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TEN-MEMBERED RING ORGANOPHOSPHORUS MOLECULES AS OBTAINED BY DIMERIZATION OF 1,3,2-DIOXAPHOSPHOLANES

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The polymerization tendency of 1,3,2-dioxaphospholanes has long been recognized [1]. Different linear structures have been proposed for the observed polymeric species. We wish to report here evidence showing that under given experimental conditions, the 2-phenyl-1,3,2-dioxaphospholane can give polymeric species among which are cyclic ten-membered ring dioxaphospholanes. Expansion reactions leading to such medium size cyclic molecules have been reported in a previous study on 1,3,2-dioxaphosphorinanes [2].

The reaction of dichlorophenylphosphine on ethylene glycol by the usual methods [3] yields after distillation a non viscous liquid which is identified as 2-phenyl-1,3,2-dioxaphospholane **1** . The identification is based on elemental analysis, mass spectrometry (molecular peak at m/e 168), and ^{1}H, ^{13}C and ^{31}P n m r spectroscopy. The ^{1}H n m r spectrum is the AA'BB' part of an AA'BB'X system (X phosphorus) with $^{3}J(PH_A) = 8.6$ Hz and $^{3}J(PH_B) = 1.5$ Hz. It must be pointed out that conversely to what has been observed on other 1,3,2-dioxaphospholanes [4] the high field protons (H_A, $H_{A'}$) exhibit the largest $^{3}J(PH)$ value.

When a toluene solution of **1** (c.a. 30 % V/V) is left for a few weeks in a closed (not sealed) n m r tube (solution A), additional lines appear in the n m r spectra. In the proton noise decoupled ^{31}P n m r spectrum, in addition to the single line at -162 ppm due to the molecule **1** , one observes two lines in an approximate 1 to 3 intensity ratio at -155.8 and -155.2 ppm respectively ($W_{1/2} = 1.5$ Hz) and a 1.2.1 triplet ($W_{1/2} = 4$ Hz) at -159 ppm. These lines correspond to three-coordinated phosphorus nuclei [5]. It must be pointed out that

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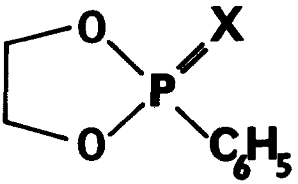
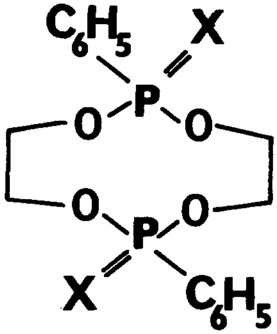
one can kept a toluene solution of **1** for several months in an n m r tube sealed under nitrogen without seeing any additional lines in the ^{31}P (^{1}H) n m r spectrum. This experimental fact suggests that traces of water is probably a determinant factor in the chemical transformation of **1** described in the present communication.



1 X lone pair

1' X sulphur



2a, **2b** X lone pair

2'a,**2'b** X sulphur

Due to the oxidizability of dioxaphospholanes, no attempts were made to isolate the new species which appeared in solution A. Their corresponding P thiono derivatives were isolated by using the technique described in a previous study on the ring expansion of the dioxaphosphorinanes [2] .

By addition of elemental sulfur to solution A and column chromatography, one can separate different molecular species denoted as **1'**, **2'a**, **2'b** and **3'**. **1'** is 2-thiono-2-phenyl-1,3, 2-dioxaphospholane which is identified by elemental analysis, mass spectrometry (molecular peak at m/e 200) and ^{1}H, ^{13}C and ^{31}P n m r spectroscopy. The ring protons are the AA'BB'* part of an AA'BB'X system with $^{3}J(PH_A)$ = 10.6 Hz and $^{3}J(PH_B)$ = 11.8 Hz.

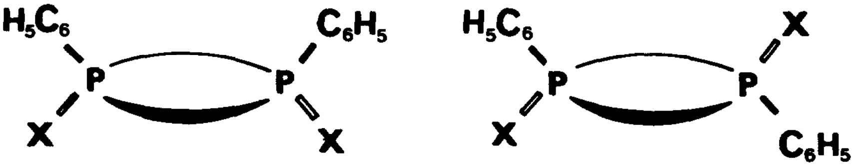
2'a (mp = 142°C), **2'b** (mp = 215°C) which can be separated by thin layer chromatography are the two diastereomeric ten-membered ring dimeric forms of the 2-thiono-dioxaphospholane **1'**. The elemental analysis is in agreement with the formula $(C_8O_2PSH_9)_n$. A molecular weight measurement shows that n = 2, and the mass spectrum exhibits a molecular peak at m/e 400 $(C_8O_2PSH_9)_2$

for both 2'a and 2'b. The ^{1}H n m r spectrum, AA'BB' part of AA'BB'XX' system (X,X' phosphorus) and the proton decoupled ^{31}P n m r spectra (a single sharp peak for each compound at -86.6 and -86.8 ppm respectively) strongly support the ten-membered ring cyclic structure of compounds 2'a and 2'b. The two diastereomeric molecules 2'a and 2'b will differ by the relative orientation of the P=S bonds with respect to the mean plane of the molecule (Figure). At the present time, we have no evidence for definitive assignment between these isomers. Such an assignment could be made by dipole moment measurement. The two species 2'a and 2'b have fairly different solubility properties. 2'b is almost insoluble at room temperature in organic solvents. Such a difference has already been noticed in the two dimeric forms obtained by polymerization of 1-methyl-5,5-dimethyl-1,3,2-dioxaphosphorinane [2].

In addition to 1', 2'a and 2'b, one obtains a fourth species 3', which exhibits a single peak in the proton noise decoupled ^{31}P n m r spectrum ($W_{1/2}$ = 2 Hz) and a complex ^{1}H n m r spectrum (signals within the OCH_2 and aromatic regions). The ^{13}C spectrum shows a triplet (coupling with two equivalent phosphorus nuclei). The elemental analysis is, within the limit of error, in agreement with the formula $(C_8O_2PSH_9)_n$. At this stage, one cannot however conclude if 3' is a large membered ring or a linear chain.

From the identification of the compounds obtained by sulfurization of solution A, one can conclude that among the new species which appear with time on storing a solution of 2-phenyl-1,3,2-dioxaphospholane, are ten-membered ring dioxaphospholanes (2a, 2b). The polymerization here described starting from the 1-phenyl-1,3,2-dioxaphospholane also takes place with 1-methyl-1,3,2-dioxaphospholane. The polymerisation process occurs at such a rate that we have not been able up to now to get a pure sample of the monomeric species without any traces of the polymeric species. Such a ring expansion reaction which can lead to new interesting molecules also occurs in the case of 1,3,2-dioxaphosphorinanes [2] and is now under examination for various heterocyclic organophosphorus molecules.

All the n m r spectra (^{1}H, ^{13}C, ^{31}P) have been recorded at the "Laboratoire Grenoblois de Résonance Magnétique Nucléaire". We thank Mr R. NARDIN and Mr. H. REUTENAUER for their skillfull assistance in recording the n m r spectra.



Schematic representation of the diastereomeric forms of the ten-membered ring 2'a and 2'b

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