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Acetylenes are convenient objects for studying the stereochemistry of the phosphorylation of unsaturated compounds by PCl₅, since a definite geometry of the alkene is fixed as the result of adding PCl₅ to the CEC bond. The products of phosphorylating alkoxyacetylenes with PCl₅ were studied only as the dichlorides of β -alkoxy- β -chlorovinylphosphonic acids AlkOCCl=CHPOCl₂ (I), and it is assumed that PCl₅ adds to the CEC bond in both the trans and cis positions [1, 2].

In our opinion, it is more correct to study the primary crystalline reaction products, namely the compounds $\text{ROCC1=CHPCl}_3^+ \cdot \text{PCl}_6^-$ (II), since isomerization with time [2] was observed in a number of cases when working with the (I) products, and the compounds were studied after fractional distillation, during which isomerization processes are not excluded. In addition, the dichlorides of β -alkoxyvinylphosphonic acids undergo both hydrochlorination and dehydrochlorination [3], which undoubtedly reflects on the ratio of the E,Z isomers. We established that, in contrast to the corresponding dichlorides of phosphonic acids, complexes of type ROCH=CHPCl}+.PCl6- do not add HCl to the C=C bond. Consequently, secondary processes have the least effect on the stereochemistry of these compounds. This could also be expected to be true of the (II) complexes.

In the present paper we studied the structure of the previously unstudied products of phosphorylating phenoxyacetylene with PCl₃, both as the β -phenoxy- β -chlorovinyltrichlorophosphonium hexachlorophosphate complex PhCOCl=CHPCl₃+·PCl₆⁻ (III) and as the dichloride of β -phenoxy- β -chlorovinylphosphonic acid PhOCCl=CHPOCl₂ (IV). The phosphorylation of phenoxyacetylene was run in cyclohexane, benzene, and AcCl solutions. The ³¹P NMR spectra of the isolated crystalline (III) complex in PhNO₂ have the signals (δ , ppm): -88.6 (JPH = 30.1 Hz), -82.5 (JPH = 33.8 Hz, E and Z isomers of PhOCCl=CHPCl₃⁺), and +296.9 (PCl₆⁻). The E/Z ratio = 1/1.7 (from cyclohexane), 1/1.9 (from benzene), and 1/1.8 (from AcCl).

The formation of the E and Z isomers of the (III) complex testifies either to the isomerization of one of the initially formed isomers, as is assumed in [2, 4], or to the stepwise electrophilic character of the phosphorylation of phenoxyacetylene, with addition in both the cis and trans positions. Our previously described E and Z isomers of $EtOCH=CHPCl_3^+ \cdot PCl_6^-$ [5], which is close to the discussed complex, do not isomerize with time. The ratio of the isomers of the (III) complex, obtained in cyclohexane, remains constant for 3.5 months. Consequently, we postulate that the electrophilic attack of the phenoxyacetylene molecule by PCl₅ in both the trans and cis positions is entirely probable by the following scheme:



In order to avoid possible thermal isomerization processes we did not purify dichloride (IV) by distillation and instead studied the freshly prepared product. The ³¹P NMR spectrum of (IV) has two doublets at -25.1 ppm (Jp_H = 17.0 Hz) and -20.8 ppm (Jp_H = 20.7 Hz), which respectively refer to the E and Z isomers (cf. [2]), in which connection the ratio of the isomers remains practically constant when going from (III) to (IV). Isomerization transformations in dichloride (IV) were also not observed for 3 months. Besides a multiplet of the protons of the benzene ring at 6.9-7.3 ppm, the PMR spectrum of (IV) has doublets at 5.84 ppm (Jp_H = 20.7 Hz, Z isomer) and 5.44 ppm (Jp_H = 17.0 Hz, E isomer).

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Institute of Petrochemical and Coal Chemical Synthesis, Irkutsk State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 898-900, April, 1981. Original article submitted July 23, 1980. On the assumption that the isomerization of Z-BuOCCl=CHPOCl₂ to the E isomer, observed in [2], can be due to the presence of HCl in the product, the addition and elimination of which would assure such a transition, we decided to check the possibility of hydrochlorinating (IV). Actually, (IV) adds HCl, as is evidenced by the appearance of a new triplet at -31.5 ppm, Jp_H = 15 Hz, in the ³¹P NMR spectrum of the reaction mixture, which refers to the P atom in PhOCCl₂--CH₂POCl₂.

In the hydrochlorination products of the dichlorides of alkenylphosphonic acids ROCClH-CH₂POCl₂ (V), isolated by us when the vinyl esters were phosphorylated, the signals of the P atoms are also observed further downfield than for the corresponding dichlorides of the alkenylphosphonic acids ROCH=CHPOCl₂ (VI): R = Et, δP (V) -38.2 ppm, doublet of triplets; δP (VI) -33.9 ppm, doublet of doublets; R = Bu, δP (V) -37.8 ppm, doublet of triplets; δP (VI) -33.7 ppm, doublet of doublets; R = Ph, δP (V) -36.5 ppm, doublet of triplets; δP (VI) -30.6 ppm, doublet of doublets.

We established that the E isomer of the dichloride of β -ethoxyvinylphosphonic acid (VI) is formed exclusively from the mixture of E and Z isomers of the complex EtOCH=CHPCl₃⁺. PCl₆⁻, which is at times also accompanied by the hydrochlorination product of (V). This confirms our viewpoint regarding the important role of HCl in the isomerization of the dichlorides of alkenylphosphonic acids of type (IV) and (VI).

EXPERIMENTAL

The NMR spectra were obtained on an XL-100/12 spectrometer, the PMR spectra relative to TMS as the internal standard, and the ³¹P NMR spectra relative to 85% H₃PO₄.

Phenoxyacetylene was obtained as described in [6]. The synthesis of (III) was run in solution using stoichiometric ratios of the reactants. The yield of (III) after fractional crystallization, washing, and drying in vacuo was 96%. The treatment of dry (III) with SO_2 , followed by vaporization of the by-products in vacuo, gave (VI). The hydrochlorination of dichlorides (IV) and (VI) was run in ether under cooling.

CONCLUSIONS

1. The reaction of phenoxyacetylene with PCl₅ gives a stable mixture of the E and Z isomers of β -phenoxy- β -chlorovinyltrichlorophosphonium hexachlorophosphate. A scheme was proposed for the phosphorylation of phenoxyacetylene.

2. The dichlorides of β -phenoxy- β -chlorovinyl- and β -alkoxyvinylphosphonic acids add HCl to the double bond, while the alkoxyvinyltrichlorophosphonium hexachlorophosphates do not react with HCl.

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