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MASS SPECTROMETRIC AND PYROLYTIC STUDIES OF DIPHENYLARSINE DERIVATIVES

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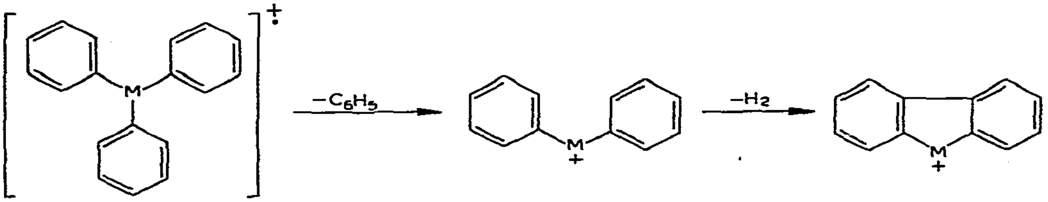
SUMMARY

The trivalent diphenylarsine derivatives studied gave molecular ions and diagnostic common fragment ions at *m/e* 229, 227, 154, 153, 152, 151, 77 and 51. The diphenylarsine odd electron ion, *m/e* 229, undergoes the "*ortho* coupling" reaction before splitting off the arsenic atom. The correlation between the ion fragmentation and the pyrolytic decompositions is discussed.

INTRODUCTION

The mass spectrometric studies of organoarsenic compounds have been reported recently in the literature[1-7]. The loss of the group attached to the arsenic atom followed by the expulsion of the arsenic atom was found to be the characteristic fragmentation mode of the organoarsenic compounds. Excellent mechanistic correlations between the two energetic processes, pyrolysis and electron impact, were observed in two series of compounds, phenoxarsine derivatives[5,8] and phenazarsine derivatives[5].

In the studies of the mass spectra of triphenyl derivatives of Group VA elements[2], the following "*ortho* coupling" reaction was found in the ion fragmentations:



where M represents phosphorus, arsenic or antimony. In this study, the detailed ion fragmentations of five diphenylarsine derivatives with the arsenic atom in the trivalent state (I)–(IV) and the pentavalent state (V) are reported. Emphasis will be placed on the "*ortho* coupling" reaction occurring in both the pyrolytic dissociation and the electron impact induced ion fragmentation.

The diphenylarsine derivatives studied are, trivalent derivatives: Ph_2AsX, (I) X=SCOPh, (II) $X=SCOC_6H_4OMe$-*o*, (III) $X=SCSNEt_2$, (IV) $X=OAsPh_2$; pentavalent derivatives: $Ph_2As(O)OH$ (V).

RESULTS AND DISCUSSIONS

Electron impact

The 70 eV mass spectra of compound (I)–(V) are shown in Fig. 1–5 respectively.

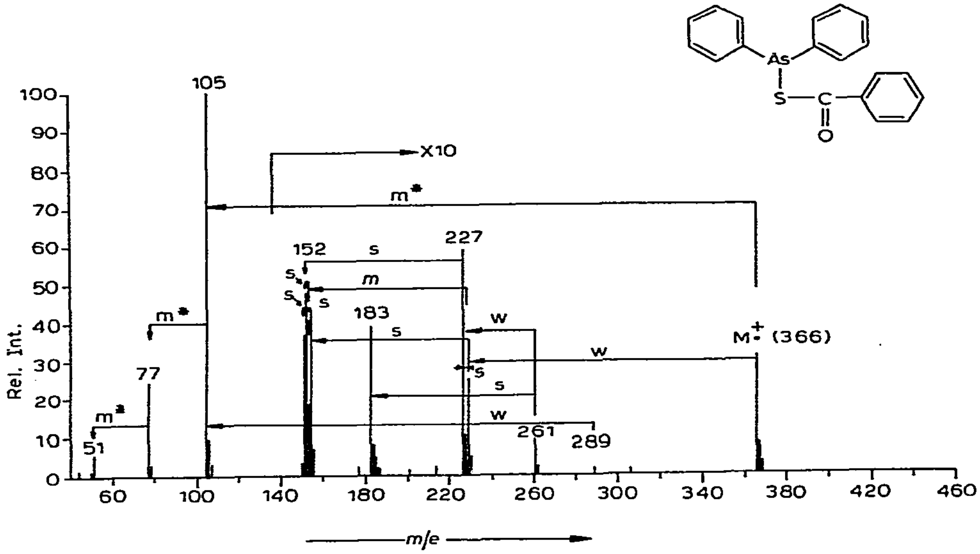


Fig. 1. Mass spectrum of *S*-diphenylarsinothiobenzoate.

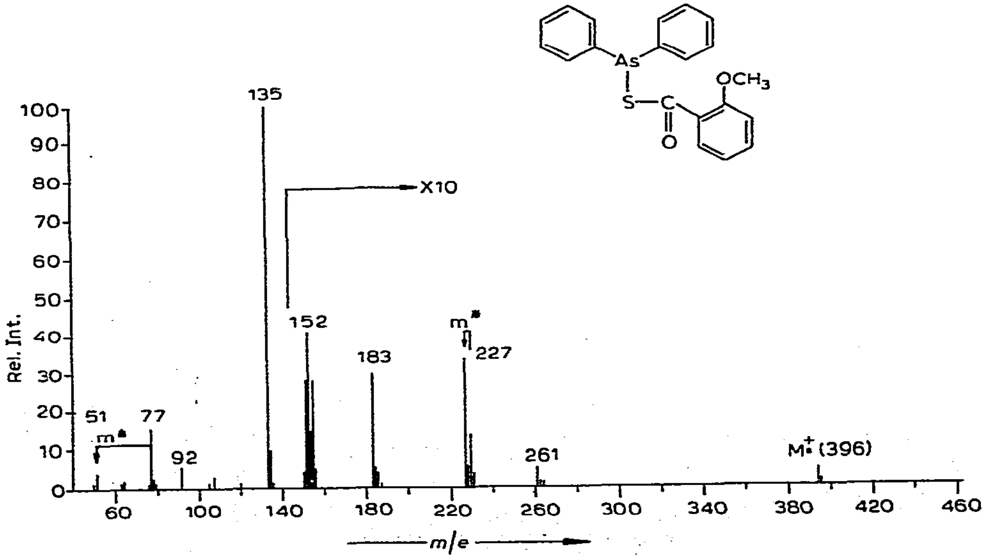


Fig. 2. Mass spectrum of *S*-diphenylarsino *o*-methoxythiobenzoate.

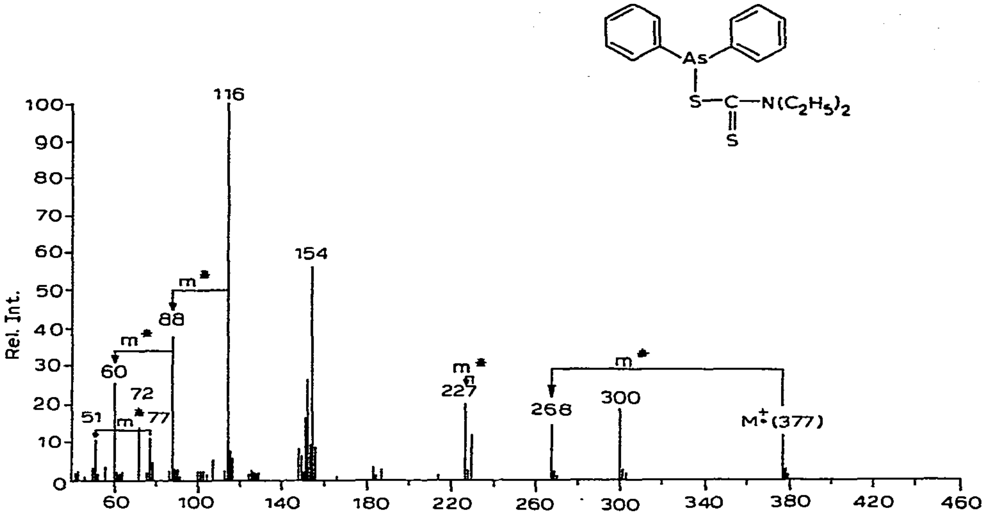


Fig. 3. Mass spectrum of S-diphenylarsino-N,N-diethyldithiocarbamate.

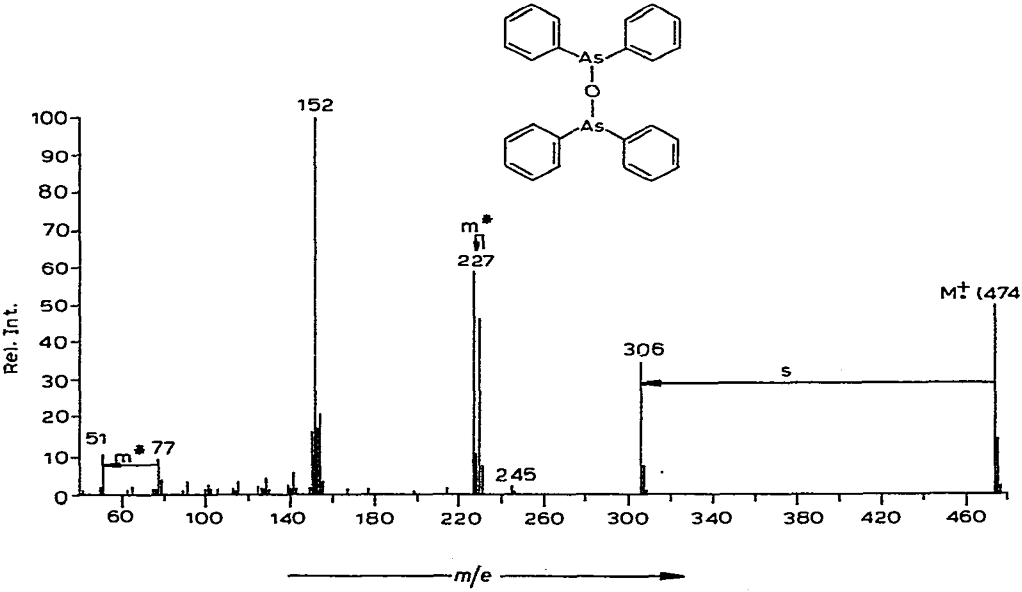
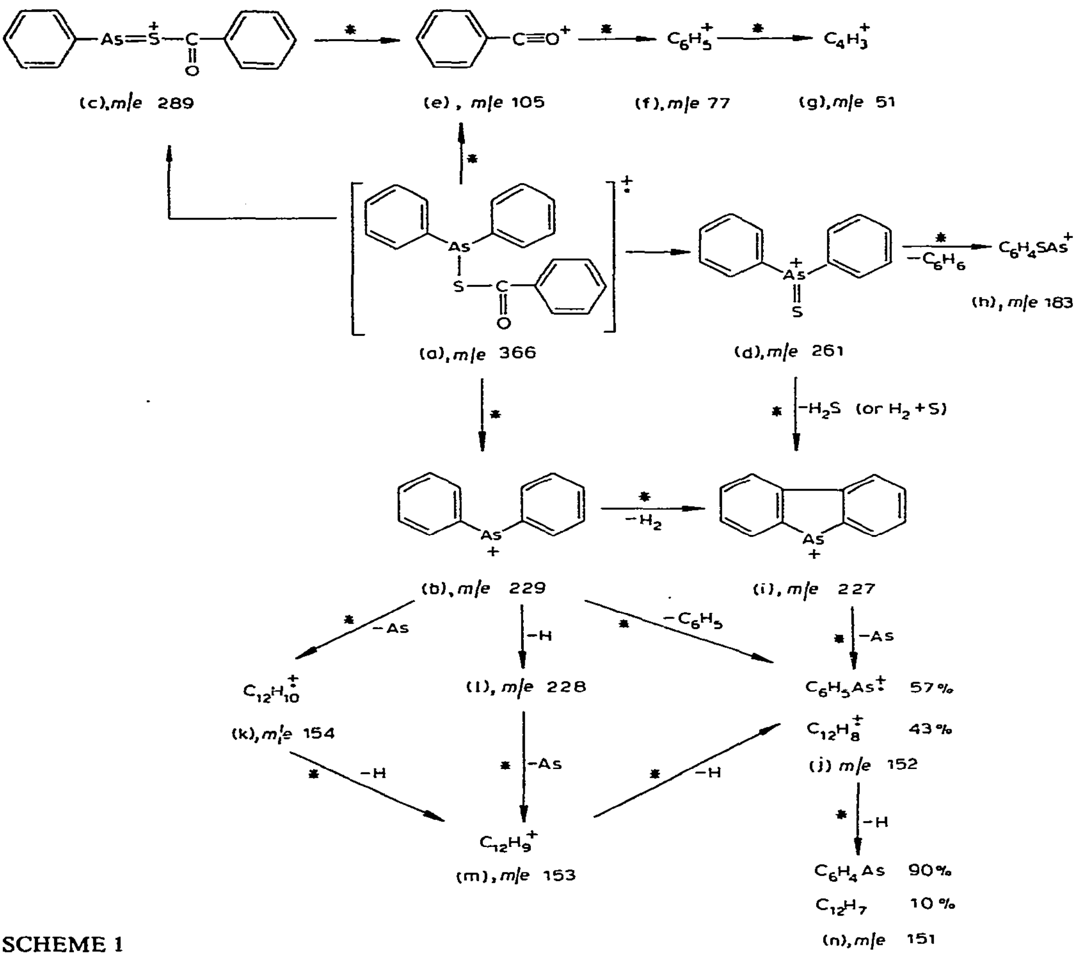


Fig. 4. Mass spectrum of oxybis(diphenylarsine).

Comparing these five spectra, there are several important common ions of interest. They are the ions at m/e 51, 77, 151, 152, 153, 154, 227 and 229. The genesis of these ions will be discussed later. The elementary compositions of the major ions in the mass spectra were determined by high resolution mass measurement. The metastable ions shown in Fig. 1–5 were obtained either with a single focussing mass spectrometer (m^*) or from a beam defocussing experiment[9,10] using a CEC 21-11OB double focus-



SCHEME 1

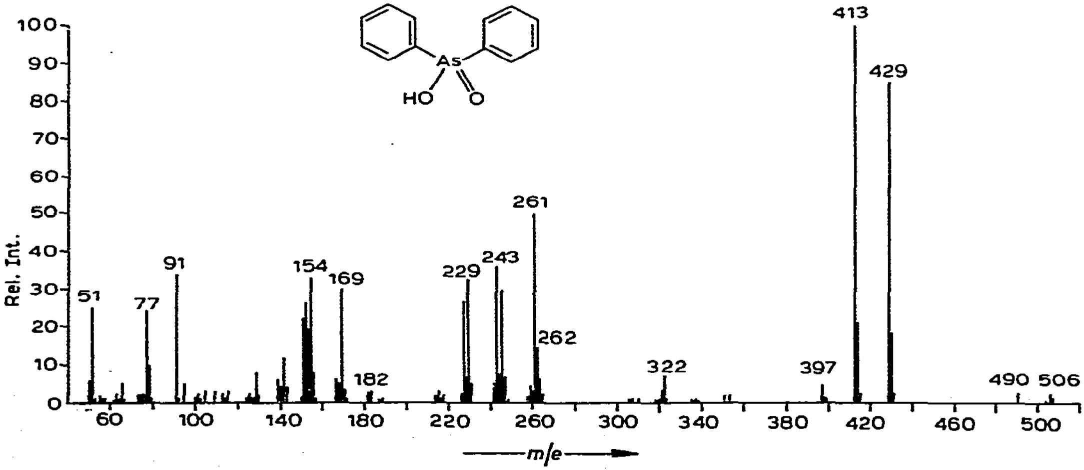


Fig. 5. Mass spectrum of diphenylarsinic acid (335°).

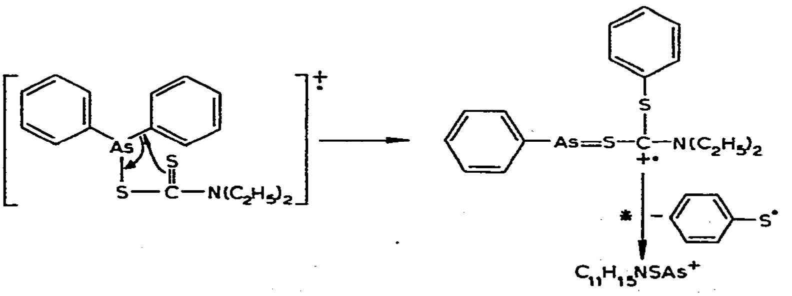
sing mass spectrometer. The intensity of the metastable ion obtained using the latter method is designated as w (weak), m (medium), s (strong) in the spectrum.

Based on the details of ion compositions and metastable ion transitions, the fragmentation mechanism of compound (I) is rationalized. Using the information gained thereby, the decomposition pathways of the other compounds are inferred.

The molecular ion, (a), at *m/e* 366, shows four competing reactions, two of which are the losses of the substituents on the arsenic atom, *i.e.* the thiobenzoate radical and the phenyl radical. The other two are the expected loss of the benzoyl radical and the formation of a stable benzoyl even electron ion. These reactions give ions (b)–(e), at *m/e* 229, 289, 261 and 105 respectively as shown in Scheme 1. Ion (c) also fragments to give ion (e) as supported by the observation of an appropriate metastable ion. That the ion at *m/e* 105 is a benzoyl ion is established from the determined elementary composition as well as the appearance of its two consecutive fragment ions (f) and (g) at *m/e* 77 and 51. Evidence discussed below also shows these two fragment ions can be generated from other routes. Ion (d) shows the loss of a benzene molecule, in the generation of ion (h) at *m/e* 183. A metastable ion was observed corresponding to the loss of H_2S from ion (d) substantiating one of the mechanisms for the formation of ion (i), at *m/e* 227. This metastable ion could well be a consecutive metastable ion[11] indicating the stepwise losses of H_2 and S in the field free region. This is analogous with the hydrogen–hydrogen "*ortho* coupling" reaction observed directly from the case discussed below. The necessity of the existence of the sulfur atom in the pyrolytic reaction will be discussed later. One of the most interesting phenomena is the "*ortho* coupling" reaction of diphenylarsine even electron ion, (b), in a one step generation of ion, (i), at *m/e* 227.

The intense metastable ion corresponding to this reaction was observed. Ion (b) also shows a loss of the arsenic atom giving the fragment ion (k) at *m/e* 154. The ion peak at *m/e* 152 was found to be a doublet with compositions of $C_{12}H_8$ and C_6H_5As, generated from the competitive losses of phenyl radical and arsenic atom from ion (b) and ion (i) respectively. In contrast to the case with the presence of the arsenic atom in the ion moiety, the hydrocarbon ion, (k), at *m/e* 154 appears to lose two hydrogen atoms stepwise.

Because of the presence of a methoxy group on the benzoyl ring, the peak at *m/e* = 105 is now shifted to *m/e* = 135 for compound (II) as shown in Fig. 2. The existence of the ions at *m/e* 77 and 51 in this case should suggest that the ion $C_6H_5{}^+$ can also be generated by other fragmentation modes than the one discussed in compound (I).

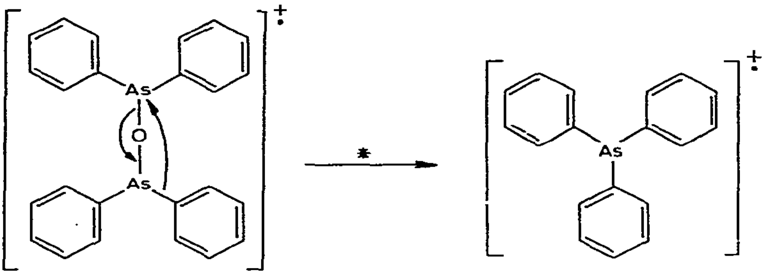


(o), *m/e* 268

An interesting loss of 109 mass units from the molecular ions of compound (III) is a phenylthio radical which is supported by high resolution mass measurement. This can be rationalized from the rearrangement of a phenyl group to the thiocarbonyl group before the fragmentation takes place.

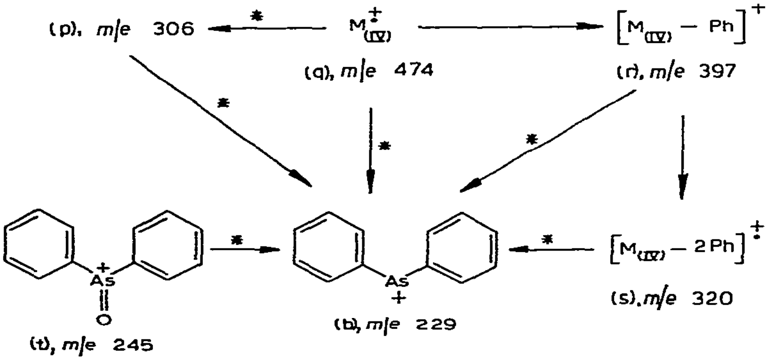
The rearrangement reactions involving an aryl group in mass spectrometry for other systems have been reported by many investigators[12]. The intense ion peak at m/e 116 in the mass spectrum of compound (III) is reasonably explained to be due to a $(C_2H_5)_2NC{\equiv}S^+$ ion, which decomposes successively to give ions at m/e 88 and 60 with hydrogen rearrangements.

The phenyl group rearrangement occurs also in the fragmentation of molecular ion of compound (IV) in the production of an ion at m/e 306 with moderate intensity. An intense metastable ion was detected for the above transition.

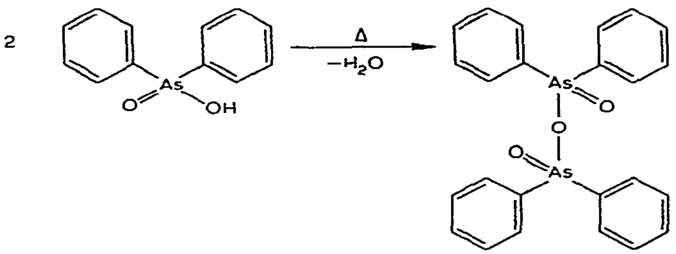


(p), m/e 306

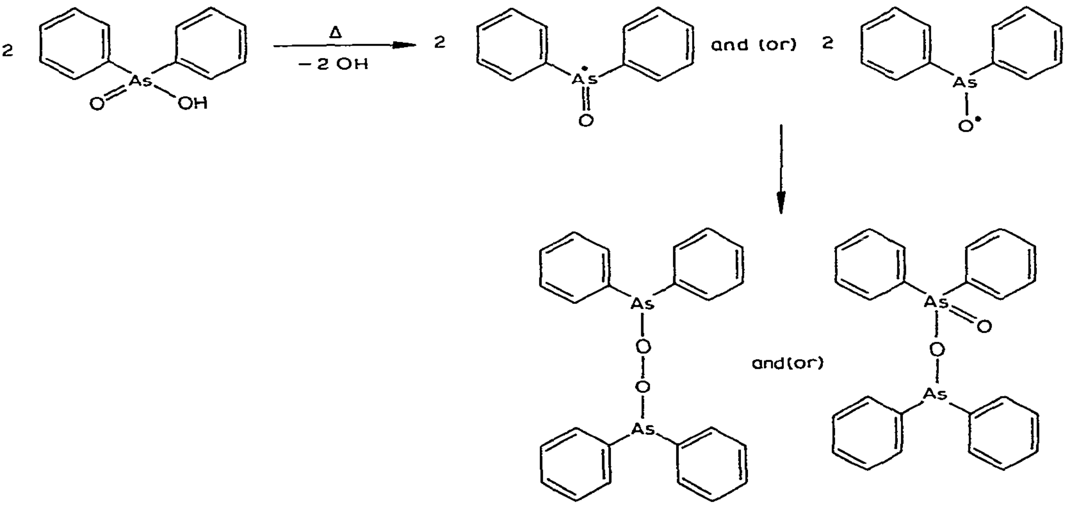
The beam defocussing technique was used to study the generation of the ion at m/e 229, the most important ion responsible for the production of the ions with lower masses. This ion is assumed to be a diphenylarsine even electron ion (b). Five significant transitions were observed which can be rationalized from the structure of molecular ion, $M^{+\cdot}_{(IV)}$ of compounds (IV), even though the ions at m/e 397 and 320 are very weak.



The mass spectrum of diphenylarsinic acid as shown in Fig. 5 is complex and clearly indicates that the diphenylarsinic acid molecule is not stable in the gaseous phase at the temperature investigated. Two main components are observed in the gaseous phase. One is the anhydride.



The formation of anhydride is supported by the presence of the ions at *m/e* 506 and 429 with composition of $C_{24}H_{20}O_3As_2$ and $C_{18}H_{15}O_3As_2$ respectively. Similar reaction was also reported in the cases of 10-phenoxarsinic acid and 2-chloro-10-phenoxarsinic acid[4]. Another component giving ions at *m/e* 490 and 413 with compositions of $C_{24}H_{20}O_2As_2$ and $C_{18}H_{15}O_2As_2$ respectively is believed to be a peroxide and (or) an oxide formed from the coupling of two diphenylarsinoxy radicals before electron impact.

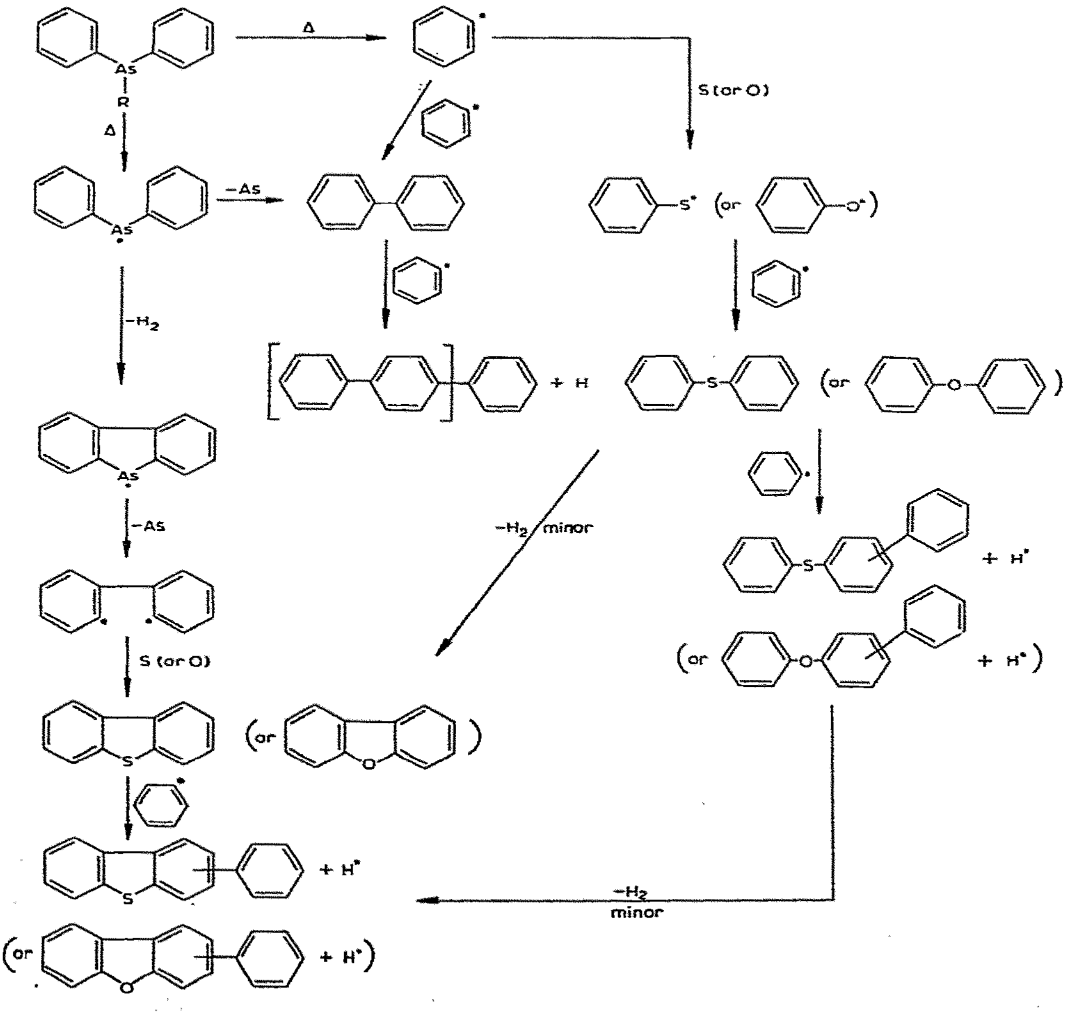


Pyrolysis

Many striking similarities between pyrolytic reactions and electron impact induced ion fragmentation have been reported in the literature[5,8,13]. The mass spectrum of an organic molecule can be used not only to correlate with the structure but also to predict and explain certain pyrolytic reaction. If the neutral molecule corresponding to an intense fragment ion in the mass spectrum is stable at the pyrolytic temperature, the predicted pyrolyzate would be that molecule. If it is not stable, then a further reaction at high temperature would occur. Furthermore, the pyrolytic reactions are usually carried out in a much higher pressure than the electron impact. Hence if certain reactive radicals exist in the pyrolytic system, a further reaction is also predicted. The above criterion should be borne in mind in correlating the two energetic processes.

The main purpose of the pyrolysis experiment in this study is an attempt to determine if the "*ortho* coupling" reaction observed in the electron impact ion decomposition is also operable in the pyrolytic reactions of the compounds of interest. The trapped pyrolyzates of the reaction at 600° were separated into two portions, ether insolubles and ether solubles. As in the case of phenarsazine derivatives[5], arsenic (As_4) and arsenic oxide (As_4O_6) were found to be in ether insoluble portion. This is consistent with the prediction from the mass spectra which show the loss of the arsenic atom to be one of the major ion fragmentation modes. The formation of As_4O_6 is believed to be the oxidation product of arsenic at high temperature.

The ether soluble portion was analyzed by a combination technique of gas chromatography and mass spectrometry. The tentative identifications are shown in Table 1. It is obvious that the products formed are complex. However, correlation with the electron impact ion decomposition is possible.



SCHEME 2

As discussed previously, the diphenylarsine derivatives show a loss of phenyl radical, which plays a very important role in the formation of major products like biphenyl, terphenyl etc.[14,15]. The mechanism of the generation of the major pyrolytic products is proposed in Scheme 2. For the sulfur containing compounds the phenyl radical reacts with sulfur atom in the formation of diphenylsulfide. The sulfur atom is believed to be the one attached to the arsenic atom of diphenylarsine derivatives evidenced from the loss of sulfur atom in the ion fragmentation reaction (d)$\rightarrow$(i)$+H_2+S^{\cdot}$ in the mass spectra discussed previously. As expected, the phenyl radical reacts with diphenyl sulfide in the formation of phenyl biphenylyl sulfide by splitting off a hydrogen atom. Also found in the ether solubles of the pyrolyzates are dibenzothiophene and phenyldibenzothiophene. It is expected that phenyldibenzothiophene is formed from the reaction of phenyl radical with dibenzothiophene. In order to determine the extent of dibenzothiophene formed from diphenyl sulfide, diphenyl sulfide was pyrolyzed under the same conditions as diphenylarsine derivatives. The results are also listed in Table 1. It is obvious that diphenyl sulfide gives a very small percentage of dibenzothiophene in a non-catalytic system[17] (for the pyrolysis of diphenyl ether, see ref. 16). Hence, dibenzothiophene must be formed from another route in the pyrolysis of diphenylarsine derivatives. By correlating with the ion fragmentation mechanism, it is suggested that the diphenylarsine radical is formed initially, which undergoes the "*ortho* coupling" reaction and then the loss of the arsenic atom in the possible formation

TABLE 1

PYROLYTIC PRODUCTS OF THE LISTED COMPOUNDS AT 600°

Pyrolyzates	Gas chromatographic peak area percentage						
	(I)	(II)	(III)	(IV)	(V)	DPE[a]	DPS[b]
Benzene						2	10
Phenol						11	
Naphthalene						1	
Thiophenol[c]							7
Diphenyl ether						74	
Dibenzofuran		3		8	3	5	
Phenyl biphenylyl ether				4		6	
Diphenyl sulfide	40	34	48				77
Dibenzothiophene	18	27	11				3
Phenyl biphenylyl sulfide	8	3	2				2
Biphenyl	21	16	7	51	66		1
Terphenyl	3	3		36	13		
Phenyldibenzofuran					< 1		
Phenyldibenzothiophene	7	3	2				
Thianthrene			1				
Diphenyl disulfide			3				
Stilbene			2				
Methylbiphenyl			2				
Benzonitrile			2				
Benzo[*b*]thiophene			12				
Phenylbenzo[*b*]thiophene			3				
Unknowns	3	11	5	1	18	1	< 1

[a] DPE diphenyl ether. [b] DPS diphenyl sulfide. [c] Identification was based on the gas chromatographic retention time.

of the biphenylylene diradical. The insertion of a sulfur atom into the biphenylylene diradical is expected, which results in the formation of the stable molecule, dibenzothiophene. The reactions discussed are shown in Scheme 2. Similar discussions can also be applied to the cases of the oxygen containing compounds, as also shown in Scheme 2. However, diphenyl ether was not detected in the pyrolyzates of compounds (IV) and (V) as noted in Table 1.

CONCLUSIONS

The trivalent diphenylarsine derivatives studied gave molecular ions with different degrees of intensities and diagnostic common fragment ions at *m/e* 229, 227, 154, 153, 152, 151, 77 and 51. Diphenylarsinic acid was found to be unstable in the gaseous phase and shows the formations of anhydride and peroxide (and/or oxide) at the temperatures investigated. The diphenylarsine odd electron ion, *m/e* 229, undergoes the "*ortho* coupling" reaction and then the splitting off of the arsenic atom. It was found that the details of the ion fragmentation modes were very useful in the interpretation of pyrolytic data in the present cases. The detailed mechanisms of ion fragmentations can be studied by using mass spectrometers, but that of the pyrolytic reaction would be difficult, if not impossible, to be investigated.

EXPERIMENTAL

Melting points were determined in a "Thomas Hoover Capillary Melting Point Apparatus" (Arthur H. Thomas Co.). Elemental analyses were done by the staff of Mr. L. Swim, The Dow Chemical Company. Infrared spectra were recorded on a Perkin–Elmer spectrophotometer, Model 237.

S-Diphenylarsino thiobenzoate (I)

In a 500 ml, 3-necked round bottomed flask equipped with a mechanical stirrer, reflux condenser and Dean–Stark trap was placed 11.9 g (0.025 mole) of oxybis(diphenylarsine), 6.9 g (0.05 mole) of thiobenzoic acid and 300 ml of thiophene free benzene. The mixture was refluxed for 24 h with vigorous stirring to azeotrope off the water of reaction. A purple solution was formed. The benzene solution was filtered and the filtrate was concentrated on a rotary evaporator. The residual oil obtained was placed in a refrigerator overnight. It turned to a solid mass which was collected on a filter, washed with a small amount of acetone to give a light purple solid, m.p. 68–73°. After drying overnight in a desiccator under reduced pressure, 15 g (82%) of a crystalline solid was obtained. Two recrystallizations from acetone raised its m.p. to 75–77°. It showed a carbonyl absorption peak at ν 1656 cm^{-1}. (Found: C, 62.2; H, 4.28; S. 8.9. $C_{19}H_{15}AsOS$ calcd.: C, 62.30; H, 4.10; S, 8.74%.)

S-Diphenylarsino o-methoxythiobenzoate (II)

The same procedure as that for the preparation of *S*-diphenylarsinothiobenzoate was applied. In this case *o*-methoxythiobenzoic acid was used instead of thiobenzoic acid. A pink solution resulted. After complete removal of benzene, the residual oil was placed in a refrigerator overnight. The light pink solid thus obtained was washed with a small amount of acetone and dried overnight in a dessicator under reduced pressure. Two more recrystallizations of the solid from acetone gave a light pink crystalline material, m.p. 97–99°, 68.2 % in yield. Its carbonyl absorption occurred at ν 1631 and 1665 cm^{-1}. These two bands probably result from rotation about the $\rangle C{=}O$ band so that for the higher frequency band the C=O group was in a configuration in which it was near the oxygen atom of the $-OCH_3$ group. The lower frequency band resulted from the configuration in which the $-OCH_3$ group was away from the C=O group. (Found: C, 60.3; H, 4.12; S, 8.15. $C_{20}H_{22}AsO_2S$ calcd.: C, 60.61; H, 4.29; S, 8.08 %.)

S-Diphenylarsino N,N-diethyldithiocarbamate (III)

In a 500 ml, 3-necked round bottomed flask equipped with a mechanical stirrer, a reflux condenser and a dropping funnel was placed 16.5 g (0.1 mole) of diphenylchloroarsine and 100 ml of absolute ethanol. To the refluxing solution, 22.5 g (0.1 mole) of sodium *N,N*-diethyldithiocarbamate trihydrate in 100 ml absolute ethanol was added slowly from the dropping funnel. The mixture was refluxed overnight and then filtered to remove the white precipitate of sodium chloride. The filtrate was concentrated on a rotary evaporator to 70 ml and placed in an icebox for crystallization. Yellowish-white crystalline solids, m.p. 88–93°, were obtained, which on one more recrystallization gave 20 g (53 %) of light yellow crystalline solid, m.p. 93–95° (lit.[18] m.p. 95°).

Oxybis(diphenylarsine) (IV)

This compound was synthesized according to the method known in the literature[19], m.p. 85–90° (lit.[19] 90°).

Diphenylarsinic acid (V)

The synthesis of this compound is similar to that of 10-phenoxarsinic acid described previously[4], m.p. 170–172° (lit.[19] 172°).

Mass spectra

The mass spectra were recorded with an Atlas CH4B mass spectrometer equipped with an EF4B source and a direct probe inlet system. The ionization chamber was kept at about 180°. The energy of the ionizing electrons and the ion accelerating potential were maintained at 70 eV 3 kV respectively. The accurate masses were measured with a Nier peak matching unit attached to a CEC21-110B double focussing mass spectrometer. The accuracy of the measurement is within 10 ppm. The beam defocussing technique for obtaining the metastable ion transitions has been described elsewhere[9,10].

Pyrolytic experiment

The pyrolytic experiment was carried out using a 0.2" ID, 18" long quartz tube. One half of the quartz tube was packed with Vycor beads which was used a 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 TiO_2 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°. Solids of the diphenylarsine compounds were dropped on the top of the reactor and the volatilized material then swept through the reactor to an outside glass trap by the nitrogen flow. The residence time in the reactor was 3 sec 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. The ether soluble portion was identified by the combination technique of VPC/mass spectrometry and the ether insoluble portion was analyzed by mass spectrometry.

ACKNOWLEDGEMENT

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