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Structure-Memorization Phenomenon During the Hygrolysis of a Spirophosphorane to a Phosphonate

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STRUCTURE-MEMORIZATION PHENOMENON DURING THE HYDROLYSIS OF A SPIROPHOSPHORANE TO A PHOSPHONATE

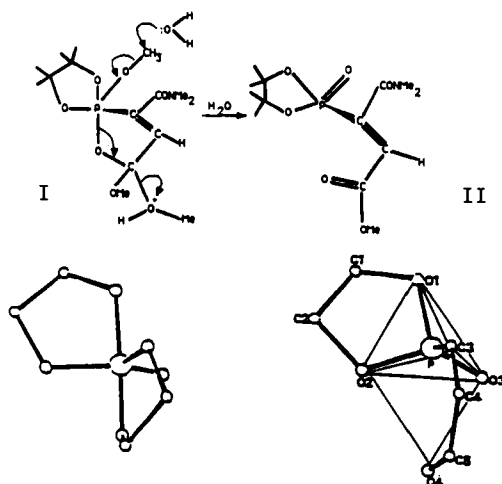
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Phosphonate II is obtained by hydrolysis of the spirophosphorane I (1). IR, ^1H and ^{31}P NMR spectra confirm the phosphonate structure. However, one question remains about the relative position of the amide and ester function relative to the phosphonate group. In front of this difficulty, we resolved it through X-Ray crystallography of II. Phosphonate II structure shows a slightly distorted figure of the spirophosphorane I of which it comes from. This observation is quite astonishing because of the lot of possible carbonyl positions of the new ester function. We can reasonably rationalize this phenomenon as a memory effect, phosphonate II "keeping in mind" even in solid state, i.e. in the more comfortable conformation, the memory of the phosphorane structure.

More, this observation allows to justify unambiguously the hydrolysis mechanism of spirophosphorane I. This one involves the apical bond break with the concomitant formation of the $\text{P}=\text{O}$ bond. We agree with the work of MC Castelijns and al (2) and we give a complementary information about the hydrolysis mechanism of the phosphorane I which have a $\text{P}-\text{C}$ bond.

In conclusion, we have proved a very important memory effect which permits to explain easily the opposite reaction paths we need for the $\text{P}_{\text{IV}} \rightarrow \text{P}_{\text{V}}$ way.



(1) Ph. D. Thesis L. LABAUDINIÈRE (PARIS)

(2) M. MCF CASTELIJNS, P. SCHIPPER, D.V. AKEN and H.M. BUCK.
 J. Org. Chem. 1987, 46, 47-53.