 739 (1979); Y. Balitskii, Y. Gololobov, V. Yurchenko, M. Antipin, Y. Struchkov and I. Boldeskul, Zh. Obshch. Khim., **50**, 219 (1980).
2. Y. Balitskii, V. Negrebetskii and Y. Gololobov, Zh. Obshch. Khim., **51**, 475 (1981).
3. Y. Gololobov and L. Nesterova, Zh. Obshch. Khim., **51**, 2638 (1981).
4. Y. Gololobov, L. Nesterova, V. Kuchar and V. Lukjanchuk, Zh. Obshch. Khim., **51**, 477 (1981).
5. M. Sanchez, J. F. Brazier, D. Houalla, A. Munoz and R. Wolf, J. Chem. Commun., 1976, 730.
6. J. I. G. Cadogan, N. J. Stewart, N. J. Tweddle, J. C. S. Chem. Commun., 1978, 182; H. B. Stegmann, G. Bauer, E. Breitmaier, E. Herrmann and K. Scheffler, Phosphorus, **5**, 207 (1975).
7. Y. Gololobov, I. Zhmurova and L. Kasukhin, Tetrahedron, **37**, 437-472 (1981).
8. M. Chaus, N. Gusar and Y. Gololobov, Zh. Obsh. Khim., **52**, 24 (1982).
9. J. I. G. Cadogan, I. Gosney, E. Henry, T. Naisby, B. Nay, N. J. Stewart and N. J. Tweddle, J. C. S. Chem. Commun., 1979, 189.