



## An unusual cascade reaction of 4,5-dihydro-4,4-bis(trifluoromethyl)-2-phenyl-6,7-(4-chlorobenzo)[e]-1,3,2-dioxaphosphepin-5-one with chloral

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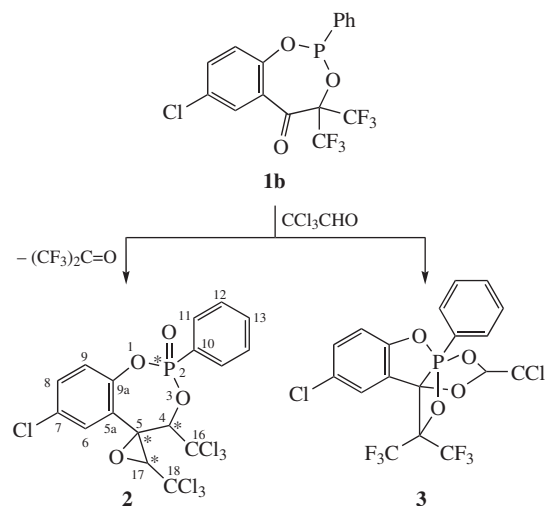
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The reaction of 4,5-dihydro-4,4-bis(trifluoromethyl)-2-phenyl-6,7-(4-chlorobenzo)[e]-1,3,2-dioxaphosphepin-5-one with chloral (1:2) proceeds with evolving hexafluoroacetone and gives spiro{2-oxo-4-trichloromethyl-4,5-dihydro-2-phenyl-6,7-(4-chlorobenzo)[f]-1,3,2-dioxaphosphepine-5,2'-(3'-trichloromethyl)oxirane} with a high stereoselectivity. Configuration of the four chiral centres ( $P_3^2C_4^3C_5^3/P_R^2C_R^4C_R^5C_R^3$ ) was determined by a single crystal X-ray diffraction.

The reactions of P<sup>III</sup> derivatives with carbonyl compounds are important for the synthesis of compounds bearing pentacoordinated phosphorus, which are the intermediates in the nucleophilic displacement reaction at tetracoordinated phosphorus species.<sup>1–6</sup> Recently,<sup>7,8</sup> we found that the reaction of  $\lambda^3\sigma^3$ -1,3,2-dioxabenzophospholes having a  $\gamma$ - or  $\delta$ -carbonyl group to the phosphorus atom in exocyclic substituent leads to the formation of ‘carcass’ phosphoranes. In spite of the formation of a few chiral centres, the process has a high regio- and stereoselectivity. The reaction was also applied to the P<sup>III</sup> derivatives bearing  $\gamma$ -endocyclic carbonyl group relative to the phosphorus atom, such as 4,5-dihydro-4,4-bis(trifluoromethyl)-2-phenyl-6,7-benzo[e]- and 4,5-dihydro-4,4-bis(trifluoromethyl)-2-phenyl-6,7-(4-chlorobenzo)[e]-1,3,2-dioxaphosphepin-5-ones **1a,b**. The 5-carbaphosphatrane derivatives with pentacoordinated phosphorus atom, containing three oxygen atoms in equatorial sets and two less apicophilic carbon ones in apical sets were unexpectedly obtained in the reaction of compounds **1a,b** with hexafluoroacetone.<sup>9</sup>

In this work, we attempted to use chloral as another reactive compound for the synthesis of 5-carbaphosphatranes. However, the interaction of chloral with dioxaphosphepine **1b** is more complex and proceeds by two main directions. The first direction leads to the formation of the unusual derivative with tetra-coordinated phosphorus atom – spiro{2-oxo-4-trichloromethyl-4,5-dihydro-2-phenyl-6,7-(4-chlorobenzo)[f]-1,3,2-dioxaphosphepine-5,2'-(3'-trichloromethyl)oxirane} **2**. The evolving of hexafluoroacetone, detected owing to the characteristic odour, took place in the course of the reaction. The content of compound **2** in the reaction mixture is about 70%.<sup>†</sup> The second direction involves the formation of 5-carbaphosphatrane derivative **3** as a minor compound.

The stereoselectivity of the formation of product **2** is very high. In spite of three additional asymmetric centres, only one diastereoisomer was formed and isolated in view of crystals suitable for X-ray diffraction (as a solvate with one CH<sub>2</sub>Cl<sub>2</sub> molecule).<sup>‡</sup> The molecular geometry of compound **2** is shown in Figure 1. The phosphorus atom has a distorted tetrahedral configuration, a seven-membered heterocycle has a distorted boat conformation and includes the planar four-atoms fragment C(5)C(5a)C(9a)O(1), the atoms P(2), O(3) and C(4) being situated on one side and at



Scheme 1

various distances of the latter. Phenyl and trichloromethyl substituents, as well as oxirane carbon atom [C(11)], are in pseudo-equatorial sets, the phosphoryl oxygen and the oxirane cycle

<sup>†</sup> Solvents and commercial reagents were purified by conventional methods before use. All experiments were performed under an atmosphere of dry argon. Melting points are uncorrected. Measurements involved a Boetius melting point apparatus. NMR experiments were performed in CDCl<sub>3</sub> at 20 °C with Varian Unity-300 (<sup>31</sup>P, <sup>31</sup>P-{<sup>1</sup>H}) at 121.42 MHz; <sup>19</sup>F at 282.4 MHz) and Bruker Avance-600 spectrometers with a 5 mm diameter inverse probe head with Z-active shielded gradients working at 600 MHz for <sup>1</sup>H and 150.864 MHz for <sup>13</sup>C. The  $\delta_H$  and  $\delta_P$  values were determined relative to internal (HMDS) or external (H<sub>3</sub>PO<sub>4</sub>) standard. The  $\delta_F$  values were determined relative to internal standard (C<sub>6</sub>F<sub>6</sub>) and then re-calculated relative to CFCl<sub>3</sub>. The  $\delta_C$  values were determined relative to the deuterated solvent signal. IR spectra were recorded on a Specord M-80 instrument in Nujol. EI mass spectra were obtained with a TRACE MS Finnigan MAT instrument; the ionization energy was 70 eV and the ion source temperature was 200 °C. The samples were introduced into the ion source *via* a direct inlet system. The evaporating ampoule was heated from 35 to 150 °C at a rate of 35 K min<sup>-1</sup>. The mass spectrometric data were processed using the Xcalibur system program.