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ISOMERISATION OF cis, trans 4-METHYL-2-OXO-2H-1,3,2-DIOXAPHOSPHORINANES

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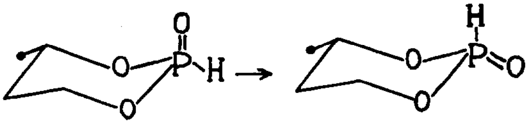
Recently, the stereochemistry of the phosphorus-containing six-membered heterocycles has been studied extensively. Compounds investigated were either cyclic phosphates, thiophosphates, phosphonates containing a pentavalent four-coordinated phosphorus[1], or cyclic phosphites whose phosphorus was three-coordinated[2]. The present authors[3] and Mikolajchyk[4] have synthesised stereoisomeric 4-methyl-2-oxo-2H-1,3,2-dioxaphosphorinanes which may be expected to show the peculiarities characteristic of each of the groups mentioned above. We have found that the trans isomer, when heated, isomerises to give the cis isomer while the transformation rate relates to just the change in the configuration at the phosphorus[5]. The isomerisation is catalysed by acids and bases.

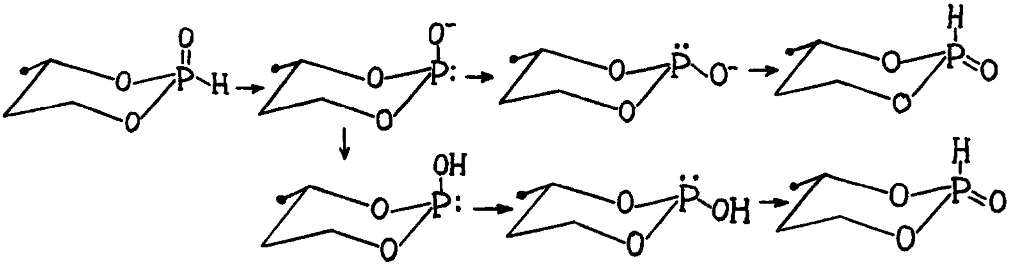


The reaction is, probably, related to prototropic processes resembling the phosphonate-phosphite tautomerism of hydrogenphosphonates. The tautomerism is known to have been studied rather qualitatively. Therefore, the isomerisation kinetics seems to be a challenging problem. The sample was 4-methyl-2-oxo-2H-1,3,2-dioxaphosphorinane (90% trans-, 10% cis-isomer). The conversion was measured by PMR in the sample tube of a T-60 (Varian) or C-60HL (JEOL) instrument.

Table

t°C	35	79	125	148
rate constant sec^{-1}	$1.31 \cdot 10^{-8}$	$1.40 \cdot 10^{-6}$	$5.34 \cdot 10^{-5}$	$3.48 \cdot 10^{-4}$

The reaction is first-order, the activation energy is 23.0±0.8 kcal/mole. This is somewhat lower than the barrier to the inversion in optically active tertiary phosphines[6]. We assume that the isomerisation starts with a deprotonation of the phosphite. The resulting anion which contains a three-coordinated phosphorus, or the respective hydroxy derivative, undergoes the inversion at the phosphorus. The process is terminated with the usual prototropic transformation resulting in the phosphoroyl form of the ester.



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