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Mass spectrometry of derivatives and heterocyclic analogues of 9,10-dihydroanthracene

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ABSTRACT. The fragmentation of derivatives of 9,10-dihydroanthracene and of its heterocyclic analogues containing atoms of O, S, N, P, Si, As, Se and Te at positions 9 and/or 10 is examined. The conditions reviewed are electron impact and chemical ionisation with recording of positive and negative ions. It has been shown that depending on its nature, the heteroatom may be eliminated together with substituents from the molecular ion or a substituent may be lost both as a radical and together with an additional H atom. The fragmentation of compounds in which the substituting groups are adjacent to the hetero atom is explained by the '*peri*-effect'. The elimination of substitutents from phenylene rings, at the *meso* position and at the hetero atom occurs in a similar manner to elimination in the corresponding aromatic derivatives.

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I. Introduction

Derivatives of 9,10-dihydroanthracene and its heterocyclic analogues are widely distributed in nature. The anthracyclines, which are antibiotics possessing antitumour activity, belong to this class. The aglycone of the anthracyclines is a tetrahydronaphthacenequinone which contains an anthraquinone fragment. Phenothiazine derivatives possess various physiological activities and are applied in medicine as antihistamine preparations, for the treatment of Parkinsonism and also for the treatment of psychiatric disorders (Aminazine). Antibiotics of the actinomycin series possess strong bactericidal properties and contain a dibenzoxazine (phenoxazine) ring in the molecule. Up to the present a large number of analogues of 9,10-dihydroanthracene have been synthesised which contain in positions 9 and 10 not only the traditional heteroatoms O, N, S and P but also the elements Si, Se, Te, As, etc.

While possessing specific chemical properties the derivatives of 9,10-dihydroanthracene and its heterocyclic analogues also differ in their specific fragmentation under conditions of electron impact (EI). First there are processes eliminating fragments of the central ring, leading to its contraction and the formation of dibenzohetarene ions. No less important fragmentation processes are fission of this ring and elimination of substituents depending on their nature and disposition in the molecule. Knowledge of the rules for dissociation on ionisation is necessary when studying the reactivity of ions in the gas phase and in the solution of structure-analytical problems (the establishment of the composition and structure of molecules, the determination of trace amounts of the appropriate physiologically active compounds and the products of their metabolism).

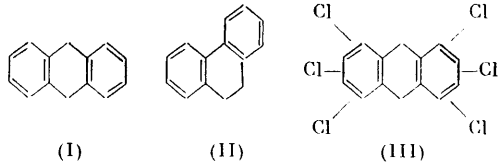
There are no special reviews in the literature of studies in which the features of the dissociation of 9,10-dihydroanthracenes and their heterocyclic analogues on ionisation have been correlated and systematised. The EI mass spectra of anthraquinones are considered only in old monographs[1,2] and the mass spectral characteristics of individual types of heterocyclic analogues of 9,10-dihydroanthracene have been given in a monograph.[3] It should be noted that in this review the EI method is implied even when not specially stipulated.

II. 9,10-Dihydroanthracene and its derivatives

The mass spectrum of 9,10-dihydroanthracene (I) contains three most significant peaks corresponding to the ions M^+, $[M-H]^+$ and $[M-2H]^+$ with a ratio of intensities 92:100: 63. A similar triplet of peaks also dominates the mass spectrum of 9,10-dihydrophenanthrene (II), however in this case the ratio of intensities is 100:55:30. The higher intensity peak for the $[M-H]^+$ ion in the case of compound (I) is explained by the fact that on elimination of a hydrogen atom from a methylene group a carbocation is formed with two benzyl group fragments in the stabilisation of which both phenylene rings participate. In the analogous carbocation which is formed from compound (II) there is one benzyl fragment and only one phenylene ring participates in its stabilisation. In addition there are seven resonance forms possible for the $[M-H]^+$ ion for compound (I) and four for compound (II).

The $[M-2H]^+$ ions (I) and (II) have the structures of anthracene and phenanthrene ions respectively.[4]

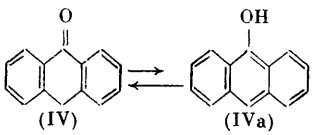
There are low intensity peaks for $[M-CH_3]^+$, $[M-C_2H_4]^+$, $[C_7H_5]^+$ and $[C_6H_4]^+$ ions in the mass spectrum of compound (I) and others the formation of which is linked with the isomerisation of M^+ and the fission of bonds in the central ring.



(I) (II) (III)

Detection of the toxic hexachloro-9,10-dihydroanthracenes (III) with chlorine atoms at various positions in the phenylene rings was effected by gas chromatography-mass spectrometry (GC-MS). Two of the most intense peaks with *m/z* 388 and 390 were used out of the multiplet of peaks of their molecular ions.[5]

9(10H)-Anthracenone, anthrone (IV), is characterised by a tautomeric equilibrium with 9-hydroxyanthracene, anthrol (IVa). The keto form is thermodynamically the more favourable and anthrone predominates in the gas phase.

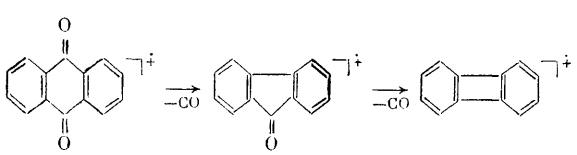


(IV) (IVa)

It was established that the enthalpy of formation of anthrone is 3 kcal mol^{-1} less than for anthrol and the enthalpy of formation of M^+ for the keto form is 77 kcal mol^{-1} greater than that of M^+ of the enol form.[6] Consequently the main decomposition of M^+ for compound (IV) is linked not with ejection of CO (as is characteristic of cyclic ketones) and the formation of a fluorene cation radical but with loss of HCO. However this process does not occur in practice in the case of 10,10-diaryl-9-anthrones.[7]

Much work has been devoted to the mass spectrometric study of anthraquinone (V) and its derivatives.[2] The main routes for the decomposition of anthraquinone on EI are determined by the sequential elimination of two CO groups, which was established by ^{18}O-labelled analogues,[8] with the formation of ions of fluorenone and biphenylene (Scheme 1).

Scheme 1



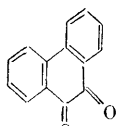
M^+, (V) $[M-CO]^+$ $[M-2CO]^+$

This fragmentation scheme for anthraquinone has become classical and is cited in many monographs and original papers.[1-3] The individual steps of this reaction sequence have been separated in the various field free regions of a reversed geometry double focussing mass spectrometer.[8] It was established that different amounts of energy are liberated in the formation of $[M-CO]^+$ ions depending on where they are generated, either in the ion source or in a field free region. But this in its turn means that $[M-CO]^+$ ions formed in these two regions have different structures. The structure of the ion in the second case is unknown. The $[M-CO]^+$ ions generated in the ion source most probably have the structure of the fluorenone ion since the mass spectrum of the latter is very similar to the spectrum of anthraquinone below the peak with *m/z* 180, which corresponds to the $[M-CO]^+$ ion. Attempts to detect all of the two-step reaction

$$M^+ \rightarrow [M-CO]^+ \rightarrow [M-2CO]^+$$

in the first field free region proved to be unsuccessful, which indicates the low rate of the second stage.

9,10-Phenanthrenequinone (VI) is decomposed on EI by an analogous scheme. Ejection of the first molecule of CO is predominant which is explained by the ease of the initial fission of the C–C bond between the α-diketo groups.[9]

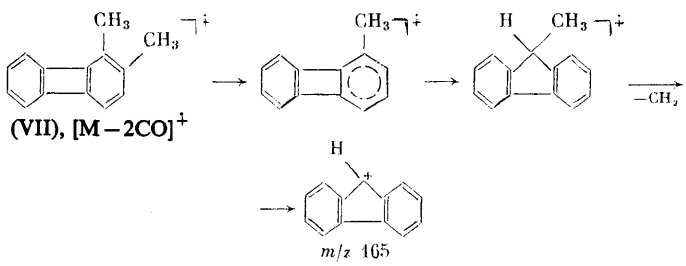


(VI)

It must be mentioned that anthracene is readily oxidised to anthraquinone on chemical ionisation in a mixture of $O_2/N_2/CO_2$ gases. Only the M^+ peak of anthraquinone was present in the negative ion mass spectrum recorded in this manner.[10]

In the case of 1(2)-methyl- and 1,2-methyl-9,10-anthraquinones (VII) a complex skeletal rearrangement occurs in the $[M-2CO]^+$ ions with the formation of a fluorene cation (Scheme 2).[11]

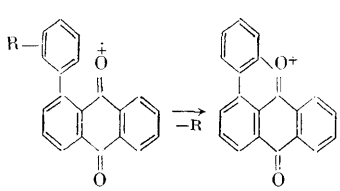
Scheme 2



(VII), $[M-2CO]^+$ *m/z* 165

The presence of a carbonyl group in anthraquinones has a special influence on fragmentation at the expense of substituents in the aromatic ring. In the spectra of 1-aryl derivatives of anthraquinone (VIII) containing an *ortho* substituent there was a main peak with *m/z* 283 caused by elimination of this substituent from M^+ (Scheme 3).[1]

Scheme 3



M^+, (VIII), R = H, *o*-CH_3, *o*-OCH_3, *o*-NO_2 *m/z* 283

This type of dissociation on ionisation has been investigated in detail[12] in a study of *o*, *m* and *p* isomers in a series of 1-aryl-anthraquinones (VIII, R = CH_3, OCH_3, F, Cl, Br, and NO_2). A substituent in the *ortho* position of the aryl group is readily eliminated by the process shown in Scheme 3. The same substituent in the *meta* or *para* position leaves with difficulty. In this case a hydrogen atom is readily lost from the *ortho* position (Table 1).

The main routes of fragmentation of 1- and 2-chloroanthraquinones and also of 1,5- and 1,8-dichloroanthraquinones on EI are linked with the loss of two molecules of CO from M^+. The $[M-CO]^+$ ions also exist as two structures in all these cases.[8]

After the ejection of two CO groups monohydroxyanthraquinones eliminate a third CO molecule and HCO.[13] Using [9,10-di-^{18}O]-1-hydroxy-9,10-anthraquinone as an example it was established[8] that the M^+ of this compound gives up $C^{16}O$ and $C^{18}O$ in the ratio 1:4, i.e. the elimination of CO from the carbonyl groups is preferred to elimination from the hydroxyl group. The $[M-C^{18}O]^+$ ions give up

$C^{16}O$ and $C^{18}O$ with a proability ratio of 1:5. The ejection of a second CO molecule from $[M-C^{18}O]^+$ ions is similar to that which occurs on decompositon of [9-^{18}O]-1-hydroxy-9-fluorenone.

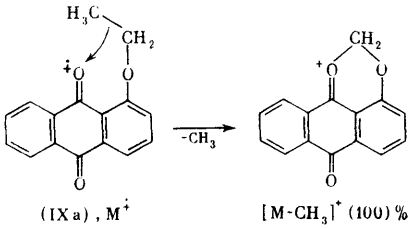
Table 1. Intensities ($\%\sum_{60}$) of peaks of characteristic ions in the mass spectra of compounds (VIII).

R	M^+	$[M-H]^+$	$[M-R]^+$	R	M^+	$[M-H]^+$	$[M-R]^+$
o-CH_3	6.5	1.5	36.5	*o*-Cl	0	0.2	43.0
m-CH_3	8.0	11.3	15.4	*m*-Cl	14.1	23.9	12.2
p-CH_3	8.6	12.2	8.3	*p*-Cl	16.4	26.5	9.4
o-OCH_3	3.0	0.3	36.5	*o*-Br	0	0.02	35.9
m-OCH_3	14.4	13.1	15.4	*m*-Br	9.5	13.9	14.8
p-OCH_3	10.4	9.7	8.3	*p*-Br	13.9	19.6	10.6
o-F	12.8	14.0	15.0	*o*-NO_2	0.02	0.09	39.6
m-F	15.8	27.4	2.8	*m*-NO_2	5.8	6.8	7.4
p-F	18.6	33.3	2.2	*p*-NO_2	2.3	2.6	3.5

The ease of formation of $[M-OH]^+$ ions in the case of dihydroxanthraquinones depends on the disposition of the hydroxyl groups.[13] The corresponding peaks were much more intense if the OH groups were in different rings. It was noted[13] that anthraquinones containing an OH group at positions 2, 3, 6, or 7 were more inclined to eject an OH radical from M^+ than were the 1, 4, 5 or 8 isomers for which the formation of an intramolecular hydrogen bond is possible.

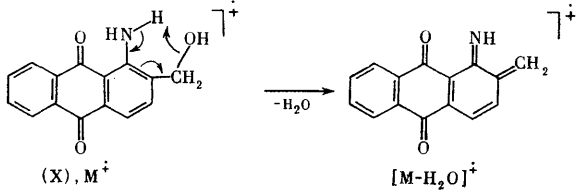
Marked differences were observed between the spectra of 1- and 2-methoxyanthraquinones.[13] Peaks for $[M-OH]^+$ and $[M-H_2O]^+$ were present only in the first case. The generation of the second ion is caused by the *peri* disposition of the CH_3O and CO groups providing migration of two H atoms to the carbonyl group. The principal differences between the mass spectra of the higher 1- and 2-alkoxyanthraquinones are explained by the *peri*-effect.[14] With the aid of 1- (IXa) and 2-ethoxyanthraquinones (IXb) labelled with deuterium in the ethyl group it was shown that the *peri* effect determines the loss of a CH_3 radical from compound (IXa) (Scheme 4), while in the case of compound (IXb) fragmentation of the ethoxy group is linked only with ejection of C_2H_4.

Scheme 4



In the general case substituted anthraquinones decompose on EI like the corresponding derivatives of aromatic compounds although the character of the fragmentation is determined by the nature of the substituent.[15] The double elimination of CO from M^+ typical of anthraquinones is, as a rule, completely suppressed but the CO molecules may be ejected from the fragment ions formed on elimination of substituents. For example the main decomposition of 1-amino-2-hydroxymethylanthraquinone (X) is linked with the elimination of a molecule of water (Scheme 5) and the elimination of CO is effected from the dehydrated ion.[16]

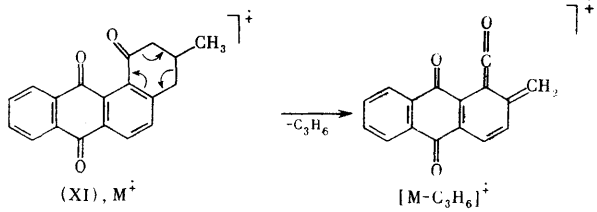
Scheme 5



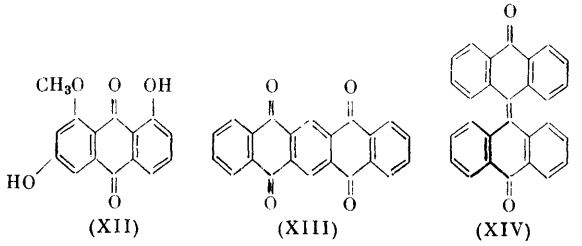
The decomposition of 1-arylamino- and 1,4-di(arylamino)anthraquinones on EI is linked with expulsion of the ArNH group from position 1. The resulting ions $[ArNH_2]^+$, $[ArNH]^+$ and $[M-ArN]^+$ may decompose further and the latter is capable of eliminating CO twice.[17]

The presence of an additional annelated ring on the anthraquinone molecule may introduce specificity into the character of the decomposition. For example in the case of the methyl ester of ochromycinone (XI) in addition to decarbonylation of M^+ there is also elimination of a C_3H_6 particle probably by a retrodiene decomposition (Scheme 6). Later OH, CO and HCO may be lost from the $[M-C_3H_6]^+$ ion.[18]

Scheme 6



An anthraquinone fragment is often encountered in natural compounds such as anthraquinone antibiotics in whose structure determination mass spectrometry was used.[19–25] For example on analysis of the mass spectrum, in which $[HOC_6H_3CO]^+$, (*m/z* 120, 12%) and $[HO(CH_3O)C_6H_3CO]^+$ (*m/z* = 150, 2%) ions were detected, the pigment isolated from the bacterium *Xenorhabdus luminescens* was assigned the structure 1,6-dihydroxy-8-methoxyanthraquinone (XII) and not 1,3-dihydroxy-8-methoxyanthraquinone.[26]



Fragmentation on EI of more complex anthraquinones of the type of pentacene-5,7,12,14-diquinone (XIII)[27] and 9,9′-dianthraquinone (XIV)[2,28] is also linked with repeated expulsion of a molecule of CO from M^+ and also of HCO at some stage.

III. Analogues of 9,10-dihydroanthracene with a heteroatom at position 9(10)

The mass spectral characeristics of heteroanalogues of 9,10-dihydroanthracene containing only one heteroatom (N, O, S, Si, P, etc.) in the central ring are considered in this section. Both general and specific routes of decomposition on EI are characteristic of compounds of this series depending on the nature of the heteroatom at position 9. One of the frequently encountered routes of fragmentation is the expulsion of the heteroatom from position 9 or the carbon atom with substituents from position 10. In both cases contraction of the central ring occurs with the formation of fluorene structures or their 9-hetero analogues (Scheme 7). The presence in the molecule of substituents inclined towards independent fragmentation may suppress these processes or cause them to occur in the later stages of ion fragmentation resulting in loss of the substituent. Some compounds of the type under consideration (XV) for which the disappearance of position 9 and/or 10 occurs at the first fragmentation of M^+ are shown in Table 2.

Scheme 7

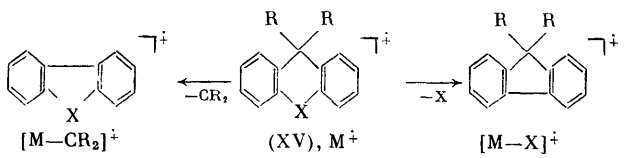


Table 2. Characteristic ions in the EI mass spectra of compounds (XV) (intensities are given in % maximal peak).

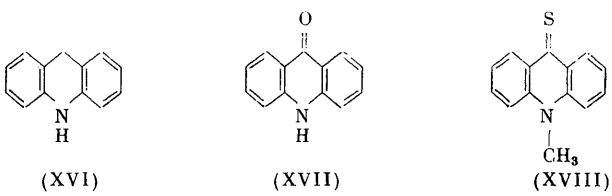
CR_2	X	Other substituents	$J_{[M-CR_2]^+}$	$J_{[M-CR_2]^+}/J_{M^+}$	$J_{[M-X]^+}$	$J_{[M-X]^+}/J_{M^+}$	Refs.
CO	O	–	50	0.50	–	–	[29]
CO	O	2,7-Cl_2	28	0.28	–	–	[29]
CO	O	2,7-F_2	40	0.40	–	–	[29]
CH_2	S	–	–	–	15	0.25	[30]
CO	S	–	38	0.38	–	–	[30]
CH_2	SO_2	–	–	–	25	0.31	[30, 31]
CO	SO_2	–	–	–	40	1.40	[30]
CO	NH	–	53	0.53	–	–	[32, 33]
CO	NH	1-CH_3	7	0.07	–	–	[34]
CO	NH	2-CH_3	8	0.08	–	–	[34]
CO	NH	4-CH_3	11	0.11	–	–	[34]
CO	NCH_3	–	11	0.11	–	–	[32]
CH_2	P(O)OH	–	–	–	62	0.75	[35]
CH_2	$P(O)OCH_3$	–	–	–	69	0.80	[35]
CO	P(O)OH	–	64	0.80	100	1.25	[35]
CO	$P(O)OCH_3$	–	30	1.15	23	0.97	[35]
CH_2	$SiClCH_3$	–	–	–	20	0.25	[36]
CH_2	SiF_2	–	–	–	18	0.18	[54]
CH_2	$Si(OCH_3)_2$	–	–	–	7	0.30	[54]

In one of the first studies on the mass spectrometric investigation of thioxanthene (XV, $CR_2 = CH_2$, X = S) and its 10,10-dideutero analogue it was established that their M^+ readily lose CH_2 and CD_2 (the corresponding peak has 60% intensity). This result was extremely unexpected since ejection of a carbene particle under EI conditions is energetically not favoured. In fact in more recent work[30,31,38] on the investigation of xanthene (XV, CR_2, CH_2, X = O), thioxanthene and their 10,10-dideutero analogues no peaks corresponding to ejection of $:CH_2$ and $:CD_2$ were detected. The elimination of CO from M^+ is a common process for carbonyl derivatives of these compounds.

In certain cases the process of forming $[M-X]^+$ ions is not a single step. This is a characteristic for example of phosphorus compounds [XV, $CR_2 = CH_2$, CO and X = P(O)OH or $P(O)OCH_3$] the molecular ions of which lose OH, OCH_3 and PO sequentially.[35]

After elimination of the heteroatom X from compounds (XV, $CR_2 = CH_2$) leading to a fluorene cation-radical, the fission of H is often a characteristic accompanied by the formation of a more stable fluorenyl cation.

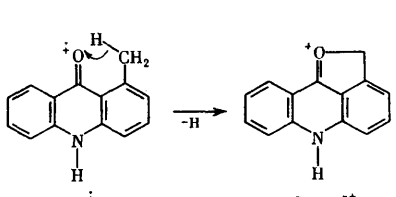
9,10-Dihydroacridines (acridanes). The mass spectrum of acridane (XVI) contains two peaks for M^+ (51%) and $[M-H]^+$ (100%) ions the intensities of which fell to 6–7% in the spectrum of 9-n-propylacridane where the base peak was the $[M-C_3H_7]^+$ ion. The character of the fragmentation is practically unchanged in the case of 4-ethyl- and 4-phenylacridanes, but in the case of 4-ethylacridane a noticeable peak for the $[M-1-28]^+$ ion appeared which is caused by the ejection of a molecule of ethylene from the C_2H_5 group as a result of a McLafferty rearrangement in the $[M-H]^+$ ion.[34]



(XVI) (XVII) (XVIII)

The mass spectral date of some acridones are given in Table 2. The molecular ion of acridone (XVII) may lose H and HCN after ejection of CO and the formation of a carbazole ion-radical.[32,33] Elimination of CS is a characteristic of 10-methylthioacridone (XVIII).[3] Competition between fragmentation of the side chain and ejection of CO was observed on fragmentation of substituted acridones (1-, 2-, 3-, and 10-methyl, 2-ethyl, 2-n-butyl, 4-isopropyl, 4-t-butyl, 1-isopropyl-4-methyl). In all cases apart from the methylacridones, β-fission (benzylic) dominates accompanied by loss of part of the alkyl substitutent.[33,39] It was proposed[34] that this process in the M^+ of 1-methylacridone is facilitated by the possibility of forming an oxonium ion (Scheme 8). In all these cases the ejection of CO occurs after the given reactions.

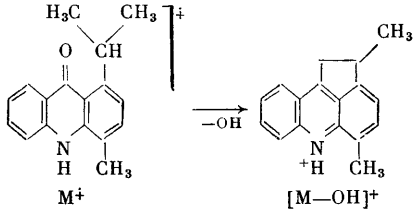
Scheme 8



A special feature of the dissociation of 1-isopropyl-4-methylacridone on ionisation is the ready formation of the $[M-OH]^+$ ion, the peak of which reached 80%.[34] The composition of this ion was

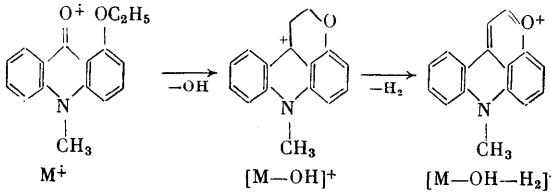
proved by high resolution mass spectrometry, and the one-step character of its formation by the presence of the appropriate metastable peak (Scheme 9).

Scheme 9



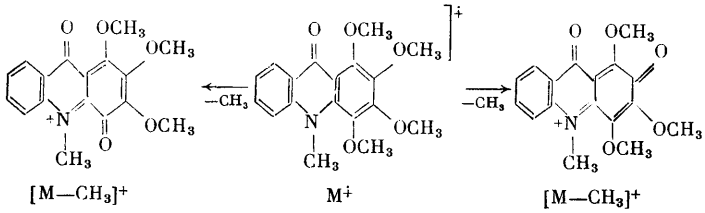
A series of specific fragmentation routes was discovered for alkoxy substituted acridones,[32] which in the general case decompose as alkylaryl ethers. Stepwise expulsion of OH and H_2 is a characteristic of 2-ethoxyacridone. It was proposed that the driving force of these reactions is the formation of cyclic oxonium ions (Scheme 10).[32,40]

Scheme 10



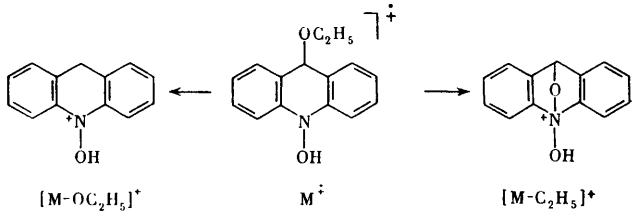
The form of the decomposition of 1,2,3,4-tetramethoxy-10-methylacridone is an example of the high regioselectivity of fragmentation. It was shown that deutero analogues that in this case the elimination of CH_3 occurs only from positions 2 and 4 in a 60:40 ratio. Such selectivity of fragmentation is caused by the possibility of forming well-stabilised ions (Scheme 11).

Scheme 11



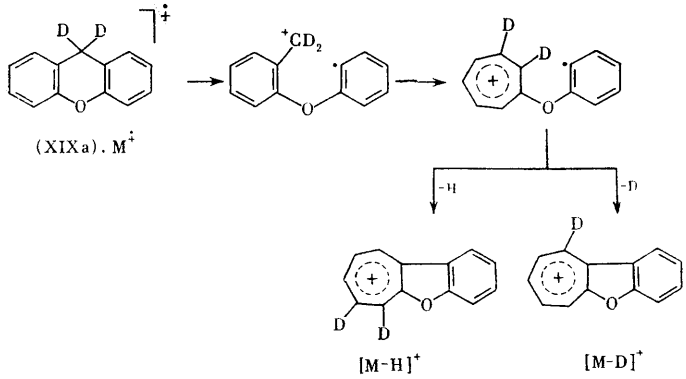
Like the 9-alkylacridanes, 9-ethoxy-10-hydroxyacridane loses the substituent from position 9 very readily on EI leading to the maximum peak in the mass spectrum. A less intense peak corresponds to loss of C_2H_5 from M^+ (Scheme 12).[41]

Scheme 12



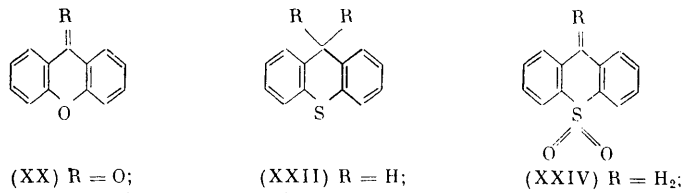
Xanthenes. The mass spectrum of unsubstituted xanthene (XIX) is very sparse and contains the base peak of the $[M-H]^+$ ion together with an M^+ peak (~45%).[30,42] In the spectrum of 9,9-deuterated xanthene (XIXa) in place of the expected peak for the $[M-D]^+$ ion a doublet was observed of peaks for $[M-H]^+$ and $[M-D]^+$ ions which were close in intensity.[31] Thus randomisation of H atoms occurs in the M^+ of xanthene even before decomposition, possibly according to the following scheme (Scheme 13).

Scheme 13



The mass spectra of complex derivatives of xanthene[43–45] and of tetrachloroxanthene[42] have been described in the literature. A series of papers is devoted to a detailed mass spectrometric investigation of xanthone (XX) and its dimethyl, hydroxy and methoxy derivatives.[29,46,47] The sequential elimination of two molecules of CO is a characteristic feature of the decomposition of the M^+ of xanthone (XX). It was shown[29] with an ^{18}O-labelled analogue that the first molecule of CO is wholly ejected from the carbonyl group. However it was discovered[8] that ejection of CO from M^+ in the second field free region of the reversed geometry mass spectrometer may also proceed with the participation of the ether oxygen in the first act of CO elimination. It must be noted that the molecular ion of thioxanthone (XXI) readily loses CS.[3]

A correlation was observed in the case of dihaloxanthones between elimination of CO and the halogen from M^+. In a series of fluorinated, chlorinated, brominated and iodinated derivatives it was shown that the stronger the C–Hal bond the higher became the intensity ratio $[M-CO]^+/[M-Hal]^+$.[29] The decomposition rule described has enabled ready detection of tetrachloroxanthone among environmental contaminants[42,48]



(XX) R = O;
(XXI) R = S

(XXII) R = H;
(XXIII) R = CH_3;
(XXV) R + R = O

(XXIV) R = H_2;
(XXVI) R = O

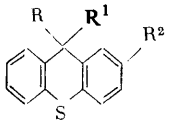
Thioxanthenes. Thioxanthene (XXII) is readily distinguished from xanthene by the character of the fragmentation involving ring fission since its M^+ loses S and HCS. However the peak of the $[M-H]^+$ ion is the base peak and exceeds the intensity of M^+ almost twofold in the mass spectrum of thioxanthene,[30] while in the spectrum of 9,9-D_2-thioxanthene the same doublet of peaks for $[M-H]^+$ and $[M-D]^+$ ions was observed as in the spectrum of deuteroxanthene. Thus the same mechanism for the fission of H occurs for thioxanthene as for xanthene (Scheme 13).[31] It must be

noted that in the mass spectrum of 9,9-dimethylthioxanthene (XXIII) the peak for the $[M-CH_3]^+$ ion possesses maximal intensity and may then lose S.[49]

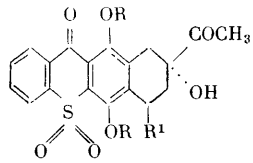
Decomposition of thioxanthene S,S-dioxide (XXIV) on EI proceeds by several parallel routes, viz. sequential elimination of 1) OH, CO and H, 2) SO and H and 3) SO_2 and H (the latter process leads to the maximal peak in the mass spectrum).[30] As was shown[31] with the aid of the 9,9-dideutero analogue of compound (XXIV) the H atom from position 9 participates in the expulsion of OH. At the same time $[M-SO_2]^+$ ions preferentially split off a H atom from the benzene ring and, to a lesser extent, from position 9.[31]

The main decomposition of the M^+ of thioxanthone (XXV) is linked with the sequential expulsion of CO and S, and also of CO, CS, and H.[30] In the case of thioxanthone S,S-dioxide (XXVI) the main reaction is the elimination of SO, seemingly as a result of isomerisation into the sulphonate form.[50]

On investigating chlorprothixene (XXVII) and its analogues (XXVIIa, b) by chemical ionisation (CH_4 as gas reagent) and negative ion recording, the unexpected formation of $[M+H]^-$ was detected in addition to the normal $[M-H]^-$ ion.[51] The generation of the former is caused by the presence of an S atom in the molecule. The strong formation of $[M+H]^-$ ions was also noted in a study of sulphur-containing anthracycline compounds (XXVIII) by secondary ion mass spectrometry (Cs^+, 12 and 23 keV) and negative ion recording.[52]



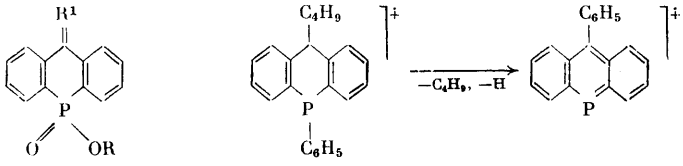
(XXVII) R + R^1 = $CHCH_2CH_2N(CH_3)_2$; R^2 = Cl;
(XXVIIa) R + R^1 = $CHCH_2CH_2N(CH_3)_2$, R^2 = H;
(XXVIIb) R = $CH_2CH_2CH_2N(CH_3)_2$, R^1 = H, R^2 = Cl



(XXVIII) R = H, CH_3, R^1 = H, OCH_3

9,10-Dihydro-9-phosphanthracenes. The individual routes for the fragmentation of these compounds are given above in Table 1. The molecular ion of compound (XXIX) is able to lose H_2O and then PO with the formation of the fluorenyl cation. The latter is also formed from the M^+ of ester (XXIXa) by the stepwise expulsion of CH_3 and PO_2H or $HOCH_3$ and PO.[35] The molecular ion of ketone (XXX) may sequentially lose CO and OH or PO_2H and CO. The seqential elimination of CH_2O and PO is a characteristic of the methoxy derivative (XXXa).[35]

Scheme 14



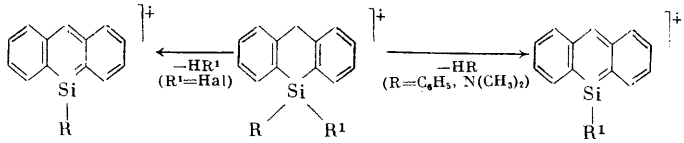
(XXIX) R = H, R^1 = H_2; (XXXI), M^+
(XXIXa) R = CH_3, R^1 = H_2;
(XXX) R = H, R^1 = O;
(XXXa) R = CH_3, R^1 = O.

The stepwise elimination of C_4H_9 and H (Scheme 14) is observed for 9-phenyl-10-t-butyl-9,10-dihydro-9-phosphanthracene (XXXI), in addition to expulsion of C_4H_8 as a result of a McLafferty rearrangement. It was proposed that transannular 1,4-migration of the phenyl group occurs in this process.[53]

9,10-Dihydro-9-silanthracenes. In the simplest compounds of this series (XXXII) the character of the fragmentation on EI depends on the nature of the substituent at the silicon atom. The molecular ion of 9,10-dihydro-9-silanthrene (XXXII, R = R_1 = H) decomposes by the sequential elimination of three H atoms with the formation of a fluorenyl cation. Derivatives containing alkyl groups on the silicon atom undergo fragmention like alkylsilanes. For example the weakly stable M^+ of 9,9-diethyl-9-sila-9,10-dihydroanthracene (XXXII, R = R^1 = C_2H_5) sequentially loses C_2H_5 (causing the base peak) and C_2H_4.[54]

A new fragmention route was detected for compounds (XXXII) with halogen substituents at the silicon atom such as (R = CH_3, R^1 = Cl),[36] (R = R^1 = Cl) and (R = H, R^1 = Cl),[54,55] (R = R^1 = F) and [R = $N(CH_3)_2$, R^1 = Cl][54] and (R = C_6H_5, R^1 = Cl or Br).[56–58] The molecular ions of such compounds readily lose hydrogen halide with the formation of silanthracene cation-radical which, in the case of compounds containing halogen and phenyl or a dimethylamino group, may also arise as a result of parallel expulsion of molecules of C_6H_6 and $(CH_3)_2NH$ respectively (Scheme 15). Both these ions are able to lose SiR and SiR^1 which leads to a fluorenyl cation (*m/z* 165).

Scheme 15



(XXXII), M^+

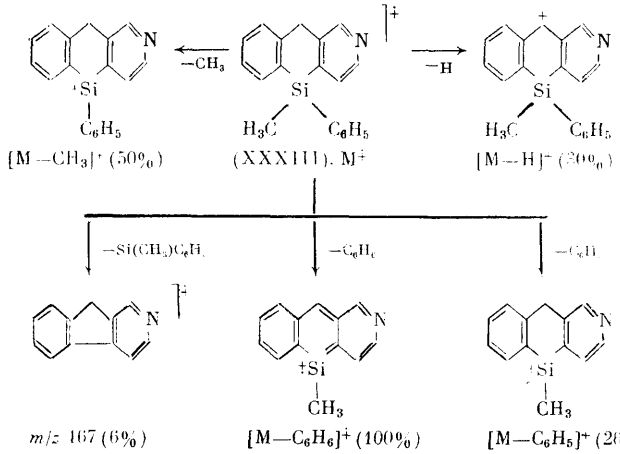
Elimination from M^+ of the substituent from the silicon atom together with an additional H atom from position 10 is also observed in the case of other types of substituent such as in compounds (R = R^1 = OCH_3) and [R = R^1 = $N(CH_3)_2$].[54] In the first case CH_3OH is readily lost (then CH_3 or CH_2O) and in the second, initially $(CH_3)_2NH$ [$N(CH_3)_2$ to a lesser extent] and then $N(CH_3)_2$.

Similar routes for fragmentation by EI also occur in the case of 10-methyl-10-phenyl-9,10-dihydro-10-sil-2-azanthracene (XXXIII). Two processes compete, viz. elimination from M^+ of a CH_3 radical and of a molecule of C_6H_6.[59,60] It was shown that with the aid of 9,9-dideutero analogues of compound (XXXIII)[59] that elimination of a hydrogen atom and also of a molecule of C_6H_6 occurs solely with the participation of hydrogen from position 9. These and several other decomposition processes for compounds of the 10-sil-2-azanthracene series are shown in Scheme 16.

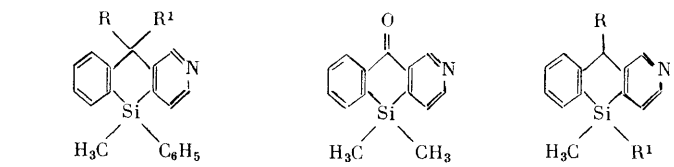
The character of the dissociation on ionisation of more complex analogues of compound (XXXIII) containing substituents or functional groups at position 9 is determined by the latter to a significant extent. Thus the presence of a carbonyl group in the molecule of 10-methyl-10-phenyl-10-sil-2-azanthrone (XXXIV) inhibits the expulsion of C_6H_6 mentioned above and the most intense peaks in the mass spectrum are the peaks for $[M-CH_3]^+$ (100%) and $[M-C_6H_5]^+$ ions. Expulsion of CO from M^+ for the compound in question is not important but a more significant reaction takes place accompanied by the elimination of H_2O,

$SiOCH_3$ and $Si(CH_3)C_6H_5$.[59] A series of specific fragmentation routes, facilitating the identification of regioisomers, was detected in the mass spectra of 4-, 5-,. 6-, 7- and 8-nitro-10,10-dimethyl-10-sil-2-azanthrones (XXXV).[61]

Scheme 16



The tertiary alcohol (XXXVI) behaves specifically on EI. Its molecular ion is capable of losing two CH_3 radicals sequentially (contrary to the even-electron rule) with the formation of a silazanthracenyl ion.[59] Other decomposition routes are linked with the sequential elimination of CH_3 (maximum peak) and H_2O, CH_3 and C_6H_6. The fission of OH and H_2O from M^+ occurs weakly. The oxime obtained from ketone (XXXIV) is capable on EI of losing OCH_3, and also 1) CH_3 and H, 2) CH_3 and H_2O and 3) H, CH_3 and C_6H_5 sequentially.[59]



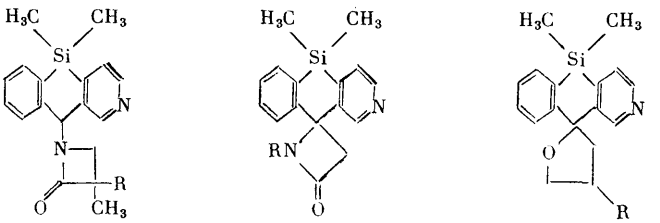
(XXXIV) R + R¹ = O;
(XXXVI) R = CH3, R¹ = OH

(XXXV)

(XXXVII)
R = CH2CH2CN, CH2CH2CH2NH2, NH2, NHCOOCH3, NHCO(CH2)3CN;
R¹ = CH3, C6H5

The main decomposition of substituted 9,10-dihydro-10-sil-2-azanthracenes (XXXVII) is caused by the loss of long alkyl substituents of the alkyl type from position 9 (loss of CH_2CH_2CN, $CH_2CH_2CH_2NH_2$ from M^+) or by the elimination of the substituent from the silicon atom (expulsion of CH_3 or C_6H_6). In the case of amines (R = NH_2) the intensity of the peak for $[M-H]^+$ ions is sharply increased and in contrast to the previous compounds significant peaks appear for $[M-SiR_2]^+$ ions. Decomposition at the expense of the amide substituent is characteristic of amides.

Compounds containing an azetidine substituent at position C(9) (XXXVIII) and also spiranes with azetidine (XXXIX) or tetrahydrofuran (XL) groups undergo fragmentation by fission of the four- and five-membered heterocycles respectively but a CH_3 radical is split away from the Si atom most frequently in the later stages of the decomposition.[63] For the derivatives (XXXVIII) for example the main process is elimination of the azetidine ring from M^+. Also typical is fission of the four-membered ring into two halves which occurs readily in $[M-CH_3]^+$ ions (formation of $[M-CH_3-CH_2CRCH_3]^+$ and $[M-CH_3-COCRCH_3]^+$ ions).



(XXXVIII)
R = H, Br

(XXXIX)
R = H, Br, CH2CH2CN

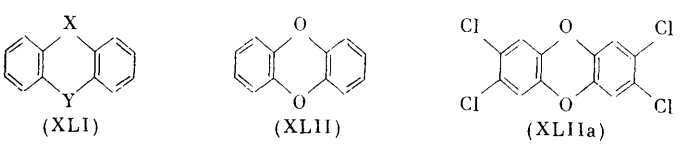
(XL)
R = Br, N3

In spiro-compounds (XXXIX) fragmentation is caused mainly by the typical fission of the four-membered ring into two halves,[64] as a result of which $[M-RNCO]^+$ and $[M-CH_2CO]^+$ ions are formed and then lose a CH_3 radical. Ions with *m/z* 222 and 224, obtained by elimination of $RCHCH_2O$ and CH_2CRCH_3 from M^+, are diagnostically important in compounds of the (XL) series.

IV. Analogues of 9,10-dihydroanthracene with heteroatoms at positions 9 and 10

The character of the dissociation of the type of compound represented by general formula (XLI) on ionisation is determined by the nature of the substituents in the aromatic ring and on the heteroatoms at positions 9 and 10. In the simplest representatives of this series the primary decomposition of M^+ is expulsion of carbenoid particles X or Y, the ease of eliminating which increases with an increase in the stability of the latter. As in the previous section these typical routes for decomposition leading to a heterocyclic analogue of fluorene ion-radicals are demonstrated in the example of compounds in which it occurs most (Table 3).

Compounds of this series may contain the same or different heteroatoms at positions 9 and 10. In view of this further consideration will be given to their mass spectral characteristics.



(XLI) (XLII) (XLIIa)

1. Analogues of 9,10-dihydroanthracene with the same heteroatoms at positions 9 and 10

Dibenzo-*p*-dioxins. Unsubstituted dibenzo-*p*-dioxin (XLII) possesses a very stable M^+ which is not capable of losing the heteroatom with the formation of the dibenzofuran system. The M^+ expels only two molecules of CO or HCO and CO to a marked extent.[67,77] The fragmentation of 2-nitrodibenzo-*p*-dioxin is linked with elimination of CO, HCO, NO_2 and also NO_2 + CO and NO_2 + HCO.[77]

Much work has been carried out on the mass spectrometric investigation of polychlorinated dibenzo-*p*-dioxins, the detection and identification of which in the environment has become an important problem in recent years. The exception toxicity of some of the isomers reinforces the need to develop highly sensitive, selective and isomer-specific analytic methods. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (XLIIa) possesses such high toxicity that even standards of

this substance are not recommended to be held in analytical laboraties.

It has been shown using 2,7- and 1.6-dichloro-, 1,3,6-trichloro- and 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxins and compound (XLIIa) as examples that their decomposition on EI is linked with the sequential elimination of CO and Cl. There are also marked peaks for $[M-2COCl]^+$ ions.[77,78] These features of the fragmentation are used for creating highly sensitive methods for the detection of compound (XLIIa) and its isomers chiefly using gas chromatography-mass spectrometry.[5,48,79–84] Mass spectrometry with chemical ionisation (gas-reactant O_2 or CH_4/NO_2) and negative ion recording possesses the greatest sensitivity and isomer specificity.[85–88] No less sensitive and specific is the method of tandem mass spectrometry (MS/MS) which was applied to M^+ and M^- ions generated from (XLIIa).[48,89] Decomposition of M^+, activated by collision with argon, leads to $[M-COCl]^+$ and $[M-2COCl]^+$ ions which characterise tetrachlorodibenzo-*p*-dioxins but do not permit their isomers to be distinguished. On activation by collision with argon, only $[M-Cl]^-$ and Cl^- ions are formed from M^-, which are not suitable for structural assignment. However with low energy collisions M^- ions form $[M-Cl+O]^-$, $[C_6H_{4-n}O_2Cl]_4^-$, $[M-HCl]^-$ and $[Cl]^-$ ions. With these, either directly or on the basis of peak intensity ratios, discrimination between 1,2,3,4-, 1,2,3,6-, 1,2,3,7- and 2,3,7,8-tetrachlorodibenzo-*p*-dioxins has been successful.[90]

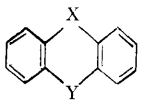
Table 3. Intensities of $[M-X]^+$ and $[M-Y]^+$ ions (as % maximal peak) in the mass spectra of compounds (XLI).

X	Y	$J_{[M-X]^+}$	$J_{[M-X]^+/J_{M^+}}$	$J_{[M-Y]^+}$	$J_{[M-Y]^+/J_{M^+}}$	Refs.
S	S	48	0.5	–	–	[65,66]
O	S	–	–	21	0.2	[67]
O	SO	–	–	100	1.2	[67]
O	Se	–	–	100	1.1	[67]
O	Te	–	–	100	1.3	[67]
O	AsCl	–	–	100	4.0	[68]
O	$SiCl_2$	–	–	100	1.1	[54,69]
O	$SnCl_2$	–	–	100	2.5	[70]
O	$SiHCH_3$	–	–	17	0.2	[54]
NH	S	–	–	53	0.5	[71]
NH	SO_2	–	–	12	0.1	[30]
NCH_3	SO	–	–	100	3.1	[72]
NH	AsCl	–	–	36	0.5	[73–75]
NH	$AsCH_3$	–	–	25	1.6	[73]
NC_2H_5	$SiHCH_3$	–	–	16	0.2	[54]
Se	Se	100	1.0	–	–	[76]*
NH	Te	–	–	100	1.1	[76]*
SiF_2	SiF_2	100	1.3	–	–	[54]
$SiCl_2$	$SiCl_2$	100	1.2	–	–	[54]

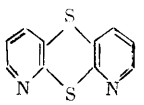
*Spectra were recorded on a laser microprobe mass spectrometer.

Some polybromo[91] and polybromochlorodibenzo-*p*-dioxins[92] have also been investigated by EI. It was shown that the M^+ of polybromo compounds lose Br, COBr, (Br + COBr) and (2Br + COBr). The formation of a large quantity of doubly charged ions was recorded.

Thianthrenes. The molecular ion of unsubstituted thianthrene (XLIII) is very stable and is capable of losing only S, CSH or S and CSH sequentially.[65,76] A similar type of fragmentation is also characteristic for diazathianthrene (XLIV).[66]



(XLIII) X = Y = S;
(XLV) X = S, Y = SO;
(XLVI) X = Y = SO;
(XLVII) X = S, Y = SO_2.

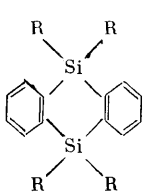


(XLIV)

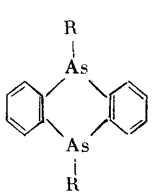
The sequential expulsion of S and H from M^+ was also observed for 2,3,7,8-, 1,4,6,9- and 1,3,7,9-tetramethylthianthrenes but elimination of CS and CSH was insignificant. The molecular ions of these compounds also lose CH_3 and then S.

The dissociation of the monosulphoxide (XLV)' and the disulphoxide (XLVI) of thianthrene on ionisation is fairly simple and is linked with the elimination of O and SO. In both cases the ion-radical of dibenzothiophene is formed in such processes and is generated from the M^+ of sulphone (XLVII) on expulsion of SO_2. SO is eliminated from the M^+ of (XLVII) as a result of skeletal rearrangment.[93]

Other compounds. The character of the fragmentation of 9,10-disila-9,10-dihydroanthracenes (XLVIII) depends on the nature of the substituents on the Si atoms.[54] The stable M^+ of the ancestor compound (R = H) may lose up to four H atoms, while seemingly $:SiH_2$ is lost from $[M-H]^+$ ions. The tetramethyl derivative (XLVIII, R = CH_3) has a weakly stable M^+ which readily loses CH_3 and then $:Si(CH_3)_2$. Decomposition of the tetramethoxy derivative (XLVIII, R = OCH_3) on EI is more complex. In this case the peaks for $[M-HSi(OCH_3)_2]^+$ and $[M-HSi(OCH_3)_2-CH_2O]^+$ ions are the most intense. In the case of the tetrahalogen compounds (XLVIII, R = F, Cl) the process of expelling dihalodisilyene from M^+ is clearly expressed and continues in the case of fluoride by elimination of H_2SiF_2 and of chloride by loss of a Cl atom.



(XLVIII)



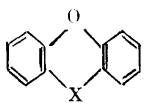
(XLIX) R = CH_3;
(L) R = Cl.

A specific character was observed for the fragmentation of derivatives of dihydroarsanthracenes (XLIX) and (L).[94] The molecular ion of the methyl derivative (XLIX) readily loses CH_3 and then As, CH_3 and As sequentially. In the case of the dichloro compound (L) the ions $[M-Cl]^+ \rightarrow [M-2Cl]^+ \rightarrow [M-2Cl-As]^+ \rightarrow [M-2Cl-2As]^+$ were formed sequentially from M^+ (the peak for the $[M-2Cl-As]^+$ ion possesses maximal intensity).

2. Analogues of 9,10-dihydroanthracene with different heteroatoms in positions 9 and 10

Phenoxathiins. The molecular ion of phenoxathiin (LI) is very stable and is capable of expelling CO, CHO and S and CHO sequentially.[67] 2,3,7,8-Tetramethylphenoxathiin is also stable on EI and the most marked decomposition of its M^+ is linked with the

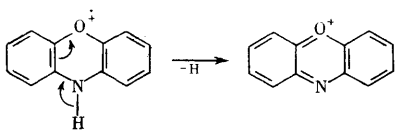
elimination of CH_3 and S or CH_3.[65] The main decomposition of its S-oxide (LII) is linked with ejection of SO, the M^+ loses an O atom to an insignificant extent. Sulphone (LIII) loses SOC in preference to SO_2 in the first stage of the decomposition.[93]



(LI) X = S;
(LII) X = SO;
(LIII) X = SO_2.

Phenoxazines. Phenoxazine (LIV) possesses a very stable M^+ the noticeable decomposition of which begins with fission of H (Scheme 17), after which CO is lost.[95,96] Nitro substituted phenoxazines lose a NO_2 group, 4,6-dinitro derivatives and a molecule of HNO_2 from the M^+.

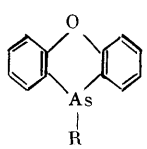
Scheme 17



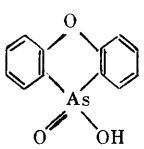
(LIV), M^+ $[M-H]^+$

In the latter case $[M-OH]^+$ ions are also formed with the participation of a hydrogen atom from the NH group.[95]

Phenoxarsines. Peaks for M^+ were recorded in the mass spectra of a large series of phenoxarsines (LV) and (LVI) which decomposed with the formation of $[M-R]^+$ and $[M-AsR]^+$ independent of the nature of the substituent R in the case of the compounds (LV) (the latter ions corresponding to dibenzofuran may be formed both in one step or several)[68,97]



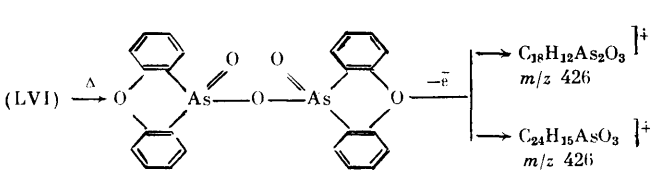
(LV) R = Cl, *p*-ClC_6H_4, 2-$C_6H_5OC_6H_4$, *p*-ClC_6H_4O.



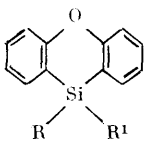
(LVI)

An interesting temperature dependence was observed for the mass spectrum of compound (LVI). At an ion source temperature below 350 °C it decomposed in a similar manner to compound (LV) with the formation of M^+ and $[M-HAsO_2]^+$ (*m/z* 243) ions. However at 390 °C condensation of two molecules occurred with elimination of water and a peak of M^+ with *m/z* 534 was present in the recorded mass spectrum and also a peak with *m/z* 426 corresponding to $[M-C_6H_4O_2]^+$ and $[M-AsO_2H]^+$ ions which decomposed further to ions with *m/z* 243 (Scheme 18).

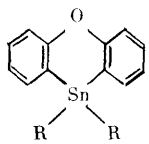
Scheme 18



Phenoxasilines and phenoxastannines. Decomposition on EI of 10,10-dimethyl- (LVII) and 10,10-diphenylphenoxasilines (LVIII) occurs mainly by expulsion of CH_3 and C_6H_5.[49,98] Fission of H and CH_3 from M^+ also leads to the most intense peak in the spectrum of their 10-methyl analogue (LIX).[54] However in the latter case $HSiH_3$ is lost from M^+ to a noticeable extent and such a process is not a characteristic of the first two compounds (here the formation of $[SiRR^1]^+$ ions is marked). A large number of rearrangement processes occurs on fragmentation of compounds (LVII) and (LVIII), in particular expulsion of SiO from $(M-R-R^1]^+$ ions or CH_2O, SiH_2O and SiHO from $[M-R]^+$ ions. The main and only fragmentation process for dichloro compound (LX) is ejection of $:SiCl_2$ from M^+.[54]



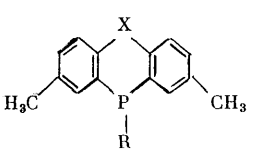
(LVII) R = R^1 = CH_3;
(LVIII) R = R^1 = C_6H_5;
(LIX) R = H, R^1 = CH_3;
(LX) R = R^1 = Cl.



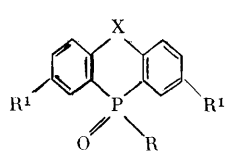
(LXI)

The nature of the substituent on the tin atom appreciably influences the fragmentation of the phenoxastannines (LXI) although the formation of $[M-R]^+$ ions is natural for all of them.[49,99,100] After elimination of radical R in the case of compounds (LXI, R = C_2H_5 and C_4H_9), olefin (R−H) is readily lost and the resulting ion then eliminates C_6H_4 two times. The methyl and phenyl derivatives (LXI, R = CH_3 and C_6H_5), after expulsion of R, lose fragments C_6H_4O, $C_{12}H_8O$ or C_6H_4. Fission of $SnCl_2$ is the main fragmentation route for the M^+ of dichloro compound (LXI, R = Cl).

Phenoxaphosphines and phenothiaphosphines. Phenoxaphosphines (LXII) and phenothiaphosphines (LXIII) are similar in their character of dissociation on ionisation.[101–104] Loss of RHP is a characteristic of their M^+.



(LXII) X = O, R = C_6H_5;
(LXIII) X = S, R = C_6H_5,
p-$CH_3C_6H_4$

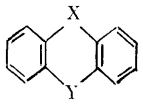


(LXIV) X = S, R = OH, OCH_3, R^1 = CH_3;
(LXV) X = SO_2, R = CH_3, C_6H_5,
p-$CH_3C_6H_4$, R^1 = F, Cl, CH_3.

The oxides of derivatives (LXIV) form very stable M^+ which may lose PO_2H and SH (when R = OH). The loss of SH is insignificant for the corresponding esters (R = OCH_3) but OCH_3 is readily eliminated and then S or PO. The peaks for M^+ and $[M-CH_3]^+$ ions possess the greatest intensity in the mass spectra of compounds (LXV). In all cases noticeable peaks were encountered for $[M-HPOR]^+$ ions.[102,103]

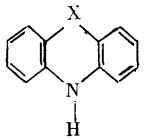
Phenoselenine (LXVI) and phenotellurine (LXVII) are fairly stable on EI and the sole primary route for their decomposition is expulsion of Se and Te respectively.[67] The resulting dibenzofuran

ions lose CO and CHO. A similar decomposition is characteristic of their sulphur analogues (LXVIII).[105]



(LXVI) X = O, Y = Se;
(LXVII) X = O, Y = Te;
(LXVIII) X = S, Y = Se, Te

Phenothiazines. This series of compounds is of interest since it includes a large number of pharmacologically active compounds, particularly tranquilisers. Unsubstituted phenothiazine (LXIX) possesses a very stable M^+, the most noticeable decomposition of which is caused by elimination of H, S or SH.[30,71] Its *S*-oxide (LXX) and *S,S*-dioxide (LXXI) differ fairly strongly in fragmentation character.[30] The former is intensively decomposed with the formation of $[M-O]^+$, $[M-OH]^+$, $[M-CO]^+$, $[M-CO-H]^+$ (base peak) and $[M-SO]^+$ ions and the second has a very stable M^+ which loses OH, CO, SO and H, SO and CO or SO_2.



(LXIX) X = S;
(LXX) X = SO;
(LXXI) X = SO_2

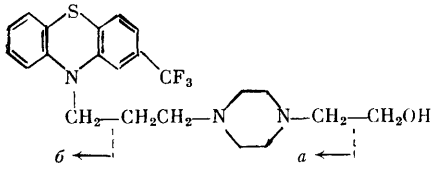


(LXXII) R = H;
(LXXIII) R = Cl.

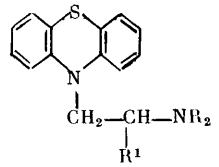
The main peaks in the mass spectra of the large series of physiologically active compounds of the phenothiazine series, among which are promazine (LXXII) and chlorpromazine (LXXIII),[71,72,106] are caused by ions formed on breaking the α-C−C bond relative to the nitrogen of the side chain, e.g. $CH_2=\overset{+}{N}(CH_3)_2$ (*m/z* 58) for (LXXII) and (LXXIII). The groups $HN(CH_3)_2$ or $H_2N(CH_3)_2$ may be lost from M^+ and also the substituent from the exocyclic nitrogen atom with migration of H atom to the heterocyclic ion. In the case of methoxyphenothiazines decomposition begins with expulsion of a CH_3 group and continues with loss of CO and S. Fragmentation of phenothiazine *S*-oxides with *N*-alkyl groups is complicated due to decomposition involving the sulphoxide group.[106,107]

The fragmentation regularities recorded for phenthiazine are used for the determination of chlorpromazine (LXXIII) metabolites in man.[108]

The GC−MS method (EI) in combination with silylation is used for the quantitative determination of the tranquiliser fluorphenazine (LXXIV) in plasma at the 50 pq ml^{-1} level.[109] It is proposed to carry out the determination with ions *a* and *b*.



(LXXIV)



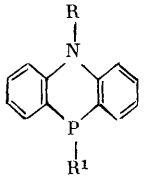
(LXXV) R = R^1 = CH_3;
(LXXVI) R = C_2H_5, R^1 = CH_3;
(LXXVII) R = C_2H_5, R^1 = H.

The metabolites of promazine (LXXII), which are volatile with difficulty, have been investigated with combinations of microliquid chromatography and mass spectrometry to provide mass spectra by chemical ionisation. Previously, using (LXXIII), 2-hydroxy- and acetopromazine as examples, it was shown that such mass spectra contain practically only peaks for $[M+H]^+$ ions.[110]

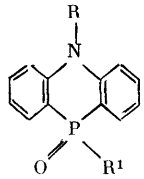
Mass spectra were obtained for a large series of phenothiazines under conditions of chemical ionisation (gas reagent was NH_3, CH_4/N_2O) recording negative ions.[111] For the majority of these compounds among which are (LXXII), (LXXIII), promethazine (LXXV), propiomazine, prochlorperazine, ethopropazine (LXXVI) and diethazine (LXXVII), the presence of peaks for $[M-H]^-$ ions in such spectra is characteristic.

The peaks for $[M-CH_2CH_2CH_2N(CH_3)_2]^-$ ions were the base peaks in the spectra of compounds of the type of (LXXII) and (LXXIII) with three C atoms between the nitrogen atoms. In the case of compounds of type (LXXV)−(LXXVII), containing two C atoms between the nitrogen atoms, the base peaks in the spectra corresponded most frequently to $[M-H_2NR_2]^-$ ions although peaks for $[M-CH_2CHR^1NR_2]^-$ ions were also present.

9,10-Dihydrophenophosphazines. The EI mass spectra of 9,10-dihydrophenophosphazines (LXXVIII) have stable M^+ which decompose by loss of R^1 and then R, since $[M-R^1]^+$ ions are the base peaks even at low electron energies. In the case of the 10-oxide derivative (LXXIX) the stability of M^+ is increased but the most noticeable dissociation processes are caused by the elimination of R^1 and PO.[74,112]



(LXXVIII)

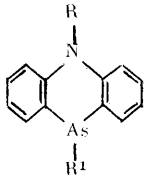


(LXXIX)

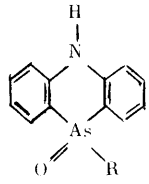
The adiabatic ionisation potentials of compounds (LXXVIII, R = CH_3, R^1 = CH_3, or C_6H_5) and (LXXIX, R = CH_3, R^1 = CH_3, or C_6H_5) were measured by photoionisation mass spectrometry. They were 7.03, 6.90, 7.50 and 7.40 eV respectively. Comparison of these values shows that the influence of the substituent is transmitted in the same way through both a trivalent and a pentavalent phosphorus atom.[113]

9,10-Dihydrophenarsazines. The EI mass spectra of substituted 9,10-dihydrophenarsazines (LXXX) contain M^+ peaks which readily lose the R^1 radical with the formation of the base ion and the latter ejects an As atom.[73−75,114] In some cases the one-step nature of the $M^+ \rightarrow [M-AsR^1]^+$ transition was demonstrated with metastable ions. In the case of (LXXX, R = H, R^1 = SCN) the formation was recorded of $[M-HSCN]^+$ ions which later eliminate As.[114]

The mass spectra of compounds (LXXXI, R = CH_3, C_6H_5, 2-ClC_6H_4) [74] and (LXXXI, R = OH) [114] contain M^+ peaks but the base peaks were of $[M-R]^+$ ions in the first case and $M-H_2O]^+$ ions in the second.



(LXXX) R = H, CH_3, C_6H_5; R^1 = Cl, OCH_3, CH_3, C_6H_5, 2-ClC_6H_4



(LXXXI)

* * *

The main influence of the fragmentation on the EI of derivatives and heterocyclic analogues of 9,10-dihydroanthracene therefore proved to be the nature of the heteroatom, the character of the substitution at positions 9 and 10 and also the type of substituent in the phenylene rings. In the case of such derivatives of dihydroanthracene as anthraquinones and also its analogues containing heteroatoms of the type S, SO, SO_2, Se, Te and also substituted Si, P, and As atoms in positions 9 or 10, the principal be the elimination of particles of the carbene type from these positions with contraction of the central ring to a five-membered ring. The ease of this process increased with the increase in stability of the eliminated carbenoid particle. For example the elimination of dihalosilyene, and of AsCl, Te, Se and P(O)OH determines the main character of the decomposition of the corresponding analogues of 9,10-dihydroanthracene.

A specific route for the fragmentation of 9-alkyl- or aryl-substituted 9,10-dihydro-9-silanthracenes is the expulsion from M^+ of the corresponding alkane or arene. It is possible that silanthracene ions are formed containing a Si=C double bond having no analogue in the unionised state.

Fragmentation of substituents in the series being considered depends on their location in the molecule. If the substituting group is side-by-side with the heteroatom the '*peri*-effect' is decisive. Fission of substituents in the phenylene rings and also in the *meso* position or at the heteroatom occurs in a similar manner to the decomposition of the corresponding aromatic or heterocyclic derivatives.

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