Mass-spectrometric study of As-substituted 10*H*-phenoxarsines

R. R. Musin,[a]* ***Yu. Ya. Efremov,***[b] ***V. I. Gavrilov,***[a] ***and F. R. Garieva***[a]

[a]*Kazan' State Technological University,*
68 ul. K. Marksa, 420015 Kazan', Russian Federation.
Fax: +7 (843 2) 36 7542
[b]*A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Research Center of the*
Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420088 Kazan', Russian Federation.
Fax: +7 (843 2) 75 2253

High-resolution mass spectrometry and analysis of kinetic energies of ions were used to establish the main routes of electron impact-induced fragmentation of several As-substituted 10*H*-phenoxarsines.

Key words: As-substituted 10*H*-phenoxarsines, mass spectrum.

Phenoxarsine derivatives are used as components of antifouling paints.[1,2] However, the number of As-containing heterocycles studied by mass spectrometry is rather small.[3—5]

In this work, we studied electron impact high-resolution mass spectra of several As-substituted 10*H*-phenoxarsines ($(C_6H_4)_2OAsR$ (R = Me (**1**), Et (**2**), Pr^n (**3**), Pr^i (**4**), Bu^i (**5**), C_7H_{15} (**6**), C_8H_{17} (**7**), C_9H_{19} (**8**), C_3H_5 (**9**), C≡CPh (**10**), Cl (**11**), and Br (**12**)) and bis(10*H*-phenoxarsin-10-yl)oxide (**13**).

Results and Discussion

Mass spectra of all the compounds studied contain peaks of molecular ions, whose intensities vary over wide limits and depend on the nature of the substituent R (Table 1). The main route of their fragmentation is related to the elimination of the substituent R at the As atom. The peaks of the $[M-R]^+$ ions that formed have the maximum intensity except for that of compound **10** (R = C≡CPh): in its mass spectrum, the peak of the $[M-Ph]^+$ ion is a maximum.

Subsequent fragmentation of the $[M-R]^+$ ions occurs in several directions to form two types of ions that contain or do not contain As atoms (Scheme 1). The elemental composition of some ions was established by measuring their exact masses (Table 2).

The $[M-R-As]^+$ ions most likely have the structure of the molecular ion of dibenzofuran, since both of them undergo fragmentation with consecutive loss of the CHO•

Table 1. Mass spectra of 10-R-10*H*-phenoxarsines

Ion	I_{rel} (%)												
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13***
$M^{\cdot +}$	28.4	18.6	21.1	18.2	14.9	25.5	10.7	11.0	5.9	91.0	43.0	6.8	22.8
$[M-R]^+$ (A)	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	4.1	64.0	100.0	100.0
$[A-O]^+$	—	0.1	0.2	0.4	0.6	0.1	—	0.2	—	0.2	0.2	—	—
$[A-CHO]^+$	3.3	3.1	3.2	2.4	3.1	2.0	3.4	3.5	2.3	1.2	3.9	3.5	1.6
$[M-R-As]^+$ (B)	32.1	34.3	30.2	25.3	30.3	21.2	29.3	23.1	28.2	11.6	100.0	43.5	27.2
$[M-C_6H_5]^+$	—	—	—	—	—	—	—	—	—	100.0	—	—	—
$[B-OH]^+$	0.2	0.2	0.1	0.1	0.1	0.1	—	0.1	0.1	1.1	—	2.7	—
$[AsC_6H_4]^+$	2.1	1.3	1.7	1.5	1.8	0.7	1.0	0.9	1.2	4.0	2.9	0.2	0.9
$[B-CHO]^+$	11.0	11.0	9.5	7.6	9.2	4.3	6.7	7.3	82.0	10.0	15.0	18.3	4.3
$[AsC_5H_4]^+$	1.2	1.0	0.9	0.7	0.7	0.4	0.6	0.6	0.6	0.8	2.8	1.3	0.4
$[AsC_4H_2]^+$	1.2	1.1	1.0	0.8	0.7	0.2	0.3	—	0.7	1.5	1.6	2.3	0.3
$[B-CHO-C_2H_2]^+$	0.9	0.8	1.5	0.5	0.5	0.1	0.2	0.2	0.5	1.9	1.0	1.8	0.1
$[AsC_3H_2]^+$	2.6	2.0	0.6	1.3	1.4	0.5	0.6	0.7	1.5	1.6	2.9	4.1	0.5
$[C_6H_5]^+$	2.1	1.7	0.7	0.8	0.7	0.4	0.3	0.3	1.5	2.0	0.5	0.5	0.3
$[As]^+$	0.4	0.5	0.3	0.3	0.2	0.1	0.5	0.1	0.4	1.2	0.3	1.2	0.3

* Peaks of ions containing the most abundant isotopes are indicated.

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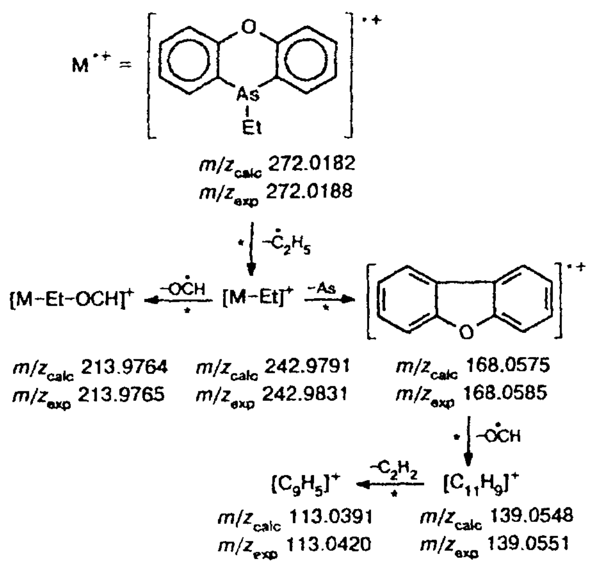
Scheme 1



radical and C_2H_2 molecule, and the ratios of intensities of the peaks of ions that formed are approximately the same in the mass spectra of dibenzofuran[6] and compound 2. Similar fragmentation to form $[M-R-P]^+$ ions is also typical of phosphorus-containing analogs (10-phenyl-10*H*-phenoxaphosphines).[7]

Thus, dissociative ionization of 10-R-10*H*-phenoxarsines is determined by the structure of the heterocyclic system, and the nature of the substituent at the As atom affects the ratio of relative intensities of ion peaks.

Experimental

Mass spectra were obtained on an MX-1310 instrument with an ionizing voltage of 30 V and average temperature of the ion source 120 °C. An SVP-5 system with direct inlet was used.

Table 2. Exact masses of fragmentation ions for compound **2**

Ion	*I* (%)	*m/z*	
		Experiment	Calculation
$C_{11}H_7$	11.0	139.0551	139.0548
C_5H_4As	1.0	138.9535	138.9529
C_9H_5	0.8	113.0420	113.0391
C_3H_2As	2.0	112.9403	112.9373

Exact automated mass measurements were performed by reference peaks of perfluorokerosene with resolution capability *R* = 15000.

Metastable peaks were analyzed by the defocusing method.[8]

The compounds studied were synthesized according to the known procedure.[9]

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