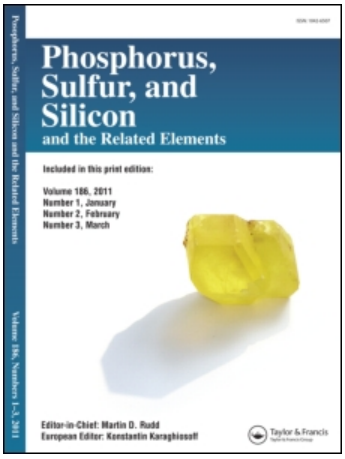

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R. Corriu[a]; A. Daffi[a]; G. Lanneau[a]
[a] Institut de Chimie Fine - Université des Sciences et Techniques du Languedoc - Hétérochimie et amino-acides - UA 1097, Montpellier-cédex, France

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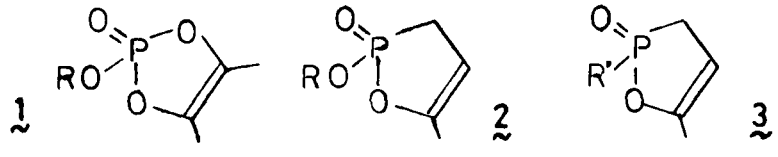
Catalyzed Methanolysis of Five Membered Ring Phosphoenolates

R. CORRIU, A. DAFFI, G. LANNEAU*

Institut de Chimie Fine - Université des Sciences et Techniques du Languedoc - Hétérochimie et amino-acides - UA 1097 - Place Eugène Bataillon - 34060 MONTPELLIER-cédex - France

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 process[1]. The same type of intermediates has been recently considered in the solvolysis of halogenophosphorus derivatives, activated by nucleophiles [2].

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



1 2 3

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

$$Et_3N > DMAP > NmI$$

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.