HYDROLYSIS OF 2-ETHYL-1,2-OXAPHOSPHOLAN-5-ONE 2-OXIDE

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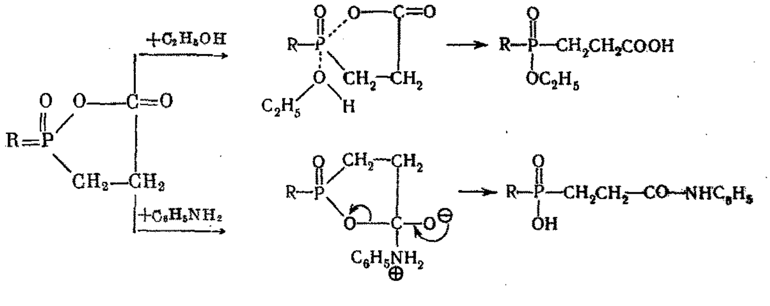
The reactions of substituted 1,2-oxaphospholan-5-one 2-oxides, which are ambident reagents, with alcohols and amines proceed by two different routes [1]:



This reaction sequence is in accord with the Pearson principle [2]. The alcohol attacks the center having the highest electron density, viz., the phosphorus atom, while the stronger base (amine) attacks the electron-poor center, viz., the carbon of the carbonyl group of the phospholane oxide.

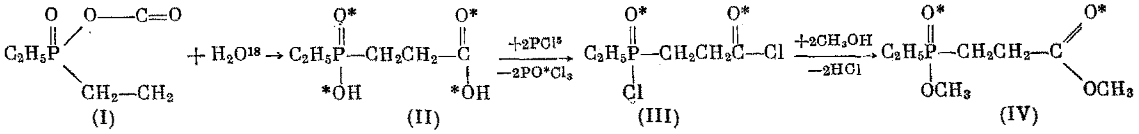
Considering the inductive effects, one may expect that alcohols should be more basic than water. However, comparison of the data on the basicity of water and alcohols gives contradictory results [3-5]. According to [6], water is a stronger base than alcohols, and the basicities of the latter arrange themselves in order of the inductive effect of the hydrocarbon radicals.

It was thus of interest to find out which reaction center water would attack during hydrolysis of the oxaphospholane oxide.

Using O^{18}-labelled water, we have determined the orientation in the opening of the ring during hydrolysis of 2-ethyl-1,2-oxaphospholan-5-one 2-oxides (I).

EXPERIMENTAL

By hydrolysis of (I) with 12% heavy-oxygen water we obtained ethyl-β-carboxyethylphosphinic acid (II) with mp 99.5°C, which is virtually nonvolatile at residual pressure of ca. $1 \cdot 10^{-6}$ mm. To obtain a volatile compound, we treated acid (II) with PCl_5 in CCl_4; the solvent and phosphoryl chloride obtained were removed from the reaction mixture in vacuo, and the residue, ethyl-β-chloroformylethylphosphinic chloride (III), was treated with methanol without distillation. The methyl ethyl-β-carbomethoxyethylphosphinate acid (IV) obtained was distilled, and the percentage of O^{18} in it was determined.



By mass spectrometer, 6% O^{18} was found in ester (IV) (according to the lines 165 and 167, which correspond to $M - C_2H_5$, $179.181 = M - CH_3$). Of this amount, ca. 3% O^{18} is found in the carbonyl group

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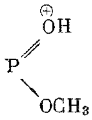
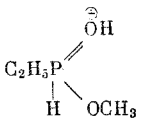
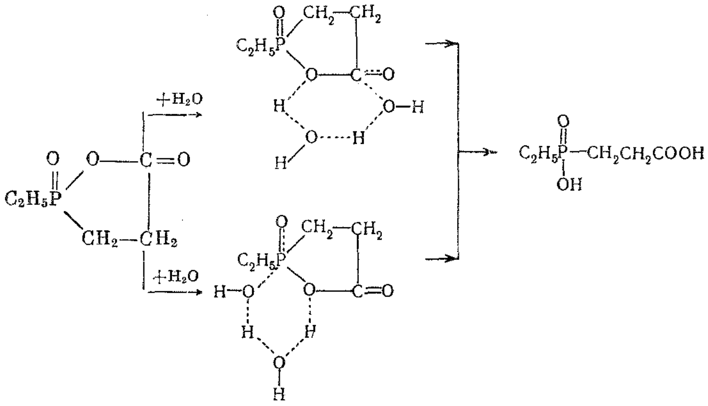
A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR, Kazan'. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2314-2315, October, 1969. Original article submitted April 14, 1969.

(according to the lines 79 and 81, and 109 and 111). The lines at 87, 79, and 109 correspond to ions of the composition $(CH_2CH_2COOCH_3)^+$,  $P(=\overset{\oplus}{O}H)OCH_3$, and  $C_2H_5P(=\overset{\ominus}{O}H)(H)OCH_3$, respectively.

These data allow one to conclude that water attacks both reaction centers of phospholane oxide (I), viz., the phosphorus atom and the carbonyl carbon, to approximately the same degree. Isotopic exchange at the P(O)OH and CO_2H groups was also established.

The hydrolysis of phospholane oxide (I) apparently proceeds via intermediate complexes with subsequent decomposition of the latter



It is most likely that attack of the water proceeds along a line perpendicular to the plane of the carbonyl group. This leads to maximum superposition of the bonding orbitals of oxygen on the π-electron cloud of the carbonyl group.

CONCLUSIONS

Hydrolysis of 2-ethyl-1,2-oxaphospholan-5-one 2-oxide proceeds via attack of water at both reactive centers, the phosphorus atom and the carbonyl carbon.

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