Reports of the Academy of Sciences of the USSR

CHEMISTRY

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1965. Volume 164, No. 3

CHEMISTRY

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ON THE COMPLEX FORMATION OF SIMPLE VINYL ETHERS WITH CHLORIDES OF PENTAVALENT PHOSPHORUS

(Presented by Academician A. E. Arbuzov, January 9, 1965)

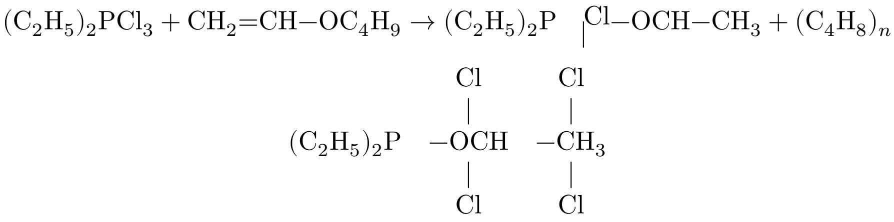
It is known ([1]) that, upon thermal cleavage of complexes obtained by the interaction of ethyltetrachlorophosphorane with simple vinyl ethers, the acid chloride of ethyl-β-chlorovinylphosphinic acid is formed. Somewhat later this reaction was reproduced with phenyltetrachlorophosphorane. The complex obtained in benzene corresponded to the formula $C_6H_5PCl_3 \cdot CH = CH—OC_4H_9$, which agrees with the literature data ([2]). Its thermal cleavage, as expected, led to the formation of the acid chloride of phenyl-β-chlorovinylphosphinic acid. It should be noted that in all the above cases considerable amounts of dichloroanhydrides of either ethyl- or phenylphosphonic acid were obtained, the formation of which, of course, is not explained by the overall scheme.

Naturally, such a peculiar course of the reaction prompted interest in extending it to other phosphorus chlorides, in particular to phosphorus pentachloride and dialkyl- or diaryltrichlorophosphoranes. Contrary to the expected analogy, the pattern of the reaction in these cases was different. In the case of phosphorus pentachloride, the complexes with simple vinyl ethers decomposed upon heating with the formation of a wide range of products; however, we were unable to isolate the acid dichloride of β-chlorovinylphosphonic acid, which is described in the literature ([3]).

We then turned to the complexes formed by the interaction of vinyl ethers with diethyl- and diphenyltrichlorophosphoranes. When the components were mixed in benzene or n-octane, after brief heating (80°, 30 min), complexes precipitated on cooling; they fumed and were very hygroscopic in air. After careful washing with octane and drying in vacuum, the resulting snow-white crystals were analyzed. In the case of diethyltrichlorophosphorane and butyl vinyl ether, the gross formula corresponded to $C_6H_{11}OCl_3P$.

Found, %: C 29.85, 29.72; H 6.14, 5.97; P 13.17, 12.99; Cl 44.13, 43.98
Calculated, %: C 30.09; H 5.89; P 12.93; Cl 44.43

With hydrogen sulfide the complex readily decomposed in benzene; however, subsequent distillation of the decomposition products in vacuum was accompanied by the evolution of volatile products and ultimately gave, in high yield, the acid chloride of diethylphosphinic acid. Decomposition of the complex with excess water gave diethylphosphinic acid; decomposition with alcohols in the presence of tertiary amines led to the isolation either of the acid chloride of diethylphosphinic acid or of its corresponding esters. We add that, after decomposition of the complex with excess water, acetaldehyde dinitrophenylhydrazone was isolated from the aqueous solution (m.p. 143.5—145°, mixed-melting test 144.5—146°). On the basis of the foregoing, it may be assumed that the reaction of diethyltrichlorophosphorane with *n*-butyl vinyl ether proceeds according to the scheme:



$$(\mathrm{C_2H_5})_2\mathrm{PCl_3} + \mathrm{CH_2{=}CH{-}OC_4H_9} \rightarrow (\mathrm{C_2H_5})_2\mathrm{P}\ \vert\mathrm{Cl{-}OCH{-}CH_3} + (\mathrm{C_4H_8})_n$$

$$(\mathrm{C_2H_5})_2\mathrm{P}\ \begin{array}{c}\mathrm{Cl}\\ |\\ -\mathrm{OCH}\\ |\\ \mathrm{Cl}\end{array}\ \begin{array}{c}\mathrm{Cl}\\ |\\ -\mathrm{CH_3}\\ |\\ \mathrm{Cl}\end{array}$$

and the complex corresponds to diethyl-α-chloroethoxydichlorophosphorus.

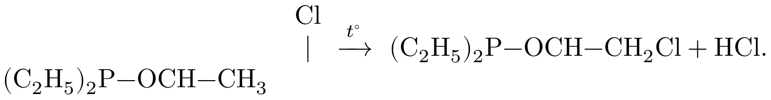
Confirmation of this scheme was the isolation of isooctylene from the benzene residue (after separation of the complex). Similar results were obtained in the reactions of diethyltrichlorophosphorus with phenyl vinyl ether and of diphenyltrichlorophosphorus with *n*-butyl vinyl ether. In the first case the already described diethyl-α-chloroethoxydichlorophosphorus was obtained; in the second, diphenyl-α-chloroethoxydichlorophosphorus. Finally, a study of the reaction of triphenyldichlorophosphorus with butyl vinyl ether also showed that a triphenyl-α-chloroethoxy-chlorophosphorus complex is formed, with simultaneous elimination of butylene.

Thermal decomposition of the complex obtained from diethyltrichlorophosphorus and butyl vinyl ether proceeded with considerable resinification and with isolation of the main fraction with b.p. 94-95° (9 mm), n_D^{20} 1.4783, d_4^{20} 1.2040. Yield 44% $\mathrm{C_6H_{13}OCl_2P}$.

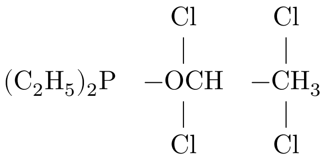
Found, %: Cl 35.38, 35.36; P 14.84, 15.00
Calculated, %: Cl 34.91; P 15.25

Repeated distillations of the product proceeded with decomposition and formation, ultimately, of the acid chloride of diethylphosphinic acid. The initial product is readily decomposed by water, and from the aqueous solution chloroacetaldehyde was isolated in the form of the dinitrophenylhydrazone (m.p. 152-153.5; mixed sample 152.5-154).

On the basis of the data presented, the product could have been assigned the structure of the α,β-dichloroethyl ester of diethylphosphinic acid according to the scheme:



$$(C_2H_5)_2P{-}OCH{-}\overset{Cl}{\overset{|}{CH_3}} \xrightarrow{t^\circ} (C_2H_5)_2P{-}OCH{-}CH_2Cl + HCl.$$

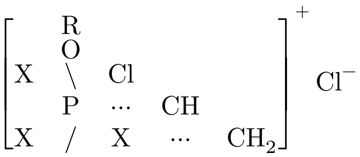


$$(C_2H_5)_2P \quad {-}O\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{CH}} \quad {-}\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{CH_3}}$$

However, the product is not oxidized and does not react with sulfur, although it reacts vigorously with bromine.

Reaction with alcohols, in the presence of tertiary bases, led to the formation of the corresponding esters of diethylphosphinic acid. Thus, on going from phosphorus pentachloride to alkyl or aryl chlorides of pentavalent phosphorus, the nature and properties of their complexes with simple vinyl ethers change. It seems to us that this can be explained by assuming the presence of additional phosphorus-chlorine bonds due to the $3d$-orbitals of phosphorus and the unshared electron pairs of chlorine, in accordance with the concept of increased bond multiplicity for halides of elements possessing d-orbitals ([4]).

Although, as applied to phosphorus chlorides, such a possibility is, on the contrary, denied ([5]), nevertheless, taking into account the criticism to which the method of determining double-bond character according to Pauling ([6]) has been subjected, it seems to us that such a possibility must be taken into account. Then the following reasoning can be given: the molecule of a vinyl ether with phosphorus chloride forms a multicenter system, caused by the presence of free d-orbitals of phosphorus and the conjugated system of $p\pi$-electrons (a π-complex)



$$\left[\begin{array}{ccccc} & R & & & \\ & O & & & \\ X & \backslash & Cl & & \\ & P & \cdots & CH & \\ X & / & X & \cdots & CH_2 \end{array}\right]^{+} Cl^{-}$$

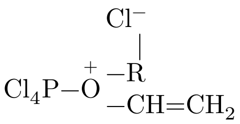
(I)

Stabilization of this complex will evidently depend on the probability of the presence of vacant d_π-orbitals.

In the case of phosphorus pentachloride the probability of occupation of the phosphorus d_π-orbitals by chlorine p-electrons is greatest; therefore stabilization of the π-complex proceeds mainly at the expense of the phosphorus d_σ-orbitals in two variants:

$$\mathrm{Cl_4P{-}CH{=}CH{-}OR} \quad \mathrm{(II)}$$

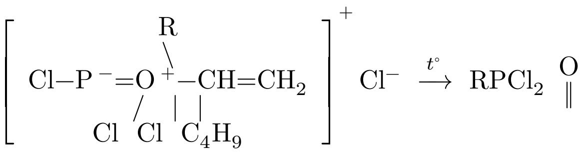
or



$$\mathrm{Cl_4P{-}\overset{+}{O}}\begin{matrix}\mathrm{Cl^-} \\ | \\ \mathrm{-R} \\ \mathrm{-CH{=}CH_2}\end{matrix} \quad \mathrm{(III)}$$

An oxonium compound of type III is evidently unstable and on heating decomposes into the initial components or forms chlorination products.

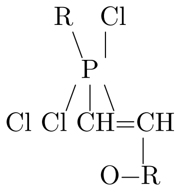
With transition to chlorides of the type $RPCl_4$, the probability of the presence of a phosphorus d_π-orbital increases; stabilization of the π-complex in IV subsequently leads to significant amounts of V



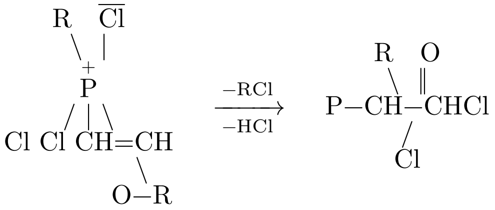
(V)

(IV)

σ-Stabilization gives product VI



in which (especially in the ionized state VII)



(VII) (VIII)

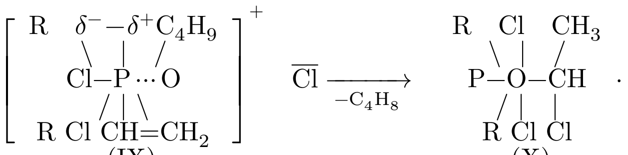
the probability of intramolecular or intermolecular interaction of the oxygen p-electrons with the phosphorus d-orbitals is retained. Evidently this explains

Fig. 1. IR spectra: a —diethyl-α-chloroethoxychlorophosphorane; b —diethylphosphinic acid chloride; c —α,β-dichloroethyl ester of diethylphosphinic acid.

Figure 1: Fig. 1. IR spectra: a —diethyl-α-chloroethoxychlorophosphorane; b —diethylphosphinic acid chloride; c —α,β-dichloroethyl ester of diethylphosphinic acid.

the formation of the chloranhydrides of ethyl-(phenyl)-β-chlorovinylphosphinic acid VIII on heating the complexes.

And, finally, with transition to phosphorus chlorides of the type R_2PCl_3 and R_3PCl_2, the probability of the presence of unfilled d_π-orbitals increases; therefore stabilization of the π-complex proceeds chiefly through oxygen via structure IX



(IX) (X)

In the spectrum of diethyl-α-chloroethoxydichlorophosphorane, obtained by the interaction of phenyl vinyl ether with diethyltrichlorophosphorane (Fig. 1a), in agreement with the structure shown, intense absorption bands are observed in the ranges 480-600 cm^{-1} (ν_{PCl_2}), 700-800 cm^{-1} (ν_{C-Cl}), 1040 cm^{-1} (ν_{P-O-C}), 1250-1300 cm^{-1} of the C_2H_5—P grouping.*

* We express our gratitude to R. R. Shagidullin for assistance in obtaining the spectra.

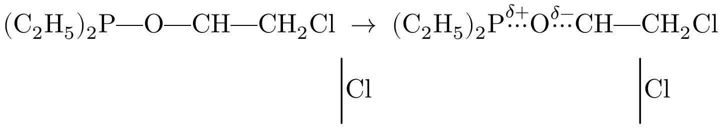
In the spectrogram of the product of thermal decomposition of complex X (Fig. 1 c), absorption bands of diethylphosphinic acid chloride are observed with sufficient intensity, which indicates the presence of significant amounts of this acid chloride.

Fig. 1. IR spectra: *a* —diethyl-α-chloroethoxychlorophosphorane; *b* —diethylphosphinic acid chloride; *c* —α,β-dichloroethyl ester of diethylphosphinic acid.

At the same time, the intense bands with maxima at 1139 and 1279 cm^{-1}, present in the spectrum of the thermal-decomposition product, are absent from the spectrum of diethylphosphinic acid chloride (see Fig. 1 b).

From this it may be concluded that thermal decomposition of complex X gives a mixture of diethylphosphinic acid chloride and the α,β-dichloroethyl ester of diethylphosphinic acid. The absorption bands at 1139 and 1279 cm^{-1} may be assigned to the symmetric and asymmetric vibrations of the P · · · O · · ·

C grouping, and thus the possibility of the existence of this trivalent ester is explained by the presence of a stabilized structure:



$$(C_2H_5)_2P\text{—}O\text{—}CH\text{—}CH_2\underset{\displaystyle |\,Cl}{Cl} \rightarrow (C_2H_5)_2P\overset{\delta+}{\cdots}O\overset{\delta-}{\cdots}CH\text{—}CH_2\underset{\displaystyle |\,Cl}{Cl}$$

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Received
28 XII 1964.

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