MASS SPECTROMETRIC STUDY OF L-ARABITOL AND RIBITOL DIPHOSPHITES

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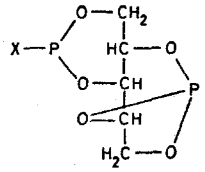
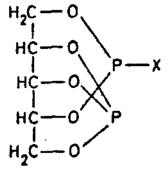
The mass spectra of a number of diphosphites were recorded in order to ascertain their structures. Probable schemes for the formation of the characteristic ions are proposed. The possibility of the identification of isomeric diphosphites from mass-spectral data is demonstrated.

Previous mass-spectrometric studies [1-3] of cyclic esters dealt with the elucidation of the principles involved in the fragmentation upon electron impact of cyclic phosphites containing five-membered [1] (1,3,2-dioxaphospholane) and six-membered [2] (1,3,2-dioxaphosphorinane) rings.

It seemed to us that it would be helpful to use mass spectrometry to obtain information regarding the structures of more complex phosphites, which were synthesized for the first time. We selected the diphosphites (I-VI) obtained from the stereoisomeric five-carbon alcohols L-arabitol (I-III) and ribitol (IV-VI) as the subjects for the investigation:



I – III



IV – VI

I, IV X = Cl ; II, V X = OCH_3 ; III, VI X = OC_2H_5

TABLE 1. Relative Intensities (in percent relative to the total ion current) of the Peaks of the Ions Characteristic for Diphosphites I-VI

m/e of the ion	I*	II	III	IV*	V	VI
	M with Cl^{35}=244 M with Cl^{37}=246	M=240	M=254	M with Cl^{35}=244 M with Cl^{37}=246	M=240	M=254
M	1,8 0,60	5,4	3,0	0,48 0,16	1,8	1,5
M−27	—	—	4,3	—	—	1,7
M−28	—	—	1,2	—	—	0,4
M−43	2,8 0,93	1,0	—	0,81 0,27	3,1	0,2
M−28, −43	—	—	1,0	—	0,40	3,9
M−X	5,2	0,40	1,2	4,9	0,50	1,1
132	0,90	1,5	1,6	2,7	2,9	3,5
119	0,90	2,0	2,6	1,4	2,3	3,1
103	3,6	0,90	1,8	2,1	1,6	5,3
102	5,2	1,9	4,3	3,0	2,7	3,5
89	5,7	3,2	6,5	3,8	3,4	4,7
M−106	2,1	2,2	0,1	—	0,40	0,1
M−28, −106	0,70 0,80 —	—	3,1	— 0,4 —	0,40	1,1
125	1,3	0,30	—	—	0,80	—
127	0,43	—	0,3	—	—	0,3

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*The intensities of the ion peaks with Cl for I and IV are due to ions with Cl^{35} and Cl^{37}, respectively.

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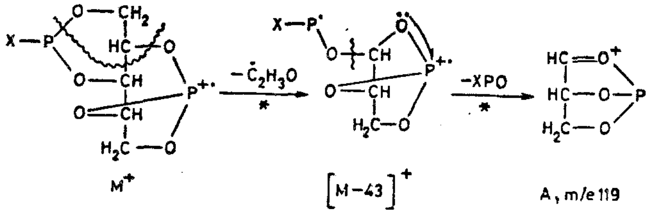
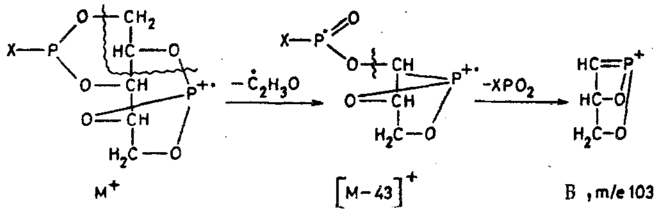
The data in Table 1, in which the relative intensities (in percent relative to the total ion current) of the peaks of the characteristic ions are presented, show that the mass spectra of all of the investigated compounds contain molecular ion peaks ($M^{+\cdot}$). This fact is in agreement with the structure of these compounds, since they consist of condensed rings and do not contain branched radicals. The mass spectrum consequently makes it possible to determine the molecular mass of these compounds.

As in the case of the previously investigated cyclic phosphites [2], the presence of a substituent X at the phosphorus atom is readily identified from the appearance in the mass spectra of intense $(M - X)^+$ ion peaks. In addition, as expected, the formation of $[M - C_2H_3]^+$ and $[M - C_2H_4]^{+\cdot}$ ions is characteristic for ethoxy derivatives III and VI. The detachment of X from the molecular ions is confirmed by the presence in the mass spectra of the corresponding peaks of metastable m* ions with m/e 179 for I and IV, while detachment of $\dot{C}_2H_3$ and C_2H_4 particles is confirmed by the presence of m* 202.9 and m* 201.1 for III.

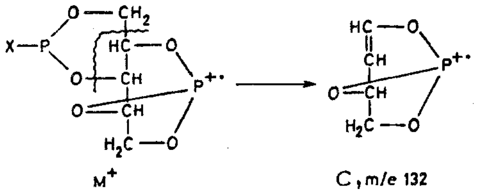
The common pathway of fragmentation for the entire investigated series of compounds is the formation of $[M - 43]^+$ ions for I, II, IV, and V and $[M - 28, - 43]^+$ ions for III and VI, which in the case of I is confirmed by the peak of the corresponding metastable ion (m* 165.6). The $[M - 43]^+$ ions are probably formed as a result of ejection of a $C_2H_3O\cdot$ radical from the molecular ions via at least two competitive mechanisms, according to an analysis of their subsequent fragmentation, since the subsequent fragmentation of the $[M - 43]^+$ ions proceeds via two different pathways with ejection of XPO of XPO_2 molecules and the formation of A and B ions, respectively (see the scheme below). Fragmentation of the molecular ions via the first pathway leads to A ions, the intensity of the peaks of which is significant in the mass spectra of all of the investigated compounds. In the mass spectrum of V this pathway is confirmed by all corresponding metastable ion (m* 71.9). The formation of $[M - C_2H_4, C_2H_3O]^+$ ions in the mass spectra of diphosphites III and VI is due to the facile detachment of an ethylene molecule from the molecular ion at the expense of the ethoxy group [2] and subsequent elimination of a $\dot{C}_2H_3O$ radical; in the case of VI this is also confirmed by a metastable ion (m* 73.4).



Fragmentation of the molecular ions via the second mechanism subsequently does not lead to A ions but rather to B ions, the peaks of which are also present in the mass spectra of all of the diphosphites:

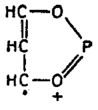


Among the remaining intense peaks for this series of diphosphites one should note the peaks of C ions that are encountered in all of the mass spectra. The ion peaks with this mass number are probably due to ions that contain the cellular fragment. Their formation presupposes cleavage of the C—C and C—O bonds in the molecular ion:

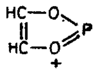


For diphosphites based on ribitol the schemes of the formation of the $[M - 43]^+$, A, B, and C ions can be represented similarly.

Let us further note that peaks of ions of the D and E type are common to all of the investigated compounds. These ions are formed from C and A ions with cleavage of P—O and C—C bonds and ejection of a CH_2O molecule (for III metastable ion m* 66.6 corresponds to the reaction $A \xrightarrow{-CH_2O} E$).



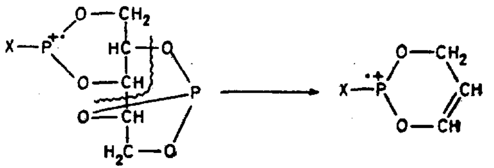
D, m/e 102



E, m/e 89

The formation of similar ions due to splitting out of a molecule of formaldehyde has been demonstrated repeatedly for a number of 1,3,2-dioxaphosphorinanes [2] and 1,3,2-dioxaphospholanes [1].

The pathways of dissociative ionization described above are common to all of the diphosphites based on L-arabitol (I-III) and ribitol (IV-VI). It was extremely important for the chemistry of these compounds to isolate those pathways of dissociative ionization by means of which these two isomeric groups of compounds can be identified. It follows from the data in Table 1 that the $[M - 106]^{+\cdot}$ ion peaks for I and II and the $[M - 28, - 106]^{+\cdot}$ ion peaks for III have higher relative intensities as compared with the mass spectra of IV-VI. It is most probable that these ions are formed from the molecular ions as a result of the following process:



M^+

$[M-106]^{+\cdot}$

The process involving the formation of these ions for diphosphites I-III is energically more favorable as compared with IV-VI, since for this the cleavage of only two bonds (C—C and C—O) is necessary, whereas the cleavage of at least three bonds is necessary for IV-VI. In the case of diphosphite III the $[M - 28, - 106]^{+\cdot}$ ion contains X = OH, in view of the previously mentioned competitive detachment of C_2H_4 from the ethoxy group of the molecular ion.

A difference in the intensities of the peaks of the ions with the composition $C_2H_3O_2PCl$ is observed for isomeric I and IV; the peaks of the ions of this composition are more intense for isomer I based on L-arabitol.

Thus the data obtained relative to the pathways of dissociative ionization of the investigated diphosphites confirmed the assumption of their structure. The differences in the mass spectra of the isomeric diphosphites of L-arabitol and ribitol derivatives are sufficient for the identification of isomeric pairs by a mass-spectrometric method.

EXPERIMENTAL

The mass spectra of the investigated compounds were obtained with an MI-1305 mass spectrometer equipped with a system for direct introduction of the substances into the ion source at an ionizing-electron energy of 50 eV, an emission current of 0.5 mA, and an ion-source temperature of 80°C.

6-Chloro-2,5,7,11,12-pentaoxa-1,6-diphosphatricyclo[7.2.1.$0^{1,9,3,8}$]dodecane (I). A mixture of 10.0 g (0.066 mole) of L-arabitol and 19.0 g (0.139 mole) of PCl_3 in 100 ml of dry dioxane was stirred at 20°C for 1 h and at 40-50°C for 1 h, after which the dioxane and excess PCl_3 were removed in vacuo, and 50 ml of dry ether was added to the residue. The resulting precipitate was removed by filtration and recrystallized from dry benzene to give 7.1 g (44%) of I with mp 141-143°C and $\delta\ ^{31}P - 146$ and 120 ppm. Found: C 24.67; H 3.12; Cl 14.46; P 25.40%. $C_5H_7ClO_5P_2$ Calculated: C 24.56; H 2.88; Cl 14.50; P 25.33%.

6-Methoxy-2,5,7,11,12-Pentaoxa-1,6-diphosphatricyclo [7.2.1.$0^{1,9,3,8}$]dodecane (II). A solution of 10.9 g (0.044 mole) of I in 150 ml of dry benzene was added dropwise with stirring and cooling (−5 to 0°C) to a solution of 1.4 g (0.044 mole) of dry methanol and 3.5 g (0.044 mole) of dry pyridine in 400 ml of a mixture (3 : 1) of dry diethyl ether and benzene, and the mixture was stirred for 3 h. It was then allowed to stand at room temperature for 15 h, and the precipitated pyridine hydrochloride was removed by filtration and washed with ether. The solvents were removed from the filtrate in vacuo, and the residual crystalline mass was purified by sublimation at 70°C (0.04 mm) to give 7.4 g (70%) of II with mp 74-76°C and δ ^{31}P − 125 and 120 ppm. Found: C 29.86; H 4.13; P 25.65%. $C_6H_{10}O_6P_2$. Calculated: C 30.01; H 4.19; P 25.80%.

6-Ethoxy-2,5,7,11,12-pentaoxa-1,6-diphosphatricyclo[7.2.1.$0^{1,9,3,8}$]dodecane (III). Compound III, with bp 98°C (0.07 mm), n_D^{20} 1.4990, and δ ^{31}P − 124 and 120 ppm, was obtained in 26% yield was obtained by a method similar to that used to prepare II. Found: C 33.37; H 4.97; P 24.45%. $C_7H_{12}O_6P_2$. Calculated: C 33.085; H 4.75; P 24.37%.

8-Chloro-2,4,7,9,12-pentaoxa-3,8-diphosphatricyclo[4.4.1.$1^{3,11}$]dodecane (IV). A mixture of 10 g (0.066 mole) of ribitol and 19.0 g (0.139 mole) of PCl_3 in 100 ml of dry dioxane was stirred at 40°C for 1 h, after which the dioxane was removed in vacuo, and the residue crystallized completely in 10 h. The crystals were dissolved in 70 ml of dry benzene and reprecipitated by the addition of dry diethyl ether. The crystals were then removed by filtration and dried at 40°C (10 mm) for 2 h to give 11.8 g (73%) of IV with mp 100-102°C and δ ^{31}P − 165 and 121 ppm. Found: C 24.42; H 2.98; Cl 14.26; P 25.25%. $C_5H_7ClO_5P_2$. Calculated: C 24.56; H 2.88; Cl 14.50; P 25.33%.

Compounds V and VI were obtained by a method similar to that used to prepare II.

8-Methoxy-2,4,7,9,12-pentaoxa-3,8-diphosphatricyclo[4.4.1.$1^{3,11}$]dodecane (V). This compound, with mp 111-112°C and δ ^{31}P − 130 and 121 ppm, was obtained in 70% yield. Found: C 30.20; H 4.27; P 25.91%. $C_6H_{10}O_6P_2$. Calculated: C 30.01; H 4.19; P 25.82%.

8-Ethoxy-2,4,7,9,12-pentaoxa-3,8-diphosphatricyclo[4.4.1.$1^{3,11}$]dodecane (VI). This compound, with bp 152-154°C (0.4 mm), mp 48-50°C, and δ ^{31}P − 128 and 121 ppm, was obtained in 34% yield. Found: C 32.94; H 4.98; P 24.08%. $C_7H_{12}O_6P_2$. Calculated: C 33.085; H 4.75; P 24.37%.

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