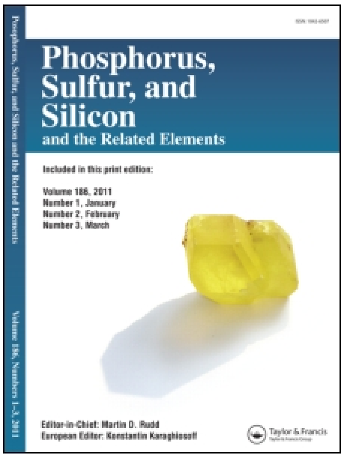

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Phosphorotropic Tautomerism in Amidine Systems

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PHOSPHOROTROPIC TAUTOMERISM IN AMIDINE SYSTEMS

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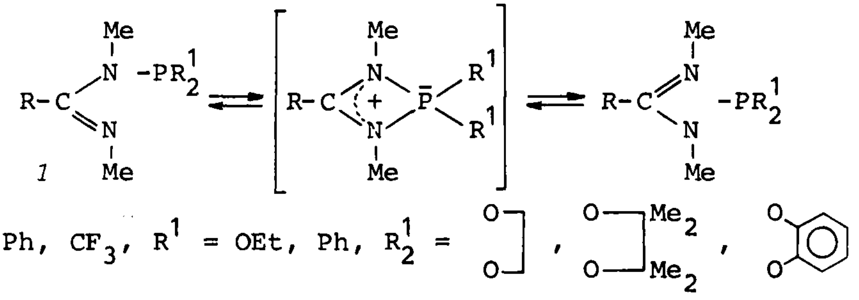
During the last years considerable progress was made in the study of phosphorotropic tautomeric transformations, which involves quick reversible migrations of phosphorus groups between nucleophilic centers of molecule. Phosphorotropic systems may serve as simple and clear models for study of the mechanism of substitution reactions at the phosphorus atom.

The phosphorylated amidines are universal systems for realization of migrations of groups with phosphorus atom in various valence and coordination state. In this report the examples of phosphorotropic tautomeric transformations in amidine systems are demonstrated and main principles of their realization are established.

Degenerative migrations of tricoordinated phosphorus groups for phosphorylated symmetrical N^1,N^2-dimethyl amidines of benzoic and trifluoroacetic acid *1* containing 1,3,2-dioxaphospholane, 4,4,5,5-tetramethyl-1,3,2-dioxaphospholane, 4,5-benzo-1,3,2-dioxaphospholane, dietoxyphosphine and diphenylphosphine groups were studied in detail.[1]

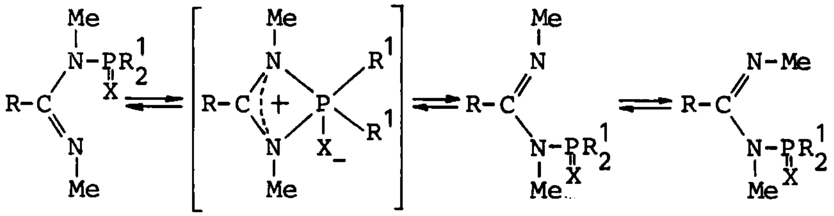


1

R = Ph, CF_3, R^1 = OEt, Ph, R^1_2 =

The migrations are mainly intramolecular, but in polar solvents at higher temperatures the tricoordinated phosphorus groups undergo both intramolecular and slower intermolecular migrations.[1]

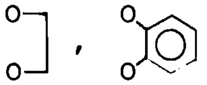
In contrast to the derivatives of tricoordinated phosphorus *1*, the phosphoryl and iminophosphoryl groups containing dimethylamidines *2*, exist as equilibrium mixture of Z,E-isomeres at C=N bond. In compounds *2* two dynamic processes occur the Z,E-isomerization at the C=N bond and phosphorotropic tautomerism.[2]



2

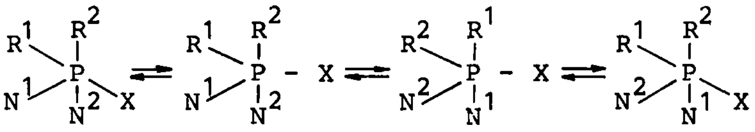
R = Ph, CCl_3, CF_3, $CHCl_2$, R^1 = OEt, $OCH_2CF_2CHF_2$, Cl, F

R^1_2 =



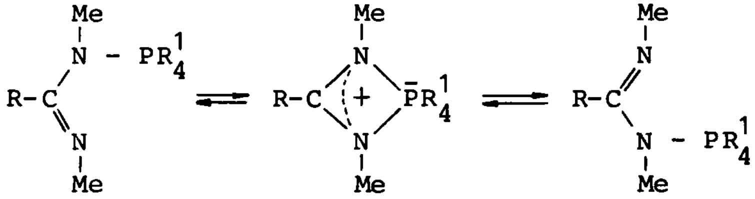
, X = O, NPh

The primary act of migration involves the attack of the lone electron pair of imino nitrogen on phosphorus atom and formation of cyclic intermediates *3* with a trigonalbipyramidal phosphorus configuration. The amidine triad geometry provides only axial-equatorial position for attacking and leaving nitrogen atoms in intermediate *3*. To allow the nitrogon atom to leave the axial position according to the principle of microscopic reversibility the process must include the stage of permutational isomerisation.

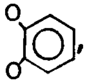


3

During the migration of tri- and tetracoordinated phosphorus the pentacoordinated intermediates have a short lifetime and cannot be detected even by spectral methods. In contrast to this, hexacoordinated structures *4*, being intermediate products of the pentacoordinate phosphorus groups, migration in amidines *5* have been isolated and identified.[3]

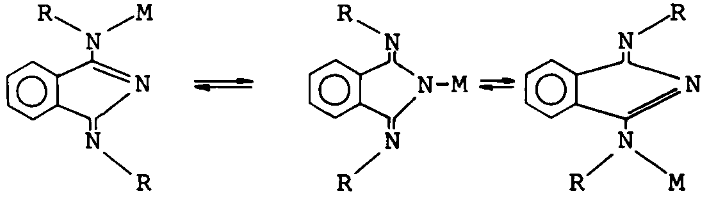


5 *4*

R = Ph, CCl_3, CF_3, R^1 = Cl, F, R^1_2 = , PR^1_2 = PF_3Ph

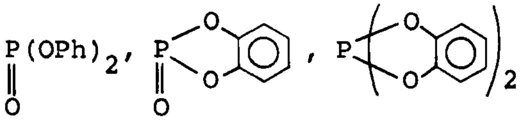
Quantitative investigations of tautomeric migrations of tri-, tetra- and pentacoordinated phosphorus groups revealed that the process of migrations depends upon the nature of substituents at phosphorus, carbon and nitrogen atoms of amidine triad. The character of substituents at the migrating phosphorus atom produces the most pronounced effect on the process. Migration is considerably accelarated by electron-withdrawing substituents enhancing properties of the phosphorus atom. Similar effect is produced by the inclusion of the phosphorus atom into a dioxaphospholanic cycle which is capable to stabilize the hypervalent state of phosphorus cyclic intermediate. At the same time, the nature of solvent produces little effect on the course of intramolecular migrations. Free activation energies $\Delta G^{\neq}$ of migrations lie in range from 8 to 26 Kcal/mol.

Intramolecular 1,5-phosphorotropic transfer occurs in the ambident pentad N-C-N-C-N of 1-amino-3-iminoisoindolenines *6* containing phosphoryl and phosphoranyl groups.[4]



6 *7*

R = Me, Ar, M =



$P(O)(OPh)_2$

As the pentad geometry hinders simultaneous involvement of both exocyclic nitrogen atoms in the formation of hypervalent cyclic intermediate the process proceeds as two consecutive 1,3-migrations via the bridging nitrogen atom in the structure *7*. The intramolecular migrations of phosphoryl and phosphoranyl groups are intermediated by diazaphosphetidine structures with penta- and hexacoordinated phosphorus atoms respectively.

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