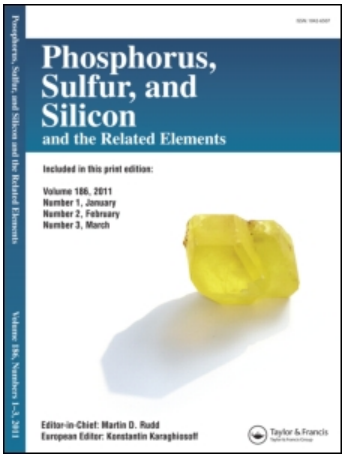


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Sigmatropic Rearrangements in Phosphorylated 2-Azaallylic Systems

P. P. Onys'ko[a]; T. V. Kim[a]; E. I. Kiseleva[a]; A. D. Sinytsa[a]
[a] Institute of Organic Chemistry, Academy of Sciences of the Ukrainian; SSR, Kiev, USSR

To cite this Article Onys'ko, P. P. , Kim, T. V. , Kiseleva, E. I. and Sinytsa, A. D.(1990) 'Sigmatropic Rearrangements in Phosphorylated 2-Azaallylic Systems', Phosphorus, Sulfur, and Silicon and the Related Elements, 49: 1, 73 — 76
To link to this Article: DOI: 10.1080/10426509008038910
URL: http://dx.doi.org/10.1080/10426509008038910

Phosphorus, Sulfur, and Silicon, 1990, Vols. 49/50, pp. 73-76
Reprints available directly from the publisher
Photocopying permitted by license only

SIGMATROPIC REARRANGEMENTS IN PHOSPHORYLATED 2-AZAALLYLIC SYSTEMS

P.P.ONYS'KO, T.V.KIM, E.I.KISELEVA, and A.D.SINYTSA
Institute of Organic Chemistry, Academy of Sciences
of the Ukrainian SSR, Kiev 252660, USSR

Allylic and heteroallylic compounds are classical objects of organic chemistry and can serve as models in the investigation of various theoretical problems. The anions and 1,3-dipoles generated from azaallylic derivatives are widely used in the synthesis of cyclic and acyclic nitrogen-containing compounds.

Our communication deals with the migrations of proton, phosphoryl and dithiophosphate groups in 2-azaallylic triad.

1,3-Prototropic rearrangements

The methylene-azomethine system is one of the least labile prototropic triads. Thus, prototropic equilibrium $p\text{-}RC_6H_4CH{=}NCH_2Ph \rightleftharpoons p\text{-}RC_6H_4CH_2N{=}CHPh$ occurs only at high temperature in the presence of a strong base, the equilibrium constant (lg K) being linearly dependent on the σ_p-constants of substituents.[1] We have shown that phosphorylation of imidoylchlorides 1, containing both electron withdrawing and electron donating substituents in benzene rings, leads initially to imidoylphosphonates 2 which isomerize to phosphonates 3 under mild conditions, even in the absence of a base.

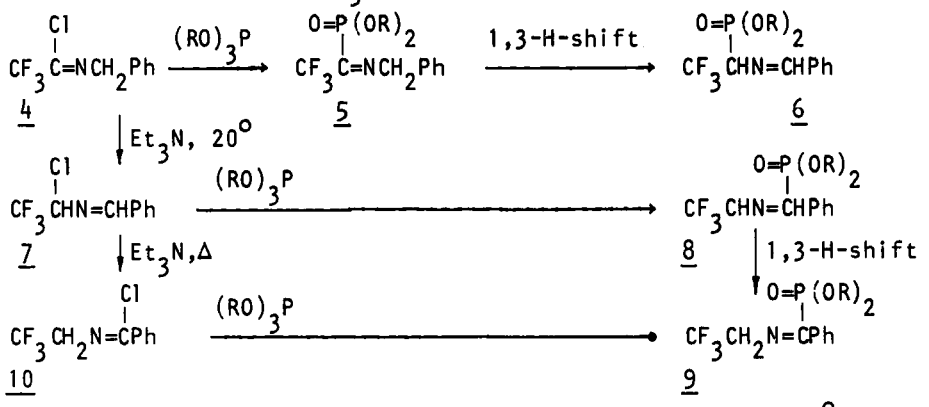
$$XC_6H_4\underset{\underset{\mathbf{1}}{}}{\overset{Cl}{\overset{|}{C}}}{=}NCH_2C_6H_4Y \xrightarrow{R_2POR'} XC_6H_4\underset{\underset{\mathbf{2}}{}}{\overset{O{=}PR_2}{\overset{|}{C}}}{=}NCH_2C_6H_4Y \xrightarrow[-\text{shift}]{1,3\text{-H-}} XC_6H_4\underset{\underset{\mathbf{3}}{}}{\overset{O{=}PR_2}{\overset{|}{C}}}HN{=}CHC_6H_4Y$$

Y = H; X = 4-MeO, 4-Me, H, 4-Cl, 2-Cl, 4-Br, $4\text{-}NO_2$; X = H; Y = 2-F, 3-F, 4-F, $4\text{-}NO_2$

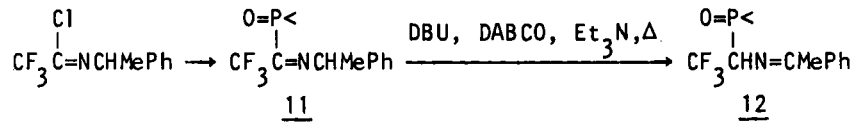
Thus, the electronic nature of X- and Y-substituents has no influence on the prototropic equilibrium: in all cases the equilibrium is completely shifted towards the compounds in which the phosphoryl group is attached to the sp^3-carbon atom of C=N-C triad. This is explained by the effective conjugation of the benzene ring and the C=N bond in isomers 3 and steric hindrance to such conjugation in compounds 2.

Interesting results were obtained in phosphorylation of chloro-

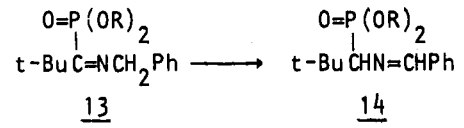
azomethines containing CF_3-group instead of Ph-substituent:



Chloroazomethines 4, 7, 10 are kinetically stable at room t° but undergo base catalyzed irreversible isomerisation by prototropic and chlorotropic shifts.[2] Unlike this, phosphorus derivatives 5, 8 undergo 1,3-H-shift to give phosphonates 6 and 9, even at 20° in the absence of base. In phosphonates 11 the lability of the NCH-proton is decreased due to the Me-group and the conversion to 12 can be performed only at high temperature under base catalysis.

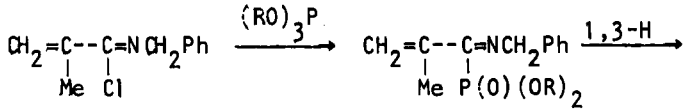


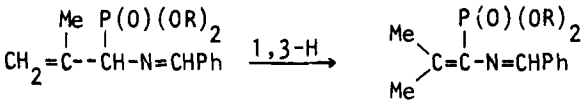
If CF_3- in 5 is replaced by t-Bu-group, the 1,3-H-shift in 13 occurs only at 140-160°. This difference is connected mainly with the polar



effects of CF_3- and t-Bu-groups. In 13 the steric properties of phosphoryl groups in series $(MeO)_2P(O)$ < $(EtO)_2P(O)$ < $(i\text{-}PrO)_2P(O)$ < $(Me_3SiO)_2P(O)$ have little influence on 1,3-H-shift. As a result of steric hindrance to conjugation of the C=N bond with the Ph-ring on the contrary, the facility of isomerization 8 → 9 is decreased in the series EtOP(O)F > i-PrP(O)F; $(EtO)_2P(O)$ > $(i\text{-}PrO)_2P(O)$.

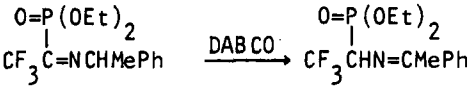
When alkenyl- and Ph-substituents are attached to 1,3-atoms of C=N-C triad, phosphorylated azadienes with longest conjugation chain are formed:





Stereoselectivity of 1,3-H-shift. Asymmetric induction

We have found that the base-catalyzed isomerization 15 → 16 is stereoselective and leads to asymmetric induction at chiral center formed as a result of 1,3-H-shift.



15 16

Enantiomeric purity (E.P.) of 16 was determined from its PMR-spectra. It must be noted that isomerization 15 → 16 can be accompanied by a racemization of 15 and/or 16 in reaction conditions. So the values of E.P. for 16 at different degrees of conversion 15 → 16 (Et_3N, 90°) were determined:

[16]/[15]	0.4	0.6	2.2	6.7
E.P. %	80	40	34	22

From the obtained data it follows that at low conversion levels the value of E.P., and consequently the degree of stereoselectivity, exceeds 80%. Thus, stereospecifity of proton transfer in the α-phosphorylated imines, models of biochemical trans-amination reactions, can be accomplished without any participation of enzymes.

Phosphorotropic migrations

We have shown the possibility of phosphoryl groups migration in the C-N-C-system

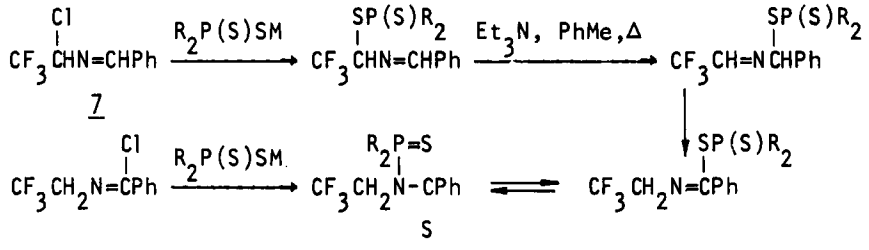
17 18

The facility of migration decreases in the series $Ph_2P(O)$ > $(Me_3SiO)_2P(O)$ > $(EtO)_2P(O)$. In some cases thermal phosphorotropic shift is accompanied by E-Z-isomerization at the C=N bond. One of the driving forces in rearrangement 17 → 18, which is accompanied by the destruction of preferable N-benzylidene structure, is apparently the steric hindrance at the sp^3-carbon atom in 17. At the same time the migration of Ph_3P-group in the nitrophenyl-substituted C-N-C triad proceeds under the mild conditions, the equilibrium being settled at 20°:

19 20

Migration of dithiophosphoryl groups

We have found that imines 21, when heated in the presence of nitrogen bases, undergo migration of dithiophosphoryl-substituent followed by prototropic rearrangements and phosphorotropic tautomerism in the S-C-N-triad.



7

The results presented above provide a basis for the synthesis and mechanistic study of phosphorylated azaallylic derivatives.

REFERENCES

1. P.A.S.Smith, Chi Van Dang, J. Org. Chem., 41, 2013 (1976).
2. Tanaka Kiyoschi, Daikaku Hiroki, Mitsuhaschi Keiryo, Heterocycles, 21, 611 (1984).
3. V.A.Palm: "Introduction in Theoretic Organic Chemistry", Moscow (1974).