

MASS SPECTRA AND PYROLYSIS OF PHENARSAZINE DERIVATIVES

JAMES C. TOU

Chemical Physics Research Laboratory

and

CHUN-SHAN WANG

Organic Chemicals Production Research,

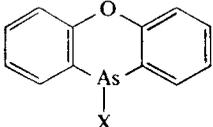
The Dow Chemical Company, Midland, Michigan 48640, USA

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Abstract—Five phenarsazine derivatives with arsenic in the trivalent state and the pentavalent state are studied by mass spectrometry. Their characteristic fragmentation modes and the fragment ions with common structures are discussed. Experimental results show that the pyrolytic decompositions of the phenarsazine derivatives are closely parallel to the unimolecular ion fragmentation.

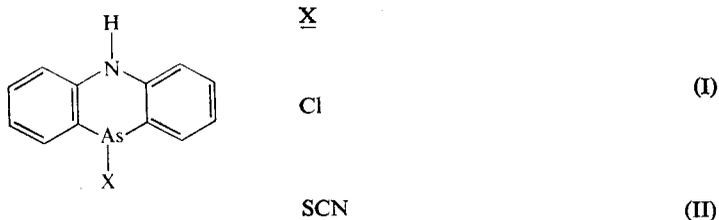
INTRODUCTION

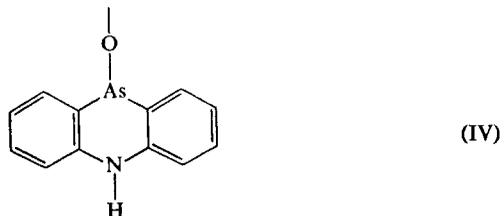
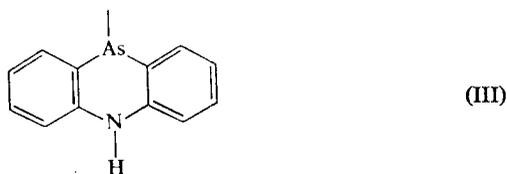
THE SYNTHESSES of organoarsenic compounds have appeared occasionally in the literature¹ since 1760.² The unusual biological activities of the compounds were also cited in many patents.³ The mass spectrometric studies of the phenoxarsine derivatives¹ and triphenyl arsine⁴ were reported recently. It was found¹ in the cases of

phenoxarsine derivatives, , that the rupture of the bond between

the arsenic atom and the substituent, and the subsequent loss of the arsenic atom were the major fragmentation modes. Intense ion peaks at m/e 243 and 168 were observed for which a phenoxarsine even electron ion and a diphenylene oxide odd electron ion were assumed respectively. A good correlation between electron-impact fragmentation and pyrolytic reaction was observed. As predicted from the mass spectra, diphenylene oxide was found to be the major pyrolyzate of the phenoxarsine derivatives.⁵ In order to extend our knowledge of the electron-impact fragmentation and the pyrolytic reaction of organoarsenic compounds, five phenarsazine derivatives with the arsenic atom in the trivalent state and in the pentavalent state were synthesized and studied by mass spectrometry. The ion fragmentation mechanisms are discussed and their predicted pyrolyzates are verified by experiment.

Phenarsazine derivatives studied:





RESULTS AND DISCUSSION

Mass spectra

The mass spectra of the five phenarsazine derivatives studied are shown in Figs. 1 to 5. The results of the high resolution mass measurements for the major ion peaks in the spectra are tabulated in Table 1. The metastable ions shown in Figs. 1 to 5 are either obtained with a single focusing mass spectrometer or from a defocusing experiment⁶ using a CEC 21-110B double focusing mass spectrometer. The latter experiment is performed when a detailed understanding of the fragmentation mechanism is desired.

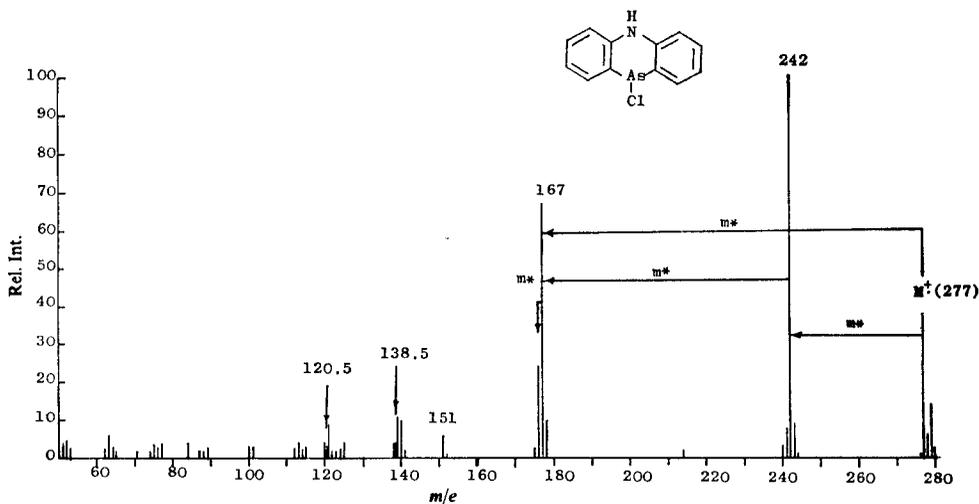


FIG. 1. Mass spectrum of 5,10-dihydro-10-chlorophenarsazine. Direct probe temperature 186°C (uncalibrated).

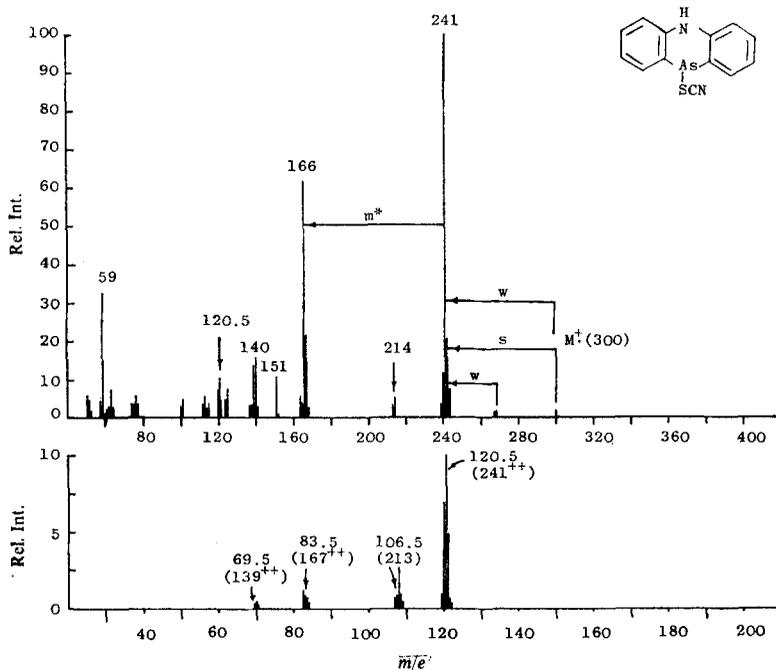


FIG. 2. Mass spectrum of 5,10-dihydro-10-thiocyanatophenarsazine. Direct probe temperature 193°C (uncalibrated).

The intensity of the latter metastable ion is designated as s (strong), m (medium) or w (weak) in the spectrum.

A detailed investigation of the fragmentation modes of the major ions in the mass spectra of compounds III and IV was performed. Using the information gained thereby, the decomposition pathways of the other compounds are inferred.

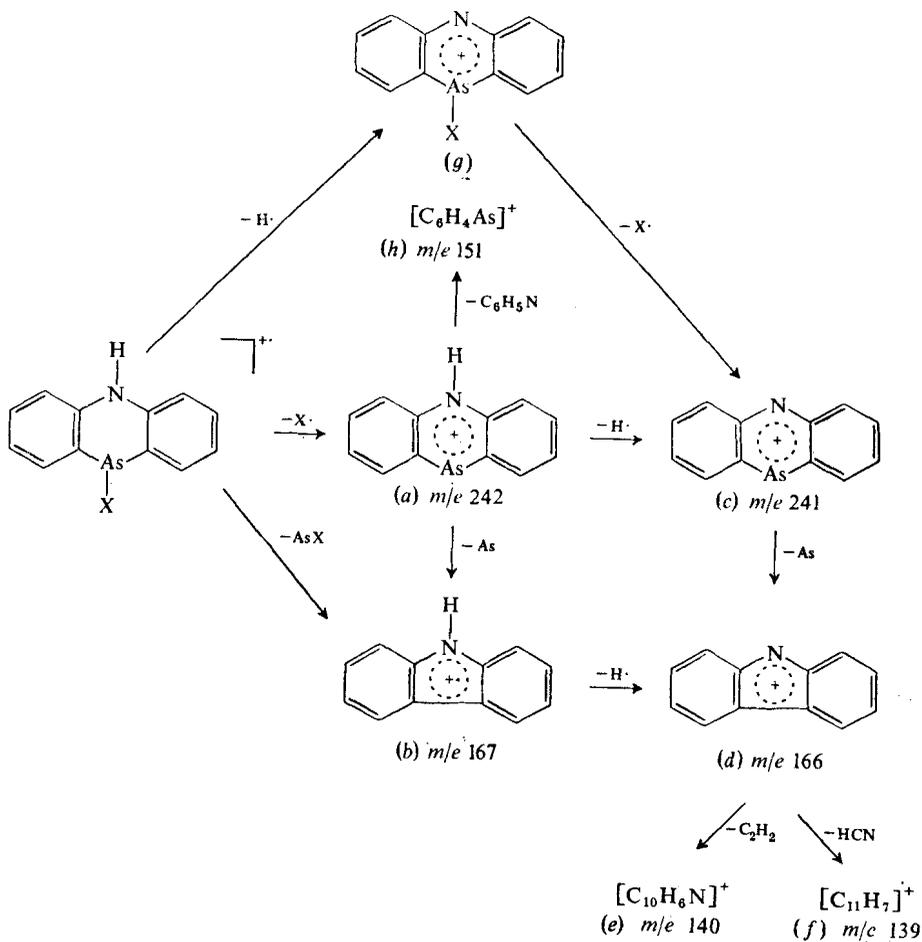
Combining information from the metastable ion transitions and the accurate mass measurements, the main fragmentation modes can be rationalized as in Scheme 1. Similarly to the phenoxarsine derivatives,¹ the molecular ions of phenarsazine derivatives show the bond rupture between the arsenic atom and the substituent, X, and the subsequent elimination of the arsenic atom in the generation of ions at m/e 242 and 167 respectively. The metastable ions corresponding to these transitions were detected in most cases studied. The loss of AsX radical as a whole was observed only in the case of compound I, however, with the presence of a weak metastable ion at m/e 100.7. This might not be an important process in the genesis of the ion m/e 167. The ion m/e 166 was found to be generated from the elimination of a hydrogen atom and an arsenic atom from the ions at m/e 167 and 241 respectively. The latter ion might be generated from the ion m/e 242, by a hydrogen atom elimination from the path, $[M]^{+\cdot} \rightarrow [M - H]^+ \rightarrow [M - H - X]^+$. Two metastable ions were found in the defocusing experiments corresponding to the competing eliminations of C_2H_2 and HCN from the ion, m/e 166. High resolution mass spectrometry established the ions at m/e 140 and 139 as two singlets with empirical formulae $C_{10}H_6N$ and $C_{11}H_7$ respectively. A metastable ion of medium intensity corresponding to the transition $140^+ \rightarrow 139^+$ was observed, however, as shown in Figs. 3 and 4. Hence a weak

TABLE 1. COMPOSITIONS OF MAJOR IONS IN THE MASS SPECTRA OF THE LISTED COMPOUNDS

Compound	Ion	Empirical formula	
(II)	268	C ₁₃ H ₉ N ₂ As	
	267	C ₁₃ H ₈ N ₂ As	
	59	HCNS	
(III)	243	C ¹³ C ₁₁ H ₉ NAs	
	242	C ₁₂ H ₉ NAs	
	241	C ₁₂ H ₈ NAs	
	167	C ₁₂ H ₉ N	
	166	C ₁₂ H ₈ N	
	151	C ₆ H ₄ As	
	140	C ₁₀ H ₆ N	
	139	C ₁₁ H ₇	
	(IV)	259	C ₁₂ H ₁₀ ONAs
		242	C ₁₂ H ₉ NAs
241		C ₁₂ H ₈ NAs	
167		C ₁₂ H ₉ N	
166		C ₁₂ H ₈ N	
151		C ₆ H ₄ As	
140		C ₁₀ H ₆ N	
139		C ₁₁ H ₇	
pyrolyzate of III	167	C ₁₂ H ₉ N	
	140	C ₁₀ H ₆ N	
	139	C ₁₁ H ₇	
pyrolyzate of IV	167	C ₁₂ H ₉ N	
	166	C ₁₂ H ₈ N	
	140	C ₁₀ H ₆ N	
		C ₁₁ H ₈ } ~15% C ¹³ C ₁₀ H ₇ } (not resolved)	
	139	C ₁₁ H ₇	
diphenylenimine	140	C ₁₀ H ₆ N	
		C ₁₁ H ₈ } ~16% C ¹³ C ₁₀ H ₇ } (not resolved)	
	139	C ₁₁ H ₇	
		C ₁₀ H ₆ N	
	139	C ₁₁ H ₇	

[C₁₁H₈]⁺ ion must exist. This will be discussed later. The two important ion peaks, *m/e* 242 and 167, responsible for the genesis of low mass ions in the spectra are assumed to be due to phenarsazine even electron ion (*a*) and diphenylenimine odd electron ion (*b*). It is surprising that the ion *b* does not show a strong direct loss of HCN in the generation of the ion at *m/e* 140, as is seen in the mass spectra of other nitrogen containing heterocyclic compounds.⁷ This prompted us to study the fragmentation mechanisms of diphenylenimine in order to seek support for the assumed ion structure.

The mass spectrum of diphenylenimine is simple and shows the molecular ion at *m/e* 167, the fragment ions at *m/e* 166, 140, 139 and a doubly charged molecular ion at *m/e* 83.5, with relative intensities 100, 16, 12, 14 and 8 respectively. The high resolution mass measurement as noted in Table 1 shows the ion peaks at *m/e* 140 and 139 as a doublet and a singlet respectively. When the C¹³ isotopic contribution from the ion *m/e* 139 is subtracted, it is found that only 5% of the ion *m/e* 140 is due to the ion



SCHEME 1

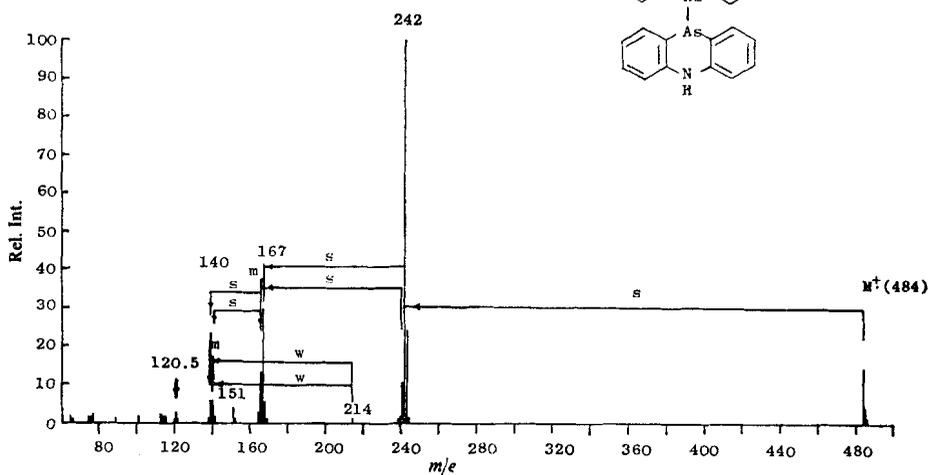


FIG. 3. Mass spectrum of 10,10'-(5H,5'H)-Bisphenarsazine. Direct probe temperature 222°C (uncalibrated).

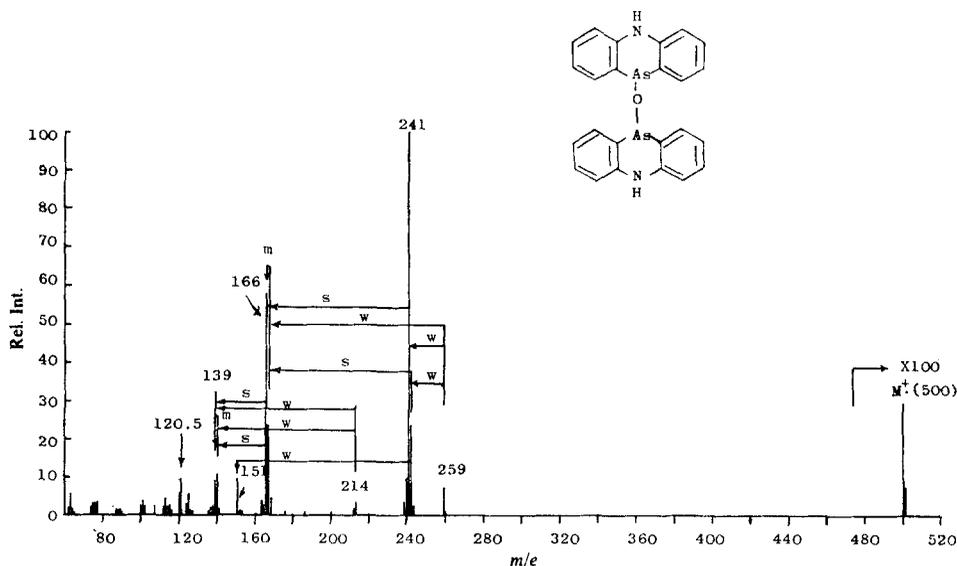
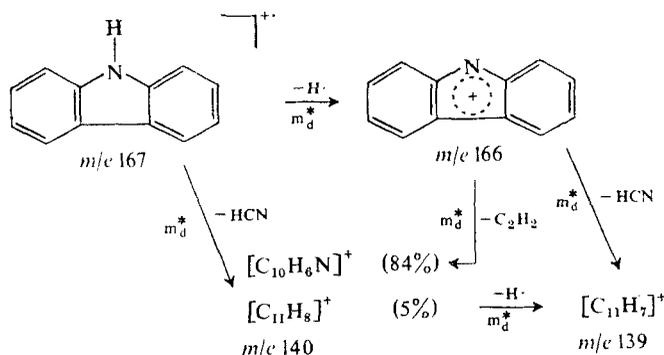


FIG. 4. Mass spectrum of 10,10'-oxybis(5,10-dihydrophenarsazine). Direct probe temperature 300°C (uncalibrated).

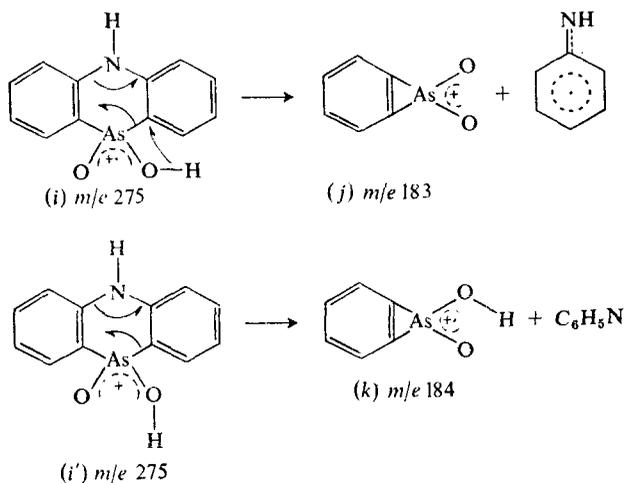
$[\text{C}_{11}\text{H}_8]^+$. The metastable ions obtained through the defocusing experiments for the generation of ions m/e 166, 140 and 139 indicate that the following ion fragmentation mechanisms are followed. Similar competitive losses of $\text{H} + \text{C}_2\text{H}_2$ and HCN in N



heterocyclic compounds were also reported in the case of phenazine.⁸ By comparing these with the fragmentation modes of the common ion, m/e 167, from phenarsazine derivatives (Scheme 1), it is highly likely that the structure of the ion at m/e 167 is a diphenylenimine odd electron ion as assumed previously.

The m/e 151 ion was observed in all the mass spectra of the compounds studied. This ion was found to be generated from the ion at m/e 242 by the loss of $\text{C}_6\text{H}_5\text{N}$ radical as shown in Scheme 1. The ion $[\text{C}_{11}\text{H}_8]^+$ was not detected in the mass spectra of phenarsazine derivatives probably because of the difference in the internal energy between the fragment ion b and the molecular ion of diphenylenimine. Ion b might not have sufficient energy to generate the ion $[\text{C}_{11}\text{H}_8]^+$ intense enough to be observed. This ion must exist, however, evidenced from the observation of the metastable transition $140^+ \rightarrow 139^+$ discussed previously.

The mass spectrum of compound II shows two weak peaks due to $[C_{13}H_9N_2As]^+$ and $[C_{13}H_8N_2As]^+$, apparently generated from the losses of S and SH from the molecular ions. The infrared spectrum of this compound shows the presence of the thiocyanato group rather than the isothiocyanato group. Hence, it is logical to assume that some extent of isomerization from thiocyanate to isothiocyanate is occurring in the gaseous phase. This is induced either by thermal activation or by electron-impact excitation. As contrasted to phenoxarsinic acid,¹ there is no indication of the formation of the anhydride of phenarsazinic acid at the temperatures studied. Two ion peaks were observed at m/e 183 and 184, possibly generated by way of the following mechanisms which are similar to those proposed for phenoxarsinic acid.¹ Many



doubly charged ions were observed in the mass spectra shown in Figs. 1 to 5. As a representative case, the doubly charged ions in the mass spectrum of compound II are shown in Fig. 2. It is noted that intense singly charged ions are always accompanied by their doubly charged ions, which apparently decompose in a fashion similar to that of their singly charged counterparts.

Pyrolysis

Many striking similarities between pyrolytic reactions and electron-impact induced ion fragmentations have been reported in the literature.^{5,9,10} Hence, certain pyrolytic products can be predicted from the unimolecular ion fragmentations of the parent compound in the mass spectrometer.

If the assumed ion structures shown in Scheme 1 are correct, then the predicted pyrolyzate of the phenarsazine derivatives would be diphenylenimine.

The mass spectra taken at higher temperatures show the ion peaks due to As_4 for the non-oxygen containing compounds I and III, and As_4 and As_4O_6 for oxygen containing compounds IV and V. This demonstrates the formation of As_4 and As_4O_6 as the phenarsazine is being thermally decomposed. All of compound II was found to be vaporized from the probe before it reached $\sim 200^\circ C$, however.

The pyrolyzates from the five phenarsazine derivatives at $600^\circ C$ were identified by mass spectrometry. As expected, diphenylenimine was found to be the only major

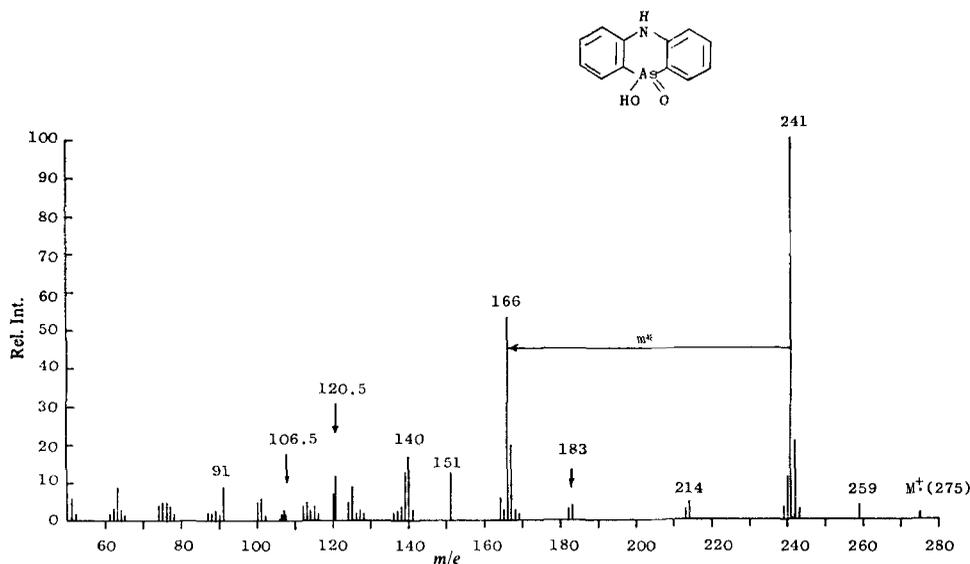


FIG. 5. Mass spectrum of 5,10-dihydro-10-phenarsazinic acid. Direct probe temperature 415°C (uncalibrated).

organic component in the pyrolyzate as evidenced from the general feature of the mass spectrum, the high resolution mass measurement as shown in Table 1 and the metastable ion transitions. The mass spectrum of each pyrolyzate shows the presence of both As_4 and As_4O_6 . For non-oxygen containing phenarsazine derivatives, As_4O_6 might be formed from the oxidation of As_4 at 600°C by the air present in the pyrolytic vycor[®] column. The mass spectrum of the ether insolubles of the pyrolyzate from compound IV shows the ion peaks at m/e 91 ($[AsO]^+$), 182 ($[As_2O_2]^+$), 198 ($[As_2O_3]^+$), 289 (As_3O_4), 300 ($[As_4]^+$), 305 ($[As_3O_5]^+$), 380 ($[As_4O_5]^+$), 396 ($[As_4O_6]^+$), with relative intensities 56, 6, 1.3, 48, 2, 1, 0.9 and 100 respectively. The mass spectrum is different from the mass spectra of the arsenic oxides in known crystalline forms.¹¹ The arsenic oxide formed in the pyrolysis might be in an amorphous form. Other spectra of the arsenic inorganics in the pyrolyzates show similar features but with different degrees of intensities of the ion peaks due to As_4 and As_4O_6 .

CONCLUSIONS

All the phenarsazine derivatives studied gave molecular ions and important common fragment ions at m/e 242, 241, 167, 166, 140, 139. The ions at m/e 242 and 167 were assumed to be the phenarsazine ion and the diphenylenimine ion respectively, evidenced by the resemblance of the fragmentation modes of the latter fragment ion and the diphenylenimine molecular ion. Experimental results show that the pyrolytic decompositions of the phenarsazine derivatives are closely parallel to the unimolecular ion fragmentation.

EXPERIMENTAL

The mass spectra were recorded with an Atlas CH-4B mass spectrometer equipped with an EF-4B source and a direct probe inlet system. The ionization chamber was kept at about 180°C. The energy of ionizing electrons and the ion accelerating potential were maintained at 70 eV and 3 kV

respectively. The accurate masses were measured with a Nier peak matching unit attached to a CEC 21-110B double focusing mass spectrometer. The accuracy of the measurement is within 10 ppm. The beam defocusing technique for obtaining the metastable ion transitions was described elsewhere.¹

The mass spectra of all the compounds studied show the presence of small amounts of 10-chloro phenarsazine and 10-bromo phenarsazine, even though, no evidence was found for the presence of halogen atoms, except for compound I, from elemental analysis. Hence the above two compounds must be generated in the mass spectrometer. The ion peaks due to these two components were deleted from the calculated mass spectra shown in Figs. 1 to 5.

An 0.2" ID, 18" long quartz tube was used to pyrolyze the phenarsazine compounds. One half of the quartz tube was packed with Vycor beads which was used as reactor, the other half of the tube was used as preheater for the inert dilution gas. This quartz tube was placed inside a nichrome heating coil insulated with TiO₂ and equipped with two thermocouple wells for measuring the quartz tube temperatures of the reactor and preheating zones. Nitrogen gas was used as eluent which was passing through the tube at a rate of 2.5 ml/min. Both reactor and preheater were kept at 600°C. Solids of the phenarsazine compounds were dropped on the top of the reactor and the volatilized material was then swept through the reactor to an outside glass trap by the nitrogen flow. The residence time in the reactor is 3 seconds measured by the appearance of white fume from the outlet of the quartz tube. The organics and the inorganics of the collected solids were separated by ether extraction and identified by mass spectrometry. For some cases, no separation was performed before analysis.

Melting points were determined in a 'Thomas Hoover Capillary Melting Point Apparatus' of Arthur H. Thomas Co. Elemental analysis was done by the staff of Dr P. Boyd, The Dow Chemical Company. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer, Model 237.

5,10-Dihydro-10-chlorophenarsazine. 5,10-dihydro-10-chlorophenarsazine was purchased from Aldrich Chemical Co, Inc. It was recrystallized several times from an acetone-ethanol mixture to give green needles, m.p. 193 to 194° (lit.^{12,13} 193°).

5,10-Dihydro-10-Thiocyanatophenarsazine. 5,10-Dihydro-10-chlorophenarsazine (7.6 g, 0.1 mole) was dissolved in a mixture of 300 ml ethanol and 200 ml benzene. Sodium thiocyanate (10.5 g, 0.13 mole) in 100 ml of ethanol was added to the above solution. The reaction mixture turned to dark red immediately and was refluxed with stirring for 4 hrs. followed by stirring at 50° overnight. After the reaction mixture was cooled to room temperature, it was suction filtered. The yellow solid which collected on the filter was recrystallized three times from tetrahydrofuran to give 17.8 g (60%) of yellow needles, m.p. 240 to 241° (lit.^{3a} 235 to 240°).

10,10'-Oxybis(5,10-Dihydrophenarsazine). 5,10-Dihydro-10-chlorophenarsazine (10 g, 0.036 mole) was dissolved in 300 ml of acetone-ethanol mixture with heat. To the refluxing solution, 50 ml of conc. ammonium hydroxide were added. Yellowish white crystals deposited from the solution immediately. The reaction mixture was refluxed for a further 6 hrs. and then allowed to cool to room temperature. The solid was filtered, recrystallized three times from an ethanol-acetone mixture to give greenish white crystals, m.p. > 350° (lit.^{12,3a} > 350°) yield > 7.9 g (91%).

10,10'-(5H,5'H)-Biphenarsazine. To the refluxing solution of 10,10'-oxybis(5,10-dihydrophenarsazine) (5 g, 0.01 mole) in 250 ml ethanol, 3 g of crystalline phosphorus were added. The greenish white solution changed to yellowish orange immediately. The resulting solution was refluxed for another 4 hrs. and then filtered hot. The solid which collected on the filter was washed with 200 ml of acetone and then dried in a desiccator under a reduced pressure. A yellowish orange crystalline solid, m.p. 304 to 305° (lit.^{14,15} 304 to 305°), yield 3.9 g (84%) was obtained.

5,10-Dihydro-10-phenarsazinic acid. 10,10'-Oxybis(5,10-dihydrophenarsazine) (3.5 g, 0.0073 mole) was added to a solution containing 100 ml of water and 20 ml of 15% aqueous sodium hydroxide. Hydrogen peroxide (20 ml, 30%) was added to the above solution with stirring. The resulting solution was then heated at 60° until complete solution took place. The excess hydrogen peroxide was decomposed by boiling. The solution was filtered, cooled and the filtrate acidified with acetic acid. The phenarsazinic acid which precipitated from solution was recrystallized from 70% acetic acid to give gray crystals, m.p. 327 to 327° (lit.^{18,14} > 300°), yield 2.75 g. (68%).

Anal. Calcd. for C₁₂H₁₀AsNO₂: C, 52.39; H, 3.66; N, 5.09. Found: C, 52.33; H, 3.96; N, 4.85.

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