Configurational Assignments to 2-X-2-Y-4-methyl-1,3,2-dioxaphosphorinans

W. J. STEC, R. KINAS, and A. OKRUSZEK
Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, 90-362 Łódź, Poland
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It has been reported from this Laboratory that $J_{PH}$ and $J_{PSe}$ absolute values showed the clear dependence on the spatial orientation of H and Se substituents in several pairs of ring C-substituted 2-X-2-Y-1,3,2-dioxaphosphorinans and may therefore provide information about the conformation of the ring and configuration at phosphorus atom.

In this communication we wish to report further examples of usefulness of this observation to the cis-trans-geometry assignment of several new pairs of 2-X-2-Y-4-methyl-1,3,2-dioxaphosphorinans. Thirteen pairs of them were prepared and spin-spin coupling values between directly bonded phosphorus and selenium-77, fluorine-19 and carbon-13, respectively, were measured. Preliminary cis-trans assignments were concluded from deductive reasonings concerning stereochimical course of reactions in which they were obtained and also from the analysis of their $^1$H, $^{13}$C and $^{31}$P NMR spectra. Results of measurements are collected in the Table.

Inspection of the Table reveals that the difference in spin-spin coupling between directly bonded phosphorus and selenium-77 can be applied as useful criterium for cis-trans assignment in diastereoisomeric pairs of 2, 3, 4, 5, 6, 7, 8 and 12. It has to be emphasized that the structure of both cis- and trans-2-tert-butylamino-2-seleno-4-methyl-1,3,2-dioxaphosphorinans (7) were determined by X-ray crystallography and in the solid state both isomers possess equatorially oriented 4-methyl group and selenium atom axial in cis-7 and equatorial in trans-7, respectively. It is also worthwhile to mention that the equatorial P = Se bond is shorter (trans-7, 2.080 and 2.082 Å) than that in the axial disposition (cis-7, 2.086 Å).

Although the solid state structure determination did not elucidate the conformation of both isomers in solution, our preliminary $^1$H NMR analysis confirmed that the cis-isomer is conformationally stable (Ca $^1$D$_8$ solution, 25°C) and it has the same conformation as determined by X-ray technique. The trans-7 in the same experimental conditions exists in the chair-chair equilibrium with ca. 70% of conformation with both 4-methyl and selenium atom equatorially orientated. Conformational mobility of trans-7 may be responsible for the lower than average value of $\Delta J/J$ min and suggests also the similar situation in pair of 6, where detailed $^1$H NMR analysis has not been performed due to the complexity of spectra recorded at 90 MHz.

Pairs of 8, 9 and 10 represent the case, when the criterium of absolute values of direct spin-spin couplings between directly bonded phosphorus-31 and carbon-13 can be applied to cyclic phosphonates. Again, spin-spin coupling between directly bonded phosphorus and carbon-13 atoms has higher absolute value when the alkyl group is equatorially orientated. Additionally, pair of 8 shows the complementary character of spin-spin coupling constants between phosphorus and carbon-13 or selenium-77. Thus $|J_{PSe}|cis < |J_{PSe}|trans and |J_{PC}|cis > |J_{PC}|trans.

Pairs of 1, 11, 12 and 13 represent the dependence of $J_{PP}$ absolute values on the spatial orientation of fluorine atom in dioxaphosphorinanyl ring system. The striking feature of these pair is the lower than in the case of other X substituents $J$ value. In pairs 1, 11 and 12 always $|J_{PF}|$ axial $< |J_{PF}|$ equatorial. In pair 13 the situation is reversed. This case requires of special comment. As it has been shown in our previous work, there is a lot of evidence that the cis-isomers of 1, 11, 12 and 13 exist in the chair-chair equilibrium and it is very probable that in the case of 13 (X = O) the equilibrium is shifted towards B.

This fact suggests that the direct spin-spin coupling can be used for estimation of the conformational equilibria. Work on this problem is in progress. However, the case of 13 warns against the use of $|J_{FX}|$ value as the only criterium for the cis-trans geometry assignment in family of compounds under consideration.

Recent literature reports confirm the usefulness of our empirical rule $|J_{XYAX}| < |J_{XYeq}|$ to other cyclic systems like phosphorinans and cyclohexane derivatives. QUIN reported the synthesis and configurational assignments to several substituted phosphorinans and their sulphides. In the case of sulphides $J_{P-C}$ for the equatorial phosphorus substituent is higher than for the axial one. However, for the corresponding trivalent compounds the situation is reversed.

BOCK and PEDERSEN pointed out that one-bond coupling between anomeric carbon and proton in $\alpha$- and $\beta$-hexapyranoses are different and always

X = l.p., O, S, Se.
Table. $^{31}$P NMR parameters* of 2-X-2-Y-4-methyl-1,3,2-dioxaphosphorinans (1–13).

<table>
<thead>
<tr>
<th>Compound</th>
<th>X</th>
<th>Y</th>
<th>$\delta^{31}$P [H$_3$PO$_4$]</th>
<th>$\Delta$</th>
<th>$^{1}$J$_{P-X}$ [Hz]</th>
<th>$^{1}$J$_{P-Y}$ [Hz]</th>
<th>$^{1}$J$_{P-C}$ [Hz]</th>
<th>Solvent</th>
<th>Reference</th>
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<tbody>
<tr>
<td>1</td>
<td>cis</td>
<td>F</td>
<td>98.5</td>
<td>99.5</td>
<td>-1180</td>
<td>24</td>
<td>2.0</td>
<td>Neat</td>
<td>2</td>
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<tr>
<td>2</td>
<td>cis</td>
<td>Se</td>
<td>88.5</td>
<td>94.0</td>
<td>-960</td>
<td>85</td>
<td>7.3</td>
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<tr>
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<td>cis</td>
<td>SeMe</td>
<td>78.5</td>
<td>87.5</td>
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<td>75</td>
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</tr>
<tr>
<td>4</td>
<td>cis</td>
<td>NMe2</td>
<td>76.0</td>
<td>75.0</td>
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<td>-930</td>
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<tr>
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<td>NHPh</td>
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<td>62.5</td>
<td>-942</td>
<td>-887</td>
<td>6.2</td>
<td>Dioxane</td>
<td>6</td>
</tr>
<tr>
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<td>cis</td>
<td>NMePh</td>
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<td>72.5</td>
<td>-941</td>
<td>-925</td>
<td>1.7</td>
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<tr>
<td>7</td>
<td>cis</td>
<td>NHBu</td>
<td>-68.7</td>
<td>66.5</td>
<td>916</td>
<td>900</td>
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<tr>
<td>8</td>
<td>cis</td>
<td>CH$_2$Ph</td>
<td>-92.0</td>
<td>96.9</td>
<td>909</td>
<td>883</td>
<td>26 (P –C)</td>
<td>9.0 (P –C)</td>
<td>C$_6$D$_6$</td>
</tr>
<tr>
<td>9</td>
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<td>8.0</td>
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<td>-12</td>
<td>9.0</td>
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<td>11</td>
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<td>-1130</td>
<td>-10</td>
<td>0.9</td>
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<tr>
<td>12</td>
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<td>-61.0</td>
<td>1122</td>
<td>1110</td>
<td>12 (P –F)</td>
<td>1.2 (P –F)</td>
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<tr>
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<td>1024</td>
<td>-6</td>
<td>-0.8</td>
<td>Benzene</td>
<td>2</td>
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</table>

* Proton-decoupled $^{31}$P NMR spectra were taken on a JEOL C-60H or Bruker HX-72 (Fourier transform) spectrometer and are referenced to external 85% H$_3$PO$_4$. Standard deviation ± 3 Hz. Proton-decoupled Fourier transform $^{13}$C spectra were obtained on a Bruker HX-72 system at 22.63 MHz. C–P coupling constants are ± 1.5 Hz.

Very recently Subbotin and Sergeyev have determined the direct spin-spin couplings between carbon-$^{13}$ and fluorine-$^{19}$ in fluorocyclohexane and found at $-100$ °C the values 167.0 Hz for axial and 172.2 Hz for equatorial fluorine.

At the same temperature in cyclohexane $^{1}$J$_{C-H}$ for the axial proton is 122.6 Hz and for equatorial one 126.6 Hz. Anet et al. found also the meaningful difference in values of $^{1}$J$_{CIS-H19}$ in cyclohexyl mercurials depending on the spatial orientation of mercury atom. In all cases $|J_{axial}| < |J_{equatorial}|$.

Presented above informations are indicative of the generality of the criterium of absolute value of direct spin-spin coupling between the central atom and exocyclic substituent in diastereoisomeric pairs of cyclic compounds for determination of axial/equatorial orientation of exocyclic substituent and thus, may form the basis for configurational assignment.
7 W. J. Stec and R. Kinas, unpublished results.
15 O. A. Subbotin and N. M. Sergeyev, J. Amer. Chem. Soc. 97, 1080 [1975].