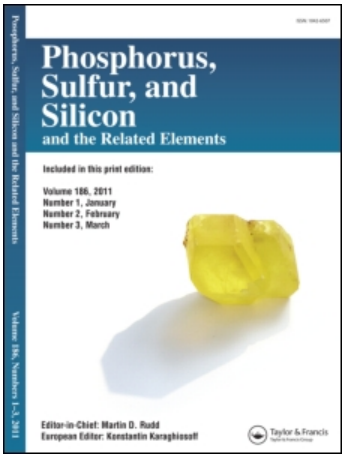



**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# Phosphorylated 2-Azaallylic Systems. Synthesis, Properties, and Rearrangements.

T. V. Kim; E. I. Kiseleva; P. P. Onys'ko; A. D. Sinitsa

**To cite this Article** Kim, T. V. , Kiseleva, E. I. , Onys'ko, P. P. and Sinitsa, A. D.(1996) 'Phosphorylated 2-Azaallylic Systems. Synthesis, Properties, and Rearrangements.', Phosphorus, Sulfur, and Silicon and the Related Elements, 109: 1, 397 — 400
**To link to this Article: DOI:** 10.1080/10426509608545174
**URL:** http://dx.doi.org/10.1080/10426509608545174

*Phosphorus, Sulfur, and Silicon*, 1996, Vols. 109–110, pp. 397–400
Reprints available directly from the publisher
Photocopying permitted by license only



# PHOSPHORYLATED 2-AZAALLYLIC SYSTEMS. SYNTHESIS, PROPERTIES, AND REARRANGEMENTS.

T.V. KIM, E.I. KISELEVA, P.P. ONYS'KO, A.D. SINITSA
Institute of Organic Chemistry, NAS of Ukraine
Kiev 252660, 5 Murmanskaya St., Ukraine

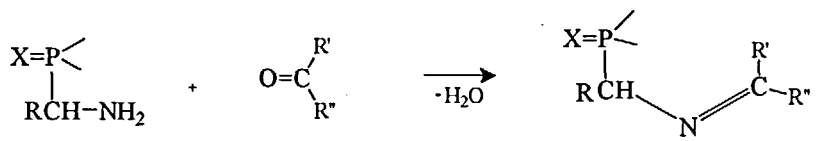


Abstract The methods for synthesis of mono- and bisphosphorylated 2-azaallylic compounds were developed. The relevant proto- and phosphorotropic rearrangements in the C=N-C triad were studied.

Isomerization reactions in azaallylic systems are of general importance as an integral part of heteroallylic rearrangements. Among them, the proton 1,3-transfer in azomethine-azomethine isomerizations, which is often considered as model for biochemical trans-amination reactions, has been most extensively investigated. The effects of phosphoryl groups on prototropic migrations in azaallylic compounds were hitherto not studied.

In the present work we report on developed in our Laboratory synthetic approaches to mono- and bisphosphorylated 2-azaallylic derivatives with phosphorus bonded to $sp^2$- or $sp^3$- carbon atoms in the C=N-C triad, specific effects of the phosphoryl substituents on their properties and elementotropic rearrangements within the triad.

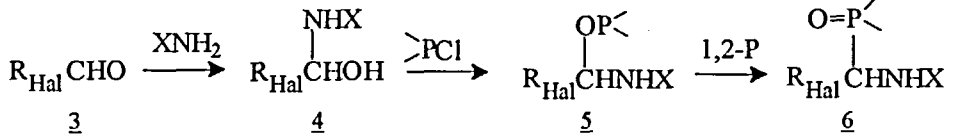
One of the general routes to $sp^3$-C-phosphorylated 2-azaallylic systems consists in condensation of a-aminophosphoryl and carbonyl compounds.




1 2

R: H, Alk, Ar, $CF_3$; R', R": H, Alk, Ar, Het; X: O, S

The limitations of the method in large measure are determined by availability of α-aminophosphonates 1. Traditional preparative pathways to compounds 1 are often unacceptable in synthesis of polyhaloalkyl derivatives. We proposed a suitable method for preparing their N-acylated precursors.



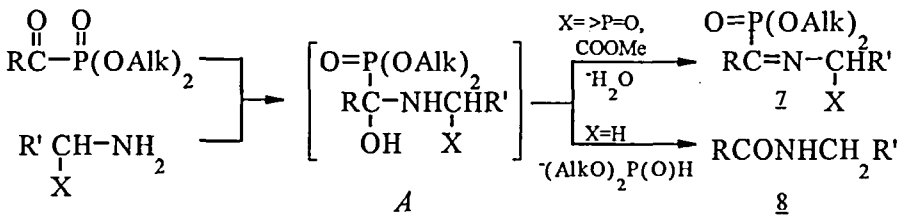
3 4 5 6

$R_{Hal}$: $CCl_3$, $H(CF_2)_4$, $H(CF_2)_6$ X: PhCO, $P(O)(OEt)_2$, $P(O)Ph_2$;

>PCl: $(AlkO)_2PCl$, $(R_2N)_2PCl$, $Ar_2PCl$

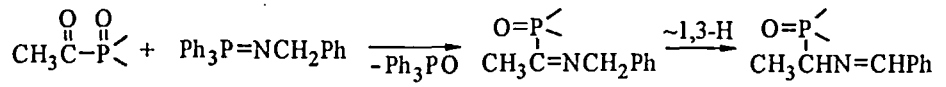
A key step in the scheme is formation of a P-C bond via phosphorotropic rearrangement 5 → 6 proceeding even at an ambient temperature. It should be noted that the reported method [1,2] based on the reaction of carbonyl compounds with carboxamides and phosphorus (III) chlorides is inapplicable to 2-haloalkylaldehydes [1].

Desired $sp^2$-C-phosphorylated azaallylic products 7 we obtained by treating α-oxophosphonates with amines containing an electron-accepting substituent in α-position. In the case of alkyl- and arylamines the reaction results in corresponding amides 8.



A 7 8

N-Benzyltriphenylphosphinimine reacts with α-oxophosphonates by the aza-Wittig scheme to give imidoylphosphonates undergoing phosphinimine-catalyzed 1,3-shift.



This method, however, is not of general application.

The reaction of N-alkyl substituted imidoyl chlorides with nucleophilic phosphorus (III) derivatives was found to be a versatile synthetic tool for preparing phosphorylated azaallylic compounds with a P-C bond either at $sp^2$- or $sp^3$- carbon atom of the C=N-C triad.

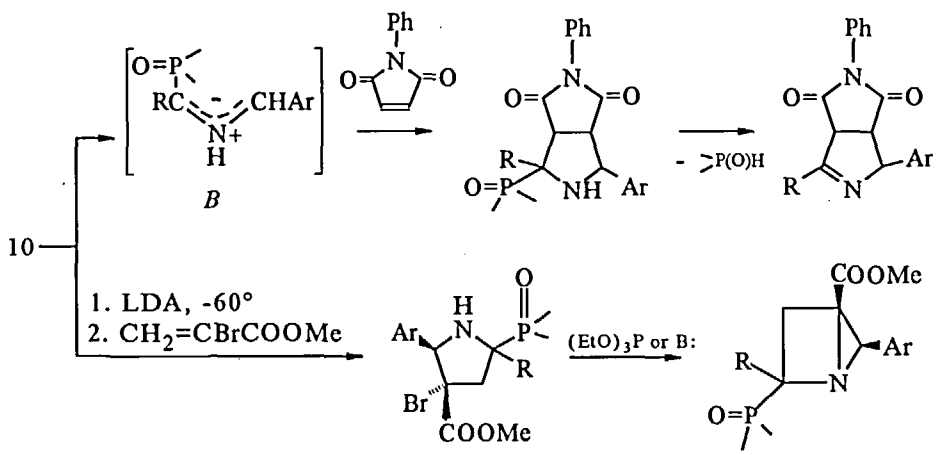
9 10

Ⓟ: $(AlkO)_2P(O)$, $(Me_3SiO)_2P(O)$, $Ar_2P(O)$, $(AlkO)_2P(=NAr)$, $Ph_3P^+Cl^-$, $Ph_2P$

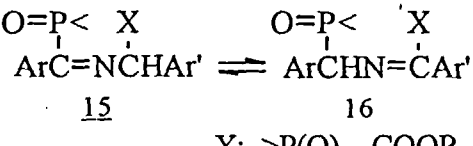
R: Alk, $CF_3$, Ar, Het; R' = H, Me

A phosphoryl group in products 9 considerably enhances mobility of the NCH proton thus facilitating their prototropic rearrangement to imines 10 obtained in preparative yields. At R'=H, isomerization 9 → 10 proceeds even in the absence of bases. With all R and Ar studied, the prototropic shift is virtually irreversible. The isomer with a phosphorus group at the $sp^3$-C-atom is thermodynamically more stable. The conjugation of the Ar substituent with the C=N bond essentially contributes to the stabilization of isomer 10. Under certain conditions compounds 9 are kinetically stable and can be isolated in the individual form. The study of the rearrangement involving optically active imines 9 has intimated that the proton transfer proceeds stereoselectively.

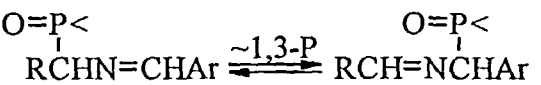
The presence of the activating phosphorus group in 10 enables, by way of 1,2-H-shift, a thermal generation of azomethine ylides *B* which can be trapped by dipolarophiles. Cycloaddition in this case is nonstereoselective. By the dipole generation in the presence of a base and subsequent reaction with an alkene containing activating (COOMe) and nucleofugic (Br) substituents, mono- and bicyclic phosphorylated heterocycles were obtained. Under these conditions the cycloaddition proceeds in a stereoselective manner.



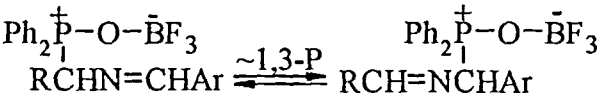
In imines 15, 16 the proton transfer is reversible that, in principle, makes it possible to perform interconversions between α-aminophosphonic and α-aminocarboxylic acid derivatives and, with regard to stereoselectivity of the H-shift, to achieve a transfer of chirality from one center to another.



Also reversible transfer of a phosphorus group in the C=N-C triad was found to be typical for 2-azaallylic systems. The isomerization is a rare in organic chemistry example of rearrangements involving cleavage-renewal of a P-C bond.



Boron trifluoride etherate is an effective catalyst of the $Ph_2P(O)$-group transfer in the azaallylic triad. The rearrangement in this case occurs in complexes formed by coordination of $BF_3$ to the phosphoryl oxygen atom of the imine.



In some cases such complexes were isolated and identified.

Thus phosphorylated azaallylic systems are suitable models for studying different elementotropic (E = H, P, S, Cl) isomerizations in the C=N-C triad. A possible occurrence of such rearrangements should be taken into account in preparative practice, particularly in synthesis of α-aminophosphoryl and α-aminocarbonyl derivatives.

The study was supported in part by grant No.U6Q 200 from the Joint Fund of the Government of Ukraine and International Science Foundation.

## REFERENCES

1. J. Oleksyszyn, J. Pract. Chem., 329, 19 (1987).
2. M. Soroka, D. Jaworska, and Z. Szezesny, Lieb. Ann., 1153 (1990).