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MASS SPECTRA OF A NUMBER OF 1,3,2-OXAZAPHOSPHORINANES

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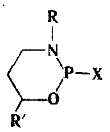
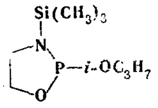
UDC 547.794:543.51

The mass spectra of a number of 1,3,2-oxazaphosphorinanes were obtained. The possibility of the mass spectrometric identification of this class of compounds, including the isomers that differ with respect to both the nature of the alkoxy groups attached to the phosphorus atom and the size of the ring, was demonstrated. The principal pathways of dissociative ionization of the investigated molecules were established by comparison of the mass spectra and the fragmentation reactions of the metastable ions.

In the present research we continued our study of the dissociative ionization, under the influence of electron impact, of cyclic esters of phosphorus acids and their derivatives. The mass spectra of some 1,3,2-oxazaphosphorinanes (I-IV) and 2-isopropoxy-3-trimethylsilyl-1,3,2-oxazaphospholane (V) were obtained:



I-IV



V

I $R=R'=H$, $X=OC_2H_5$; II $R=H$, $R'=CH_3$, $X=OC_2H_5$; IIa $R=D$, $R'=CH_3$, $X=OC_2H_5$; III $R=R'=H$, $X=i\text{-}OC_3H_7$; IV $R=Si(CH_3)_3$, $R'=H$, $X=i\text{-}OC_3H_7$

The mass spectra of substituted 1,3,2-oxazaphospholanes [1] and 1,3,2-dioxaphospholanes [2] have been previously discussed. A comparative analysis of the mass spectra of six- and five-membered cyclic phosphites in [2, 3] demonstrated the possibility of the application of mass spectrometry for the determination of the size of the rings of these compounds.

The relative intensities of the ion peaks characteristic for the investigated 1,3,2-oxazaphosphorinanes are presented in Table 1, and a portion of the mass spectrum of deutero analog IIa is presented in Fig. 1.

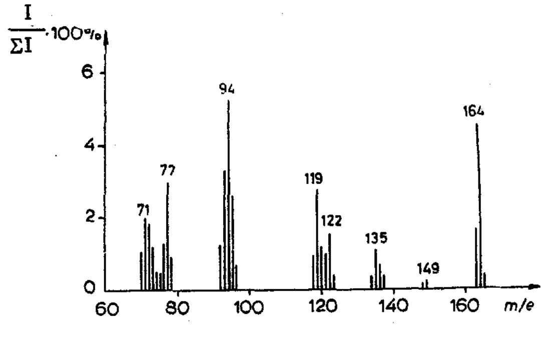


Fig. 1. Mass spectrum of deutero analog IIa.

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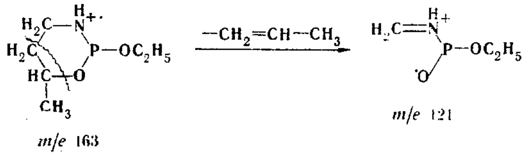
TABLE 1. Relative Intensities of the Ion Peaks Characteristic for 1,3,2-Oxazaphosphorinanes

Ion m/e	$I/\Sigma I \cdot 100\%$				
	I, M=149	II, M=163	III, M=163	IV, M=235	V, M=221
$(M)^{+\cdot}$	4,3	6,3	0,70	2.0	1,5
$(M-15)^{+}$	—	0,31	—	0,55	0,31
$(M-27)^{+}$	0.88	0,31	0.23	—	—
$(M-28)^{+\cdot}$	2,4	1,1	—	—	—
$(M-41)^{+}$	—	0,80	2,0	0,70	0,90
$(M-42)^{+\cdot}$	—	2,1	5,1	3,2	4,3
$(M-30)^{+\cdot}$	0,30	0,15	—	—	—
$(M-44)^{+\cdot}$	0,60	2,0	0.23	—	—
$(M-X)$	4,6	3,4	2.6	1,8	2,8
$[M-(42+30)]^{+\cdot}$	0,74	0.50	0.45	0,20	1,1
$[M-(42+15)]^{+}$	3,8	—	—	3,6	8,1
$[M-(42+73)]^{+}$	0,30	0.10	0,30	0.50	1,0
73	0.44	0,46	0,33	5,4	5,8
55	0.44	2,0	0.37	1,1	0,10
41	1,9	1,8	6,1	2,4	2,3
56	6,3	2,1	3,3	1,2	0.24
42	1,5	2,1	3,1	1,4	1,7

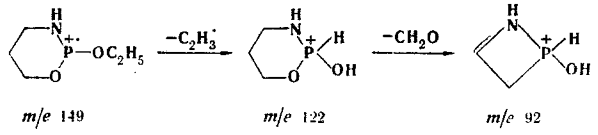
The data in Table 1 show that the mass spectra of the investigated compounds have extremely intense peaks corresponding to the molecular ions ($M^{+\cdot}$). In contrast to cyclic phosphites [1, 2], the high intensity of the molecular ion peak for II is somewhat unexpected, although this compound has a more branched structure than I.

As in the case of 1,3,2-oxazaphospholanes [1], the peaks of $(M-X)^+$ ions are the high-intensity peaks in the mass spectra of 1,3,2-oxazaphosphorinases. In addition, an alkoxy group leads to the appearance in the mass spectra of $(M-28)^{+\cdot}$, $(M-C_2H_4)^{+\cdot}$, (M-27), and $(M-C_2H_3)^+$ ions for I and II and $(M-42)^{+\cdot}$, $(M-C_3H_6)^{+\cdot}$, $(M-41)^+$, and $(M-C_3H_5)^+$ ions for III-V. The $(M-42)^{+\cdot}$ ion in the mass spectrum of II is apparently not formed through the alkoxy group but rather as a result of cleavage of the ring C-C and C-O bonds in the molecular ion with splitting out of a molecule of propylene via the scheme



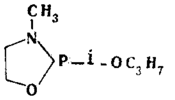
The expected shift of the peaks of $(M-OC_2H_5)^{+\cdot}$, $(M-C_2H_4)^{+\cdot}$, and $(M-C_3H_6)^{+\cdot}$ ions is actually observed in the mass spectra of deutero analog IIa. The fragmentation reactions of the metastable ions also indicate these pathways of dissociative ionization. A diffuse peak with $m^* = 98.3$ is observed in the mass spectrum of I, and a peak with $m^* = 111.8$ is observed in the mass spectrum of II; this is in agreement with fragmentation of the molecular ion to an $(M-C_2H_4)^{+\cdot}$ ion. The diffuse peaks in the mass spectra of III-V with m/e 89.8, 144.9, and 158.5 correspond to fragmentation of the molecular ion to an $(M-C_3H_6)^{+\cdot}$ ion. The examined pathways of dissociative ionization make it possible to easily identify iosmers II and III, which differ with respect to the nature of the alkoxy groups. The peaks of $(M-28)^{+\cdot}$, $(M-C_2H_4)^{+\cdot}$, $(M-45)^+$, and $(M-OC_2H_5)^+$ ions are intense in the mass spectrum of II, whereas these peaks are practically absent in the mass spectrum of isomer III, but the peaks of $(M-42)^{+\cdot}$, $(M-C_3H_6)^{+\cdot}$, $(M-59)^+$, and $(M\text{-iso-}OC_3H_7)^+$ ions are very intense.

The formation of intense peaks corresponding to $[M-(42+15)]^+$ and $[M-(C_3H_6+CH_3)]^+$ ions and less intense $[M-(42+73]^+$ and $[M-(C_3H_6+Si(CH_3)_3]^+$ ion peaks is characteristic for IV and V, which contain a trimethylsilyl group. The formation of the first ion should have been expected because of the facile loss of a methyl radical from the trimethylsilyl group [4]. The $(M-57)^+$ ion is formed via a different pathway in the case of I:



The sequence of the processes involving the loss of $C_2H_3^{\cdot}$ and CH_2O may be reversed. The mass spectrum of this compound contains both $(M-27)^+$ and $(M-30)^+$ ion peaks, and this may serve as evidence in favor of this assumption.

TABLE 2. Relative Intensities of the Ion Peaks for Isomeric Compounds

Ion m/e	$I/\Sigma I \cdot 100\%$	
	 M=163	III, M=163
$(M)^{+\cdot}$	3,5	0,70
$[M-(42+30)]^{+\cdot}$	11	0,45
44	9,5	1,1
42	8,1	3,1
30	0,81	8,2

It has been shown in [2] that ions formed by cleavage of ring P-O and C-C bonds are the most valuable in the determination of the size of the rings for five- and six-membered cyclic phosphites. The peaks of ions whose formation is associated with cleavage of ring P-O and C-O bonds are observed in the mass spectra of the investigated compounds. Thus, in the case of I the molecular ion loses a CH_2O molecule, whereas the molecular ion of II loses a CH_3CHO molecule; this is confirmed by the shift of the peak of the corresponding fragment ion in the mass spectrum of deutero analog IIa. Because of the ready occurrence of the reaction $M^{+\cdot} \rightarrow M^{+\cdot} - C_3H_6$, the peak of an $[M - (42+30)]^{+\cdot}$ $[M - (C_3H_6+CH_2O)]^{+\cdot}$ ion rather than the peak of an $(M - 30)^{+\cdot}[(M - CH_2O)^{+\cdot}]$ ion is present in the mass spectrum of III.

The formation of ions via the pathways noted above leads to a difference in the isomeric 2-isopropoxy-3-methyl-1,3,2-oxazaphospholane, investigated in [1], and 2-isopropoxy-1,3,2-oxazaphosphorinane (III). It is apparent from the data in Table 2 that a greater difference in the peak intensity is noted for the $[M - (C_3H_6+CH_2O]^{+\cdot}$ ion. The first isomer, which contains a five-membered ring, gives an $[M - (C_3H_6+CH_2O]^{+\cdot}$ ion peak with an intensity of 11% of the total ion current as against 0.45% for the second isomer, which contains a six-membered ring. This experimental result leads to the conclusion that the six-membered ring has greater energic stability than the five-membered ring because of the strain of the latter. This may explain the fact that the formation of ions associated with cleavage of the ring bonds is less likely for the investigated six-membered compounds than for the five-membered compounds. Dissociative ionization of these isomers with cleavage of the ring P-N and C-C bonds leads to ions with different m/e values, since in the first isomer the substituent attached to the nitrogen atom in the second isomer. Ions with m/e 44 (hypothetical composition $CH_2{=}\underset{\substack{|\\ H}}{\overset{+}{N}}{-}CH_3$), and m/e 42 ($CH{\equiv}\overset{+}{N}{-}CH_3$) are represented considerably more intensely in the mass spectrum of the first isomer, whereas the ion with m/e 30 ($CH_2{=}\overset{+}{N}H_2$) is represented more intensely in the mass spectrum of the second.

As in the case of 1,3,2-dioxaphospholanes [2], the hydrocarbon portion of the ring of 1,3,2-oxazaphosphorinane molecules, except for trimethylsilyl derivatives IV and V, is responsible for the formation of an ion arising as a result of cleavage of ring C-O and C-N bonds and migration of a hydrogen atom to the neutral fragment. The peaks of this ion are found at m/e 41 in the case of I and III and at m/e 55 in the case of II. In the case of trimethylsilyl derivatives IV and V these processes are accompanied by migration of a methyl group to the charged fragment, and an ion of the composition $(C_nH_{2n-1}+CH_3)^{+\cdot}$ with m/e 56 is formed in the case of IV and with m/e 42 is formed in the case of V.

One should note the intense peaks in the mass spectra of IV and V with m/e 73, which correspond to ions with the composition $[Si(CH_3)_3]^{+\cdot}$.

EXPERIMENTAL

The conditions for the recording of the mass spectra are similar to those previously described in [1] (the ionizing voltage was 50 V). The physical constants of I-III were in agreement with the literature values [5]. Deutero analog IIa was obtained by an exchange reaction by mixing a sample of II with a large excess of heavy water in the recording ampul and subsequent evacuation of the ampul. Compounds IV and V were obtained by silylation of the appropriate heterocycles containing a secondary amide group.

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SYNTHESIS OF 2-SELENOTHIENO[2,3-d]PYRIMIDINE DERIVATIVES

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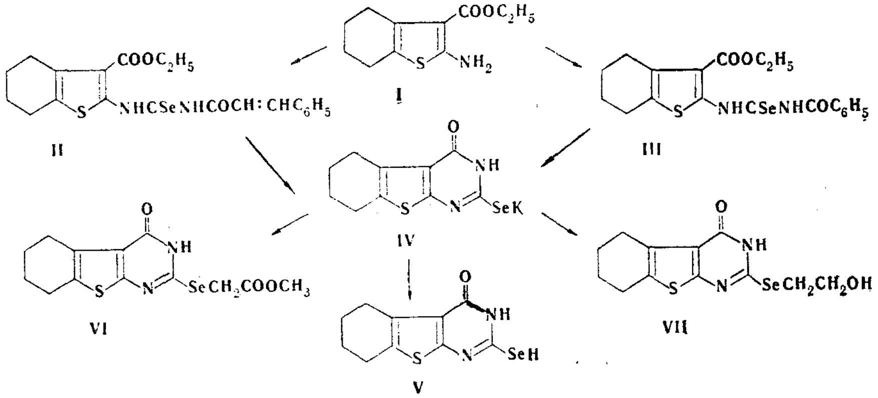
UDC 547.735'853.07

Intramolecular cyclization of 2-(N-acylselenoureido)-3-carbethoxy-4,5,6,7-tetrahydrobenzo[b]thiophenes in alkaline media leads to the formation of the potassium salt (I) of 2-seleno-4-oxo-3,4,5,6,7,8-hexahydrobenzo[b]thieno[2,3-d]pyrimidine, acidification of which yielded the corresponding base in free form. Some pyrimidine compounds containing a selenium atom in the side chain were obtained by reaction of potassium salt I with halo derivatives ($ClCH_2CH_2COOCH_3$ and $ClCH_2CH_2OH$).

A convenient method for the synthesis of thiouracil derivatives is intramolecular cyclization of compounds containing a carboxyl or ester group in the α position relative to the acylthioureido group [1, 2]. Up until now, the cyclization of similarly constructed acylselenoureides has not been studied.

2-N-Acylselenoureido derivatives of 3-carbethoxy-4,5,6,7-tetrahydrobenzo[b]thiophene (AST) undergo cyclization with splitting out of acyl groups to give the condensed 2-selenothieno[2,3-d]pyrimidine system. The AST were obtained by reaction of 2-amino-3-carbethoxy-4,5,6,7-tetrahydrobenzo[b]thiophene (I) [3] with cinnamoyl and benzoyl isoselenocyanates (II and III).



Heating II and III in an alkali solution gave potassium salt IV, which readily forms base V when it is acidified. Selenium-containing pyrimidine derivatives VI and VII were obtained by reaction of potassium salt IV with halo derivatives.

The AST undergo cyclization on treatment with a twofold excess of alkali. The same compounds (IV and V) are formed in the case of cyclization in the presence of an equimolar amount of alkali, but the yields are approximately halved.

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