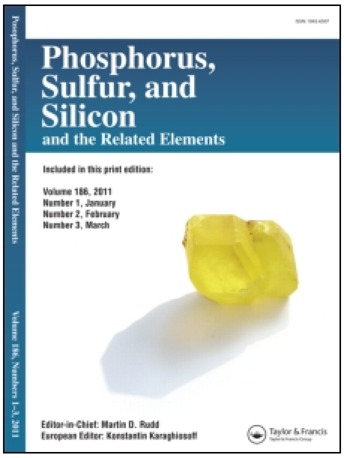

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Phosphorotropic Tautomerism in Amidines

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PHOSPHOROTROPIC TAUTOMERISM IN AMIDINES

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We have discovered and systematically studied the fast reversible 1,3-rearrangements phosphorus-containing groups with tri-, tetra- and pentacoordinate phosphorus in amidines by means of NMR ^{1}H, ^{13}C, ^{31}P spectroscopy.

The intramolecular rearrangements of P^{III}, P^{IV} groups proceeded according to the three-step scheme: "addition-polytopal rearrangement in pentacoordinate intermediate-elimination". The stereochemical correspondance between initial and transition states of the reaction is the main condition of the realizing of the phosphorotropic rearrangements. On carrying out steric and electronic conditions the free energies activation for migrations of P^{III}, P^{IV} groups is decreased to 30 KJ/mol and smaller.

Intramolecular phosphorotropic rearrangements of P^{V} groups are proceeded through the associative nucleophilic substitution at a phosphorus and may be accompanied by the formation of stable hexacoordinate cyclic amidiniumphosphorates. This stereochemically nonrigid compounds rearranged by a intramolecular bond-repture mechanism through the formation of trigonal-bipyramidal or square-pyramidal intermediates.

Intramolecular multi-central 1,3-rearrangements of P^{IV} and P^{V} groups were discovered in the system 1-amino-3-iminoisolenine == 1,3 diiminoisoindoline.

* At different stages this investigation had been preformed together with professors
N.N. MEL'NIKOV, L.N. MARKOVSKI, A.F. GRAPOV,
and doctors
V.I. KAL'TCHENKO, L.Y. BOGEL'FER and others.