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## Synthesis and Reactivity of New Pentacoordinated Phosphoenolpyruvate Derivatives

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Pentaoxyphosphoranes are closely related as intermediates to the biologically important phosphate ester reactions. Thus, the hydrolysis of phosphoenolpyruvate 1, a strong phosphorylating agent, proceeds most probably via the formation of the cyclic acyloxyphosphorane 2.

 $\frac{1}{2}$  To our knowledge, structures of type  $\frac{2}{2}$  have not yet been isolated. So, it becomes important to prepare well-defined species bearing such a ring.

This paper describes a quantitative method for the synthesis of pentaoxyphosphoranes  $\underline{5ab}$  bearing, for the first time, the requested ring.

The method involves the first step of a Perkow reaction followed by a ring closure (1).  $\mu$  .0

The first step happens without any proton transfer process observed with  $\alpha$ -ketoacids. Moreover, despite the elimination of Br, no Arbuzov reaction takes place with R=Me, since it is the major reaction with trimethylphosphite. However, the presence of the dioxaphospholane ring in  $\underline{3}$  facilitates the ring closure to give the spirophosphoranes  $\underline{5}$ . The hydrolysis, alcoholysis and aminolysis of  $\underline{5}$  under mild conditions are then studied.