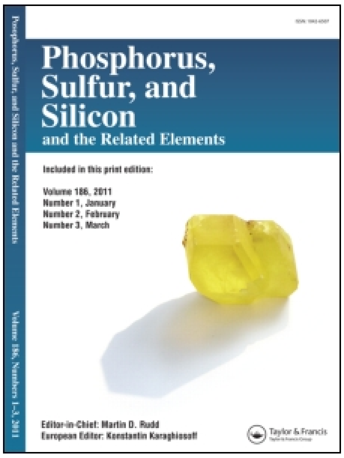


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

P...N Interaction and its Effect on the Structure and Properties of Phosphorylated α-Aminoketones Derivatives

Yuri V. Balitzky[a]; Serge E. Pipko[a]; Anatoly D. Sinitsa[a]; Alexander N. Chernega[a]; Yuri G. Gololobov[a]; A. N. Nesmeyanov[b]
[a] Institute of Organio Chemistry of the Acad. of Sci. of the Ukraine, Kiev, Ukraine [b] Institute of Organo-Element Compounds of the Russian Acad. of Sci., Moscow, Russia

To cite this Article Balitzky, Yuri V. , Pipko, Serge E. , Sinitsa, Anatoly D. , Chernega, Alexander N. , Gololobov, Yuri G. and Nesmeyanov, A. N.(1993) 'P...N Interaction and its Effect on the Structure and Properties of Phosphorylated α-Aminoketones Derivatives', Phosphorus, Sulfur, and Silicon and the Related Elements, 75: 1, 167 — 170

To link to this Article: DOI: 10.1080/10426509308037391

URL: http://dx.doi.org/10.1080/10426509308037391

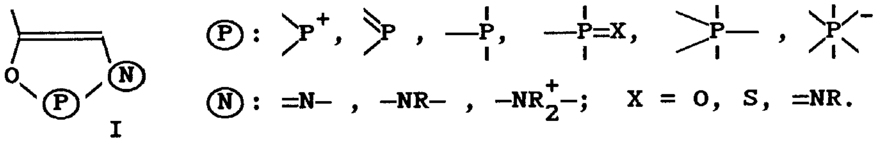
Phosphorus, Sulfur, and Silicon, 1993, Vol. 75, pp. 167–170

P...N INTERACTION AND ITS EFFECT ON THE STRUCTURE AND PROPERTIES OF PHOSPHORYLATED α-AMINOKETONES DERIVATIVES

YURI V. BALITZKY, SERGE E. PIPKO, ANATOLY D. SINITSA, ALEXANDER N. CHERNEGA and YURI G. GOLOLOBOV*
Institute of Organic Chemistry of the Acad. of Sci.
of the Ukraine, Kiev 252094, Murmanskaya Str.,5,Ukraine.
* A.N.Nesmeyanov Institute of Organo-Element Compounds of
the Russian Acad. of Sci., Moscow 117334,
Vavilova Str., 28, Russia.

Abstract Reactions of α-aminoketones with P-chlorides in a basic medium are reported. Methods for the synthesis of Δ^4-1,3,2-oxazaphospholines and β-aminovinyl esters phosphorus acids are reported. Migration of phosphorus from **N** to **O** and enamin-imine isomerization are discussed for the phosphorylated aminoketones. Nucleophylic and electrophylic reactivity of cationes **XV** and **XVI** was studied.

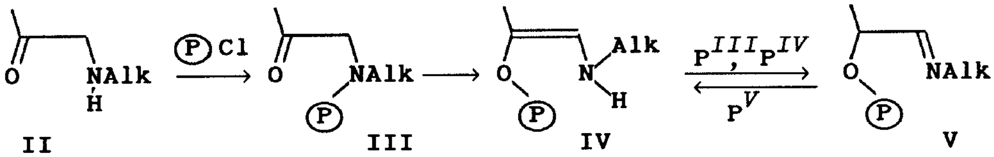
Phosphorylation of α-aminocarbonyl compounds is a facile method for the synthesis of Δ^4-1,3,2-oxazaphospholines **I** with phosphorus in all valent states [1].



I

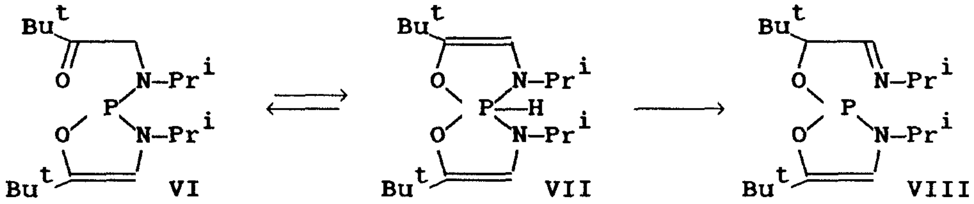
N: =N– , –NR– , –NR_2^+–; X = O, S, =NR.

The majority of the reactions of 5-alkyl-1,3,2-oxazaphospholines studied proceed with the retention of the cycle. They differ from 5-alkoxy-1,3,2-oxazaphospholines which are thermally unstable and rearrange in more stable **C**-derivatives [1]. Phosphorus acids monoclorides interact with aminoketones **II** to afford **N**-derivatives **III** that are kinetically controlled products and they are capable of transforming into more stable **O**-esters.[2,3,4]

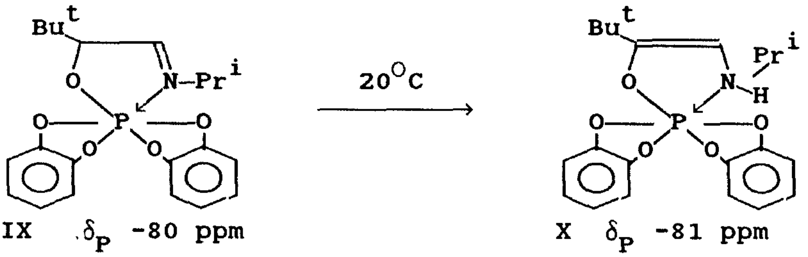


II **III** **IV** **V**

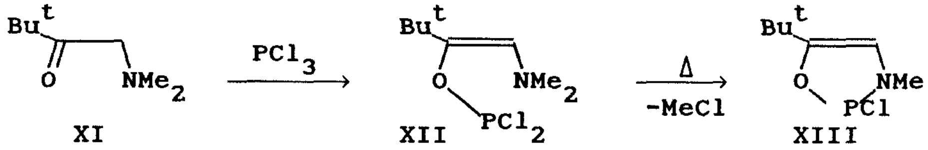
Use of P^{III}-compound **VI** allows to detect an intermediate phosphorane **VII**.



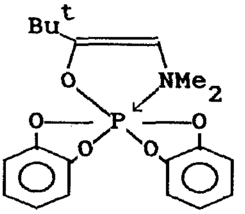
The peculliarity of isomerization is not only transformation of amides into esters. For *III*- and *IV*-coordinate phosphorus the stable form is the iminophosphate **V** and not isomeric vinylphosphate **IV** (or the corresponding phosphite). Another situation is observed for phosphorane structures. Employing **N**- or **O**-silylated aminoketone **II** and bis(o-phenylenedioxy)-chlorophosphorane, the esters **X** and **IX** was obtained instead of the corresponding amide.



Aminoketone **XI** is transformed with PCl_3 to aminovinylphosphite **XII** which is demethylated to cycle **XIII** on heating[5].



In NMR spectra we observed no interaction between **N** and **P** in vinylphosphite **XII**, but ^1H NMR spectra of spirophosphorane **XIV** testify to the existence of the **P**···**N** contact.



XIV

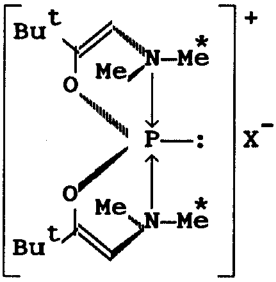
δ_P = -80.2 ppm

PMR:

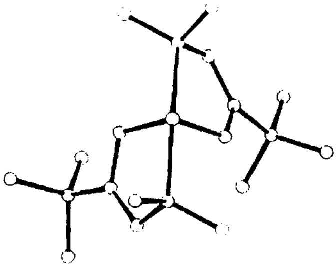
Me *d* 2.95

$^3J_{PH}$ = 5.2 Hz

A mixture of two moles of aminoketone **XI**, Et_3N and PCl_3 affords crystalline spirobis-Δ^4-1,3,2-oxazoniaphospholincloride **XV**.[6] The presence of two types of **N**-methyl groups - a singlet and a doublet, magnetic equivalence of the rest groups are accounted for by the symmetrical structure of the moieties in the molecula with Z-configuration of aminovinyloxygroups as well as by the formation of a rather rigid structure close to a trigonal bipyramid due to two intramolecular donor-acceptor bonds **N**⟶**P**.



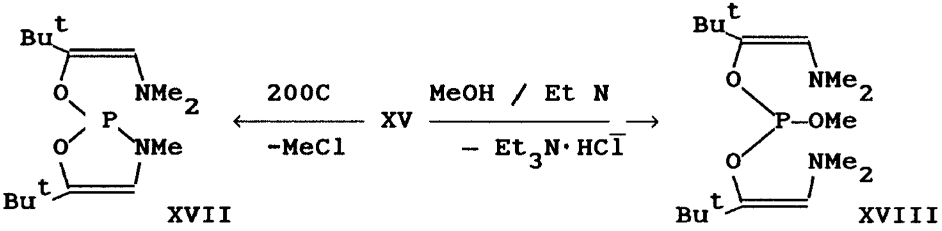
XV, X=Cl	**XVI, X=BPh$_4$**
δ_P= 103 ppm	δ_P= 103 ppm
PMR:	PMR:
$\overset{*}{Me}$ *d* 2.79,	$\overset{*}{Me}$ *d* 2.14,
$^3J_{PH}$ 7.8 Hz	$^3J_{PH}$ 7.8 Hz
Me *s* 2.98	Me *s* 2.35



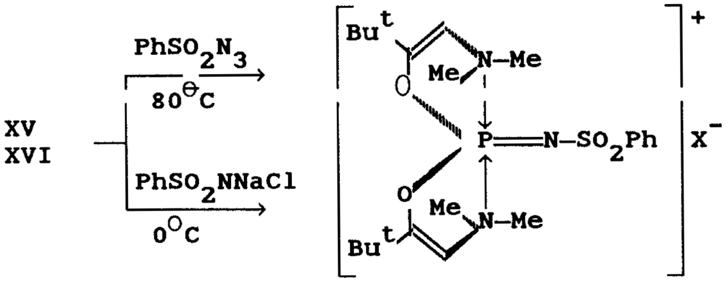
P-N 2.05 and 2.06 Å
P-O 1.63 and 1.64 Å
NPN 166.9°
OPO 102.2°
OPN_{endo} 84.5 and 84.3°

In a solution, compound **XV** is probably completely dissociated at the bond **P-Cl**, which is confirmed by the replacement of the anion Cl^- by BPh_4^-. The cationic part of the **XV** and **XVI** displays practically the same characteristics in NMR spectra.

Interaction of the cation **XV** with nucleophiles leads to the cleavage of the donor-acceptor bonds **N**⟶**P**.

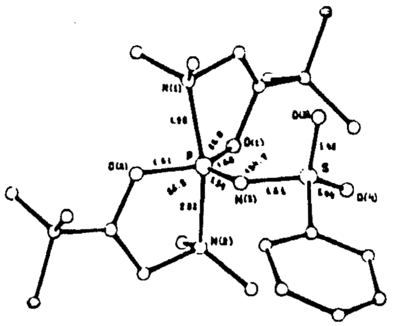


Cationes **XV** and **XVI** react with very active electrophiles with retention their cationic nature. Structure of **XIX** ($X=BPh_4$) is confirmed by X-Ray analysis.



δ_P= -32 ppm
PMR:
Me *d* 3.00,
$^3J_{PH}$ 4.8 Hz
Me *s* 2.96

XIX



P-N 1.96 and 2.02 Å
P-O 1.61 and 1.60 Å
P=N 1.54 Å
S-N 1.61 Å
NPN 160.2°
PNS 134.7°
OPN_{endo} 88.0 and 86.8°

Thus, the donor-acceptor $N \longrightarrow P$ interaction in **IX**, **X**, **XIV**, **XV**, **XVI** and particularly **XIX** opens parthways to novel phosphorus structural types.

REFERENCES

1. Yu.G.Gololobov and Yu.V.Balitsky, Reviews on Heteroatom Chemistry, 6, 25-75 (1992).
2. Yu.V.Balitsky, S.E.Pipko, T.V.Kolodka, A.L.Kovalenko, M.I.Povolotsky, A.D.Sinitsa, Zurn. Obshch. Khim., 59, N. 8, 1911-1912 (1989).
3. Yu.V.Balitsky, S.E.Pipko, T.V.Kolodka, M.I.Povolotsky, A.D.Sinitsa, Zurn. Obshch. Khim., 59, N 12, 2788-2789 (1989).
4. Yu.V.Balitsky, S.E.Pipko, T.V.Kolodka, M.I.Povolotsky, A.D.Sinitsa, Zurn. Obshch. Khim., 60, N 4, p. 963-964 (1990).
5. S.E.Pipko, Yu.V.Balitsky, T.V.Kolodka, I.V.Komarov, A.D.Sinitsa, Zurn. Obshch. Khim., 62, (1992), in press.
6. S.E.Pipko, Yu.V.Balitsky, I.V.Komarov, A.D.Sinitsa, Zurn. Obshch. Khim., 62 (1992), in press.