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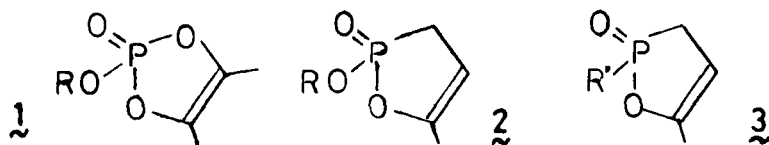
Catalyzed Methanolysis of Five Membered Ring Phosphoenolates

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Alkyl cyclic enediolphosphates, **1**, have been widely investigated to probe nucleophilic catalysis in the phosphorylation of alcohols. Hexacoordinated species have been supposed to participate into the process¹. The same type of intermediates has been recently considered in the solvolysis of halogenophosphorus derivatives, activated by nucleophiles².

In the present communication, we present kinetic and stereochemical data concerning the catalyzed methanolysis of five-membered ring phosphoenolates **2**, **3**.



The stereochemistry of the catalyzed methanolysis of **2** (R = Menthyl) is the same, whatever the effectiveness of the base :



The participation of a mechanism involving general base catalysis cannot be dismissed, but we have discarded a process of simple decomposition of the phosphoranoxide.

Complex rate laws and isotopic effects allow us to propose an alternative mechanism in which the first step is the formation of a phosphorane.

References

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- 2 - R. Corriu, G. Lanneau, J.P. Dutheil, *J. Amer. Chem. Soc.*, **106**, 1060, (1984) and references.