Stereochemistry of Organophosphorus Compounds

Communication 9. Study of the NMR-\(^1\)H and \(^{31}\)P Method of the Configuration and Conformation of Cyclic Phosphites Based on Dimethyl Esters of D- and Mesotartaric Acids


In a continuation of investigations in the field of phosphorus-containing heterocycles [1, 2], we studied the configuration and conformation of stereoisomeric 4,5-dicarbalkoxy-1,3,2-dioxaphospholanes (I)-(V) (Table 1) with various substituents at the phosphorus atom by the method of NMR-\(^1\)H, \(^{31}\)P, and NMDR-\(^1\)H-\(^{31}\)P including the Overhauser effect and the influence of paramagnetic shifting reagents. These compounds were synthesized on the basis of dimethyl and diethyl esters of D- and mesotartaric acids (VI) and (VII) [2]

\[
\begin{align*}
\text{R} = &\text{R}^1 = \text{OCH}_3 \quad (\text{Ia}); \\
&\text{OCH}_3 \quad (\text{IIa}) \\
&\text{R}^1 = \text{Cl}, \text{R} = \text{CH}_3 \quad (\text{IIIa}); \\
&\text{R} = \text{N}(\text{C}_6\text{H}_{11}), \text{R} = \text{CH}_3 \quad (\text{IVa}); \\
&\text{R}^1 = \text{Ph}, \text{R} = \text{CH}_3 \quad (\text{Vb})
\end{align*}
\]

Evidently the D- and mesoisomers of tartaric acid esters used for the synthesis, like the known examples of 2,3-disubstituted butanes, are an equilibrium mixture of molecules in one anti-conformation and two gauche-conformations, the populations of which are determined by the contribution of the torsional energy and the energy of uncoupled gauche-1,2-atom-atom interactions to the total free energy of the rotamer [3]. The most populated will be the transoid conformations (VI) and (VII), in which the voluminous

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\end{align*}
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\begin{align*}
\text{H}_A \\ \text{H}_B \\ \text{P} \quad \text{R}^1 \\
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\end{align*}
\]
TABLE 1. Chemical Shifts and Spin–Spin Interaction Constants in 4,5-Dicarbalkoxy-1,3,2-dioxaphospholanes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent temperature, °C</th>
<th>Chemical shifts, δ ppm</th>
<th>SSIC, δ Hz</th>
<th>Overhauser effect, δ Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H&lt;sub&gt;A&lt;/sub&gt;</td>
<td>H&lt;sub&gt;B&lt;/sub&gt;</td>
<td>H&lt;sub&gt;B&lt;/sub&gt;</td>
</tr>
<tr>
<td>(Ia)</td>
<td>CS&lt;sub&gt;2&lt;/sub&gt; + CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-140</td>
<td>5.04</td>
<td>3.74</td>
</tr>
<tr>
<td>(Ib)</td>
<td>CS&lt;sub&gt;2&lt;/sub&gt; + CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-140</td>
<td>4.67</td>
<td>5.00</td>
</tr>
<tr>
<td>(IIa)</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;, 20°</td>
<td>-140</td>
<td>4.67</td>
<td>5.08</td>
</tr>
<tr>
<td>(IIb)</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;, 80°</td>
<td>-140</td>
<td>4.74</td>
<td>5.04</td>
</tr>
<tr>
<td>(IIIb)</td>
<td>CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>-141</td>
<td>4.74</td>
<td>5.01</td>
</tr>
<tr>
<td>(IVb)</td>
<td>CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>-141</td>
<td>4.92</td>
<td>5.27</td>
</tr>
<tr>
<td>(Vb)</td>
<td>CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>-177</td>
<td>4.71</td>
<td>4.84</td>
</tr>
<tr>
<td></td>
<td>CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td>-177</td>
<td>4.96</td>
<td>5.24</td>
</tr>
</tbody>
</table>

*In those cases where the temperature is not indicated, the measurements were performed under room conditions at 25-30°; concentration of the substance 3-5 vol.%. 
The chemical shifts δ<sub>4</sub> were measured relative to TMS as an internal standard with an accuracy of ± 0.005 ppm; the shifts δ<sub>13</sub> were measured relative to 85% H<sub>3</sub>PO<sub>4</sub> by the NMR<sup>1</sup>H-{31}P method with an accuracy of ± 1 ppm. 
The SSIC were determined with an accuracy of ± 0.05 Hz. The relative signs of the constants in (Ib) and (IVb) were determined from the INDO<sup>1</sup>H-{31}P spectra. 
Concentration % by volume. 
Concentration 3% by volume. 
The PMR spectrum at 80° was recorded at a depth of partial scanning 250 Hz; therefore, the chemical shifts were measured relative to the resonance signal of the proton H<sub>B</sub>; the chemical shifts of which was assumed equal to 5.04 ppm. 
The chemical shifts were determined relative to benzene, δ<sub>C6H6</sub> 7.27 ppm. 
The Overhauser effect was not measured on account of the large error in the measurement of the integrals of closely situated multiplet resonance bands of the protons H<sub>A</sub> and H<sub>B</sub>. 

COOR groups are maximally distant from one another. From an equilibrium mixture of the ester of the D-form, the anti-rotamer and one gauche-rotamer with a gauche-arrangement of the OH groups participate in the event of closing of the ring, which leads to the production of trans-4,5-dicarbalkoxy-1,3,2-dioxaphospholanes initially in the A and B conformations. In the ester of the meso-form only two gauche-rotamers have a gauche-arrangement of the OH groups, which leads to closing of the ring with a cis-configuration of the COOR groups with the original equiprobable population of the formations C and D. However, if we consider that in the ester of the D-form the transoid conformation is more populated than the gauche-rotamers, the reaction of formation of trans-4,5-dicarbalkoxy-1,3,2-dioxaphospholanes should be characterized by a large rate constant. Actually, with all other conditions equal, the reaction for the cis-isomer of 2-methoxy-4,5-dicarbalkoxy-1,3,2-dioxaphospholane proceeds at a substantially lower rate than for its trans-isomer.

A subsequent study of the chemical structure of the products (I)-(V), a confirmation of the configuration, and a study of the conformations were conducted by the NMR-{31}H, {31}P, and NMR-{31}H-{31}P method.

PMR Spectra and Conformation of the Ring. The use of the NMR method permitted, in the first place, additional information to be obtained on the conformation states of the phosphorus-containing five-membered heterocycle, i.e., a cyclic fragment which, as is well known, easily undergoes a pseudorotation [3]; in the second place, it permitted a supplementary confirmation to be obtained for the qualitative conformational analysis cited above. Moreover, a study of the compounds (I)-(V) and their predominant conformations was of interest from the standpoint of the methodological question of the angular dependence of...