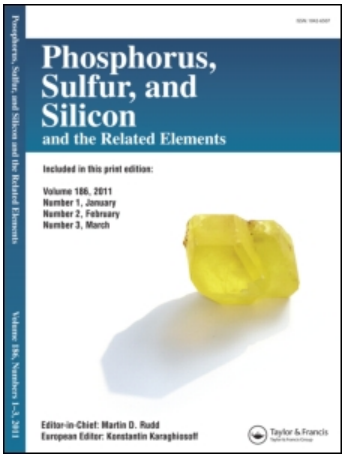

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VINYLPHOSPHITE - VINYLPHOSPHONATE REARRANGEMENT IN ACYCLIC AND CYCLIC SYSTEMS

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Acyclic vinylphosphites (1) with Π-acceptors at the β-carbon atom of vinyloxylic system and some cyclic vinylphosphites, 4-methylen-1,3,2-dioxaphosphorines (2) with electron withdrawing groups at C^5 in the heterocycle, and 4-methylen-1,3,2-oxazaphosphorines (3), may undergo earlier unknown vinylphosphite-vinylphosphonate rearrangement. This rearrangement seems formally like a migration of the phosphorus-containing fragment to α-carbon of vinyloxylic system and results in the formation of acyclic vinylphosphonates (4) in the case of (1), 2-oxo-3-methylen-1,2-oxaphospholenes (5) and 2-oxo-5-methylen-1,2-azaphospholenes (6) in the cases (2) and (3) respectively. Isomerization is favoured by electrondonating groups at the phosphorus (III) atom. It is likely that the rearrangement of (1) and (2) proceeds through the stage of formation of cyclic oxeten-cation and disubstituted phosphite-anion as intermediates, which then combine to vinylphosphonates.