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RECENT PROGRESS IN THE MASS SPECTROMETRY OF HETEROCYCLIC COMPOUNDS

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Mass spectrometry of heterocyclic compounds is reviewed with respect to (1) hydrogen scramblings and skeletal rearrangements, (2) ion structures, and (3) fragmentations. The fragmentations reviewed here are those of azoles, pyridine-carboxylic acids, polyazaindenes and related compounds, seven- and eight-membered heterocyclic rings, chromene derivatives, and heterocyclic rings containing the Group IV and V elements as a heteroatom.

ABOUT a decade has elapsed since the introduction of mass spectrometry as a tool for the investigation of organic chemistry. Our understanding of this field underwent a remarkable increase and the amount of data available on the electron impact induced fragmentations of organic compounds, especially, heterocyclic compounds has increased tremendously. There appeared a number of monographs and review articles[1-10] dealing with the mass

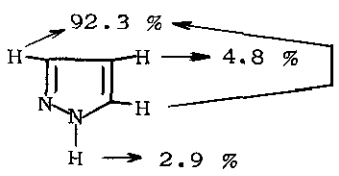
spectrometry of heterocyclic compounds, all of which are very informative not only for heterocyclic chemists but also for pharmaceutical chemists wishing to apply mass spectrometry to drug analysis.

As the basic fragmentations of heterocyclic compounds have been dealt with in these monographs and reviews to a greater or less extent, the present review has aimed to provide the up-to-date knowledge concerning (1) hydrogen scramblings and skeletal rearrangements, (2) ion structures, and (3) fragmentations discovered recently or studied in more detail. Attention is drawn to the explanation of fragmentation modes in terms of the Quasi Equilibrium Theory (QET). To limit this review to a reasonable size, the subjects taken up here are selective rather than comprehensive. Literature citations are taken from the period 1970-1973, with occasional references to earlier papers. Negative ion mass spectrometry of heterocyclic compounds is beyond the scope of the present review. Russian journals were not referred to owing to language difficulty.

(1) Hydrogen scramblings and skeletal rearrangements.

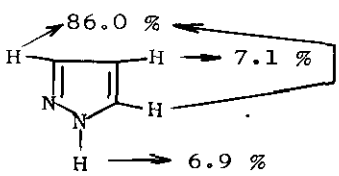
Like benzenoid compounds, ring-hydrogens of heterocyclic analogues of benzene are prone to lose positional identity (scrambling) on electron impact.[11] For instance, pyridine,[11] quinoline,[11] benzothiazole,[11] and 1,2-benzisothiazole[12] undergo hydrogen scramblings prior to the elimination of HCN from the molecular ion and the mass spectra of benzofuran-2-d and -5-d[11] indicate the occurrence of partial scramblings of H/D before loss of CHO from the molecular ion. But randomization of

ring-hydrogens of oxazole, isoxazole, thiazole, and pyrazole has not been observed to any significant extent. Pyrazole (I) is known to lose H and HCN from the molecular ion;[13] syntheses of the pyrazoles selectively deuteriated at N(1), C(3), C(4), and C(5) and determination of the intensity ratios $(M-H)^+/(M-D)^+$ and $(M-HCN)^{+\cdot}/(M-DCN)^{+\cdot}$ for each pyrazole have revealed that the hydrogen atoms at C(3) and C(5) are predominantly eliminated from the molecular ion and also incorporated into the eliminated HCN as shown below.[14]



$(M-H)^+$

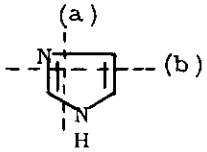
(I)



$(M-HCN)^{+\cdot}$

(I)

Occurrence of hydrogen scramblings has been suggested for imidazole (II) because the fragmentation (a) can not account for all of HCN molecules which are eliminated from the molecular ion.[15] Examination of the intensity ratios $(M-H)^+/(M-D)^+$ and $(M-HCN)^{+\cdot}/(M-DCN)^{+\cdot}$ in the mass spectra of selectively deuteriated imidazoles confirmed the preferential incorporation of the C(2)-H into the eliminated HCN and unexpectedly revealed that a hydrogen atom



(II)

eliminated from the molecular ion arises from C(4), the loss proceeding much faster than hydrogen scramblings. High specificity for loss of a hydrogen from C(4) suggests that the loss of HCN from this position (b) is also possible and casts doubt on the earlier suggestion[15] for the occurrence of randomization.[16]

The situation is quite complicated for thiophene. The studies of deuterium-labelled thiophenes indicate that considerable but not complete hydrogen scramblings preceed the decomposition into CHS^+, $C_2H_2S^+$, and $C_3H_3^+$ ions, whereas the spectra of ^{13}C-labelled thiophenes indicate the occurrence of substantial carbon scramblings. De Jong concluded from these studies that the production of CHS^+ and $C_3H_3^+$ ions is preceeded by partial carbon scramblings (hydrogen migration is of minor importance) and hydrogen scramblings predominate over carbon scramblings in the loss of C_2H_2 to give the $C_2H_2S^+$ ion.[17]

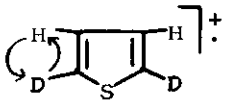
A substituent on the thiophene ring also loses its positional identity on electron impact. For instance, fragmentation of 3-phenylthiophene occurs after the migration of a phenyl group from C(3) to C(2) and 2-bromo-3-phenylthiophene decomposes after the migration of a bromine atom from C(2) to C(5).[18] It is apparent from these few examples that caution must be taken in the proposal of ion structures and fragmentation mechanisms based on labelling studies only.

Hydrogen randomization takes place for the ion of longer life time. Thus even if the randomization is incomplete for a daughter ion produced at 70 eV, hydrogen scrambling is complete for a metastable ion observed in the first and second field-free regions at this beam energy and it is also complete for a daughter ion produced at low beam energy. The intensity ratio

$(M\text{-}HCN)^{+\cdot}/(M\text{-}DCN)^{+\cdot}$ in the mass spectrum of 3-d-1,2-benzisothiazole is 1:3.3 at 70 eV, but the intensity ratio of the metastable ions in the first field-free region is 2.3:1.[12] It is evident that the slow loss of HCN from the molecular ion of 1,2-benzisothiazole proceeds with a high degree of hydrogen scramblings.

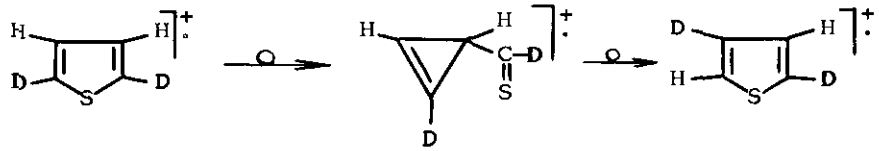
The mechanism of hydrogen scramblings is not yet clear, but at least three processes could be envisaged.[11]

(A) Reciprocal H/D exchange on the intact carbon skeleton of the molecular ion. This is explained by the change of 2,5-d_2-thiophene (III-a).



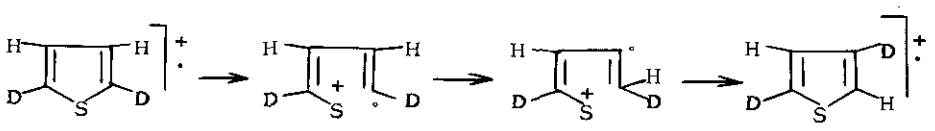
(III-a)

(B) Transposition of ring atoms of the molecular ion without breaking C-H linkages. 2,5-d_2-Thiophene (III-a) changes into 2,4-d_2-thiophene (III-c) by way of 1-cyclopropene-3-thioaldehyde (III-b). An analogous mechanism is operative in the photo-induced transpositions of thiophene and other related five-membered heterocyclic compounds.



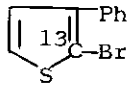
(III-a) (III-b) (III-c)

(C) Formation of open-chain radical cation followed by hydrogen randomization and its ring-closure, as illustrated by the change of (III-a) into (III-c).

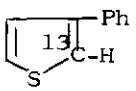


(III-a) (III-c)

In this connection it is relevant to refer to the observation of Rennekamp, et al .[18] The mass spectrum of 2-^{13}C-2-bromo-3-phenylthiophene (IV) shows the loss of ^{12}CBrS to be almost equal to that of ^{13}CBrS, indicating that breaking of a ^{13}C-Br bond precedes the formation of a ^{12}C-Br bond. An $(M-C_3H_3)^+$ ion is present in the mass spectrum of 2-^{13}C-3-phenylthiophene (V). If this process takes place by the mechanism (B), loss of ^{13}C label should be 100 %. However, the fact that it is only 43 % indicates that, at least in part, the process involves phenyl migration accompanied by C-phenyl bond cleavage, ^{13}C-H bond cleavage, and hydrogen migration back to the position from which the phenyl migrated.



(IV)

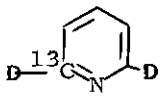


(V)

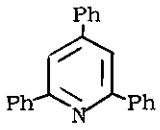
These results suggest that a substituent migrates after ring opening, and if this result could be general, it would imply that the hydrogen migration of heteroaromatic compounds mainly takes place via the mechanism (C).

As noted previously, pyridine undergoes extensive hydrogen randomization on electron impact. Detailed studies on the mass spectra of 2-^{13}C-pyridine and 2-^{13}C-2,6-d_2-pyridine (VI) have

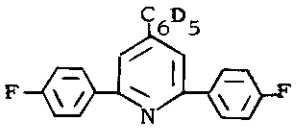
disclosed that ring carbon scramblings take place independently of any hydrogen randomization;[19] if the carbon scrambling occurs by way of the mechanism (B), the ^{13}C-deuterium bond should not be cleaved.



(VI)



(VII)

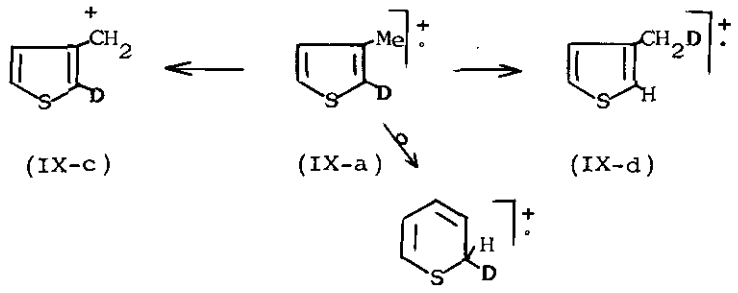


(VIII)

The molecular ions of 2,3,4,5,6-pentaarylpyridine[20] and 2,4,6-triarylpyridine (VII)[21] undergo extensive hydrogen randomization between aryl groups, but they do not undergo aryl migration. For instance, the phenyl group eliminated from the molecular ion of (VII) originates from α- (96 %) and γ-positions (4 %), whereas the corresponding pyridine (VIII) labelled with deuterium and fluorine atoms ejects $C_6H_xD_{(4-x)}F$ and $C_6H_xD_{5-x}$ in the ratio of 96 : 4. This result suggests the occurrence of inter-ring hydrogen randomization.

It is well known that the $(M-1)^+$ ion of toluene can be represented as the tropylium ion, which would arise after the irreversible isomerization of toluene radical cation into cycloheptatriene radical cation followed by loss of a hydrogen atom.[11] Studies of the mass spectrum of 2-d-3-methylthiophene (IX-a) have shown the occurrence of extensive H/D randomization; ca. 35 % of the molecular ion lose a hydrogen from Me to give an ion (IX-c) at 16-70 eV before the isomerization into the thiapyran radical cation (IX-b) and 4-6 % of the molecular ion eliminate a deuterium atom from C(2) at 16-70 eV. As loss of a vinylic hydrogen is energetically

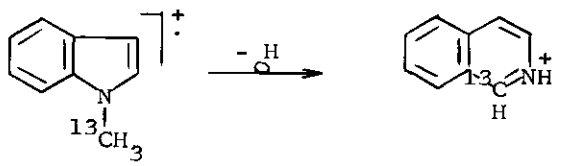
unfavourable, it appears that H/D exchange to produce the ion (IX-d) precedes a specific deuterium loss from C(2). Therefore, the greater part of the molecular ion of 3-methylthiophene appear to be randomized before loss of a hydrogen atom. However, at lower electron beam energies, elimination of hydrogen atoms from the three ring positions becomes equally probable and occurs most probably from the molecular ion that has ring-expanded to (IX-b).[22]



(IX-c) (IX-a) (IX-d)

(IX-b)

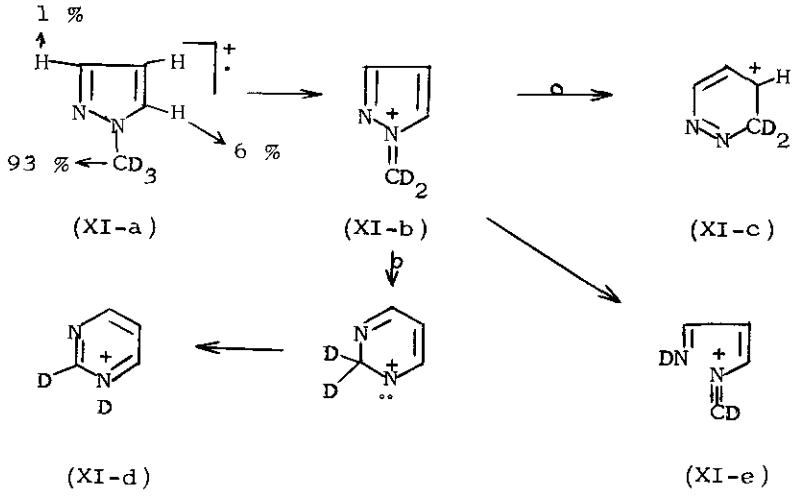
The molecular ion of 2-methyl- and 3-methyl-indoles, respectively, loses a Me hydrogen, the resulting ion undergoing ring expansion to produce the quinolinium ion.[23] The mass spectra of 2-methylindoles labelled at Me and C(2), respectively, with a ^{13}C atom have disclosed that bond-forming between the Me carbon and C(3) accounts for ≥ 58 % of the total ring enlargement processes and bond-making between the Me carbon and N(1) accounts for ≥ 28 % of the total processes.[24] The mass spectrum of 1-^{13}C-methylindole (X-a) shows the retention of 52 % of the labels in the $(M-H_2CN)^+$ ion, which implies the $(M-1)^+$ ion to be represented as the isoquinolinium ion (X-b).



(X-a) (X-b)

Both of the mass spectra of 2-methyl- and 3-methyl-indoles exhibit a metastable ion at m/e 81.6 corresponding to the transition $(M-H)^+ \longrightarrow (M-H_2CN)^+$ and the intensity ratio m/e 81.6/$(M-H_2CN)^+$ is nearly equal in both spectra. This implies that the $(M-1)^+$ ions in both spectra have the same structure (the quinolinium ion).[25] The Ion Kinetic Energy (I.K.E.) spectral studies of the $(M-1)^+$ and $(M-H_2CN)^+$ ions of methylindoles also allow a conclusion to be drawn that the $(M-1)^+$ ions of 2-methyl- and 3-methyl-indoles have a different structure from that of the $(M-1)^+$ ion of 1-methylindole.[25]

The molecular ion of 1-d_3-methylpyrazole (XI-a) predominantly eliminates one Me hydrogen (see the formula), the resulting $(M-1)^+$ ion (XI-b) decomposing by loss of N_2 and HCN.[26] The loss of N_2 implies the cleavage of the N(1)-C(5)-bond of the ion (XI-b) and its ring enlargement into the ion (XI-c). The origin of the hydrogen atom incorporated into HCN is complicated (60 % from Me, 20 % from C(3)-H, and 20 % from C(5)-H), whereas the mass spectrum of 2-^{15}N-1-methylpyrazole has disclosed that incorporation of the N(1)-atom into HCN is greater than that of the N(2)-atom. These labelling studies indicate that two processes, i.e., the ring enlargement into the ion (XI-d) and the formation of the open-chain ion (XI-e) are implicated in the loss of HCN from the $(M-1)^+$ ion of 1-methylpyrazole.



Ring enlargement of the molecular ion and/or the $(M-1)^+$ ion is a common phenomenon in the mass spectrometry of methyl-substituted heterocyclic compounds, a further few examples which have been corroborated by extensive labelling studies being 2-d_3-2-methylquinoline,[27] 2-d_3-2-methylpyridine,[28] and 4-d_3-4-methylpyridine.[28] Almost complete hydrogen randomization takes place before loss of HCN (DCN) in the molecular ion of these compounds. However, the preference for the incorporation of the C(2)-H into HCN eliminated from the molecular ion of 4-d_3-4-methylpyridine[29] could not be accounted for in an analogous way as the ring expansion of toluene radical cation into cycloheptatriene radical cation.[30]

Another factor which makes the interpretation of the mass spectra complicated is skeletal rearrangements, which are commonly encountered in the mass spectrometry of heterocyclic compounds, and hence great care is required in applying mass spectrometry to the structural elucidation. Adequate reviews[31,32] which cover the rearrangements reported before 1970 are available.

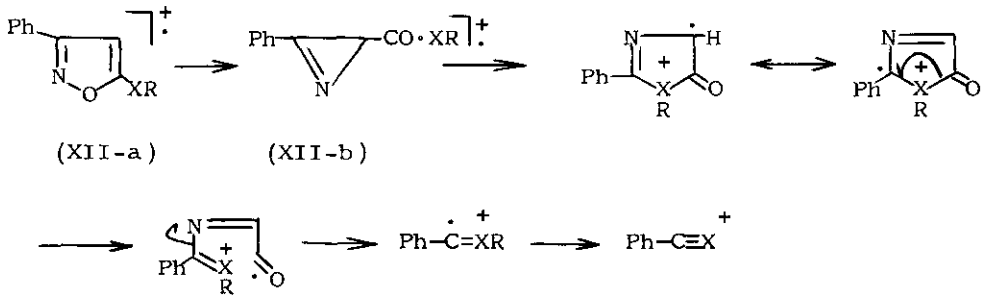
The rearrangement reaction in a mass spectrometer can be explained in terms of QET: $K=\nu(\frac{E-E^{o}}{E})^{s-1}$, which relates the rate constant K of the fragmentation reaction with the internal energy E (E^{o} is the activation energy for the reaction; ν is the frequency factor; s is the effective number of oscillators). If we assume that a simple bond cleavage reaction (the rate constant K_1 and the activation energy E_1^{o}) and a rearrangement reaction (the rate constant K_2 and the activation energy E_2^{o}) compete for an ion possessing an internal energy E, the following relationships can be written: $K_1=\nu_1(\frac{E-E_1^{o}}{E})^{s-1}$ and $K_2=\nu_2(\frac{E-E_2^{o}}{E})^{s-1}$.

In rearrangement reactions the transition state must take up a rigid orientation of atoms (or groups) in which a partial bond is being formed. The relatively low probability of attaining such a rigid orientation lowers the reaction rate and ν will be lowered than that in a simple bond cleavage reaction ($\nu_1 > \nu_2$). Further, the activation energy E^{o} for the rearrangement is lower than that of a simple bond cleavage reaction ($E_1^{o} > E_2^{o}$) because bond(s) are cleaved and newly formed. Under high electron beam energy impact the term $(\frac{E-E_1^{o}}{E})^{s-1}$ is almost equal to the term $(\frac{E-E_2^{o}}{E})^{s-1}$ and hence K_1 is larger than K_2 if ν_1 is larger than ν_2. Under low electron beam energy impact the term $(\frac{E-E_2^{o}}{E})^{s-1}$ is larger than the term $(\frac{E-E_1^{o}}{E})^{s-1}$ because of the relationship $E_1^{o} > E_2^{o}$ and hence K_1 is almost equal to K_2. Therefore, effective competition of a simple bond cleavage and a rearrangement reaction is observed only under low electron beam energy impact.

Rearrangement reactions in a mass spectrometer have been classified in a number of types,[32] the most common being the reaction $ABC^{+\cdot} \rightarrow AC^{+\cdot} + B$ which means the loss of a neutral molecule B from the radical cation $ABC^{+\cdot}$ to give a fragment radical cation $AC^{+\cdot}$.

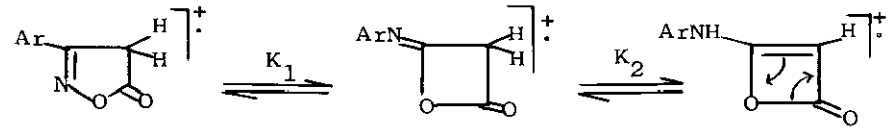
This type of the rearrangement is illustrated by the mass spectra of isoxazole derivatives as an example.

The high energy mass spectra of 3-phenylisoxazoles substituted at C(5) with a methoxy,[33] amino,[34] or methylthio[34] group (XII-a; XR=OMe), (XII-a; XR=NH_2), and (XII-a; XR=SMe) display an $(M-CO-HCN)^{+\cdot}$ ion in high abundance (it is uncertain whether CO and HCN are eliminated in one or two steps). Loss of a Me or hydrogen radical from this odd electron species is also very important and the $(M-CO-HCN-Me)^+$ ion is the base peak in the spectrum of 5-methoxy-3-phenylisoxazole.[33] As a similar behaviour is observed in the mass spectrum of 2-carbonyl-substituted-3-phenyl-2H-azirine (XII-b) which is the valence bond isomer of the isoxazole (XII-a),[34,35] the molecular ion of the isoxazole (XII-a) is postulated to decompose <u>via</u> the corresponding 2H-azirine radical cation. This rearrangement is still important in the spectra determined at low electron beam energy,[33] in agreement with the prediction from QET. The following rationalization has been advanced for this interesting rearrangement. The mass spectra of 4-phenyl-5-methyl-, 3-methyl-5-phenyl-, and 4-methyl-5-phenyl-isoxazoles also exhibit the $(M-CO-HCN)^{+\cdot}$ ion in moderate abundance at 70 and 12 eV and another mechanism could be envisaged for this rearrangement (see the original paper).[36]



(XII-a) (XII-b)

A recent study of Cum, et al. on the 70 eV mass spectra of 3-arylisoxazol-5(4H)-ones (XIII; Ar=Ph) and (XIII; Ar=p-$NO_2C_6H_4$) using modern techniques has also uncovered a very interesting 1,2-sigmatropic aryl migration followed by two hydrogen shifts to produce an arylamine radical cation.[37] There is a primary kinetic isotope effect (K_H/K_D=4.4) operating on the rate of C_3O_2 loss from the molecular ion and it was concluded that a hydrogen is transferred in the rate-determining step, preceded by a fast process (K_1) which involves the phenyl migration, i.e., $K_1 \gg K_2$ and/or K_4.



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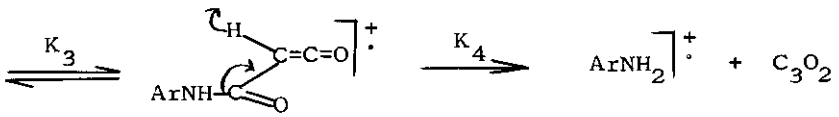
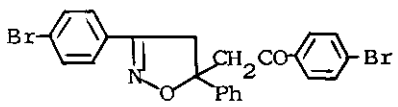
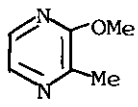


The heterocyclic compounds which undergo the $ABC^{+\cdot} \rightarrow AC^{+\cdot} + B$ type skeletal rearrangements are shown below together with the neutral molecule eliminated (for the proposed rearrangement mechanisms see the original papers).



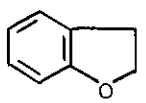
(XIV)[38]

$(M-H_2O_2)^{+\cdot}$



(XV)[39]

$(M-H_2O)^{+\cdot}$



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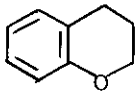

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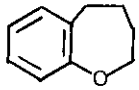

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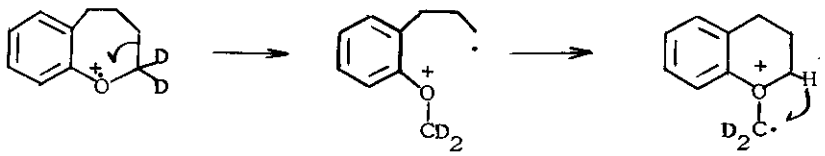
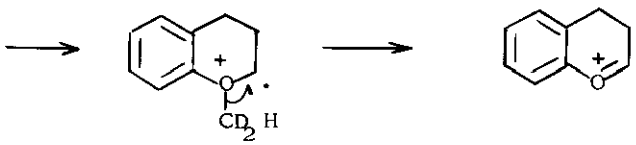


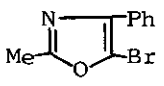
(XXIV-a)



(XXIV-b) (XXIV-c)

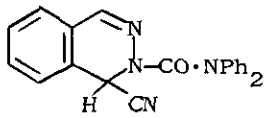
A much more complex mechanism is implicated in the genesis of the $(M-Me)^+$ ion of chroman (XXIII). Deuterium and ^{13}C labelling studies have revealed that an analogous ring contraction process as delineated above, i.e., the incorporation of the CH_2 group adjacent to the oxygen atom and C(3)-H in the Me group eliminated accounts for less than 50 % of the ion.[48]

Dependence of the skeletal rearrangement accompanied by ring contraction is also evident in the mass spectra of N-acetylpyrrolidine (XXV),[49] N-acetylpiperidine (XXVI),[49] N-acetylhexahydroazepine (XXVII),[49] and N-acetylmorpholine (XXVIII).[50] The Me group eliminated from the molecular ion arises from an acetyl group in the spectrum of (XXV), but with the increase of ring size the intensity of the $(M-Me)^+$ ion becomes larger and the leaving Me group arises from the positions other than the acetyl group. For instance, the ring contraction of the molecular ion (XXVI-a)



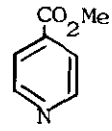
(XVI)[40]

$(M-CO)^{+\cdot}$



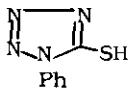
(XVII)[41]

$(M-PhNCO)^{+\cdot}$



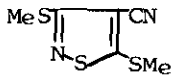
(XVIII)[42]

$(M-CO_2)^{+\cdot}$



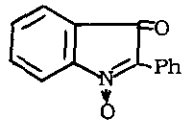
(XIX)[43]

$(M-N_2S)^{+\cdot}$



(XX)[44]

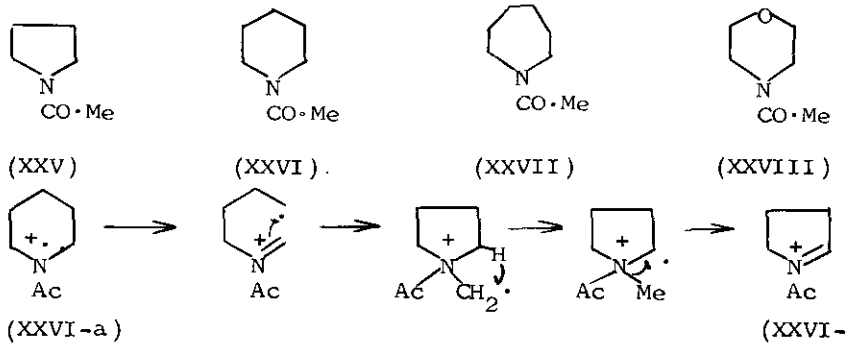
$(M-S_2)^{+\cdot}$



(XXI)[45]

$(M-CO_2)^{+\cdot}$

An interesting skeletal rearrangement depending on the ring size has been reported independently from two Laboratories. A great difference was found in the intensity of the $(M-Me)^+$ ion in the mass spectra of 2,3-dihydrobenzofuran (XXII), chroman (XXIII), and 2,3,4,5-tetrahydro-1-benzoxepin (XXIV); this ion is absent for (XXII) and appears in the relative intensity of 13 % for (XXIII), but it is very strong (R.I. 57 %) for (XXIV). Detailed deuterium labelling studies have shown that the molecular ion (XXIV-a) undergoes ring contraction to a six-membered radical cation (XXIV-b) from which the CD_2H group is ejected to give the ion (XXIV-c).[46] Operation of a similar rearrangement accompanied by ring contraction has been discovered in the spectrum of 2,3-dihydro-1-benzoxepin.[47] As the Me radical has no special stability, this rearrangement will depend on the stability of the product ion.

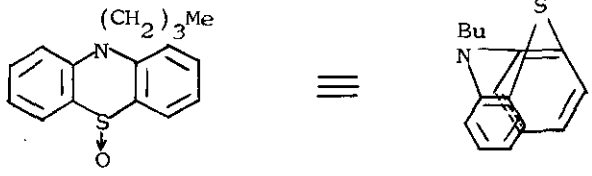


(XXV) (XXVI) (XXVII) (XXVIII)

(XXVI-a) (XXVI-b)

accompanied by the loss of Me to give an ion (XXVI-b) accounts for 40 % of the total $(M-Me)^+$ ion current (loss of the acetyl Me is 17 %),[51] whereas the ring contraction process is mostly responsible for the $(M-Me)^+$ ion in the spectrum of N-acetylhexahydroazepine (XXVII).[50]

Other examples on the skeletal rearrangement of the molecular ion accompanied by a radical loss to give an even-electron species are shown below. Loss of an OH radical from the molecular ion of 10-n-butylphenothiazine-5-oxide (XXIX) is possible only when the molecular ion takes the <u>extra-configuration</u> (XXIX').

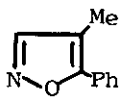


(XXIX)[52] (XXIX')

$(M-OH)^+$

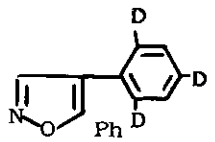
(XXX)[53] (XXXI)[54]

$(M-SeH)^+$ $(M-HS_2)^+$



(XXXII)[36]

$(M-CHO)^+$



(XXXIII)[55]

$(M-C_8H_2D_3O)^+$

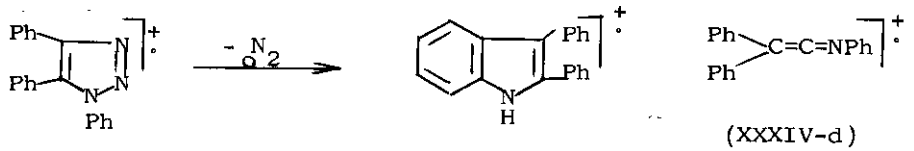
(2) Ion structures.

One of the most important yet the most troublesome problems in the mass spectrometry of organic compounds is the question of ion structures, and chemists used to rationalize the fragmentations by using organic chemically reasonable structures and corroborate the fragmentation mechanism they proposed with deuterium labelling and comparison with the mass spectrum of a substance predicted as an intermediate of the fragmentation. However, these methods have pitfalls and are far from complete; for instance, scrambling is an important pitfall in the deuterium labelling technique as noted in the section (1).

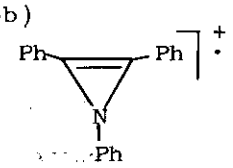
There has been an obvious need for more powerful and reliable methods to be devised for the structural inference of ions produced by electron impact. Nowadays, such elaborate techniques as (i) heats of formation of fragment ions, (ii) application of ion cyclotron resonance spectroscopy, (iii) metastable ion characteristics, and (iv) substituent effects are available. In addition, comparison with the photochemically and thermally induced reactions of the compound under consideration has often been made (see Ref. 32). However, great care should be taken in

applying any of these techniques to the structural inference of ions because these approaches often give a different and contradictory result. Some of these approaches are explained by citing examples from the field of heterocyclic chemistry.

The molecular ion of 1,4,5-triphenyl-1H-1,2,3-triazole (XXXIV-a) loses a molecule of nitrogen.[56] The radical cations of 2,3-diphenylindole (XXXIV-b), 1,2,3-triphenyl-1H-azirine (XXXIV-c), and triphenylketenimine (XXXIV-d) appear to be plausible structures for the resulting ion, among which the structure (XXXIV-b) was ruled out by comparison with the spectrum of an authentic compound. Despite the spectral similarity, the ketenimine structure (XXXIV-d) was also eliminated from thermodynamic consideration, since heat of formation (ΔH_f) of the $(M-N_2)^{+\cdot}$ ion of (XXXIV-a) (360 Kcal/mol) is different from that of (XXXIV-d) (297 Kcal/mol) (there is an important pitfall in this technique as described later). The ketenimine structure was also ruled out on the basis of metastable ion characteristics observed in the spectra of 1-m-methoxyphenyl-4,5-diphenyl-1H-1,2,3-triazole (XXXV-a) and the corresponding ketenimine (XXXV-b). Although the 1H-azirine structure (XXXV-c) has been claimed for the $(M-N_2)^{+\cdot}$ ion of (XXXIV-a) because of the good agreement of the observed (360 Kcal/mol) and the calculated (361 Kcal/mol) heats of formation of (XXXIV-c), this conclusion

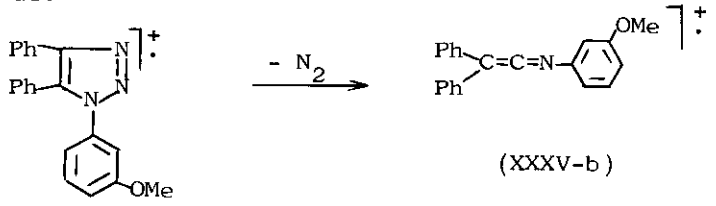


(XXXIV-a) (XXXIV-b) (XXXIV-d)



(XXXIV-c)

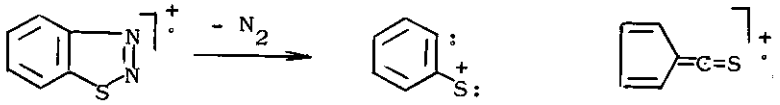
should be ragarded still tentative because energy parameters required to the calculation of ΔH_f of (XXXIV-c) have been derived by analogy and estimation of kinetic shift (vide infra) has not been made.



(XXXV-a) (XXXV-b)

The molecular ion of 1,2,3-thiadiazole (XXXVI-a) loses a molecule of nitrogen,[57-59] and plausible structures for the resulting ion are the radical cations of the carbene (XXXVI-b), the thiirene (XXXVI-c), and the thioketene (XXXVI-d). The corresponding 1,2,3-selenadiazole behaves similarly on electron impact[60] and the mass spectrum of 1,2,3-benzothiadiazole (XXXVII-a) also displays a prominent $(M-N_2)^{+\cdot}$ ion[57] which appears to have either the carbene (XXXVII-b) or thioketene (XXXVII-c) radical cation structure if the benzene ring is intact. The original

(XXXVI-a) (XXXVI-b) (XXXVI-c) (XXXVI-d)



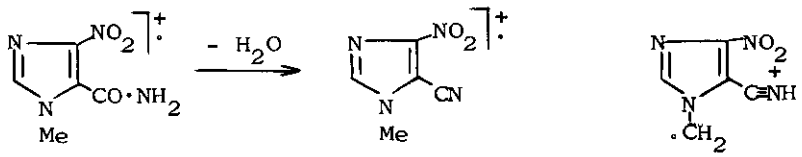
(XXXVII-a) (XXXVII-b) (XXXVII-c)

authors concluded that the $(M-N_2)^{+\cdot}$ ions of 1,2,3-thiadiazole and its benzo-analogue are the tioketene radical cations (XXXVI-d) and

(XXXVII-c) which are the Wolff rearrangement products of the carbenes (XXXVI-b) and (XXXVII-b), because (i) the $(M-N_2)^{+\cdot}$ ion loses CS and (ii) a benzyne ion (m/e 76) expected to be produced from the carbene (XXXVII-b) was virtually absent in the mass spectrum of 1,2,3-benzothiadiazole.[57] Although this appears to be a plausible conclusion in the light of the formation of thioketene and selenoketene from the photochemical reactions of 1,2,3-thiadiazole[61] and 1,2,3-selenadiazole,[62] studies by means of more elaborate techniques such as metastable ion characteristics and ion cyclotron resonance spectroscopy are awaited.

Ion cyclotron resonance spectroscopy appears to be the most reliable and suitable technique for the discrimination between plausible ion structures. This technique is based on ion-molecule reactions and the relatively longer residence time in a source (the order of milliseconds) permits the observation of ion-molecule reactions at low pressure. The double resonance technique is used in identifying the precursor of a fragment ion.

Application of this technique is illustrated by the mass spectrum of 1-methyl-4-nitroimidazole-5-carboxamide.[63] The molecular ion (XXXVIII-a) loses a molecule of water and the resulting ion could be formulated either as (XXXVIII-b) or (XXXVIII-c). An m/e 152 ion obtained by electron impact induced ionization of 1-methyl-4-nitroimidazole-5-carbonitrile and an

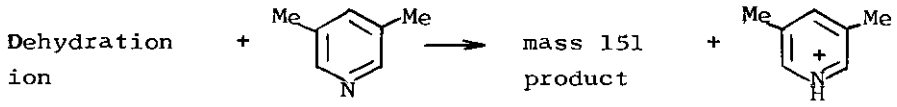


(XXXVIII-a) (XXXVIII-b) (XXXVIII-c)

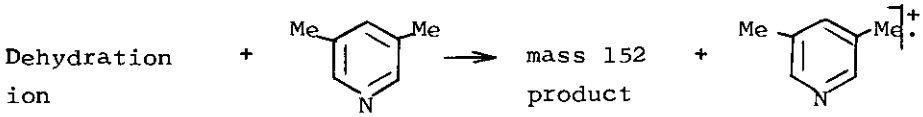
Scheme 1

m/e 152 ^{13}C or ^{15}N isotopic compound mass 108 — mass 152 ^{13}C or ^{15}N isotopic ion m/e 108

Scheme 2



Dehydration ion m/e 152 — mass 107 — mass 151 product — m/e 108

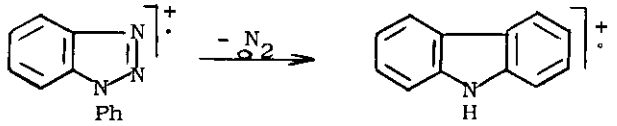


Dehydration ion m/e 152 — ^{13}C or ^{15}N isotopic compound mass 108 — mass 152 product — ^{13}C or ^{15}N isotopic ion m/e 108

m/e 152 ion obtained by electron impact induced dehydration of (XXXVIII-a) were separately caused to react with 3,5-dimethyl-pyridine. The m/e 152 ion (XXXVIII-b) reacted only by charge transfer (Scheme 1), whereas the dehydration product ion reacted both by charge transfer and by proton transfer with the base (Scheme 2). The different behaviour under identical conditions shows the non-identity of the dehydration product ion of 1-methyl-4-nitroimidazole-5-carboxamide (XXXVIII-a) with 1-methyl-4-nitro-

imidazole-5-carbonitrile radical cation (XXXVIII-b). This result, together with the metastable ion characteristics, allowed a conclusion to be made that the dehydration product ion should be formulated as (XXXVIII-c).

When the ion structure is inferred, it is preferable to reach the same conclusion by employing at least two different techniques, and hence pitfalls inherent in these methods must be well understood in order to avoid confusion. Inference of the structure of a rearrangement ion by means of an energetic approach requires special caution. The $(M-N_2)^{+\cdot}$ ion of 1-phenyl-1H-1,2,3-benzotriazole (XXXIX-a) has been proposed to have the carbazole radical cation structure (XXXIX-b) by comparing the mass spectral behaviour with the photochemically induced reaction of 1-phenyl-1H-1,2,3-benzotriazole.[64,65] However, there is a great difference between the heat of formation of the $(M-N_2)^{+\cdot}$ ion (391.5 Kcal/mol) and that of the carbazole radical cation (239.5 Kcal/mol),[66] which makes one suspect the conclusions drawn by three groups.



(XXXIX-a) (XXXIX-b)

In the reaction $A + e \rightarrow B^+ + C + 2e$, difference between the appearence potential* of B^+ and the ionization potential* of A, i.e., A.P.(B^+) - I.P.(A), is the sum of the activation energy (E_f)

* It must be recognized that the accuracy of mass spectrometric I.P. and A.P. determinations has been regarded to be poor.

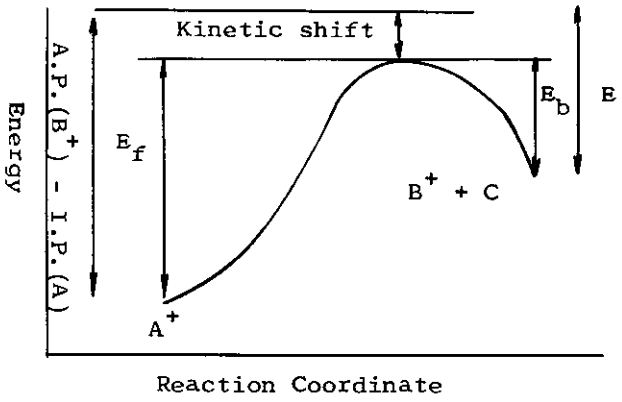


Fig. 1. Reaction Profile in a Mass Spectrometer

necessary to reach the transition state of the fragmentation and an energy required to increase the reaction rate from 0 to the order of 10^5 s^{-1} which is called kinetic shift.[67] The Fig. 1 illustrates this situation.

As a rearrangement reaction must take a rigid orientation of atoms or groups in which a partial bond is being formed, the rise of K *vs.* E curve in QET must be slower than for a simple bond cleavage reaction, and hence the value of kinetic shift increases.

Heats of formation (ΔH_f) may be calculated from the following equation.

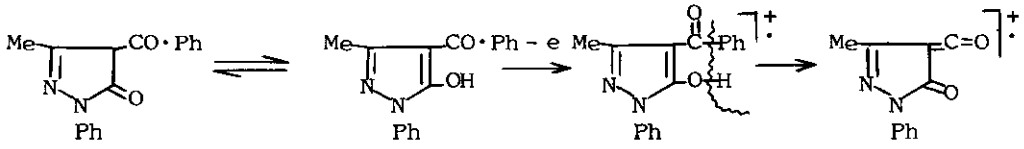
$$A.P.(B^+) = \Delta H_f(B^+) + \Delta H_f(C) - \Delta H_f(A) + E$$

As an excess energy (E) at the threshold is the sum of kinetic shift and the energy (E_b) released from the transition state when B^+ and C are produced, a large kinetic shift causes a large error in the estimation of ΔH_f. Therefore, difference between ΔH_f of the $(M-N_2)^{+\cdot}$ ion of 1-phenyl-1,2,3-benzotriazole (XXXIX-a) and that of the carbazole radical cation (XXXIX-b) does not allow the conclusion to be made that the $(M-N_2)^{+\cdot}$ ion of (XXXIX-a) does not possess the carbazole radical cation structure.

(3) Fragmentations.

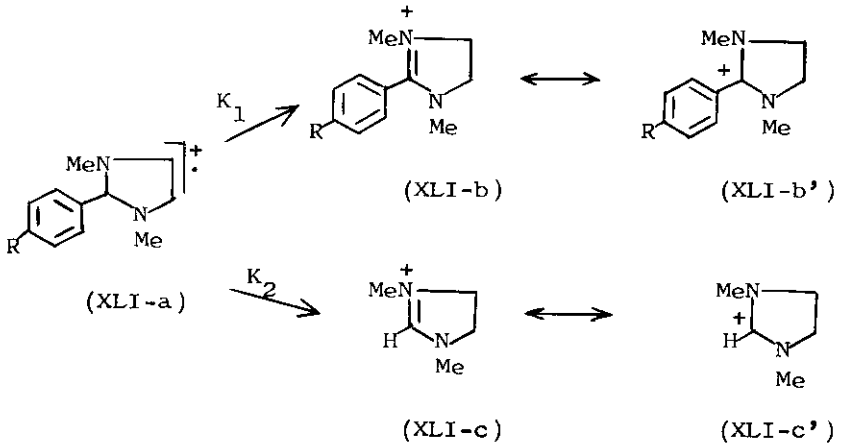
3-A. Azoles.

In contrast to the mass spectral behaviour of Δ^2-pyrazolin-5-one derivatives, which preferentially lose N_2R,[13] the spectra of the pyrazoline substituted with a benzoyl or carbethoxy group at C(4) such as (XL) display an intense $(M-C_6H_6)^{+\cdot}$ ion (or $(M-EtOH)^{+\cdot}$ ion);[68] ionization of an enolic form (XL') and operation of an ortho effect are responsible for these ions.



(XL) (XL')

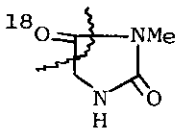
Though the ions generated by loss of Ar or H at C(2) from the molecular ion of 2-aryl-1,3-dimethylimidazolidine (XLI-a) appear to be stabilized by the positive charge which is distributed over C(2) and ring nitrogen atoms, a study of substituent effects has shown that formulations as (XLI-b') and (XLI-c') are preferable



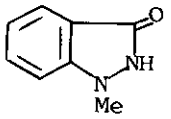
(XLI-a) (XLI-b) (XLI-b') (XLI-c) (XLI-c')

to the representations (XLI-b) and (XLI-c).[69] Plot of log z/z_0 ($z=K_1/K_2$ and $z_0=K_1/K_2$ for R=H) vs. σ^+ gives $\rho = -0.251$. Small and negative ρ value allowed the above conclusion to be made.

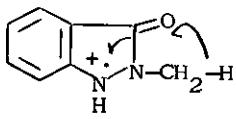
Novel fragmentations have not been reported for imidazole derivatives, but a labelling study has disclosed the exclusive loss of $C^{18}O$ from 3-methylhydantoin (XLII) and its N(1)-alkyl-derivatives.[70] The McLafferty rearrangement of alkyl-substituted hydantoins takes place for 5-alkylhydantoins but not for 3-alkyl hydantoins; this diagnostic difference will find important use in structural characterizations.



(XLII)



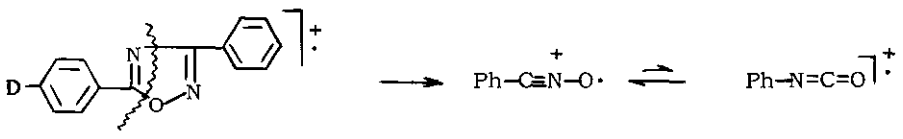
(XLIII)



(XLIV)

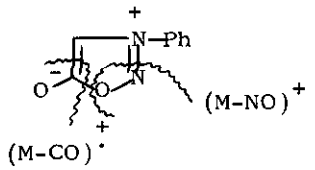
The mass spectrum of indazol-3-one displays a prominent $(M-29)^+$ ion, 90 % of the leaving 29 mass units being N_2H. However, the $(M-29)^+$ ion of 1-methyl- and 2-methyl-indazol-3-ones is comprised of three ions, among which the $(M-CHO)^+$ ion is the most abundant. As 2-methylindazol-3-one (XLIV) loses CHO five times as ready as 1-methylindazol-3-one (XLIII), a hydrogen rearrangement as shown has been proposed for (XLIV).[71]

Although the mass spectrum of 1,2,4-oxadiazole itself has not yet been reported, the spectrum of its 3,5-diphenyl derivative (XLV) indicates the generation of benzonitrile-oxide radical cation and its partial rearrangement into phenylisocyanate radical cation.[72] This heterocyclic ring appears not to undergo the cleavage of an N-O bond in sharp contrast to isoxazole derivatives.[73]

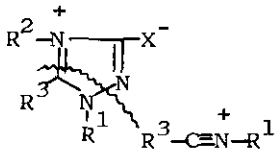


(XLV)

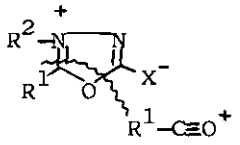
The mass spectra of a number of mesoionic compounds possessing oxadiazole, thiadiazole, and other rings have been reported.[74-77] The mesoionic compounds so far reported decompose by simple bond cleavages which depend on the nature of heteroatoms as shown in formulas (XLVI)-(LI). For instance, the intensity of the $(M\text{-}NCS)^+$ ion decreases greatly in the spectrum of the sulfide (L), whereas the spectrum of the oxide (XLIX) displays a fairly abundant $(M\text{-}NCO)^+$ ion.



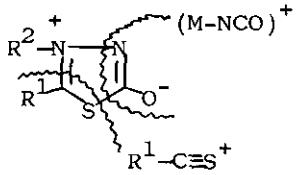
(XLVI)



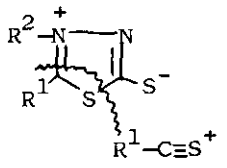
(XLVII)



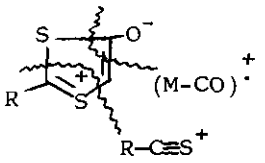
(XLVIII)



(XLIX)



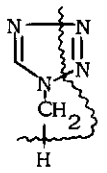
(L)



(LI)

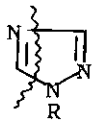
The mass spectra of tetrazole and its 2-methyl derivative have been determined.[78-80] As it is to be expected, they undergo exclusive loss of N_2. The methyl-substituted tetrazoles, however,

behave a little differently each other on electron impact; the spectrum of 2-methyltetrazole shows no molecular ion peak but instead an $(M+1)^+$ ion in the relative intensity of 2-4 % depending on repeller voltage, whereas the molecular ion of 1-methyltetrazole (LII) loses HN_2 as shown.[78]

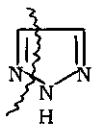


(LII)

The spectrum of 1H-1,2,4-triazole (LIII)[81-84] and that of 2H-1,2,3-triazole (LIV)[83] closely resemble each other, the $(M\text{-}HCN)^{+\cdot}$ and $(M\text{-}N_2)^{+\cdot}$ ions being intense in both spectra. The $(M\text{-}HCN)^{+\cdot}$ ion in both spectra further eliminates a nitrogen atom, the process being accompanied by a flat-topped metastable ion. As an excess energy released during the loss of N is 0.39 eV for (LIII) and 0.43 eV for (LIV), it was concluded that the $(M\text{-}HCN)^{+\cdot}$ ions of (LIII) and (LIV) have the same structure.[83]



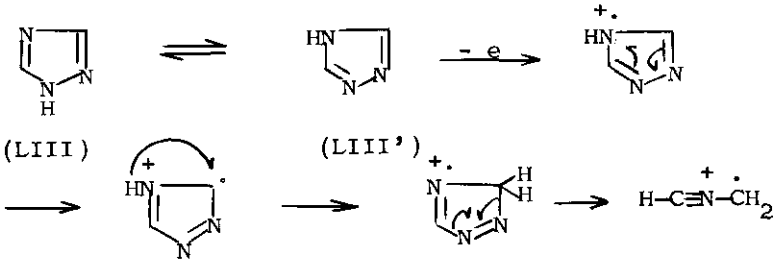
(LIII)



(LIV)

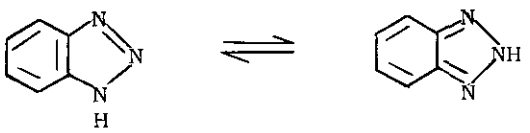
A flat-topped metastable ion is observed for the process $M^+ \rightarrow (M\text{-}N_2)^{+\cdot}$ in both spectra. An excess energy released during this process is 1.41 eV for (LIII; R=H) and 1.57 eV for (LIII; R=D) Operation of an isotope effect indicates the participation of the N(1)-H atom in the loss of N_2 and hence a proposal was made tha ionization of (LIII'), a tautomer of (LIII), and the hydrogen migr

as shown followed by nitrogen loss are involved in this process.[81] Formation of the $(M-N_2)^{+\cdot}$ ion of 2H-1,2,3-triazole (LIV) has also been accounted for in a similar way.[83]



(LIII) (LIII')

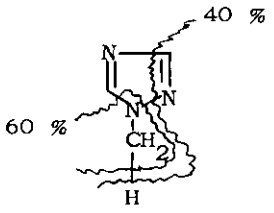
Tautomerization of 1H-benzotriazole (LV) with 2H-benzotriazole (LV') is also possible. However, a detailed study of d_1-benzotriazole has shown the exclusive presence of the 1H-tautomer (LV) in the gaseous phase and additionally revealed that the $(M-N_2)^{+\cdot}$ ion undergoes hydrogen randomization between N(1)-H and benzene ring hydrogens.[85]



(LV) (LV')

Bowie, et al. have revealed from the studies of metastable ions that three pathways are implicated in the decomposition of 1H-1-methyl-1,2,4-triazole (LVI),[86] i.e., (i) M - HCN - HCN, (ii) M - HCN - H_2CN, and (iii) M - $C_2H_3N_2$. In the first pathway a hydrogen atom of HCN initially eliminated comes from the C(5)-H. The pathway (ii) is complicated; ^{15}N and deuterium labelling studies have shown that the initially eliminated HCN arises as in

the first process and 60 % of H_2CN subsequently eliminated originate from N-Me and 40 % from N(2), C(3)-H, and one Me hydrogen as shown below. The process (iii) is the one-step formation of a CH_2N^+ ion; 60 % of this ion arise from N-Me, 35 % from N(2), C(3)-H, and one Me hydrogen, and 5 % from N(2), C(3)-H, and a hydrogen atom at C(5). The spectrum of 1-methyl-1,2,4-triazolin-5-thione was also subjected to detailed analysis and an intense m/e 60 ion was found to be produced by two independent processes, i.e., M-$C_2H_3N_2$ and M-HCN-HCN-H; 60 % of the leaving $C_2H_3N_2$ in the former pathway come from N(1)-CH_2, N(2), and C(3)-H and 40 % from N(1)-Me, N(2), and C(3).[87]



$(M-HCN-H_2CN)^+$

(LVI)

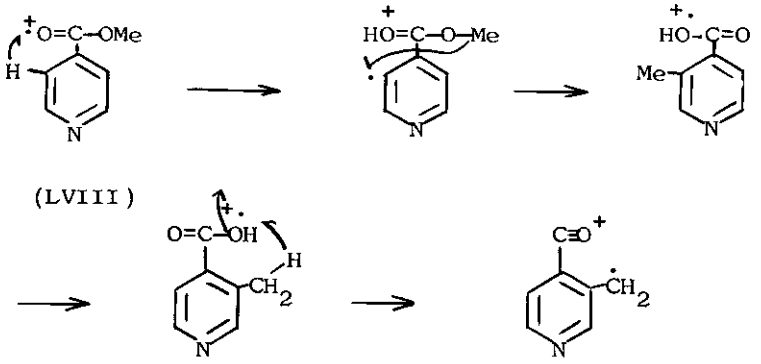
3-B. Pyridine-carboxylic acids.

The mass spectra of pyridine-carboxylic acids which had received no attention in the past were found to show interesting variations depending on the position of CO_2H. The spectrum of the 2-carboxylic acid (LVII) has an intense $(M-CO_2)^{+\cdot}$ ion,[88] whereas this ion is virtually absent in the spectra of the 3- and 4-carboxylic acids.[89] Formation of a hydrogen bond between CO_2H and the ring nitrogen atom will assist the ready ejection of CO_2 from the 2-carboxylic acid.

(LVII)

Pyridine-3- and 4-carboxylic acids decompose by consecutive losses of OH and CO from the molecular ion. However, the carboxyl group is not the sole source of the OH radical eliminated. Exchange of the carboxyl hydrogen with ring hydrogens is implicated. In the 4-carboxylic acid, a hydrogen of CO_2H exchanges with a C(3)-H only and this exchange takes place more readily for the ion of longer life-time, i.e., 53-57 % in a source, 92-97 % in the first field-free region, and 100 % in the second field-free region.[90] This should be contrasted with the behaviour of pyridine-3-carboxylic acid. The exchange occurs with a C(2)-H only and proceeds to the extent of ca. 66 % in a source, but neither in the first nor in the second field-free region. This is because the $(M-OH)^+$ ion produced from the 3-carboxylic acid is electronically stabilized, requiring lower activation energy for its formation and hence the reaction rate constant K rises with internal energy E. The molecular ion decomposes before reaching the metastable drift regions.

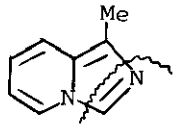
The molecular ion of methyl pyridine-4-carboxylate (LVIII) loses H_2O at the first and second field-free regions;[42] exchange of a C(3)-H with a methoxy Me and operation of an ortho effect as shown below are responsible for the dehydration. However, as a C(2)-H atom was also found to be incorporated into the eliminated H_2O, hydrogen excahnge appears to proceed extensively.



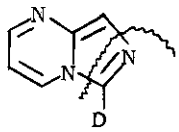
(LVIII)

3-C. Polyazaindenes, polyazanaphthalenes, and other related compounds.

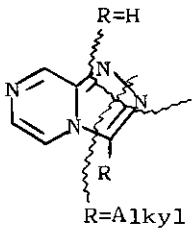
Owing to the biological and pharmaceutical importance of pyrimidine and pteridine derivatives, their mass spectra were extensively studied before 1970 by Tatematsu,[91,92] Dudeck,[91] and Nishiwaki.[91] Which of the nitrogen atoms is incorporated into the HCN initially eliminated was the central problem of these studies. Polyazaindenes, polyazanaphthalenes, and other related compounds (LIX)-(LXVII) were subsequently studied, the site of the initial ring-opening being shown by wavy lines. Tetrazolo(1,5-b)pyridazine (LXIII) and s-triazolo(4,3-b)pyridazine (LXIV) undergo ring-opening across two fused rings, but it is unknown whether N_2 and HCN are eliminated in one step or two steps.



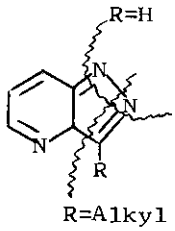
(LIX)[93]



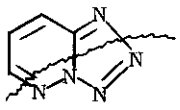
(LX)[93]



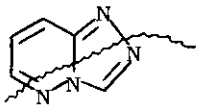
(LXI)[94]



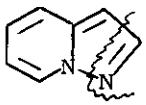
(LXII)[95]



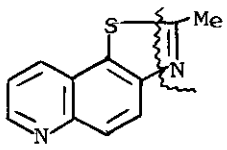
(LXIII)[96]



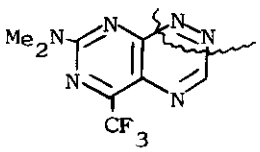
(LXIV)[96]



(LXV)[97]



(LXVI)[98]

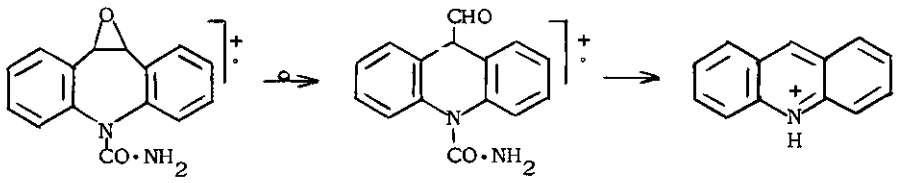


(LXVII)[99]

3-D. Seven- and eight-membered heterocyclic rings.

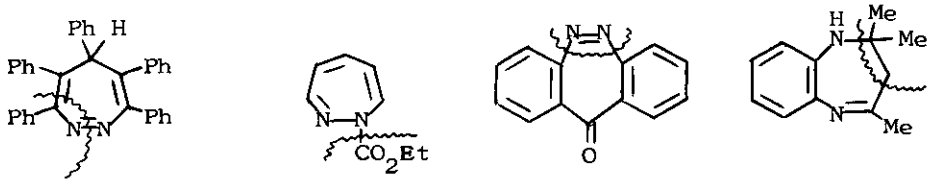
Recently the mass spectra of seven- and eight-membered heterocyclic rings are receiving attention. 10,11-Epoxy-5H-dibenzo(b,f)azepin-5-carboxamide (LXVIII-a) undergoes an interesting yet unusual fragmentation;[100] the acridinium ion (LXVIII-c) produced by successive losses of HNCO and HCO, or vise versa, from the rearranged molecular ion (10-formylacridan-5-carboxamide radical cation) (LXVIII-b) eliminates H_2CN in one-step.

3,4,5,6,7-Pentaphenyl-1,2-diazepine (LXIX) eliminates PhCN but not N_2 on electron impact,[101] whereas the decomposition of

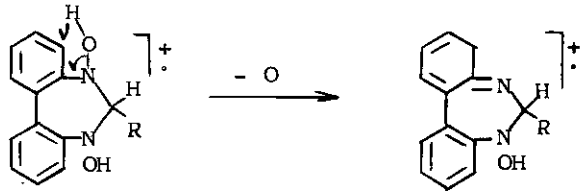


(LXVIII-a) (LXVIII-b) (LXVIII-c)

1-ethoxycarbonyl-1H-1,2-diazepine (LXX) starts from the CO_2Et moiety.[102] Preferential loss of N_2 from the molecular ion has been observed for dibenzo(c,f) (1,2)diazepine and its 11-oxo-derivative (LXXI).[103,104] The mass spectra of 2,4,4-trimethyl-4,5-dihydro-1,5-benzodiazepine (LXXII) and its derivatives indicate that the simple bond cleavage as shown is the predominant mode of fragmentation.[105] The molecular ion of 6,7-dihydro-5,11-dihydroxy-5H-dibenzo(d,f)(1,3)diazepine (LXXIII-a) eliminates an oxygen atom, as confirmed by the presence of a metastable ion.[106]



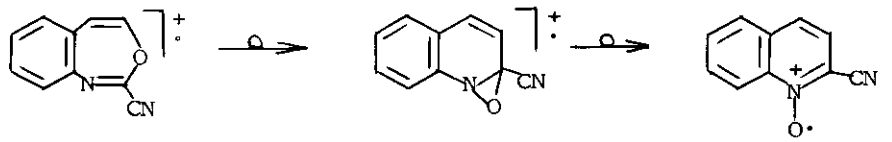
(LXIX) (LXX) (LXXI) (LXXII)



(LXXIII-a)

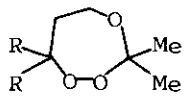
Elimination of CO is preferred to that of HCN in the mass spectrum of 1,3-benzoxazepin-2-carbonitrile (LXXIV-a). Presence of an $(M-O)^{+\cdot}$ ion in its spectrum suggests the occurrence of a

rearrangement to 2-cyanoquinoline-1-oxide radical cation (LXXIV-b).[107]

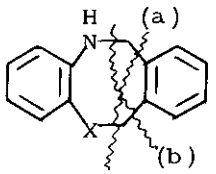


(LXXIV-a) (LXXIV-b)

Fragmentation of 3,3-dimethyl-1,2,4-trioxepane (LXXV) appears to proceed by loss of acetone.[108] The spectra of 11,12-dihydro-6H-dibenzo(b,f)(1,5)oxazocine (LXXVI; X=O), 11,12-dihydro-6H-dibenzo(b,f)(1,5)thiazocine (LXXVI; X=S), and 5,6,11,12-tetrahydro-5-methyldibenzo(b,f)(1,5)diazocine (LXXVI; X=NMe) have been determined.[109] All of them display an $(M-C_7H_7)^+$ ion which is formed through either cleavage (a) or (b) accompanied by a hydrogen rearrangement. The cleavage mode depends on the nature of an X atom of the ring; the scission (b) is more preferred for the compounds (LXXVI; X=S and O), whereas the cleavage (a) is preferred for the compound (LXXVI; X=NMe).



(LXXV)

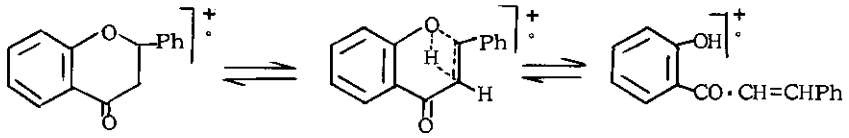


(LXXVI)

3-E. Chromene derivatives.

It is well known that flavanone (LXXVII-a) decomposes via a retro Diels-Alder fragmentation.[4,6] Detailed studies of its mass spectrum have disclosed, however, that there are several ions which can not be accounted for as produced from the intact

flavanone structure, one of them being the $(M-OH)^+$ ion. On the other hand, the $(M-Ph)^+$ ion appears as the base peak in the mass spectrum of 2'-hydroxychalcone (LXXVII-b), which is also difficult to expalin as produced by an energetically unfavourable vinylic cleavage of (LXXVII-b). The spectra of (LXXVII-a) and (LXXVII-b) closely resemble each other and have the common metastable ion characteristics, and major ions in both of the spectra have the same ΔH_f values. As thermal isomerization between them is ruled out, a proposal has been made that (LXXVII-a) is equilibrated with (LXXVII-b) in a source. If so, the formation of the $(M-OH)^+$ ion from (LXXVII-a) and the $(M-Ph)^+$ ion from (LXXVII-b) can be well rationalized.[110]

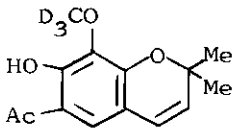


(LXXVII-a) (LXXVII-b)

Another interesting mass spectral feature found in this type of compounds concerns the $(M-15)^+$ ion of flavan. Wilhalm has claimed the occurrence of an unusual and energetically unfavourable elimination of carbene (CH_2) from the $(M-1)^+$ ion because he found a metastable ion at m/e 106.5 corresponding to the transition m/e 133 → m/e 119.[111] However, this claim was subsequently disproved by Djerassi, et al.,[112] whose study has shown that the metastable ion at m/e 106.5 is an isotope peak of a metastable ion at m/e 105.67 corresponding to the transition m/e 134 (M^+) → m/e 119.

Despite this yet unsettled dispute, Eguchi, et al. have recently claimed the occurrence of the $(M-CH_2)^+$ ion in the mass spectra of

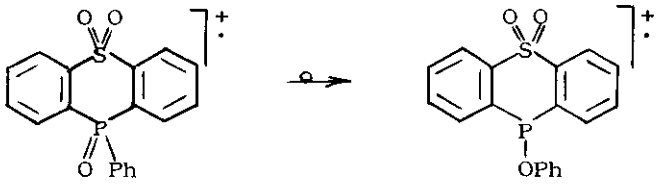
2H-chromene derivatives.[113] The mass spectrum of 2,2-dimethyl-6-acetyl-7-hydroxy-2H-chromene displays the $(M-14)^{+\cdot}$ ion in the relative intensity of 26.5 %, which can not be regarded as consisting of only an isotope peak of the $(M-Me)^{+}$ ion (the base peak). Studies on the spectrum of its 8-trideuteriomethoxy-derivative (LXXVIII) by means of I.K.E. spectroscopy and the metastable refocusing technique[114] have uncovered the presence of a transition m/e 251.6 → m/e 235.8 corresponding to the loss of CD_2 from the molecular ion. The $(M-CH_2)^{+\cdot}$ ion is also observed in the spectra of the compounds related to (LXXVIII) (2,2-dimethyl-7,8-dimethoxy- and 2,2-dimethyl-6,7,8-trimethoxy-2H-chromenes), but it is absent in the spectrum of anisole.



(LXXVIII)

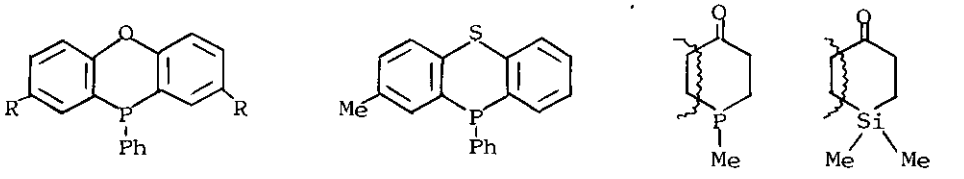
3-F. Heterocyclic rings containing the Group IV and V elements.

Nowadays a number of phosphorus-containing heterocyclic compounds are available. Their mass spectra have also been determined, among which phenothiaphosphine and phenoxaphosphine derivatives are very interesting. The spectrum of phenothiaphosphine-oxide-S,S-dioxide (LXXIX-a) has an intense $(M-PhO)^{+}$ ion besides ions associated with the fragmentations at the sulfone moiety. The presence of the $(M-PhO)^{+}$ ion indicates the occurrence of the rearrangement of (LXXIX-a) (P^{V}) into the phosphinite (LXXIX-b) (P^{III}).[115] Transannular interaction between phosphorus and



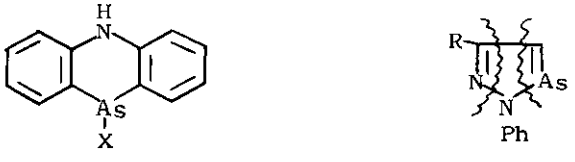
(LXXIX-a) (LXXIX-b)

oxygen atoms has been suggested for 10-phenylphenoxaphosphine (LXXX; R=H) because of the presence of an $(M-PhO)^+$ ion in its mass spectrum.[116] A strong metastable ion corresponding to the transition $M^+ \longrightarrow (M-PhO)^+$ has been observed, suggesting the elimination of the PhO radical to be a slow step. The transannular interaction appears to be virtually absent for the related 2,8-dimethyl-10-phenylphenoxaphosphine (LXXX; R=Me),[117] but it is observed in the spectrum of 2-methyl-10-phenylphenothiaphosphine (LXXXI).[117] The C_2H_7PO ion observed in the spectrum of 1-methylphosphorinan-4-one (LXXXII) is again an evidence for such an interaction.[118]



(LXXX) (LXXXI) (LXXXII) (LXXXIII)

The As-X bond cleavage is the initial step in the fragmentation of 5,10-dihydrophenarsazine derivative (LXXXIV),[119,120] whereas 1,2,5-arsadiazole (LXXXV) eliminates HC≡As and RC≡N on electron

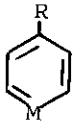


(LXXXIV) (LXXXV)

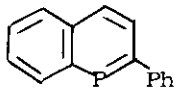
impact.[121]

Unlike cyclohexanone, the mass spectra of 1-methylphosphorinan-4-one (LXXXII)[118] and 1,1-dimethylsilacyclohexan-4-one (LXXXIII)[122] display an $(M-C_2H_4)^{+\cdot}$ ion in high abundance.

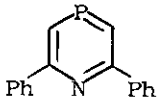
The mass spectra of arsenin (LXXXVI; M=As, R=H),[123] phosphorin (LXXXVI; M=P, R=H),[123] and antimonin (LXXXVI; M=Sb, R=H)[124] have been recorded. They reflect the great stability of the aromatic ring, the molecular ion being the base peak, but unlike pyridine they have the $(M-C_2H_2)^{+\cdot}$ ion in the relative intensity of 16-24 %. Antimonin (LXXXVI; M=Sb, R=H) deviates a little from its arsa- and phospha-analogues in that the Sb^+ ion appears in relatively high abundance. The spectra of substituted arsenin and phosphorin are also available.[125,126] There is a subtle change in their fragmentations; for instance, the compound (LXXXVI; M=As, R=C_6H_{11}) has the molecular ion as the base peak and an $(M-Me)^+$ ion in the relative intensity of 10 %, whereas the compound (LXXXVI; M=P, R=C_6H_{11}) has the molecular ion of small abundance (R.I. 10 %) and the $(M-1)^+$ ion as the base peak.



(LXXXVI)



(LXXXVII)

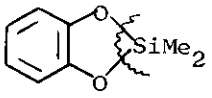


(LXXXVIII)

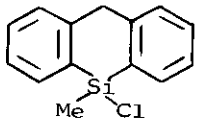
Phospha-analogues of naphthalene and pyrazine have been prepared and their mass spectral behaviours have been examined. 2-Phenylphosphinoline (LXXXVII) decomposes by loss of PH_2 and HCP,[127] whereas 1,4-azaphosphorine (LXXXVIII) decomposes by elimination of Ph and PhCN.[128] Both of these compounds have the molecular ion as the base peak in their mass spectra.

Formation of the ionized silene and germirene is an important feature in the mass spectra of 1,1-dimethylsilacyclobutane (LXXXIX; M=Si) and the corresponding germanium analogue (LXXXIX; M=Ge).[129] Formation of the ionized silene has also been observed in the spectrum of 2,2-dimethyl-1,3,2-benzodioxasilole (LC).[130] This is a very interesting feature because the formation of the ionized carbene has not been reported.

(LXXXIX)



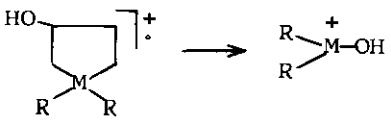
(LC)



(LCI)

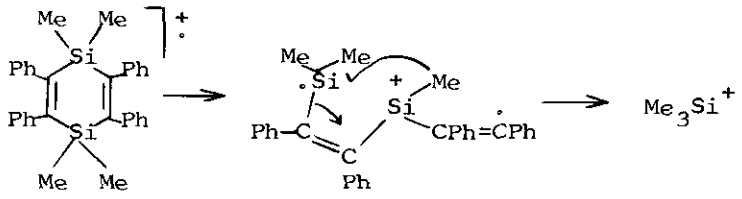
Aromatization by elimination of HCl from 9 and 10-positions of 9-chloro-9-methyl-9,10-dihydro-9-sila-anthracene (LCI)[131] and its related compounds[132] produces the most prominent ion in their mass spectra. The molecular ion peak appears in only small abundance except for the 9,9-difluoro-derivative. 9-Chloro-9-methyl-9,10-dihydro-9-germa-anthracene behaves similarly.[133]

Similarity of the mass spectra of heterocyclic rings containing the Group IV element is also evident when the behaviours of 1,1-dialkylsilacyclopentan-3-ol (LCII; M=Si)[134] and 1,1-dialkylgermacyclopentan-3-ol (LCII; M=Ge)[135] are compared. Their mass spectra exhibit an interesting ion associated with hydroxy migration to the Group IV element.



(LCII)

Aryl and alkyl rearrangement ions are present in the mass spectrum of 1,4-disilacyclohexa-2,5-diene (LCIII),[136] which arise by (i) transfer of Ph from α-carbon to Si and (ii) transfer of Me from one Si to another as shown.



(LCIII)

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