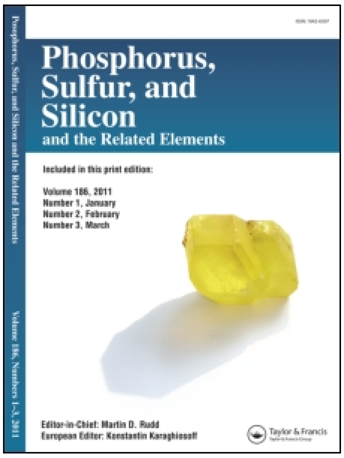

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INTRAMOLECULAR PYRIDINE-CATALYSED MIGRATION OF THE THIOPHOSPHORYL GROUP FROM SULPHUR TO OXYGEN IN SUGAR vic-HYDROXYPHOSPHORODITHIOATE SYSTEMS

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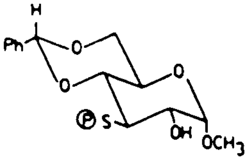
Transfer of the phosphoryl group from oxygen to vicinal hydroxyl group takes place in many important biological processes. A similar reaction occurs in vicinal hydroxy-thiolo systems, in which case the phosphoryl group spontaneously migrates from sulphur to oxygen. This type of transphosphorylation was observed in the synthetic procedures leading to episulphides or alkenes, such as the reaction of oxiranes with monothioacids of phosphorus,[1] reactions of carbonyl compounds with carbanions containing the thiophosphoryl group[2] and in the reactions of alkoxyanions generated from S-(β-oxoalkyl) thio- and selenophosphates.[3]

In the course of extensive studies on the reaction of sugar oxiranes with thio-, dithio- and selenoacids of phosphorus we have demonstrated that when 5,6-anhydro-1,2-O-isopropylidene-α-D-glucofuranose undergoes reaction with O,O-dialkyl phosphorothioic acids, the primarily formed β-hydroxyphosphorothioate undergoes spontaneous transphosphorylation to give β-mercapto sugar phosphate. ^{31}P NMR studies of this reaction provided experimental proof for the intermediacy of the pentacovalent phosphorus species in the transphosphorylation step.[1c]

The reaction of sugar epoxides with organic phosphorodithioic acids leads to β-hydroxyphosphorodithioates, which, due to the diminished electrophilic character of phosphorus in the thiophosphoryl group, do not undergo transphosphorylation and are stable under acid and neutral conditions.[4] Migration of the thiophosphoryl group occurs, however, in the presence of a basic catalyst. We have previously explored the reaction of sugar epoxides with alkylammonium salts of phosphorodithioic acids in the synthesis of sugar episulphides.[4] Under the applied conditions the intermediate β-mercaptophosphorothioates could not be isolated. Bearing in mind that generation of the mercapto function in carbohydrate moieties under mild conditions is still a problem to be solved in carbohydrate chemistry, we decided to investigate more thoroughly the reaction of sugar epoxides with phosphorodithioic acids. We found that pyridine is the basic reagent of choice in order to stop the reaction at the stage of the desired β-mercaptophosphorothioates.

By employing appropriate model sugar β-hydroxyphosphorodithioates (Scheme 1) we were able to correlate the propensity of the thiophosphoryl group to migrate with the steric arrangement of groups involved in the transphosphorylation process. We found that diequatorial geometry of the reacting groups is the most suitable for thiophosphoryl group transfer, which occurs almost spontaneously in pyridine solution. The transfer from axial to equatorial position is also possible, although it requires more time. Diaxially oriented substituents do not migrate under the applied conditions (pyridine solution, room temperature) due probably to the distance between the reacting centres which does not allow the formation of the pentacovalent species. ^{31}P NMR monitoring of the progress of the transphosphorylation step enabled us to propose the mechanistic scheme of thiophosphoryl group transfer (Scheme 2), which is consistent with our previous investigations.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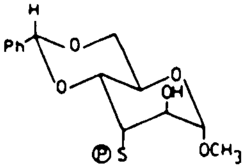
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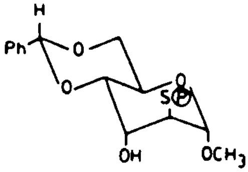
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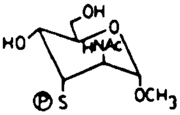
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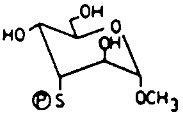
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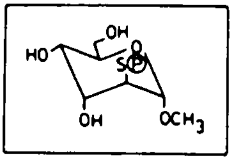
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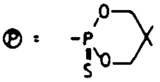
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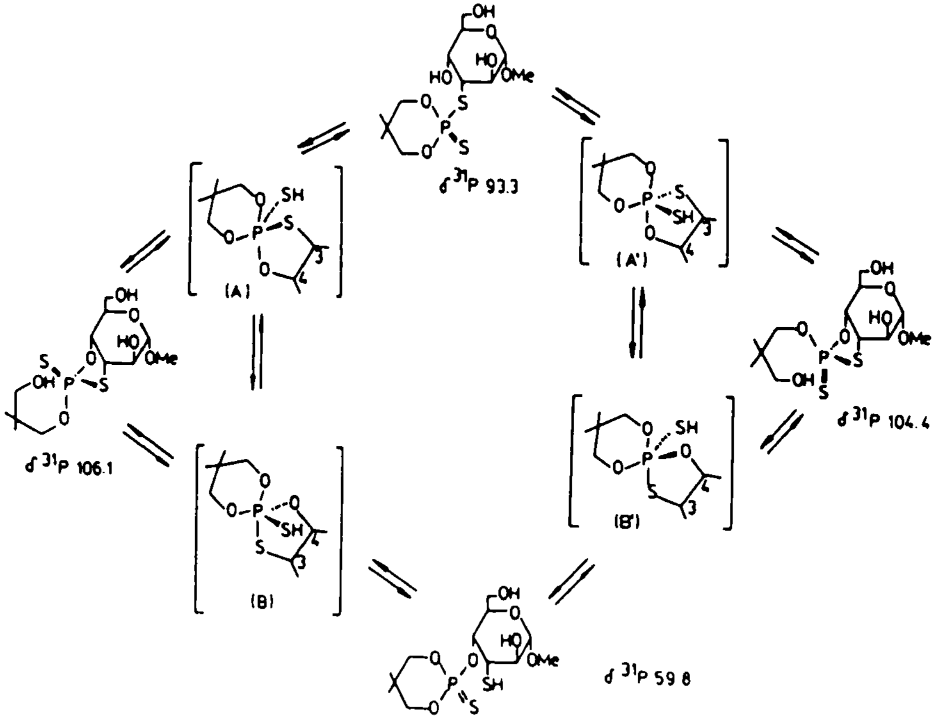
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(A)
(A')
(B)
(B')
δ ³¹P 106.1
δ ³¹P 104.4
δ ³¹P 59 8

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