The Axial Preference of Fluorine Atom
in 2-Fluoro-4-methyl-1,3,2-dioxaphosphorinanyl Ring System

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Dioxaphosphorinans, Fluorine Substituent, Axial Preference

The axial preference of fluorine substituent at phosphorus involved in 4-methyl-1,3,2-dioxaphosphorinanyl ring system was established.

Cis-trans geometry in this family of compounds was assigned by chemical correlation and by means of $^1$H, $^{13}$C, $^{19}$F and $^{31}$P NMR.

The configurational instability of phosphorus in five-membered ring phosphorochloridites is known to be very dependent on their purity.$^1$ Ring C-substituted 2-halogeno-1,3,2-dioxaphosphorinans are described as anancomeric systems$^2$ and in a number of works the axial orientation of chlorine atom has been inferred from NMR couplings and chemical shifts$^{2b}$ and deductive reasoning concerning the stereochemical course of exchanging this atom by another substituent.$^{2b}$ From investigations carried out in many research establishments it is known that 2-X-4-methyl-1,3,2-dioxaphosphorinans with such X-substituents as H$^3$, R$^4$, Ar$^4$, OR$^{5e}$, SR$^5$ and NHR$^6$ exist preferentially in the chair conformation with equatorial 4-methyl group and axial X-substituent. The striking difference has been found for dialkylaminosubstituent which, due to the special requirements of lone pairs at phosphorus and nitrogen, exist preponderantly in equatorial position.$^4,7$ However, except for X=Cl all these systems exist in an equilibrium with the thermodynamically less-stable diastereoisomers, which are usually conformationally non-rigid compounds. Mentioned above anancomerism of 2-halogeno-1,3,2-dioxaphosphorinanyl systems may result from two phenomena: i) very fast in the NMR time-scale chlorine-chlorine exchange and/or ii) low content of the minor diastereoisomer, being on the level of detectivity of $^{31}$P NMR spectroscopy. It was of interest to study other 2-halogeno-derivatives, like 2-fluoro-4-methyl-1,3,2-dioxaphosphorinane (1), which, due to the higher electronegativity and smaller atomic radius of fluorine, as compared to those of chlorine, should also exist entirely in form containing axially orientated fluorine atom. $^{19}$F NMR offered additional tool for detailed studies.

Results and Discussion

Radio-frequency spectroscopy ($^1$H, $^{19}$F, $^{13}$C and $^{31}$P NMR) and chemical correlation methods were applied for studying of sterical requirements of fluorine atom attached to trivalent phosphorus atom being a part of 4-methyl-1,3,2-dioxaphosphorinanyl ring system. 1 was obtained in the reaction of 2-chloro-4-methyl-1,3,2-dioxaphosphorinane (2) with antimony trifluoride, according to procedure developed by Schützler$^3$. Analysis of the NMR spectra of distilled 1 revealed the presence of two isomers in the ratio 1a:1b = 8:92. This ratio was left unchanged after one-hour heating of the sample of distilled 1 at 70 °C in benzene solution in the presence of ammonium fluoride, so one can expect that an equilibrium has been reached. An interpretation of $^1$H NMR spectrum of distilled 1 (see Table I) allows us to conclude that preponderant isomer (1b) exists in a rigid chair conformation with the equatorially orientated 4-methyl group and axially located fluorine atom:

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The most typical for an axial orientation of phosphorus substituent is the value of spin-spin coupling constant between phosphorus and equatorial C-6 proton (He)\(^4\). In the case under consideration \(3J_{PHc}\) equals 11.8 Hz, but for equatorially orientated fluorine this coupling was expected to be of order of 21 Hz\(^4\). Although the \(^1\)H NMR analysis of the minor component (1a) was not possible, some conclusions about its conformation were drawn out from the \(^{13}\)C, \(^{19}\)F and \(^{31}\)P NMR spectra (see Table II).

Thus, the appearance of the signal of 1a in \(^{31}\)P NMR spectrum at the lower field than that of 1b suggests cis-configuration of 1a. This conclusion has been inferred on the basis of many examples published in the literature\(^4\) and is also supported by \(^{13}\)C NMR data. The coupling constant between carbon-5 and phosphorus has much higher value in 1a (12.5 Hz) than in 1b (5.1 Hz). This fact speaks for equatorial position of fluorine in 1a and axial one in 1b. The analysis of chemical shift values of carbon-4 and carbon-5 in both 1a and 1b may suggest, however, the rapid conformational equilibrium of 1a. Typical \(\gamma\)-effect of the axial phosphorus substituent\(^4\) on the chemical shift of C-4 and C-6 is observed for carbon-4 only. Higher value of \(\Delta\epsilon\) in 1b than that in 1a may be explained by assumption of competitive occurrence of \(\gamma\)-effect of axial 4-methyl group in conformer of type B coming from chair-equilibrium of 1a (Eq. (1)).

![Eq. (1)](image)

This conclusion is subsequently supported by considerable broadening of the \(^{19}\)F NMR signal of 1a by comparison with that of 1b:

![Signal Comparison](image)

Such an effect has been observed in the range of temperature from +30 to —20 °C and apparently results from the rapid (in the NMR time-scale) equilibrium of 1a between conformer A and B (Eq. (1)) in this temperature range. For rigid structure of type A (Eq. (1)), with both 4-methyl group and fluorine atom in equatorial position, the definite splitting of fluorine by equatorial Hc-proton (W-rule) should be observed. It is worthwhile to mention, that in \(^{13}\)C NMR spectrum the splitting of

### Table I. \(^1\)H NMR spectral parameters for 1b (C\(_6\)D\(_6\)) (see Fig. 1).

<table>
<thead>
<tr>
<th>(\delta [\text{ppm}])</th>
<th>TMS</th>
<th>Ha</th>
<th>Hb</th>
<th>He</th>
<th>Hd</th>
<th>He</th>
<th>Hf</th>
</tr>
</thead>
<tbody>
<tr>
<td>(J [\text{Hz}])</td>
<td></td>
<td>4.44</td>
<td>4.22</td>
<td>3.53</td>
<td>1.72</td>
<td>1.03</td>
<td>0.925</td>
</tr>
<tr>
<td>12.0</td>
<td>3.3</td>
<td>6.6</td>
<td>4.0</td>
<td>11.8</td>
<td>13.2</td>
<td>3.3</td>
<td>4.0</td>
</tr>
</tbody>
</table>

### Table II. \(^{13}\)C, \(^{19}\)F and \(^{31}\)P NMR spectral parameters for 1, 3 and 5 (C\(_6\)D\(_6\)).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta_{C1} [\text{ppm}])</th>
<th>(3J_{C1P} [\text{Hz}])</th>
<th>(\delta_{C2} [\text{ppm}])</th>
<th>(3J_{C2P} [\text{Hz}])</th>
<th>(\delta_{C3} [\text{ppm}])</th>
<th>(3J_{C3P} [\text{Hz}])</th>
<th>(\delta_{CH2} [\text{ppm}])</th>
<th>(3J_{CH2P} [\text{Hz}])</th>
<th>(\delta(\text{PF}) [\text{ppm}])</th>
<th>(3J_{PF} [\text{Hz}])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>71.0</td>
<td>6.6</td>
<td>59.1</td>
<td>4.4</td>
<td>32.7</td>
<td>12.5</td>
<td>—129.9</td>
<td>—120.0</td>
<td>1178</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>67.0</td>
<td>7.4</td>
<td>60.7</td>
<td>7.4</td>
<td>35.5</td>
<td>5.1</td>
<td>22.4</td>
<td>2.9</td>
<td>—105.4</td>
<td>—118.8</td>
</tr>
<tr>
<td>3a</td>
<td>79.3</td>
<td>5.9</td>
<td>67.8</td>
<td>6.6</td>
<td>31.1</td>
<td>11.1</td>
<td>20.6</td>
<td>3.7</td>
<td>—94.5</td>
<td>17.4</td>
</tr>
<tr>
<td>3b</td>
<td>79.0</td>
<td>5.9</td>
<td>69.4</td>
<td>7.3</td>
<td>32.6</td>
<td>5.9</td>
<td>21.5</td>
<td>9.6</td>
<td>—78.0</td>
<td>17.5</td>
</tr>
<tr>
<td>5a</td>
<td>78.8</td>
<td>7.3</td>
<td>67.6</td>
<td>8.8</td>
<td>31.9</td>
<td>11.8</td>
<td>21.5</td>
<td>4.4</td>
<td>—146.0</td>
<td>60.8</td>
</tr>
<tr>
<td>5b</td>
<td>78.5</td>
<td>10.3</td>
<td>69.1</td>
<td>10.3</td>
<td>32.9</td>
<td>7.3</td>
<td>22.1</td>
<td>8.8</td>
<td>—127.0</td>
<td>61.0</td>
</tr>
</tbody>
</table>

\(^a\) \(3J(C-F) [\text{Hz}]\), \(^b\) \(2J(\text{Se-F}) [\text{Hz}]\), \(^c\) \(1J(\text{Se-P}) [\text{Hz}]\).
C-4 and C-6 carbons by fluorine of order 2 Hz is observed only for 1b (see Table II). Since vicinal Karplus-type relationship (between $J_{F-P-O-C}$ and dihedral angle) has not been so far established, this fact can be reported without further comment.

Presented above spectroscopic evidence for the trans-geometry of the more stable isomer of 1 (1b) was further confirmed by the chemical correlation. Oxidation of distilled 1 with trimethylamine N-oxide gave a mixture of two diastereoisomeric 2-fluoro-2-oxo-4-methyl-1,3,2-dioxaphosphorinans \(^9\) (3a and 3b) in the ratio 10:90, respectively (see Scheme I).

\[
\begin{align*}
\text{Scheme I.} & \\
\begin{array}{c}
\text{2} \\
\xrightarrow{5bF} \\
\text{1a, 8%} & \quad \text{1b, 92%} \\
\end{array}
\end{align*}
\]

The same ratio 3a:3b was obtained when dinitrogen tetroxide was used as an oxidizing agent. For to assign the cis-trans geometry of both 3a and 3b we have performed their synthesis on an independent way. Trans-2-chloro-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (4) was treated with the stoichiometric amount of ammonium fluoride in benzene solution at 80 °C. When the reaction was carried out for fifteen minutes only, reaction mixture contained 10% of unchanged 4 and 90% of phosphorofluoridate in the ratio 3a:3b = 80:20, respectively. Removal of inorganic salts and distillation allowed us to isolate pure 3 with unchanged isomer ratio. Refluxing of its benzene solution caused a slow increase of 3b content. However, addition of catalytic amounts of NH$_4$F to benzene solution of 3a:3b = 80:20 accelerated the epimerization process leading to the equilibrium 3a:3b = 12:88 (see Scheme II).

\[
\begin{align*}
\text{Scheme II.} & \\
\begin{array}{c}
\text{4} \\
\xrightarrow{A} \\
\text{3a, 80%} & \quad \text{3b, 20%} \\
\end{array}
\end{align*}
\]

Taking into account, that 3b is preponderant product of direct oxidation of distilled 1 with Me$_3$NO or N$_2$O$_4$, which are known to oxidize the trivalent phosphorus compounds with retention of configuration at phosphorus atom\(^{10-11}\), we have fully confirmed the trans-geometry of predominant isomer of 1. Oxidation of 1 has been extended to its conversion to 2-fluoro-2-seleno-4-methyl-1,3,2-dioxaphosphorinane (5) (see Scheme I).

Addition of elemental selenium to distilled 1 gave 5 as a mixture of two isomers (5a and 5b) in the ratio 20:80, respectively\(^{12}\). Oxidation of this mixture with dinitrogen tetroxide converted 5 into 3 in the ratio a:b = 20:80, respectively. Because addition of selenium to P$_{III}$ derivatives as well as oxidation of diastereoisomeric 2-seleno-1,3,2-dioxaphosphorinans with N$_2$O$_4$ are known to proceed with retention of configuration at phosphorus atom\(^{13}\), these results support the trans-configuration of 1b. The cis-trans geometry assignment of 5a and 5b was independently confirmed by nucleophilic exchange of chlorine atom of trans-2-chloro-2-seleno-4-methyl-1,3,2-dioxaphosphorinane (6) by fluorine with an aid of ammonium fluoride in benzene solution (see Scheme III).

5a, being the kinetic product of this reaction, is supposed to have the cis-geometry for the reasons discussed above for the case of oxo compounds\(^{14}\). Heating of the initially obtained mixture (5a:5b = 80:20) for three days in refluxing benzene in the presence of NH$_4$F caused its equilibration and finally the mixture contained 15% of 5a and 85% of 5b.
As an additional criterion for cis-trans geometry assignments of diastereoisomeric pairs 1, 3 and 5, spin-spin coupling constants between phosphorus and fluorine and/or selenium-77 were used. We reported previously from this laboratory\textsuperscript{15} that absolute value of spin-spin coupling constant between phosphorus, and magnetically active nucleus X directly bonded to phosphorus depends on the spatial disposition of X and fulfills the requirement $|J_{FX \text{axial}}| < |J_{FX \text{equatorial}}|$. In agreement with this empirical rule the observed couplings between phosphorus and fluorine are higher in cis-isomers (1a, 5a) and coupling between phosphorus and selenium-77 is higher in trans-isomer than in cis-one (see Table II). Both couplings $J_{PF}$ and $J_{PSe}$, in 5 demonstrate the complementary character of our criterium. However, this rule $|J_{FXax}| < |J_{FXeq}|$ does not obey in the case of diastereoisomeric pair 3 and this case requires of special comment. It has to be emphasized that in pairs 1, 3 and 5 the relative difference between coupling-constants $\Delta J/J \min$ is in the range 0.6: 2\%, that is much lower than that of other isomeric pairs of family of 4-methyl-1,3,2-dioxaphosphorinanes\textsuperscript{15}. Also the differences between $^{31}\text{P}$ NMR chemical shift values of each diastereoisomeric pair 1, 3 and 5 are much lower (0.1-1.2 ppm) than usually observed in 4-methyl-1,3,2-dioxaphosphorinanyl series (1.2-14.0 ppm). These observations may be explained by the fast conformational equilibrium between two chair forms (A and B) in cis-isomers (Eq. (3); see also Eq. (1)).

Such conclusion is supported by considerable broadening, even at $-80\,\text{°C}$, of the $^{19}\text{F}$ NMR signals of 1a, 3a and 5a and also by characteristic splitting of the signal of 4-methyl protons, observed in $^1\text{H}$ NMR spectra of 3a and 5a. In $^1\text{H}$ NMR spectra of the trans-isomers (3b and 5b) this group appears as the doublet of doublets with $^{3}J_{\text{CH}_3-\text{Ha}} \sim 6\,\text{Hz}$ and $^{4}J_{\text{CH}_3-\text{Hb}} \sim 2\,\text{Hz}$. However, the $^1\text{H}$ NMR spectra of cis-isomers (3a and 5a) reveal the presence of the doublet of triplets, due to the additional splitting ($\sim 1\,\text{Hz}$) of 4-methyl protons by vicinal axial proton and this is indicative of the considerable participation of conformer $\text{B}^{16}$ in equilibrium under consideration (Eq. (3)).

Since this work was mainly devoted to elucidation of spatial preference of fluorine atom in 2-fluoro-4-methyl-1,3,2-dioxaphosphorinane (1) we conclude that fluorine attached to phosphorus, in this system, preferentially occupies axial position. This axial preference is so strong that it predominates in part the tendency of 4-methyl group for to be equatorially orientated and may be rationalized in terms of modified gauche effect\textsuperscript{4-7}, especially due to the small atom-radius of fluorine and high electronegativity of this atom, what makes the 1,3-syn-axial interactions attractive rather than repulsive. However, in the light of findings presented in this work, it seems peculiar that 2-chloro-4-methyl-1,3,2-dioxaphosphorinane (2) exists entirely as the trans-isomer\textsuperscript{2c,19}.

**Experimental**

All m.ps and b.ps are uncorrected. Solvents and commercial reagents were distilled and dried by conventional methods before use. $^1\text{H}$ NMR spectra were recorded at 60 MHz, with a Jeol C-60 H spectrometer, equipped with Hetero-Spin-Decoupler JNH-SD-1H, with TMS as an internal standard. $^{31}\text{P}$ NMR spectra were obtained on the same instrument operating at 24.3 MHz with external $\text{H}_2\text{PO}_4$ or $\text{PhO}_2\text{P}$ as the reference. Positive chemical shift values are reported for compounds absorbing at higher fields than $\text{H}_2\text{PO}_4$. $^{19}\text{F}$ NMR spectra were recorded at 56.4 MHz with a Perkin-Elmer R-12 B spectrometer with external $\text{C}_6\text{F}_6$ as the reference. Negative chemical shift values are reported for compounds absorbing at lower fields than $\text{C}_6\text{F}_6$. $^{13}\text{C}$ NMR measurements were recorded on a Bruker-HX 72 spectrometer using TMS as an internal standard. Mass spectra were obtained on a LKB-9000 S spectrometer at 70 eV ionizing energy. The chlorophosphite (2) was synthesized from butan-1,3-diol and $\text{PCl}_3$ in CH\textsubscript{2}Cl\textsubscript{2} according to LUCAS\textsuperscript{17} procedure. Trans-chlorophosphate (4) was...
prepared by chlorination of \textit{trans}-2-hydro-2-oxo-4-methyl-1,3,2-dioxaphosphorinane with sulphuryl chloride\textsuperscript{18}. \textit{Trans}-chloroselenophosphate (6) was obtained by addition of elemental selenium to 2 \textsuperscript{2}. 

1. 2-Fluoro-4-methyl-1,3,2-dioxaphosphorinane (1) 

To finely powdered antimony trifluoride (9.0 g, 0.05 m) was added in small portions, with magnetic stirring, the chlorophosphite (2) (15.4 g, 0.1 m). An exothermic reaction was observed and the temperature arose to 60 °C. Stirring was continued at this temperature for next hour and the resulting fluorophosphite (1) was isolated by distillation, b.p. 40–42 °C/30 mm Hg, \( \eta^2_D = 1.4205 \). Yield 10.3 g (75%). Mass spectrum: \( m/e \) 55 (100%), 103 (21%), 67 (17%), 54 (64.7%). 

\[ \text{C}_3\text{H}_5\text{O}_2\text{PF} \quad (138.08) \]

Calcd C 34.80 H 5.80 P 22.40.

Found C 35.19 H 6.00 P 21.69.

\( ^{31}\text{P} \) and \( ^{19}\text{F} \) NMR analysis of the distillate revealed the presence of two isomers: 1a (8\%\text{),} \( \delta^{31}\text{P} = -120.0 \text{ ppm}, \delta^{19}\text{F} = -129.9 \text{ ppm,} \) \( ^{1}J_{PF} = 1175 \text{Hz) and 1b (92\%}, \delta^{31}\text{P} = -118.8 \text{ ppm,} \delta^{19}\text{F} = -105.4 \text{ ppm,} \) \( ^{1}J_{PF} = 1156 \text{Hz).} \)

To a solution of distilled 1 (1 g) in benzene (1 ml) was added finely powdered ammonium fluoride (0.1 g). The mixture was heated at 70 °C for one hour. The \( ^{31}\text{P} \) and \( ^{19}\text{F} \) NMR analysis showed the presence of 1 in the ratio a:b = 8:92, respectively.

2. Oxidation of 1. \textit{Trans}-2-fluoro-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (3b) 

a) To a solution of distilled 1 (3.45 g, 0.025 m) in chloroform (30 ml) was added at 0 °C, dropwise, a solution of trimethylamine N-oxide (1.9 g, 0.025 m) in chloroform (20 ml). The reaction mixture was heated at 70 °C for one hour. The \( ^{31}\text{P} \) and \( ^{19}\text{F} \) NMR analysis showed the presence of 3 in the ratio a:b = 8:92, respectively.

b) A solution of \( \text{Na}_{2}\text{O}_4 \) (0.92 g, 0.01 m) in \( \text{CCl}_4 \) (10 ml) was added dropwise at —30 °C, with stirring and cooling, into a solution of distilled 1 (2.76 g, 0.02 m) in \( \text{CHCl}_3 \) (20 ml). The reaction mixture was then degassed at 0 °C and evaporated. The NMR analysis of the residue revealed the presence of 3a (11\%\text{),} \( \delta^{31}\text{P} = +17.4 \text{ ppm,} \delta^{19}\text{F} = -94.5 \text{ ppm} \)) and 3b (89\%\text{),} \( \delta^{31}\text{P} = +17.5 \text{ ppm,} \delta^{19}\text{F} = -78.0 \text{ ppm} \). Distillation gave 2.2 g (72\%\text{) of pure 3, b. p. 78–80 °C/0.05 mm Hg, \( \eta^2_D = 1.4137 \); the isomer ratio remained unchanged.

3. Addition of selenium to 1. \textit{Trans}-2-fluoro-2-seleno-4-methyl-1,3,2-dioxaphosphorinane (5b) 

Elemental selenium (7.9 g, 0.1 m) was added to a solution of 1 (13.8 g, 0.1 m) in toluene (50 ml). The suspension was refluxed for 5 h. The unreacted selenium was filtered off and the filtrate was evaporated. The residue was distilled under reduced pressure yielding 18.0 g (53\%\text{) of 5 as pale-red liquid, b. p. 85 °C/0.2 mm Hg, \( \eta^2_D = 1.5100 \).

\[ \text{C}_3\text{H}_5\text{N}_2\text{PFSe} \quad (216.98) \]

Calcd C 22.10 H 3.69 P 14.25.

Found C 22.30 H 3.91 P 14.76.

Careful NMR analysis showed the presence of 5a (20\%\text{),} \( \delta^{31}\text{P} = -60.8 \text{ ppm,} \delta^{19}\text{F} = -146.0 \text{ ppm,} \) \( ^{1}J_{PF} = 1110 \text{Hz,} \) \( ^{3}J_{PF} = 16.0 \text{ Hz)), and 5b (80\%\text{),} \( \delta^{31}\text{P} = -61.0 \text{ ppm,} \delta^{19}\text{F} = -127.0 \text{ ppm,} \) \( ^{1}J_{PF} = 1205 \text{ Hz,} \) \( ^{3}J_{PF} = 1122 \text{ Hz,} \) \( ^{3}J_{PF} = 14.4 \text{ Hz).} \)

\( ^{1}\text{H} \) NMR (\( \text{CDCl}_3 \)): \( \delta_{\text{HCCH}} = 5.8 \text{ Hz,} \) \( ^{3}J_{\text{POCCH}} = 2.7 \text{ Hz.} \)

\[ \text{C}_3\text{H}_5\text{N}_2\text{PFSe} \quad (154.08) \]

Calcd C 31.20 H 5.19 P 20.10.

Found C 31.25 H 5.24 P 19.84.

The distillate (1 g) was dissolved in benzene (1 ml). Finely powdered ammonium fluoride (0.1 g) was added and the mixture was heated at 70 °C for two hours. The NMR analysis showed the presence of 3a (12\%\text{) and 3b (88\%).}
spectrum: m/e 101 (100%), 154 (2%), 139 (37%), 127 (82%), 126 (32.5%), 113 (7.4%), 55 (13.5%), 54 (86%).

The sample of obtained distillate (1 g) was dissolved in benzene (1 ml) and heated for 20 h at 70 °C.

An epimerization occurred and the sample contained 3a and 3b in the ratio 33:77, respectively (19F NMR analysis). Ammonium fluoride (0.1 g) was added to the examined solution and the mixture was heated at 70 °C for 1 h. 19F NMR analysis revealed the presence of an equilibrium mixture 3a:3b = 12:88.

b) Trans-2-fluoro-2-oxo-4-methyl-1,3,2-dioxaphosphorinane (3b)

The reaction of trans-4 (0.1 m) with NH₄F (0.15) was performed as in section 4a. Stirring and refluxing was continued for one hour. The 31P NMR spectrum of the crude product showed the presence of 3a (12%, δ₃¹P = +17.4 ppm) and 3b (88%, δ₃¹P = +17.5 ppm). Distillation gave 12 g (78%) of pure 3, b.p. 78–80 °C/0.05 mm Hg, nD²⁰ = 1.4140, consisting of a mixture of both 3a and 3b in unchanged isomer ratio.

5. Reaction of trans-2-chloro-2-seleno-4-methyl-1,3,2-dioxaphosphorinane (6) with ammonium fluoride.

Cis-2-fluoro-2-seleno-4-methyl-1,3,2-dioxaphosphorinane (5a)

Trans-6 (4.66 g, 0.02 m) was added to the suspension of ammonium fluoride (1.0 g, 0.03 m) in benzene (20 ml). The mixture was stirred under reflux for 2 h. The precipitate was filtered off and the filtrate was evaporated. The 31P NMR analysis of the residue revealed the presence of 24% of unchanged 6 (δ₃¹P = −54.5 ppm) and 76% of 5 as a mixture of 5a (80%, δ₅ᵣᵢ = −60.8 ppm) and 5b (20%, δ₅ᵣᵢ = −61.0 ppm). The fractional distillation let us to isolate 2.2 g (50.5%) of pure 5, b.p. 73–75 °C/0.05 mm Hg, nD²⁰ = 1.5123, containing 5a and 5b in the ratio 80:20, respectively. 1H NMR (CDCl₃): δcm = 8.99 ppm, 3J₇₋₈CH₃ = 5.6 Hz, 4J₇₋₈CH₃ = 0.8 Hz, 5J₇₋₈CH₃ = 0.8 Hz.

The distillate (1 g) was dissolved in benzene (1 ml) and ammonium fluoride (0.5 g) was added. The mixture was heated at 70 °C for 70 h. The sample contained 5a and 5b in the ratio 16:84, respectively (19F NMR analysis).

6. Oxidation of 5

a) Into a solution of 5 (4.9 g, 0.0225 m), containing 20% of 5a and 80% of 5b, in CHCl₃ (50 ml) was added, dropwise at 0–10 °C, with stirring and cooling, N₂O₄ (2.1 g, 0.0225 m) in CCｌ₃ (25 ml). The precipitation of the red selenium was observed. Stirring at room temp. was continued for 30 min. and the precipitated selenium was filtered off. The filtrate was degassed and evaporated. The 31P NMR spectrum of the residue revealed the presence of 5a (20%, δ₃¹P = +17.4 ppm) and 3b (80%, δ₃¹P = +17.5 ppm).

Distillation gave 2.8 g (81%) of pure 3 in the same isomer ratio, b.p. 105 °C/1 m mm Hg, nD²⁰ = 1.4128.

b) N₂O₄ oxidation of 5 (4.3 g, 0.02 m) (80% of 5a and 20% of 5b) performed as described in section 6a gave 2.7 g (88%) of 3 containing 81% of 3a and 19% of 3b (31P and 19F NMR analysis).

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8 R. Schmutzler, Chem. Ber. 96, 2435 [1963].
9 The synthesis of this compound was earlier described in the patent-literature (W. M. Lanham, U.S., 2,922,813; April 10, 1957); however, its stereochemistry has not been considered.
12 The lack of full stereospecificity can be explained by the higher nucleophilicity of the axially-oriented lone electron-pair in 1a, which cause the kinetic difference in the rate of reaction of both 1a and 1b with selenium (J. G. Verkade, Bioinorganic Chemistry 3, 165 [1974]).
Inversion of configuration during the halogen exchange reaction at thiophosphoryl centre has been proved earlier in this Laboratory (J. Michalski, M. Mikolajczyk, B. Halpern, and K. Prószynśka, Tetrahedron Letters 1966, 1919).

For the pure conformer of type B splitting of 4-methyl protons by vicinal axial proton of a range of 1 Hz would be expected.