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# STEREOCHEMICAL STUDY OF SEVEN-MEMBERED RING PHOSPHINES

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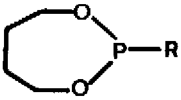
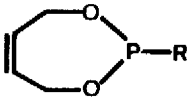
In contrast to the numerous studies available concerning the conformation of five and six-membered ring heterocyclic phosphorus compounds like dioxaphospholanes [1] and dioxaphosphorinanes [2] relatively little attention has been devoted toward the corresponding seven-membered rings [3].

Two recent papers reported stereochemical information on seven-membered ring phosphates. By using an nmr shift reagent, it was shown that 3-substituted-1,5-dihydro-2,4,3-benzodioxaphosphepin 3-oxide exists in equilibrium between two chair forms [4]. In the solid state, the seven-membered ring tetramethylene phosphoric acid ($C_4H_9PO_4$) exhibits a twist chair conformation with the phosphorus and an ester oxygen on one side of the best four atoms plane and a methylene carbon on the other [5]. To our knowledge, there are no structural data concerning similar rings in which the phosphorus atom is three co-ordinated.

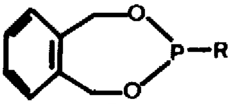
As part of our chemical [6] and stereochemical [7] studies on phosphorus heterocyclic compounds, we wish to present here some nmr data and stereochemical conclusions on three coordinated phosphorus compounds of types A, B and C.



A



B



C

1 R $OC_6H_5$ 2 R $OC_6H_5$ 3 R $OC_6H_5$

Compounds 1, 2 and 3 have been synthesized by the direct mixing of triphenyl phosphite and the corresponding diol in the presence of a catalytic amount of sodium. After distillation (1, 2) or column chromatography over alumina (3), the compounds were identified by elemental

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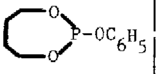
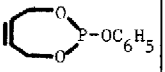
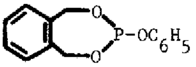
analysis, mass spectrometry and nmr spectroscopy ($^1H$, $^{13}C$, $^{31}P$).

The most important nmr parameters ($^1H$, $^{13}C$, $^{31}P$) concerning compounds **1**, **2** and **3** which are of interest for the stereochemical discussion are reported in Table I :

Table I

| | | chemical shifts (ppm) * | | | | | coupling constants ($H_2$) | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $^{31}P$ | $H_4,H_7$ | $H_{4'},H_{7'}$ | $^{13}C_4,^{13}C_7$ | $^{13}C_5,^{13}C_6$ | $^3J(PH_{4,7})$ | $^3J(PH_{4',7'})$ | $^2J(PC_{4,7})$ | $^2J(H_{4,4'})$ |
| **1** |  | 127.3 | 4.06 | 3.64 | 63.0 | 29.5 | 13.5 | 9.5 | 3.0 | 11.5 |
| **2** |  | 130.4 | 4.66 | 4.18 | 60.7 | 129.0 | 13.0 | 7.0 | 0.0 | 13.0 |
| **3** |  | 124.5 | 5.80 | 4.30 | 64.7 | 138.0 | 9.5 | 10.5 | 2.0 | 13.0 |

The examination of the $^3J(POCH)$ nmr coupling constants, which have been correlated with their POCH dihedral angle ∅ [8], can give some insight on the seven-membered ring conformation. In the three compounds under study, **1**, **2** and **3**, each with the identical R group attached to the phosphorus, the differences of the $^3J(POCH)$ values clearly indicate that the seven-membered rings, **A**, **B** and **C**, adopt different conformations in solution.

In compound **2**, the fact that the $^3J(POCH)$ values (13.0 Hz and 7.0 Hz) show a large difference (6 Hz), and that these couplings remain constant over a temperature range of 140°C (-60°C up to 80°C) is in agreement with the presence of a unique rigid chair or boat conformation. A twist conformation would give rise to more identical $^3J(POCH)$ coupling constants. The largest $^3J$ value (13.0 Hz) corresponds to the equatorial proton ($\emptyset \sim 150°$ as measured on a Dreiding model), and the smallest one to the axial proton ($\emptyset \sim 30°$). Due to the strongly preferred axial orientation of the P-R bond in 2-R-1,3,2-dioxaphosphorinanes [2], the boat conformation would be highly destabilized. Thus, we conclude that **2** exists in solution in a unique chair form with the phenoxy group lying in the axial orientation.

In compound **3**, the two $^3J(POCH)$ values differ by only 1.0 Hz at room temperature. Such a small difference excludes the existence of a unique rigid chair or boat conformation. The very strong bias of the extracyclic bond attached to the phosphorus to be axial indicates that

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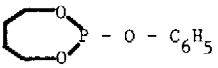
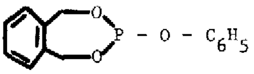
* The chemical shifts are positive to high frequency from $H_3PO_4$ (85%) as external reference for $^{31}P$ and from TMS as internal reference for $^1H$ and $^{13}C$. The $^{31}P$ and $^1H$ nmr spectra were recorded in $C_6D_6$, the $^{13}C$ spectra in $CDCl_3$.

the near zero difference between the two $^3J$(POCH) couplings cannot be due to a 50%-50% chair-chair (or boat-boat) equilibrium. Moreover, the $^3J$(POCH) values show significant variations with temperature as shown in Table II. Thus, **3** exists at room temperature as a mixture of different conformations. The increase observed in the difference between the two couplings as the temperature decreases, and the values measured at low temperature (8.5 Hz and 11.5 Hz) suggest the existence of an equilibrium between a chair form (the more stable one) and a twist form.

Table II

| | | t (°C) | -60 | 20 | 80 |
|---|---|---|---|---|---|
| **1** |  | $^3J(POCH_4)$ | 14.5 | 13.5 | 12.0 |
| | | $^3J(POCH_{4'})$ | 9.5 | 9.5 | 10.0 |
| **3** |  | $^3J(POCH_4)$ | 11.5 | 10.5 | 10.0 |
| | | $^3J(POCH_{4'})$ | 8.5 | 9.5 | 10.0 |

In compound **1**, many different conformations are plausible. The very small chemical shift difference between the two protons attached to carbons 4 and 5, even on a spectrum recorded at 250 MHz, does not allow the determination of the $^3J$(HH) couplings which would be very helpful for drawing a conclusion about conformational preferences.

The variation observed for $^3J$(POCH) between -60°C and 80°C (Table II) indicates that **1** does not exist in only one conformation or as a mixture of isoenergetic conformers at room temperature. It is noteworthy that the difference between the two $^3J$(POCH) couplings increases as the temperature decreases. Such a trend and the low temperature values suggest that the stable conformation at the low temperature is close to $C_s$ symmetry where the POCH dihedral angles are quite different. This conformation will correspond to an unexpected eclipsed conformation of the $C_5C_6$ fragment.

Further studies using labelled compounds, X-ray analysis and low temperature nmr experiments are now in progress in order to clarify this problem of seven-membered ring conformation.

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