

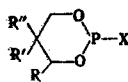
# MASS SPECTRA OF SOME SIX-MEMBERED CYCLIC PHOSPHITES

Yu. Ya. Efremov, R. Z. Musin,  
N. A. Makarova, and É. T. Mukmenev

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A comparative analysis of the mass spectra of a number of 1,3,2-dioxaphospholanes and phosphorinanes was made in order to ascertain the dependence of several pathways of dissociative ionization on the size and degree of alkylation of a phosphorus-containing ring. The principal differences in the mass spectra of five- and six-membered cyclic phosphites are due to the high (as a consequence of the presence of strain) probability of cleavage of the P-O bond in the dioxaphospholane ring. The possibility of the use of mass spectrometry for the establishment of the composition of the hydrocarbon fragment of the ring is demonstrated.

Several mass spectra of five-membered cyclic phosphites have been reported [1]. The mass spectra of seven six-membered cyclic phosphites (I-VII), which were obtained in the present research, are discussed, and the effect of the ring size on several pathways of dissociative ionization is examined.



I R=R'=R''=H, X=OC<sub>2</sub>H<sub>5</sub>; II R=CH<sub>3</sub>, R'=R''=H, X=OC<sub>2</sub>H<sub>5</sub>; III R=H, R'=R''=CH<sub>3</sub>, X=OC<sub>2</sub>H<sub>5</sub>; IV R=R'=R''=H, X=OC<sub>6</sub>H<sub>5</sub>; V R=R'=R''=H, X=Cl; VI R=CH<sub>3</sub>, R'=R''=H, X=Cl; VII R=H, R'=R''=CH<sub>3</sub>, X=Cl

The relative intensities of the ion peaks necessary for the discussion are presented in Table 1. The formation of [PO]<sup>+</sup> (m/e 47), [POH]<sub>2</sub><sup>+</sup> (m/e 65), and [HP(OH)<sub>3</sub>]<sup>+</sup> (m/e 83) ions is characteristic for five- and six-membered cyclic phosphites. For the formation of the latter, cleavage of at least three C-O bonds with migration of four hydrogen atoms to the charged fragment is required. The formation of ions with m/e 47, 65, and 83 evidently occurs in several steps. The presence of a diffuse line with m/e 62.1 in the mass spectrum of III, which is due to the disintegration of the metastable ion with m/e 111 to an ion with m/e 83, serves as some proof of this assumption. Two diffuse lines at m/e 55.7 and 40.3, the first of which is due to the disintegration  $M^{+} \xrightarrow{-93} 105$ , the second of which is due to disintegration of the metastable ion with m/e 105 to an ion with m/e 65, are observed in the mass spectrum of IV. Ions with m/e 83, 65, and 47 are also characteristic for noncyclic phosphites, except for trimethyl phosphite, which does not give ions with m/e 83 and 65 [2].

The relative intensity of the ion peak with m/e 83 increases as the number of substituents in the ring increases when an identical alkoxy group is present. When the ethoxy group is replaced by a phenoxy group, the intensity of this signal falls sharply. This can apparently be explained by the fact that cleavage of a stronger O-C<sub>6</sub>H<sub>5</sub> bond as compared with the O-C<sub>2</sub>H<sub>5</sub> bond is required for the formation of an ion with m/e 83 from IV. The energy of the C-O bond in ethanol is 90 kcal/mole, whereas the energy of the C-O bond in phenol is of the order of 107 kcal/mole [3]. In addition, migration of hydrogen from the benzene ring is required in the formation of anion with m/e 83, and this should also reduce the probability of formation of

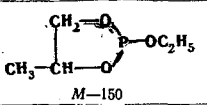
A. E. Arbuzov Institute of Organic and Physical Chemistry. Kazan Branch, Academy of Sciences of the USSR, Kazan. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 12, pp. 1620-1623, December, 1974. Original article submitted June 26, 1973.

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TABLE 1. Mass Spectra of Six-Membered Cyclic Phosphites

m/e of the ion	$\frac{I}{\Sigma I} \cdot 100\%$						
	I	II	III	IV	V	VI	VII
	M-150	M-164	M-178	M-198	M with Cl <sup>35</sup> -140 M with Cl <sup>37</sup> -142	M with Cl <sup>35</sup> -154 M with Cl <sup>37</sup> -156	M with Cl <sup>35</sup> -168 M with Cl <sup>37</sup> -170
M	4,6	3,4	3,1	8,7	5,1	2,8	3,8
M-15	—	0,10	0,35	—	—	0,1	—
M-27	8,3	3,6	1,7	—	—	1,6	—
M-28	5,3	2,1	1,8	—	—	0,5	—
M-30	0,50	—	0,35	—	1,1	0,1	—
M-44	—	1,8	—	—	—	0,7	—
M-X	4,8	1,9	1,2	30,0	24,0	4,4	6,0
M-58	3,4	—	—	3,1	0,50	—	—
M-72	0,15	2,3	—	—	0,40	0,1	0,3
85	—	0,10	0,15	—	0,60	0,3	0,2
83	1,5	0,70	5,2	0,2	2,2	1,0	0,6
82	0,40	3,8	1,4	0,20	0,20	0,1	—
77	1,5	0,70	0,50	7,2	3,8	1,0	0,6
P-X	0,20	0,2	0,2	—	0,8	0,6	0,5
65	8,3	7,0	7,6	12,0	5,6	1,0	0,6
47	5,7	3,4	2,2	4,6	10,0	4,6	2,9
69	—	—	5,0	—	0,2	—	14,0
55	0,25	9,8	4,6	0,8	0,6	15,0	4,8
41	8,2	3,8	6,1	9,9	10,5	3,8	12,4
29	7,0	5,9	4,8	1,3	7,2	11,0	4,1
27	6,2	5,6	4,0	1,6	7,0	12,0	4,1
43	1,4	4,0	1,4	0,4	1,2	5,1	1,4
86	—	—	0,9	—	—	—	0,5
72	—	0,7	—	—	—	0,3	—
58	7,2	0,2	0,9	0,4	2,4	0,2	0,3

TABLE 2. Mass Spectra of Isomeric Five- and Six-Membered Cyclic Phosphites

m/e of the ion	$\frac{I}{\Sigma I} \cdot 100\%$	
		
	I	M-150
M	2,8	4,6
M-30	1,1	0,5
M-44	1,6	—
M-28-30	2,6	3,4
M-28-44	1,7	0,2
M-74	2,6	0,2

this ion. It is known that C-H bonds in the  $\alpha$  position with respect to a double bond are stronger than C-H bonds in saturated compounds.

The presence in the molecule of a  $\text{OC}_2\text{H}_5$  group leads to the appearance of  $\text{M}^+ - \text{OC}_2\text{H}_5$ ,  $\text{M}^+ - \text{C}_2\text{H}_4$ , and  $\text{M}^+ - \text{C}_2\text{H}_3$  ions. The relative intensities of the peaks of these ions and of the molecular ion peak decrease as the number of methyl groups attached to the ring increases. The same regularity was also noted for five-membered cyclic phosphites [1]. The behavior of VI is somewhat unexpected as compared with the investigated five- and six-membered cyclic phosphites and acid chlorides. Peaks of M-27 and M-28 ions are observed in the mass spectrum of this compound, but the reason for their appearance is as yet unclear.

It should be noted that the formation of an  $\text{M}^+ - \text{C}_2\text{H}_5$  ion is not characteristic for I-III and that the formation of an  $\text{M}^+ - \text{C}_6\text{H}_5$  ion is not characteristic for IV. The M- $\text{C}_2\text{H}_5$  ion peak is of low intensity for the former compounds, while the M- $\text{C}_6\text{H}_5$  ion is altogether absent in the case of IV.

The presence of peaks of ions formed during the cleavage of P-O and C-C ring bonds is characteristic for the mass spectra of 1,3,2-dioxo- and 1,3,2-oxaazaphospholanes [1, 4]. In this case, the molecular ion lost a formaldehyde, acetaldehyde, or acetone molecule, depending on the number of methyl groups replacing the ring hydrogen atom. The M-30 ion peak (44, 58) is less intense in the mass spectra of six-membered cyclic phosphites. The principal difference in the mass spectra of five- and six-membered cyclic phosphites are observed for the M-30, M-44, M-28-44, and M-74 ions, the formation of which is associated with cleavage of one or two ring P-O bonds. This experimental result indicates that the P-O bond in five-membered cyclic phosphites is weaker than in six-membered phosphites because of the presence of strain in the five-membered ring. The relative intensities of the lines for I and the isomeric 2-

ethoxy-4-methyl-1,3,2-dioxaphospholane are presented in Table 2; these lines illustrate the difference in the above-indicated pathways of dissociative ionization. These differences can be used for the determination of the ring size of cyclic phosphites from their mass spectra.

A characteristic feature of the mass spectra of six- and five-membered cyclic phosphites is the presence of intense ion peaks due to hydrocarbon ions of the composition  $C_nH_{2n-1}$ . The heaviest hydrocarbon ion is formed by cleavage of two ring C-O bonds with migration of one hydrogen atom to the neutral fragment. This pathway of dissociative ionization makes it possible to distinctly determine the cyclic hydrocarbon portion of molecules from their mass spectra. Thus I gives ions with  $m/e$  41 and 27. Consequently, the composition of the hydrocarbon portion is  $C_3H_5 + H$ , i.e.,  $C_3H_6$ . Compound II forms ions with  $m/e$  55, 41, and 27, the heaviest of which corresponds to the  $C_4H_7^+$  ion, and hence the composition of the hydrocarbon portion of the ring is  $C_4H_8$ . Ion peaks with  $m/e$  69, 55, 41, and 27 are observed for III, and this corresponds to a  $C_5H_{10}$  hydrocarbon composition of the ring.

The hydrocarbon composition of the ring can be found independently from ion peaks of the composition  $C_nH_{2n}O$  (58, 72, 86). In the mass spectrum, these peaks are considerably less intense than the peaks due to hydrocarbon ions. However, for identification purposes they may be useful, inasmuch as it can be foreseen that the ion with  $m/e$  83 may have the compositions  $C_6H_{11}$  and  $HP(OH)_3$ . At the same time, the peak with  $m/e$  100 for the same compounds will be due only to ions of the composition  $C_6H_{12}O$ . We observed ion peaks with  $m/e$  100 in the mass spectrum of a five-membered cyclic phosphite - tetramethylethylene phosphite.

## EXPERIMENTAL

The cyclic phosphites and chlorophosphites (I-VII) used in this research were synthesized by reaction of the appropriate diols with ethyl dichlorophosphite or phosphorus trichloride in a solvent (ether, methylene chloride) in the presence or absence of a base (triethylamine). The boiling points and refractive indexes of the products were in agreement with the literature data [5-9].

The conditions under which the mass spectra were recorded were similar to those indicated in [1].

## LITERATURE CITED

1. Yu. Ya. Efremov, R. Z. Musin, L. I. Gurarii, and É. T. Mukmenev, *Khim. Geterotsikl. Soedin.*, 1329 (1972).
2. J. L. Occolowitz and G. L. White, *Anal. Chem.*, **35**, 1179 (1963).
3. N. N. Semenov, *Some Problems in Chemical Kinetics and Reactivities* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1958), p. 28.
4. Yu. Ya. Efremov, R. Z. Musin, M. A. Pudovik, and L. K. Kibardina, *Khim. Geterotsikl. Soedin.*, 894 (1973).
5. H. J. Lucas, F. W. Mitchell, and C. N. Scully, *J. Amer. Chem. Soc.*, **72**, 5491 (1950).
6. A. E. Arbuzov, V. M. Zoroastrova, and N. I. Rizpolozhenskii, *Izv. Akad. Nauk*, 208 (1948).
7. R. S. Edmundson, *Chem. Ind.*, 1828 (1962).
8. R. S. Edmundson, *Tetrahedron*, **20**, 2781 (1964).
9. D. S. Ayres and M. N. Rydon, *J. Chem. Soc.*, 1109 (1957).