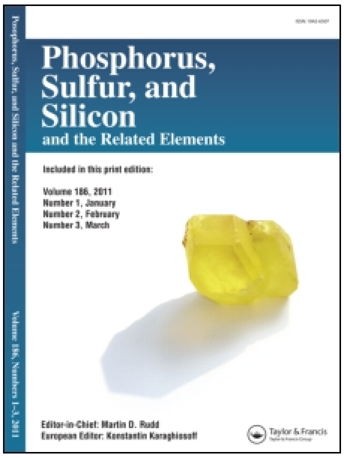

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Synthesis and Chemical Properties of Phosphobicyclic Carbohydrates

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SYNTHESIS AND CHEMICAL PROPERTIES OF PHOSPHOBICYCLIC CARBOHYDRATES

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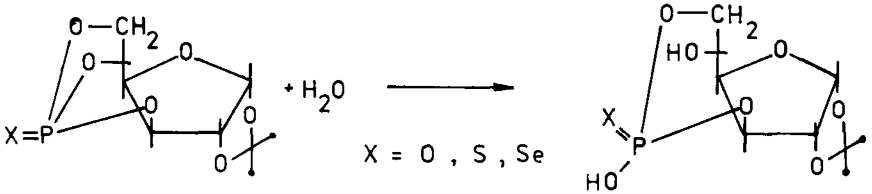
New methods of bicyclophosphorylation of partially protected and free pyranoses and furanoses with trivalent phosphorus acid derivatives are proposed. Over thirty carbohydrate bicyclophosphites belonging to the phospholane-phospholane, phospholane-phosphorinane, phospholane-phosphepane and phosphorinane-phosphepane types were obtained. Their structure and stereochemistry were studied by NMR and X-ray methods. The bicyclophosphite system was found to be strongly conjugated and the bond angles O-P-O substantially narrowed compared to the standard values. Chemical studies show that the sugar bicyclophosphites readily enter into homolytical reactions while their heterolytical reactions are impeded. Nevertheless, we succeeded in oxidizing these compounds to bicyclic phosphates, sulfides and selenides. As opposed to bicyclophosphites, the carbohydrate bicyclophosphates display a high and varied reactivity. They vigorously transfer the phosphoryl oxygen, selenium and sulfar atoms to acyclic phosphines, phosphites and phosphorous acid amides, and undergo reduction to compounds containing tricoordinated phosphorus atom. The phosphates readily enter into heterolytical reactions with water, alcohols, amines, etc. It is essential that the reactions of the phosphates with nucleophiles proceed stereo- and regioselectively, for example as follows:



The structures were also confirmed by an X-ray study.