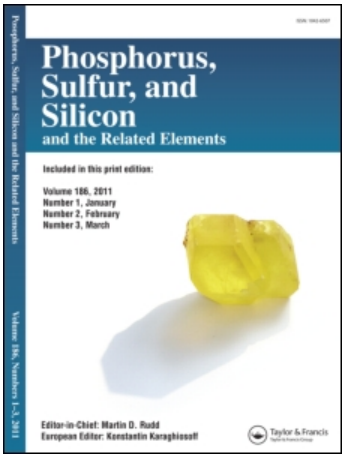

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New Phosphorus Compounds Prepared from α- Ketoacids Hydrido and Hydroxyphosphoranes Involving Enolpyruvate Moieties - Synthesis and Properties

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NEW PHOSPHORUS COMPOUNDS PREPARED FROM α- KETOACIDS HYDRIDO AND HYDROXYPHOSPHORANES INVOLVING ENOLPYRUVATE MOIETIES - SYNTHESIS AND PROPERTIES

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Abstract Synthesis and properties of new phosphoranes prepared from α-ketoacids are discussed.

INTRODUCTION

Substituted pyruvic acids can be considered either as carbonyl compounds and as potential α-enolacids. Thus, two investigation ways have been developped : - reactivity of carbonyl group of ketoacids 3 - 7 towards phosphoranides generated from phosphoranes 1, 2, - synthesis and properties of phosphoranes having substituted pyruvate moieties. These are good models of intermediate phosphoranes postulated in reactions of biological interest, involving phosphoric esters of enolpyruvic acid[1].

RESULTS AND DISCUSSION

1. α-ketoacids reactivity towards phosphoranides.

Ketoacids 3 - 5 react with phosphoranes 1, 2, in presence of triethylamine giving, with good yield, compounds 8, 9. In solution, these last slowly give adducts 10 (from 1) or phosphoranes 11 (from 2) (schemes (1)). From ketoacids 6, 7, adducts 10 were directly obtained, the formation of compound 8 being not observed.

Compounds 8, 9 react with phosphorus trichloride or (and) chloridite 12 leading to polyphosphoranes 13, 14 exhibiting an interesting diastereoisomery (schemes (1)).

2. α-ketoacids as α-enolacids.

α-ketoacids 3 - 5, as usual α-hydroxyacids[2] easely react with phosphorus trichloride giving phosphoranes 15, isolated with good yields in the case of acids 4 and 5. Concerning 15a, a tautomeric equilibrium $P^{V} \rightleftharpoons P^{III}$, takes place (scheme (2)). As phosphoranes 1, 2, compounds 15 are deprotonated by triethylamine[3]. Moreover, they form sixcoordinated phosphorus adducts with DMF, while 1, 2 do not react. They are oxidized in mild conditions (DMSO, room temperature) to the corresponding hydroxyphosphorane, not sufficiently stable to be isolated. Nevertheless, thiolo and selenoderivatives 16 and 17 have been synthetized reacting elemental sulfur or (and) selenium on compounds 15a,b, in presence of triethylamine (schemes (2)).

If hydroxyphosphoranes corresponding to compounds 15 were not isolated, homologous derivative 18 has been prepared from the reaction (3) (yield : 30-40%). Its $\delta^{31}P$, consistent with a pentaoxophosphorane, slightly varies with temperature. This phenomenum is connected to the equilibrium (3), largely desplaced towards the form 18. The hydroxyphosphorane corresponding to pyruvic acid 3, unambigously identified in solution, has not been isolated.

CONCLUSION

The synthesis of compounds 15 - 18 provides additional evidences of the existence of intermediate phosphoranes postulated in the hydrolysis of phosphoric, thio, selenophosphoric esters of enolpyruvic acid.On the other hand, reactions of ketoacids with phosphoranides, led to unusual hydroxyacids presenting interesting potential reactivity.

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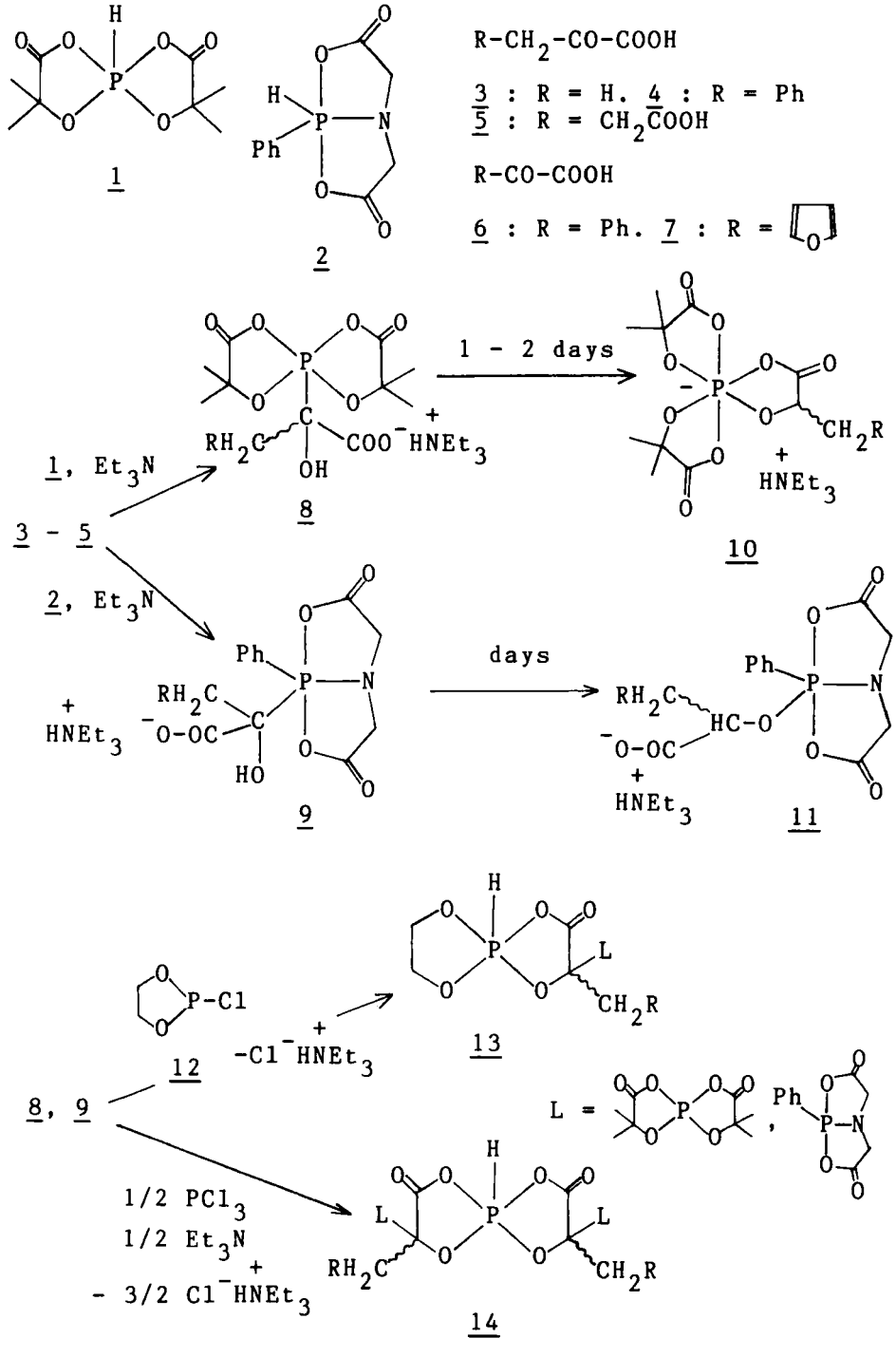
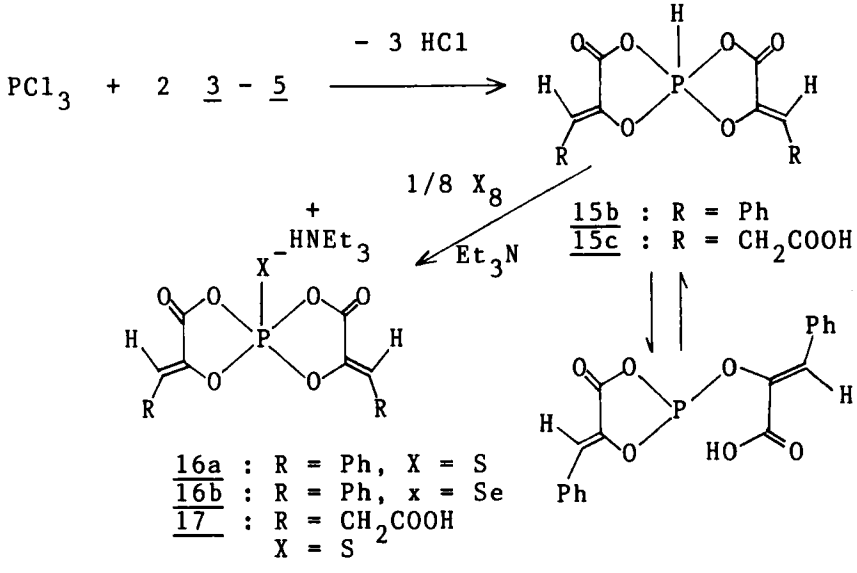
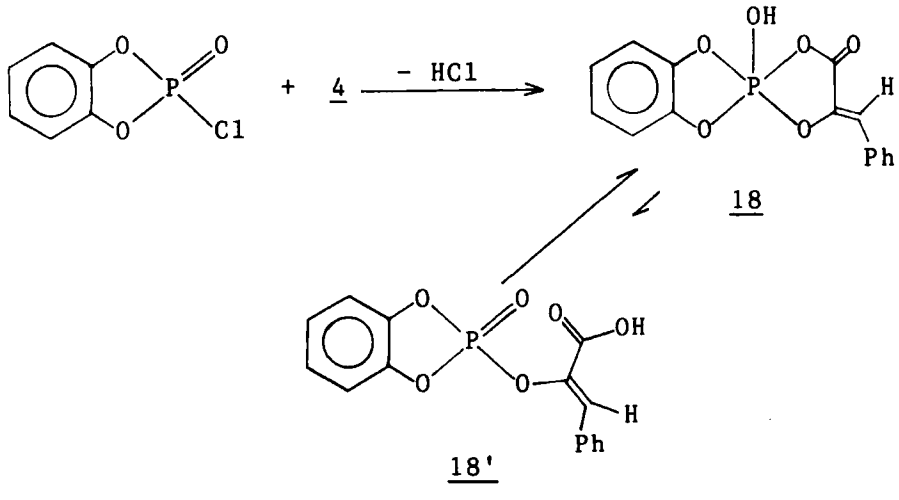


SCHEMES 1



SCHEMES 2



SCHEMES 3