MASS SPECTROMETRY OF SOME FIVE-MEMBERED CYCLIC PHOSPHITES

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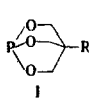
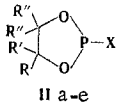
The characteristic paths of the dissociative ionization of some 1,3,2-dioxaphospholanes were established. In the case of 2-ethoxy-1,3,2-dioxaphospholane and its 4-methyl and 4,4,5,5-tetramethyl derivatives, an ethylene molecule is formed from the ethoxy group of the molecular ion, while the formation of an aldehyde (ketone) molecule is due to cleavage of the C–C and P–O bonds in the ring.

Our mass-spectrometric study of some five-membered cyclic phosphites is only one of the stages of research to ascertain the possibility of the application of mass spectrometry to establish the structures of cyclic esters of phosphorus acids and polyatomic alcohols [1-3]. At the start of our research the literature contained only one communication devoted to the mass spectrometry of cyclic phosphites I, which, however, contain condensed six-membered rings [4]. We have used mass spectrometry to study several substituted 1,3,2-dioxaphospholanes (II) (see Table 1).



I



II a-e

IIa R=R′=R″=H, X=OC_2H_5; b R=CH_3, R′=R″=H, X=OC_2H_5; c R=R′=R″=CH_3, X=OC_2H_5; d R=R′=R″=H, X=OC_6H_5; e R=R′=R″=H, X=Cl

The presence of intense molecular-ion peaks is characteristic for the mass spectra of all of the investigated compounds. As expected, the most intense M^+ peak is observed in the mass spectrum of phenyl ethylenephosphite (IId). This is in agreement with the fact that when there is an aromatic substituent present in the compound, it leads to the formation of a molecular ion that is more stable than the molecular ions of compounds that contain only aliphatic substituents.

The appearance of $(M-28)^+$ ion peaks in the mass spectra of IIa-IIc is apparently associated with splitting out of an ethylene molecule from the ethoxy group of the initially formed molecular ions. In fact,

TABLE 1

m/e	$\frac{J}{\Sigma J} \cdot 100\%$				
	IIa	IIb	IIc	IId	IIe
$M^{+\cdot}$	5,20	2,80	4,00	11,00	9,60
$(M-28)^{+\cdot}$	9,60	3,20	1,60	0,13	0,14
$(M-30)^{+\cdot}$	2,60	1,14	—	0,57	2,10* 5,90*
$(M-X)^+$	9,00	3,70	1,80	19,60	22,4

*These are the intensities of the lines caused by the $[M^{(Cl\ 37)}-30]^{+\cdot}$ and $[M^{(Cl\ 35)}-30]^{+\cdot}$ ions, respectively.

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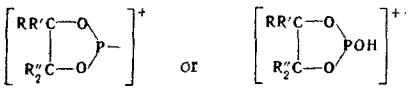
on passing from ethyl ethylenephosphite (IIa) to phenyl ethylenephosphite and ethylene chlorophosphite (IId and (IIe), the intensity of the $(M-28)^+$ ion peak decreases from 9.6 to 0.13 and 0.14%, respectively.

The loss of a C_2H_5O group by the molecular ions leads to the appearance of $(M-45)^+$ ion peaks in the mass spectra of IIa-IIc. As seen from Table 1, the intensities of these peaks, like the intensities of the $(M-28)^+$ ion peaks, clearly depend on the degree of methylation of the 1,3,2-dioxaphospholane ring. As the number of methyl groups increases, the stability of ion III or IV decreases. It is well known that the stability of ions decreases as their degree of branched character increases.



III IV

The presence in the mass spectra of IIa and IIb of $(M-30)^+$ peaks, which can be explained by splitting out of a formaldehyde molecule from the corresponding molecular ions, is of definite interest. The C–C and P–O bonds in the 1,3,2-dioxaphospholane ring are apparently cleaved. This assumption is confirmed by the fact that an $(M-44)^+$ peak is observed along with an $(M-30)^+$ peak in the mass spectrum of ethyl propylenephosphite. The appearance of the $(M-44)^+$ peak may be due to splitting out of an acetaldehyde molecule from the molecular ion. There are no $(M-30)^+$ and $(M-44)^+$ peaks in the mass spectrum of IIc, but there is an $(M-58)^+$ ion peak corresponding to splitting out of an acetone molecule from the molecular ion. Our proposed mechanism for the dissociative ionization of substituted 1,3,2-dioxaphospholane rings with cleavage of the C–C and P–O bonds also occurs in the case of ethylenechlorophosphite (IIe).

EXPERIMENTAL

The cyclic phosphites used in this study were synthesized by the reaction of glycols with ethyl dichlorophosphite or phosphorus trichloride in ether in the presence of triethylamine. Their boiling points and refractive indexes were in agreement with the data in [5].

The mass spectra of the compounds were obtained with an MI-1305 mass spectrometer equipped with a glass input system at an ionizing voltage of 50 V. The temperature of the input system was ~80°. The mass spectra were normalized in such a way that the sum of the intensities of all of the lines is taken as 100.

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