

## LETTERS TO THE EDITOR

# Regiochemistry of the Reaction of Ethoxyacetylene with 2,2,2-Trichlorobenzo[*d*]-1,3,2λ<sup>5</sup>-dioxaphosphole, as Studied by Dynamic <sup>13</sup>C and <sup>31</sup>P NMR Spectroscopy

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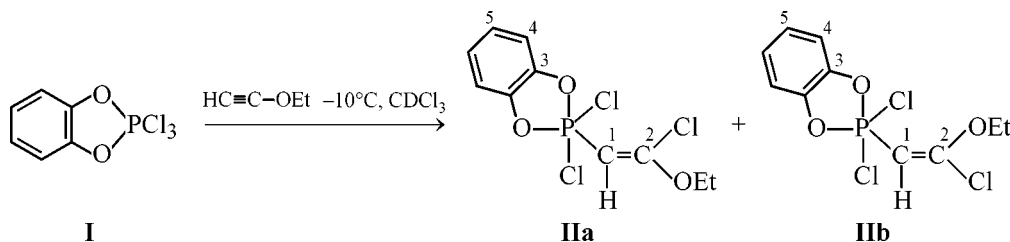
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Received July 5, 2001

It is known that alkoxyacetylenes react with PCl<sub>5</sub> to give phosphonium salts, the products of electrophilic addition across the C≡C bond, [ROC(Cl)=CHPCl<sub>3</sub>]<sup>+</sup>·PCl<sub>6</sub><sup>−</sup>. Their structure was not elucidated exactly because of their lability and low solubility [1, 2]. Contrary to PCl<sub>5</sub>, 2,2,2-trichlorobenzo[*d*]-1,3,2λ<sup>5</sup>-dioxaphosphole **I** is readily soluble in the majority of organic solvents and is therefore a convenient object for dynamic NMR experiments [3].

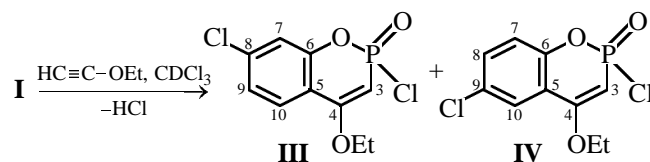
Here we report on the first dynamic <sup>13</sup>C and <sup>31</sup>P NMR study of the regiochemistry of the reaction of dioxaphosphole **I** with ethoxyacetylene in 1 : 1.1 ratio. According to <sup>31</sup>P NMR data, several compounds are formed at −10°C. They are characterized by three groups of upfield [δ<sub>P</sub> −18 to −20 (65%) and −16.1 ppm] and downfield [δ<sub>P</sub> 24–25 ppm (25%)] signals. The main direction is the preferred formation (65%) of two phos-

phorane compounds **IIa** and **IIb** (**IIa**, δ<sub>P</sub> −20.1 ppm, <sup>2</sup>J<sub>PCH</sub> 32.1 Hz; **IIb**, δ<sub>P</sub> −18.0 ppm, <sup>2</sup>J<sub>PCH</sub> 24.6 Hz) in 5 : 1 ratio. On heating to 65°C, they undergo complex disproportionation to give spirophosphoranes and phosphonates as final products. The structure of phosphoranes **IIa** and **IIb** was determined from the <sup>13</sup>C NMR spectrum (−10°C). This spectrum contains a double set of similar signals of carbon atoms related to two main isomeric phosphoranes with the P–C bond. Considering the data of [1, 2], we identified them as *Z* (**IIa**) and *E* (**IIb**) isomers of 2,2-dichloro-2-(2-chloro-2-ethoxyethenyl)benzo[*d*]-1,3,2λ<sup>5</sup>-dioxaphosphole. Thus, under very mild conditions dioxaphosphole **I** adds to ethoxyacetylene with predominant formation of the *cis* product. Formation of a small amount of the *trans*-addition product is hardly due to the *Z*–*E* isomerization, because the ratio of the isomers is approximately the same at −10 and 20°C.

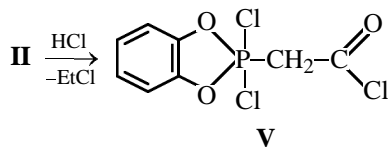


In addition, unusual insertion of ethoxyacetylene into the five-membered ring of phosphorane **I** takes place, giving 4-ethoxybenzo[*e*]-1,2-oxaphosphorins **III** and **IV** (3 : 1) in a total yield of 25%. The final products of this reaction are characterized by the signals with δ<sub>P</sub> 24.5 (d, <sup>2</sup>J<sub>PCH</sub> 10.6 Hz) and 25.0 ppm (d, <sup>2</sup>J<sub>PCH</sub> 11.3 Hz). The structure of these compounds

was determined by <sup>13</sup>C NMR spectroscopy. The signals were assigned considering the data of [4].



Hydrogen chloride released in the process reacts with ethoxyacetylene and vinylphosphoranes **II** to give  $\text{CH}_3\text{CCl}_2\text{OEt}$  and dichlorophosphorane **V**, which were also detected by  $^{13}\text{C}$  NMR.



The signal of phosphorane **V** in the  $^{31}\text{P}$  NMR spectrum is located at  $\delta_{\text{P}}$  -16.1 ppm (t,  $^2J_{\text{PCH}}$  16.0 Hz). The  $^{13}\text{C}$  NMR spectrum of the  $\text{P}-\text{CH}_2-\text{C}(\text{O})\text{Cl}$  fragment contains the following signals,  $\delta_{\text{C}}$ , ppm ( $J$ , Hz): 68.34 d.t ( $\text{CH}_2$ ,  $^1J_{\text{PC}}$  139.0,  $^1J_{\text{CH}}$  139.0), 164.31 d.t [ $\text{C}(\text{O})\text{Cl}$ ,  $^2J_{\text{PCC}}$  10.8,  $^2J_{\text{HCC}}$  7.0].

**Compound IIa.**  $^{13}\text{C}$  NMR spectrum ( $0^\circ\text{C}$ ) (here and hereinafter, the shape of signal in the  $^{13}\text{C}-\{^1\text{H}\}$  NMR spectrum is given in parentheses),  $\delta$ , ppm ( $J$ , Hz): 109.02 d.d (d) ( $\text{C}^1$ ,  $^1J_{\text{PC}}$  195.2,  $^1J_{\text{HC}}$  177.8), 154.65 d.t.d (d) ( $\text{C}^2$ ,  $^2J_{\text{PCC}}$  6.3,  $^3J_{\text{HCOC}}$  3.8,  $^2J_{\text{HCC}}$  2.2), 144.39 m (s) ( $\text{C}^3$ ,  $^2J_{\text{POC}}$  0), 111.24 d.m (d) ( $\text{C}^4$ ,  $^1J_{\text{HC}}$  168.1,  $^3J_{\text{POCC}}$  14.6,  $^3J_{\text{HCCC}}$  9.4,  $^2J_{\text{HCC}}$  4.5,  $^4J_{\text{HCCCC}}$  0.7), 123.20 d.m (s) ( $\text{C}^5$ ,  $^1J_{\text{HC}}$  162.8,  $^3J_{\text{HCCC}}$  7.8,  $^2J_{\text{HCC}}$  1.0), 69.74 t.q.d (d) ( $\text{OCH}_2$ ,  $^1J_{\text{HC}}$  149.0,  $^2J_{\text{HCC}}$  4.3,  $^4J_{\text{PCCOC}}$  0.9), 14.04 q.t (s) ( $\text{CH}_3$ ,  $^1J_{\text{HC}}$  127.8,  $^2J_{\text{HCC}}$  2.8).

**Compound IIb.**  $^{13}\text{C}$  NMR spectrum ( $0^\circ\text{C}$ ),  $\delta_{\text{C}}$ , ppm ( $J$ , Hz): 105.49 d.d (d) ( $\text{C}^1$ ,  $^1J_{\text{PC}}$  224.8,  $^1J_{\text{HC}}$  166.4), 155.84 d.t (d) ( $\text{C}^2$ ,  $^2J_{\text{PCC}}$  8.1,  $^3J_{\text{HCOC}}$  2.2), 144.13 m (s) ( $\text{C}^3$ ,  $^2J_{\text{POC}}$  0), 111.60 d.m (d) ( $\text{C}^4$ ,  $^1J_{\text{HC}}$  168.1,  $^3J_{\text{POCC}}$  14.6), 123.51 d.d (s) ( $\text{C}^5$ ,  $^1J_{\text{HC}}$  163.1,  $^3J_{\text{HCCC}}$  7.8), 69.40 t.q.d (d) ( $\text{OCH}_2$ ,  $^1J_{\text{CH}}$  147.3,  $^2J_{\text{HCC}}$  4.0,  $^4J_{\text{PCCOC}}$  3.9), 14.50 q.t (s) ( $\text{CH}_3$ ,  $^1J_{\text{HC}}$  128.0,  $^2J_{\text{HCC}}$  2.8).

**Compound III.**  $^{13}\text{C}$  NMR spectrum ( $25^\circ\text{C}$ ),  $\delta_{\text{C}}$ , ppm ( $J$ , Hz): 85.66 d.d (d) ( $\text{C}^3$ ,  $^1J_{\text{PC}}$  173.3,  $^1J_{\text{HC}}$  166.4), 163.0 m (d) ( $\text{C}^4$ ,  $^2J_{\text{PCC}}$  16.1), 116.26 m (d)

( $\text{C}^5$ ,  $^3J_{\text{PCCC}}$  12.0), 149.63 m (d) ( $\text{C}^6$ ,  $^2J_{\text{POC}}$  7.8), 119.01 d.d.d.d (d) ( $\text{C}^7$ ,  $^1J_{\text{HC}}$  170.2,  $^3J_{\text{POCC}}$  9.7,  $^3J_{\text{HCCC}}$  5.4,  $^4J_{\text{HCCCC}}$  1.0), 137.89 d.d.d (s) ( $\text{C}^8$ ,  $^3J_{\text{HCCC}}$  13.3,  $^2J_{\text{HCC}}$  4.4,  $^2J_{\text{HCC}}$  3.2), 124.84 m (s) ( $\text{C}^9$ ,  $^1J_{\text{HC}}$  164.0,  $^3J_{\text{HCCC}}$  5.3), 126.28 d (s) ( $\text{C}^{10}$ ,  $^1J_{\text{HC}}$  167.7), 64.89 m (d) ( $\text{OCH}_2$ ,  $^4J_{\text{PCCOC}}$  3.2).

**Compound IV.**  $^{13}\text{C}$  NMR spectrum ( $25^\circ\text{C}$ ),  $\delta_{\text{C}}$ , ppm ( $J$ , Hz): 86.49 d.d (d) ( $\text{C}^3$ ,  $^1J_{\text{PC}}$  173.2,  $^1J_{\text{HC}}$  166.4), 162.54 m (d) ( $\text{C}^4$ ,  $^2J_{\text{PCC}}$  15.8), 118.96 m (d) ( $\text{C}^5$ ,  $^3J_{\text{PCCC}}$  11.9), 147.50 m (d) ( $\text{C}^6$ ,  $^2J_{\text{POC}}$  7.8), 120.16 d.d (d) ( $\text{C}^7$ ,  $^1J_{\text{HC}}$  166.9,  $^3J_{\text{POCC}}$  9.5), 132.26 d.d (s) ( $\text{C}^8$ ,  $^1J_{\text{HC}}$  168.0,  $^3J_{\text{HCCC}}$  6.0), 129.88 m (d) ( $\text{C}^9$ ,  $^3J_{\text{HCCC}}$  11.2,  $^2J_{\text{HCC}}$  3.4,  $^2J_{\text{HCC}}$  3.4,  $^5J_{\text{POCCCC}}$  1.0), 65.02 m (d) ( $\text{OCH}_2$ ,  $^4J_{\text{PCCOC}}$  3.1).

The  $^{13}\text{C}$ ,  $^{13}\text{C}-\{^1\text{H}\}$ ,  $^{31}\text{P}$ , and  $^{31}\text{P}-\{^1\text{H}\}$  NMR spectra were recorded on a Bruker MSL-400 ( $^{13}\text{C}$ , 100.6 MHz;  $^{31}\text{P}$ , 162.0 MHz) spectrometer in  $\text{CDCl}_3$  relative to internal HMDS or external  $\text{H}_3\text{PO}_4$ .

## ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project no. 00-03-32835).

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