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Abstract

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On derivatives of ethyl-α-chlorovinyl- and ethyl-β-chlorovinylphosphinic acids

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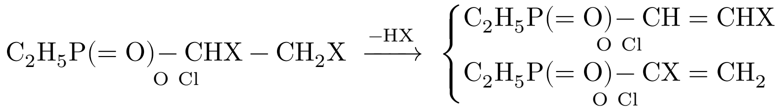
In our recent communication (^{1}) it was shown that the acid chlorides of ethyl-α, β-dihaloethylphosphinic acids readily undergo thermal or catalytic decomposition with formation of the acid chlorides of ethylhalovinylphosphinic acids.

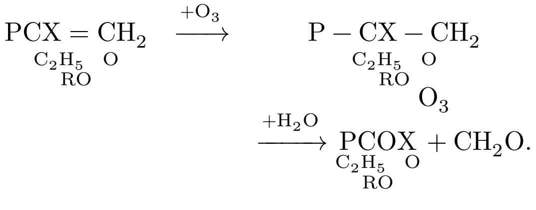
Taking into account the possibility that the reaction may proceed in two directions, namely:



$$C_2H_5P(=\underset{O\ \ Cl}{O)-}\,CHX-CH_2X \xrightarrow{-HX} \begin{cases} C_2H_5P(=\underset{O\ \ Cl}{O)-}\,CH=CHX \\ C_2H_5P(=\underset{O\ \ Cl}{O)-}\,CX=CH_2 \end{cases}$$

the question of the position of the halide in the vinyl radical was temporarily left open, although for a number of reasons preference was given to the variant with the halide located at the β-carbon atom.

To establish the structure of the compounds described, we decided to make use of the ozonolysis reaction of esters of ethylchlorovinylphosphinic acid, followed by identification of the decomposition products with the aid of dimedone. As a result of ozonolysis of the propyl and isobutyl esters of ethylchlorovinylphosphinic acid, after a series of appropriate procedures, in both cases a crystalline product was isolated which, by its melting point (189.5°), corresponded to the condensation product of dimedone with formaldehyde. The latter, obviously, can be formed only if the halide in the above-mentioned compounds is in the α-position, according to the scheme



$$\underset{\substack{C_2H_5\ \ O\\ RO}}{PCX}=CH_2 \xrightarrow{+O_3} \underset{\substack{C_2H_5\ \ O\\ RO}}{P-CX}-\underset{O_3}{CH_2} \xrightarrow{+H_2O} \underset{\substack{C_2H_5\ \ O\\ RO}}{PCOX}+CH_2O.$$

Thus, as a result of thermal or catalytic dehydrohalogenation of the acid chlorides of ethyl-α, β-dihaloethylphosphinic acids, acid chlorides of ethyl-α-

halovinylphosphinic acids are formed, and, consequently, we must change our initial opinion and agree with the view of M. I. Kabachnik and T. Ya. Medved, who recently reported the preparation of the diethyl ester of bromovinylphosphinic acid (^{2}), to which they assign a structure with the bromine atom in the α-position.

It seemed of interest to obtain derivatives of ethyl-β-halovinylphosphinic acid in order to compare their physical constants and properties with those of the previously described derivatives of ethylhalovinylphosphinic acid, in which, as was shown above, the halide is located at the α-carbon atom. We succeeded in doing this, however, in a somewhat unexpected way. As is known, phosphorus pentachloride readily reacts

with various ethylene derivatives, including simple vinyl ethers, as was first reported by K. N. Anisimov and A. N. Nesmeyanov (^{3}). According to the general scheme

$$2PCl_5 + CH_2 = CHOR \rightarrow ROCHCl - CH_2PCl_4 \cdot PCl_5 \xrightarrow{+2SO_2}$$

$$\rightarrow ROCH = CH_2POCl_2 + POCl_3 + 2SOCl_2 + HCl,$$

they obtained a series of acid chlorides of β-alkoxyvinylphosphinic acids.

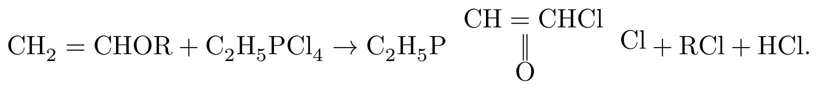
We intended to carry out the reaction with ethyltetrachlorophosphine, expecting that the reaction would proceed analogously and ultimately give the acid chlorides of ethyl-β-alkoxyvinylphosphinic acids. However, in studying the reaction of ethyltetrachlorophosphine with butyl vinyl ether, we found that the suspension of ethyltetrachlorophosphine in absolute benzene decreases as the vinyl ether is added (in the cold) and disappears completely when the latter is added in an equimolecular ratio; the solution becomes homogeneous. This seemed interesting, since in the case of the interaction of vinyl ethers with phosphorus pentachloride, crystalline intermediate products are formed that are insoluble in the reaction medium—benzene.

Since the reaction mixture in our case had become homogeneous, we decided to omit the stage of treatment with sulfur dioxide and proceeded directly to distillation. After distilling off the benzene and applying a vacuum, approximately half of the residue consisted of a gum of comparatively low-boiling, as yet unidentified fractions. The other half, after two repeated distillations, gave a fraction which, according to the analytical data and comparison of the molecular refractions found and calculated, most probably corresponded to the acid chloride of ethylchlorovinylphosphinic acid. The product was a slightly yellow, mobile liquid with a somewhat pungent odor, fuming slightly in air and decomposed by water. When a sample of the substance was added to a chloroform solution of bromine or directly to bromine, no noticeable interaction was observed; however, after several days the bromine became decolorized.

A product identical with that described above was also obtained in the interaction of ethyltetrachlorophosphine with vinyl isopropyl ether. By treating the product obtained with ethanol according to the generally accepted procedure, i.e., in absolute diethyl ether in the presence of pyridine, a substance was obtained which, according to analytical data, corresponded to the ethyl ester of ethylchlorovinylphosphinic acid.

The assignment of the indicated structure is confirmed by the infrared spectrum of the latter product. Intense absorption bands in the regions of 760 cm^{-1}, 1020–1060 cm^{-1}, and 1250 cm^{-1}, according to the literature data (^{4}), indicated, respectively, the presence of C—Cl, P—O—C, and P=O bonds; confirmation of the presence of a double bond was provided by an absorption band in the region of 1635 cm^{-1} (stretching vibrations of the C=C bond) and an intense absorption band in the region of 820 cm^{-1} (out-of-plane deformation vibrations of the C—H bond in —CH=CHCl (^{4})).

On the basis of the results obtained, we considered it possible to conclude that the reaction of ethyltetrachlorophosphine with simple vinyl ethers differs substantially from the reaction of the latter with phosphorus pentachloride and, ultimately, leads to the formation of the acid chloride of ethyl-β-chlorovinylphosphinic acid, according to the general scheme



$$CH_2 = CHOR + C_2H_5PCl_4 \rightarrow C_2H_5\overset{CH = CHCl}{\underset{\substack{\| \\ O}}{P}}Cl + RCl + HCl.$$

Assignment of the structure with chlorine located at the β-carbon atom in the present case followed from the fact that the boiling point, refractive index, and specific gravity proved to be appreciably higher than the same constants for the acid chloride of ethylchlorovinylphosphinic acid obtained by catalytic dehydrochlorination of the acid chloride of ethyl-α,β-dichloroethylphosphinic acid, in which chlorine is in the α-position. A similar discrepancy in physical constants is also observed in the case of the ethyl esters of the indicated acids.

The study of the reaction of ethyltetrachlorophosphine with vinyl ethers is continuing.

We express our gratitude to R. V. Lindval' and N. V. Oslina for carrying out the spectral analyses.

Experimental Part

1. Into a one-liter three-necked flask were placed 500 ml of anhydrous benzene and 115 g of ethyldichlorophosphine. The system was swept with a stream of carbon dioxide. After the mixture had been cooled to −10°, with vigorous stirring, a stream of gaseous chlorine was passed into the flask at a rate that allowed the temperature to be maintained within −10 to +10°. After 1 hour had elapsed, chlorination was stopped. A white

crystalline suspension formed in the flask. Directly into the reaction mixture, at −5°, 56 g of vinyl butyl ether was added dropwise from a dropping funnel, as a result of which the amount of precipitate noticeably decreased. The next day a further 33 g of butyl vinyl ether was added to the mixture, after which the precipitate disappeared completely. After 2 h the reaction mixture was transferred to a Würtz flask and the benzene was distilled off. The residue was transferred to an Arbuzov flask of appropriate capacity and distilled in vacuum. As a result of repeated distillations, one of the fractions isolated proved to be a fraction (50 g): b.p. 113–118° at 13–14 mm Hg; n_D^{20} 1.5070; d_4^{20} 1.3210; MR_D found 38.91, calculated 38.41; yield 32.5%.

Found, %:	P 17.51; 17.63;	Cl 40.58; 40.64
$C_4H_7OCl_2P$. Calculated, %:	P 17.9;	Cl 41

As is evident from the analytical data, the product is the acid chloride of ethylchlorovinylphosphinic acid.

2. 24 g of the acid chloride of ethyl-β-chlorovinylphosphinic acid was reacted with 6 g of ethanol in the presence of 10 g of pyridine in 250 ml of anhydrous diethyl ether. After separation of pyridine hydrochloride and removal of the ether, the filtrate, during vacuum distillation, gave 19 g of a substance with b.p. 115° at 15 mm Hg; n_D^{20} 1.4710; d_4^{20} 1.1520; MR_D found 44.32, calculated 44.05; yield 75%.

Found, %:	P 16.48; 16.70;	Cl 19.22; 19.44
$C_6H_{12}O_2ClP$. Calculated, %:	P 16.90;	Cl 19.44

Thus, the substance is the ethyl ester of ethyl-β-chlorovinylphosphinic acid.

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