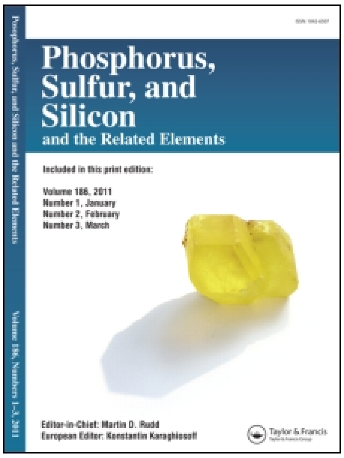

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# A Step by Step Synthesis of Polythiooazaphospholidines

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# A STEP BY STEP SYNTHESIS OF POLYTHIOOXAZAPHOSPHOLIDINES

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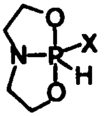
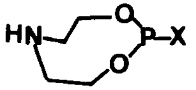
## Abstract

In the majority of the numerous complexes of transition metals obtained with (I) (X=$C_6H_5$) the starting molecule is present under the tautomeric form (I') (phosphocine). Conversely, the present contribution demonstrates that the phospholidines tautomers (I") play an essential role in the sulfuration of (I) (X=OR, $C_6H_5$). This allows to propose a step by step synthesis of polythiooxazaphospholidines.

Organyl bicyclophosphoranes I (X=$C_6H_5$, $CH_3$ ...) are readily available. As such, they are expected to have a poor donor capacity as ligand : indeed phosphorus has no free electrons available and nitrogen is very likely planar. However, under the action of transition metal derivatives, these compounds were shown to yield adducts of their "open form" tautomers (I') (phosphocine tautomers). After hydrogen abstraction in H-P, (I) can also play the role of 3 electrons donor, giving complexes containing a three membered metallacycle $>P\overset{M}{—}O$ and $>P\overset{M}{—}N$ (where M is a 15 electrons transition metal moiety). This versatility allowed to prepare more than 200 complexes, with 10 different metals, and about 25 X ray structures are known. These investigations, mainly developed by Riess, Tkatchenko et al., were nicely reviewed by Agbossou (1). It is worth to notice that the second tautomeric form of (I), that is (I") (phospholidine tautomer), is rarely taken in consideration (2). In the following, the existence of this latter, with a sangling alcohol function, is demonstrated, then making the sequential synthesis of polythiooxazaphospholidines possible.


I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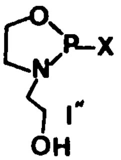
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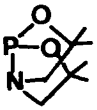
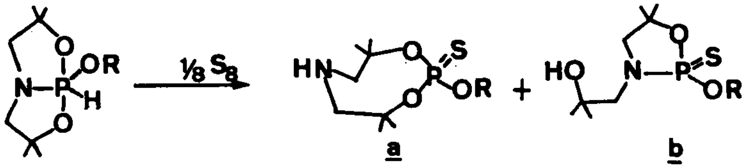

1

The wealth of the chemistry of (I) (mainly with X=$C_6H_5$) prompted us to prepare and study the alkoxyhydridobicyclophosphoranes (I) (X=OR). The reaction of $ROPCl_2$ with aminodiols $(HO{\sim\!\sim})_2NH$ in presence of a base gives medleys which are difficult to share. Therefore, we used the oxidative addition on a constrained bicyclophosphane (3) ; only 1 is used in this investigation.

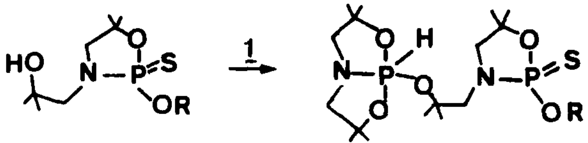
Reactions were monitored by $^{31}P$ NMR at room temperature in benzene solution. Quantitative NMR yield were formed and we are limited only by the difficulty to maintain the purity of the reagent 1 (90-95 %) due to its very high affinity for protic compounds. Phosphoranes 2 ($\delta^{31}P$ = -33.8 ppm $^{1}J_{P-H}$ = 791$_5$ Hz), 3 ($\delta^{31}P$ = -36.9 ppm $^{1}J_{P-H}$ = 798 Hz), 4 ($\delta^{31}P$ = -34.7 ppm $^{1}J_{P-H}$ = 779 Hz) were firstly prepared, using respectively methanol, isopropanol and t-butanol, and the stoechiometric sulfuration was studied. $^{31}P$ NMR spectra of solutions, recorded about one hour after the mixing of reagents, revealed the disappearence of the phosphorane and the presence of two compounds with the following chemical shifts and peaks intensities



2 R=Me 3 R=i.Pr 4 R=t.Bu

| R | a | b | Δδ |
|---|---|---|---|
| 2 (Me) | 54.1 (25 %) | 86.8 (75 %) | 32.7 |
| 3 (i-Pr) | 51.0 (30 %) | 83.5 (70 %) | 32.5 |
| 4 (t-Bu) | 42.4 (45 %) | 75.3 (55 %) | 32.9 |

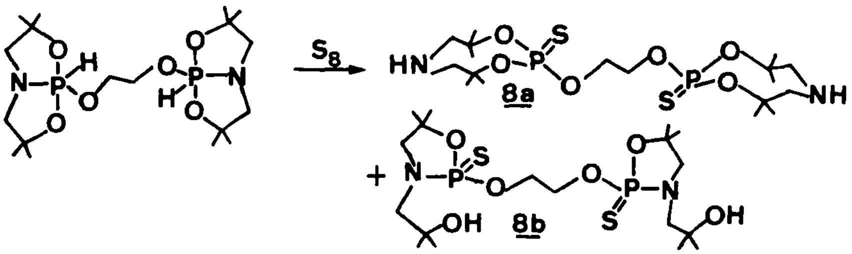
The peak close to ~ 80 ppm increases in time at the expense of that at ~ 50 ppm demonstrating so that one hour after the beginning of the reaction, the mixture is not at the thermodynamic equilibrium. These assignments are supported by (i) the comparison of chemical shifts values with those of similar molecular models (4) (ii) the study of the fine structure of $^{31}P$ peaks ; for example in 4, the 42.4 ppm $^{31}P$ resonance remains a simple peak with and without $^{1}H$ decoupling, whereas a second order fine structure due to $^{3}J_{P-N-CH2}$ appears in the coupled spectra (~ 75 ppm region) (iii) the presence of the t-butylalcohol function in 2b, 3b and 4b which is revealed by the reaction of a second molecule of 1 leading quantitatively to the corresponding bicyclophosphoranes 5 ($\delta^{31}P$ = -36.1 ppm), 6 ($\delta^{31}P$ = -37.0 ppm) and 7 ($\delta^{31}P$ = -36.8 ppm). These results allow to propose the following course of the reaction : the formation of



5 R=Me 6 R=i.Pr 7 R=t.Bu

the thiophosphate (phosphocine tautomer) is followed by an intramolecular attack of nitrogen to phosphorus which displaces the t-butyl alcohol function. In the overall reaction, starting from an alcohol reacting on 1 to obtain an alkoxyphosphorane, we can recover the alcohol function by sulfuration of this latter. We are now in a situation where we may check for the possibility of synthesizing polythiooxazaphospholidines as stated in the tittle.

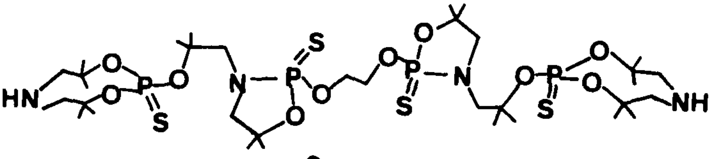
Starting with the ethylene glycol bisphosphorane (δ = -36.6 ppm, $^1J_{P\text{-}H}$ = 797.8 Hz), the stoechiometric sulfuration gives a mixture of 8a-8b, one hour after mixing the reagents (8a δ = 51.7 ppm 8b δ = 84.3 ppm) and only 8b stays present 24 h later. A second phosphoranylation of



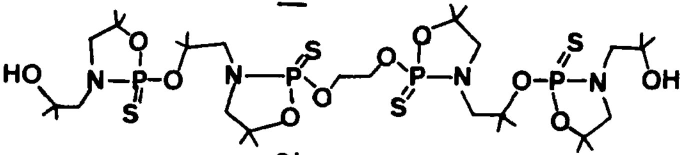
8a

8b

8b followed by a second sulfuration leads to a mixture of 9a-9b.



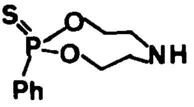
9a

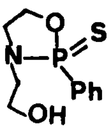


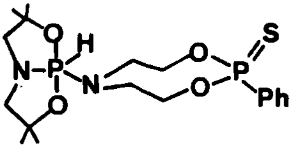
9b

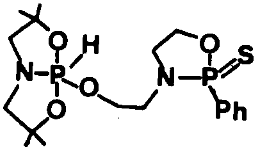
Here also we observe a decreasing of 9a which disappears almost completely 24 h later. Thus, it appears that alkoxyhydridobicyclophosphoranes represent a suitable starting material for the step by step preparation of polythiooxazaphospholidines (6).

The same scheme could be applied to phenylbicyclophosphorane (I) (X = $C_6H_5$). We have re-investigated the sulfuration of this compound as it was recently achieved by Bentrude et al. (5). We have established that the kinetic reaction product is the thiooxazaphospholidine 10b ($\delta^{31}P$ = 94.0 ppm) while the thermodynamic one is the thiophosphate 10a ($\delta^{31}P$ = 82.5 ppm) identified by Bentrude et al. (5). It is interesting to notice that in the case of alkoxybicyclophosphoranes (X=OR) the thiooxazaphospholidine form is both the kinetic and thermodynamic product of the sulfuration. We have also showed that the phosphoranylation of both 10a and 10b is accomplished, at room temperature, by means of the bicyclophosphane 1 and leads to a mixture of 11a ($\delta^{31}P$ = -60 ppm $^1J_{P-H}$ = 756 Hz) and 11b ($\delta^{31}P$ = -39.8 ppm $^1J_{P-H}$ = 797 Hz). This result allows, again, a step by synthesis of another type of compounds bearing the thiooxazaphospholidine moiety.


10a


10b


11a


11b

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6 - The collaboration of Latifa Chahoua on a part of this work has been appreciated