MASS SPECTRAL FRAGMENTATION PATTERNS OF 3,6-DIHYDRO-1,2-OXAZINES

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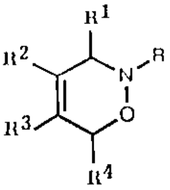
Abstract - Electron impact induced fragmentation of twenty-nine 3,6-dihydro-1,2-oxazines occurs via two competitive pathways. The first is the formation of a pyrrole system by loss of water from the molecular ion. The second pathway involves a retro Diels-Alder reaction to generate the butadienyl system as the most stable fragmentation product. The spectra contain low intensity peaks corresponding to the nitroso component of the retro cycloaddition process.

INTRODUCTION

3,6-Dihydro-1,2-oxazines have been shown to be potentially extremely versatile synthetic intermediates.[1] However, mass spectra of compounds containing this system have not been examined in detail. In order to identify major fragmentation processes to be expected for the 1,2-oxazine system, mass spectra of several N-unsubstituted,[2] N-aryl-,[1] and N-pyridyl[3] substituted 3,6-dihydro-1,2-oxazines have been examined. Electron impact ionization at 70 ev applied to the oxazine afforded pyrrole and butadienyl systems as the most stable fragmentation products. In view of the results obtained it could be concluded that thermal dehydration of the oxazine to yield pyrrole and the retro Diels-Alder reactions were two main processes of fragmentation.[4] The principal modes of fragmentation for the pyrrole systems and the retro Diels-Alder products are presented. The mass spectral data for all the oxazines examined are reported in Table 1.



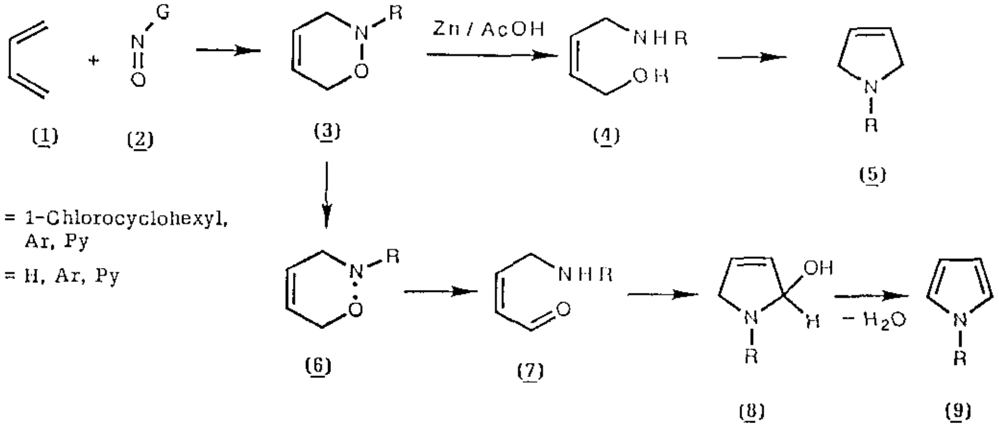
I. $R^1, R^3, R^4 = H; R, R^2 = Ph$
II. $R^3, R^4 = H; R^1, R^2 = CH_3; R = Ph$
III. $R^1, R^2 = H; R^3 = CH_3; R, R^4 = Ph$
IV. $R^3, R^4 = H; R^1 = CH_3; R, R^2 = Ph$
V. $R^1, R^2 = H; R^3 = Et; R, R^4 = Ph$
VI. $R^3, R^4 = H; R^2 = CO_2CH_3; R, R^1 = Ph$
VII. $R^2 = H; R^1, R^3, R^4 = CH_3; R = Ph$
VIII. $R^3 = H; R^1 = CH_3; R^2, R^4 = Et; R = Ph$
IX. $R^1, R^2 = H; R^3 = CH_3; R^4 = \underline{p}\text{-}C_6H_4OCH_3; R = Ph$
X. $R^1, R^2 = H; R^3 = Et; R^4 = \underline{p}\text{-}C_6H_4OCH_3; R = Ph$
XI. $R^1, R^2 = H; R^3 = CH_3; R^4 = \underline{p}\text{-}C_6H_4OCH_3; R = \underline{p}\text{-}C_6H_4CH_3$
XII. $R^1, R^2 = H; R^3 = Et; R^4 = \underline{p}\text{-}C_6H_4OCH_3; R = \underline{p}\text{-}C_6H_4CH_3$
XIII. $R^1, R^2 = H; R^3 = CH_3; R^4 = Ph; R = \underline{p}\text{-}C_6H_4CO_2CH_3$
XIV. $R^1, R^2 = H; R^3 = Et; R^4 = Ph; R = \underline{p}\text{-}C_6H_4CO_2CH_3$
XV. $R^1, R^2 = H; R^3 = CH_3; R^4 = \underline{p}\text{-}C_6H_4OCH_3; R = \underline{p}\text{-}C_6H_4CO_2CH_3$
XVI. $R^1, R^2 = H; R^3 = Et; R^4 = \underline{p}\text{-}C_6H_4OCH_3; R = \underline{p}\text{-}C_6H_4CO_2CH_3$
XVII. $R, R^1, R^4 = H; R^2 = CH_3; R^3 = Ph$
XVIII. $R, R^2, R^3 = H; R^1 = CH_3; R^4 = Ph$
XIX. $R, R^3 = H; R^1, R^2, R^4 = CH_3$
XX. $R, R^3 = H; R^1 = CH_3; R^2, R^4 = Et$
XXI. $R, R^1, R^2 = H; R^3 = Et; R^4 = Ph$
XXII. $R, R^1, R^2 = H; R^3 = CH_3; R^4 = \underline{p}\text{-}C_6H_4OCH_3$
XXIII. $R, R^1, R^2 = H; R^3 = Et; R^4 = \underline{p}\text{-}C_6H_4OCH_3$

XXIV. $R^1, R^3, R^4 = H; R^2 = CH_3; R = 4\text{-}CH_3Py$
XXV. $R^1, R^2 = H; R^3 = CH_3; R^4 = Ph; R = Py$
XXVI. $R^1, R^2 = H; R^3 = CH_3; R^4 = Ph; R = 4\text{-}CH_3Py$
XXVII. $R^1, R^2 = H; R^3 = CH_3; R^4 = Ph; R = 6\text{-}CH_3Py$
XXVIII. $R^1, R^2 = H; R^3 = Et; R^4 = Ph; R = Py$
XXIX. $R^1, R^2 = H; R^3 = CH_3; R^4 = \underline{p}\text{-}C_6H_4OCH_3; R = 4\text{-}CH_3Py$

Py = 2-pyridyl

DISCUSSION

The pyrrole system. The 3,6-dihydro-1,2-oxazines (3) can be prepared by Diels-Alder reaction of conjugated dienes (1) with the 1-chloro-1-nitrosocyclohexane,[2] nitrosoaromatic,[1], or nitrosoheteroaromatic[3] compounds (2) (Scheme 1).



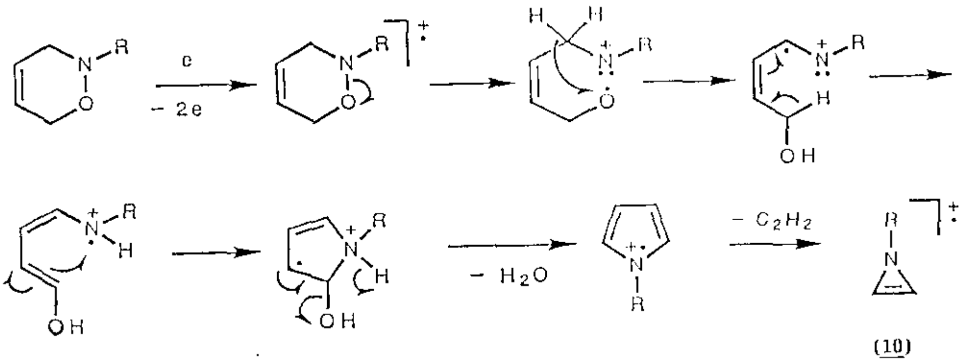
G = 1-Chlorocyclohexyl,
Ar, Py
R = H, Ar, Py

Scheme 1

The nitrogen-oxygen bond in the oxazine ring can be cleaved chemically using zinc and acetic acid,[5] or photochemically by irradiation with ultraviolet light.[6,7] The initial product of the reductive cleavage, an unsaturated aminoalcohol (4), under suitable conditions may undergo dehydration and subsequent cyclization to form pyrroline (5). The photolysis of dihydro-1,2-oxazines results in homolytic cleavage of the N-O bond (6) and the formation of an γ-amino-α,β-unsaturated carbonyl compound (7) which cyclizes to hydroxypyrroline (8). The latter consequently undergoes dehydration to pyrrole (9). Thus, in both chemical or photochemical transformations, dehydration is an essential step leading to formation of the pyrrole system.

A similar phenomenon is observed during electron impact ionization. The formation of the molecular ion is presumably followed by the cleavage of the N-O bond in the oxazine ring[8] and the subsequent cyclization of the initially formed aminoalcohol radical-cation to a pyrrole (Scheme 2). The mass spectra of all 1,2-oxazines examined are characterized by peaks which correspond to ions formed by successive loss of water from the molecular ion. Peaks corresponding to dehydration products are prominent in all the spectra and in some cases are present as the base peaks (XI, XV, XVI). The ratios of these ions ($M^{+\cdot} - H_2O$) to molecular ions ($M^{+\cdot}$) are shown in Table 2.

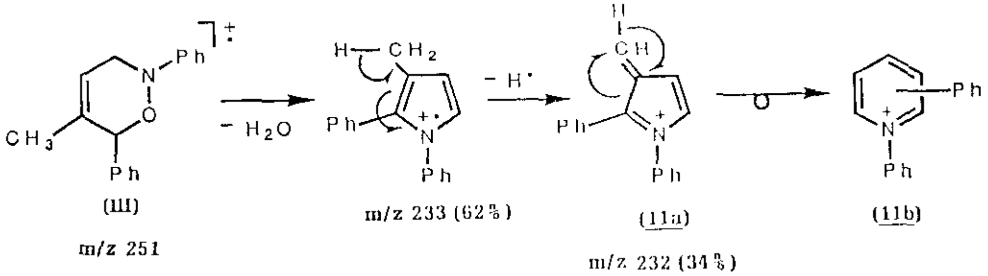
Further degradation processes result in fragmentation of the pyrrole system. The most abundant ions observed as high intensity peaks are the cyclopropenyl cation and the radical-cation (10), the latter resulting from loss of acetylene.[9,10]



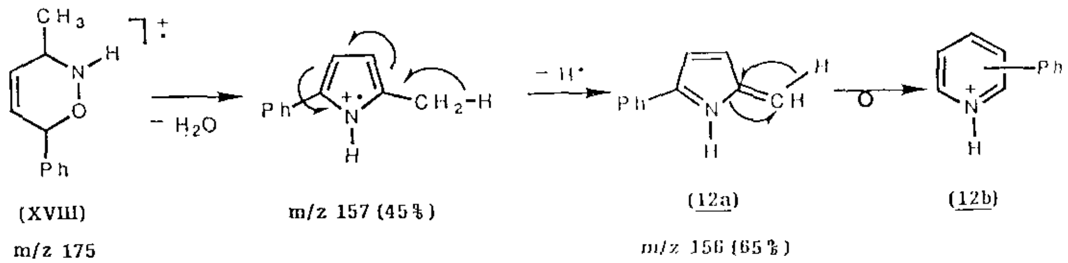
Scheme 2

The most characteristic fragmentation mode of the pyrrole nucleus containing C-methyl or C-ethyl substituents involves loss either of a hydrogen radical from the methyl group or methyl radical from the ethyl substituent to afford an azafulvene ion (11a) or its *rearrangement product*.[9-11] The spectra of N-arylpyrroles with only one C-methyl substituent contain peaks which correspond to an azafulvene cation formed by loss of a hydrogen radical from the methyl group. These initially formed cations may undergo ring expansion to more stable pyridinium ions (11b) (III-34 %, IV-32 %, IX-23 %, XIII-34 %, XXIV-12 %, XXV-41 %, XXVI-35 %, XXVII-30 %, XXIX-35 %; Scheme 3a). The *latter rearrangement* is analogous to the formation of the tropylium cation observed in the mass spectrum of toluene[12-14].

N-Unsubstituted pyrrole systems with one C-methyl group also produce azafulvene-type cations (12a) which may rearrange to pyridinium cations (12b) (XVII-100 %; XVIII-65 %; Scheme 3b).

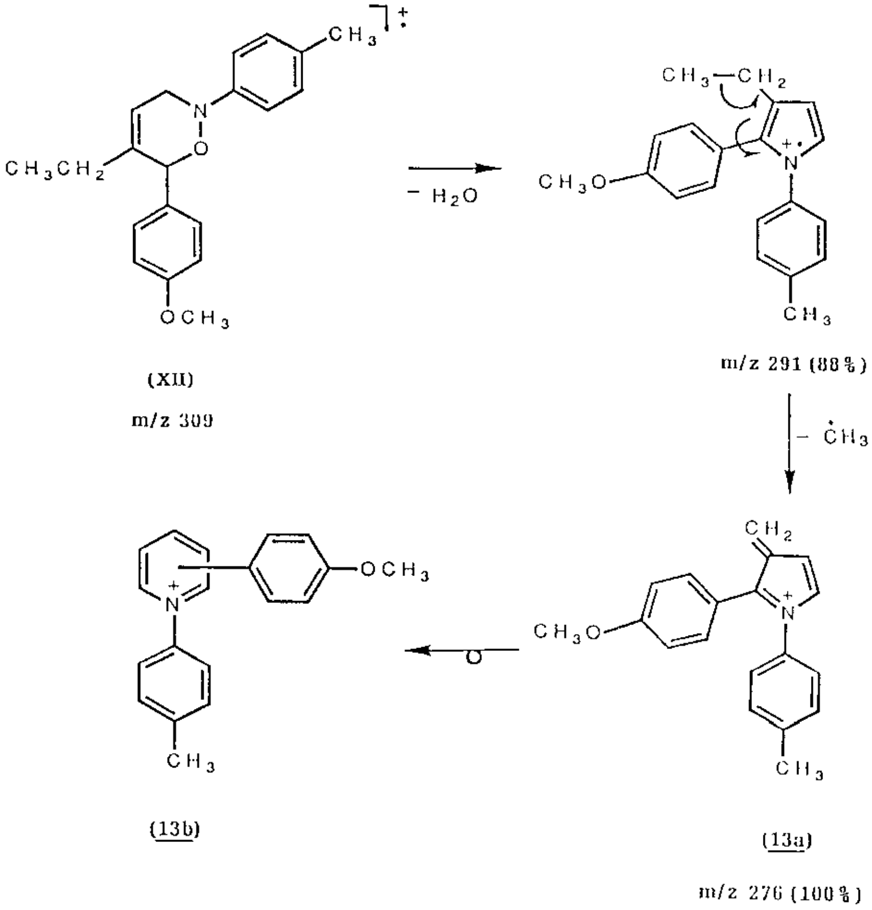


Scheme 3a



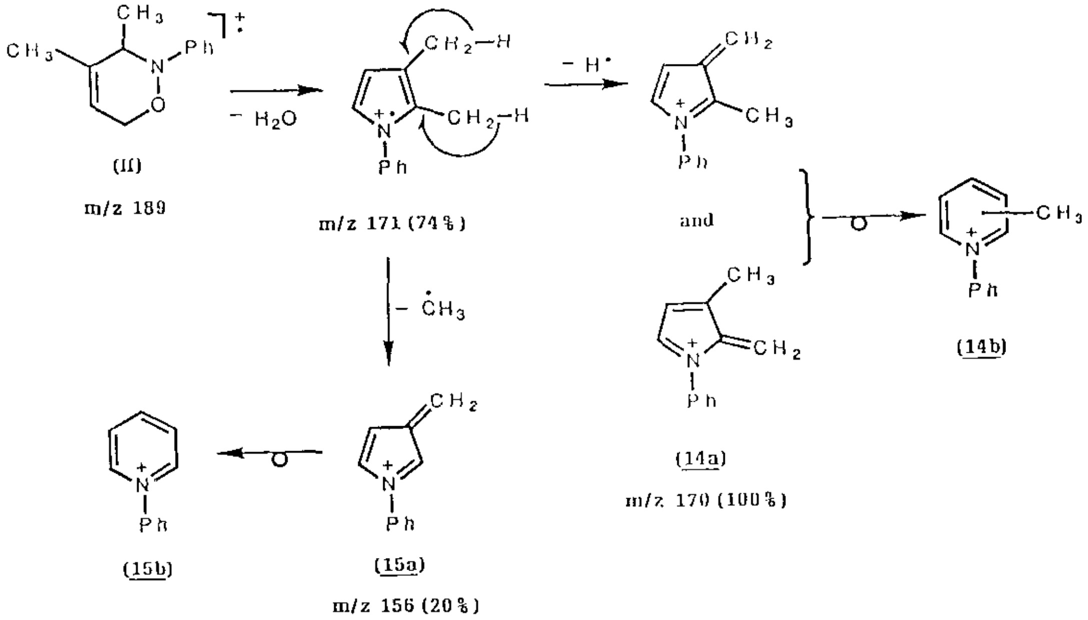
Scheme 3b

The β-cleavage of a C-ethyl group in the 2- or 3-position of the pyrrole moiety yields an azafulvene cation (13a) which may subsequently undergo ring expansion to provide the pyridinium ion (13b) (V-42%, X-96%, XII-100%, XIV-78%, XVI-86%, XXI-94%, XXIII-100%, XXVIII-42%; Scheme 4). It appears that the loss of a methyl radical from a C-ethyl group is energetically more favorable than the loss of a hydrogen radical from a C-methyl group.



Scheme 4

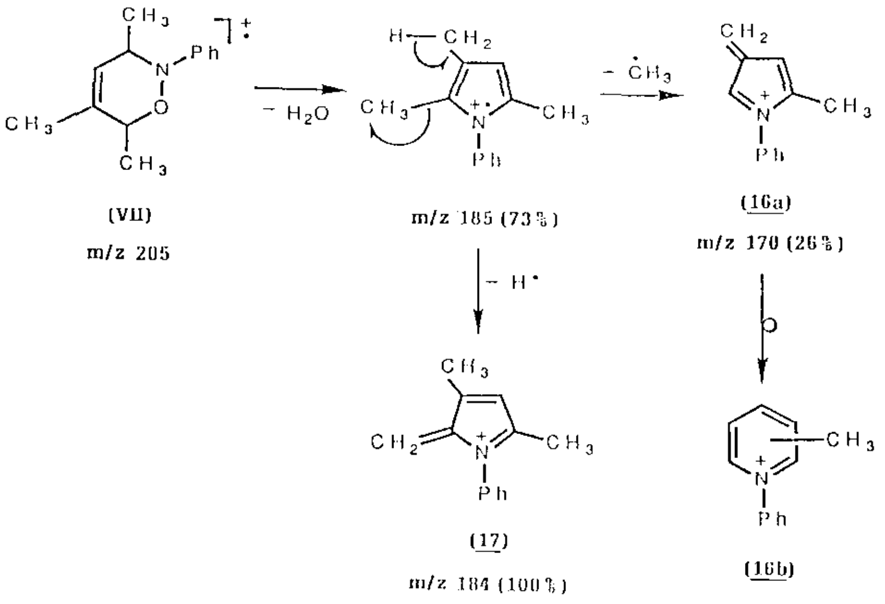
Pyrroles containing two (II) or three (VII, XIX) C-methyl groups generally produce very stable fragments. The β-cleavage resulting in the loss of a hydrogen radical may occur at any methyl substituent. In such a case rearrangement of the initially formed ion of an azafulvene-type (14a) to form the pyridinium ion (14b), appears to be very favorable (II,VIII-100%, XIX-87%; Scheme 5).



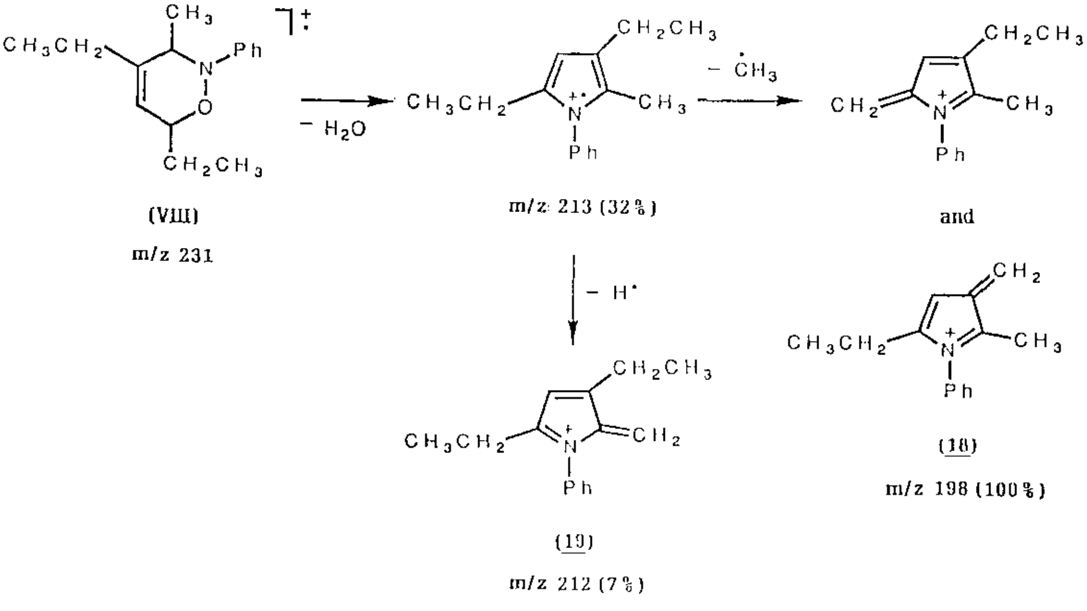
Scheme 5

The loss of nuclear methyl or ethyl groups as radicals from the monoalkylpyrroles would result in the formation of energetically unstable species (Table 3). The corresponding loss of the methyl radical from di- or trimethylpyrroles is, however, more appreciable (II-20 %, VII-26 %). This could be due to rearrangement involving the participation of a neighboring methyl group[13] in the formation of a fragment ion which may exist as an azafulvene cation (15a, 16a) or as the pyridinium cation (15b, 16b; Schemes 5 and 6). This type of rearrangement was previously reported for pyrroles, indoles, and thiophenes, all of which contained vicinal methyl groups.[13] The fragmentation involving loss of a nuclear methyl group as a radical may compete with the loss of a hydrogen radical from a methyl group. In the latter case the ejection of a hydrogen radical from any methyl group present to furnish azafulvene cation (17) which may also produce the pyridinium cation by ring expansion (Scheme 6) seems, however, to be more favorable.

In the case of pyrroles containing both methyl and ethyl substituents (VIII, XX), the β-cleavage at the ethyl group resulting in the loss of a methyl radical and the formation of an ion (18), appears energetically more preferred to the corresponding β-cleavage at the methyl group which affords a fragment ion (19) of quite low intensity.

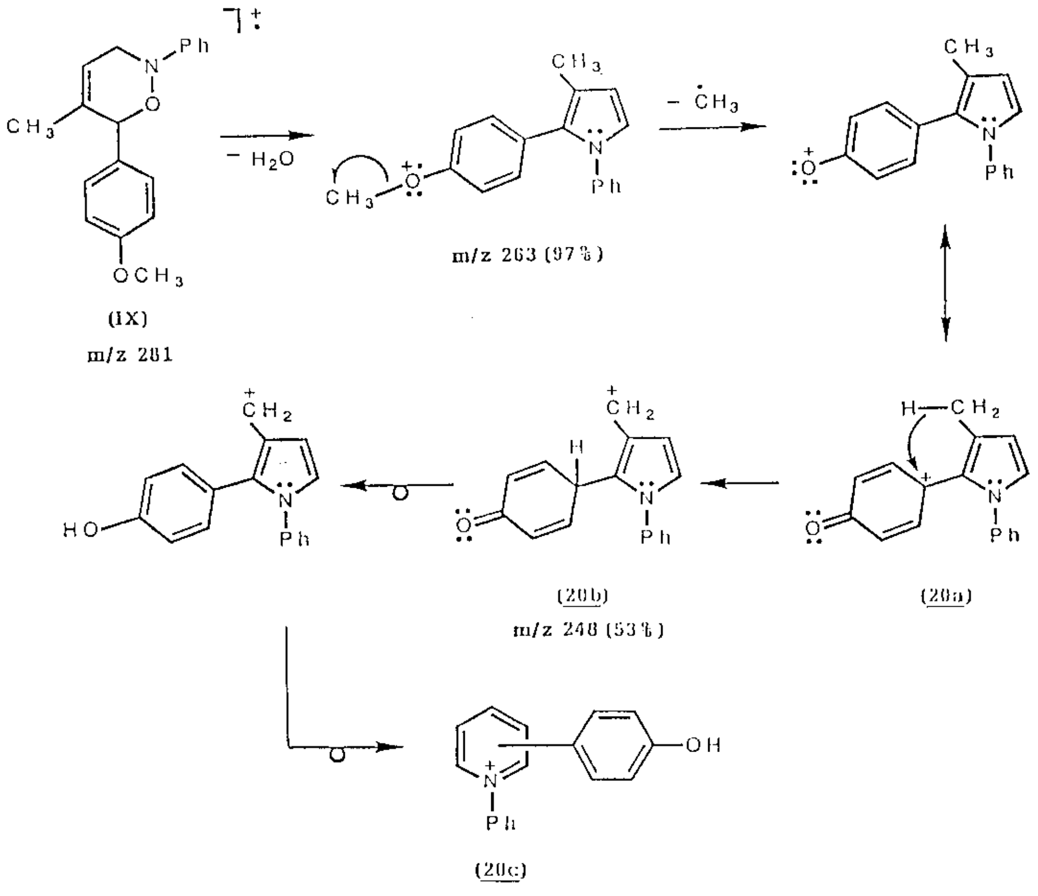


Scheme 6



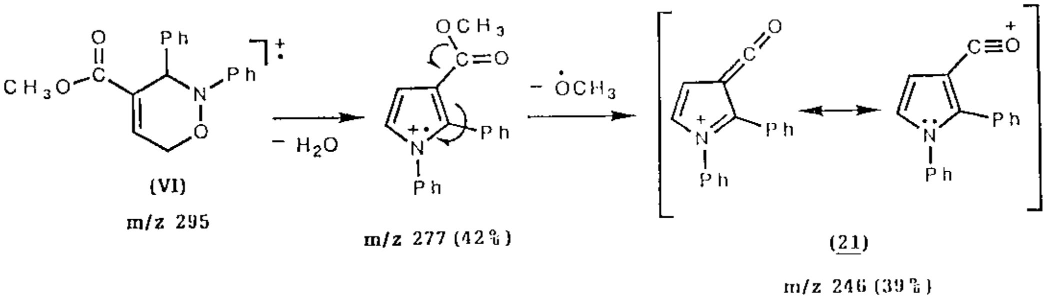
Scheme 7

The mass spectra of 3-methyl-2-(p-methoxyphenyl)pyrroles contain peaks of quite appreciable intensity which may be attributed to fragments formed by loss of a methyl radical from an original methoxy group (IX-53%, XI-60%, XV-33%, XXII-100%, XXIX-30%). The product-cation (20a) might be stabilized by hydride transfer from an adjacent methyl group to produce an azafulvene cation (20b) which may consequently rearrange to the corresponding pyridinium cation (20c; Scheme 8). Similar rearrangement has been observed for isomeric methyl anisoles.[13]



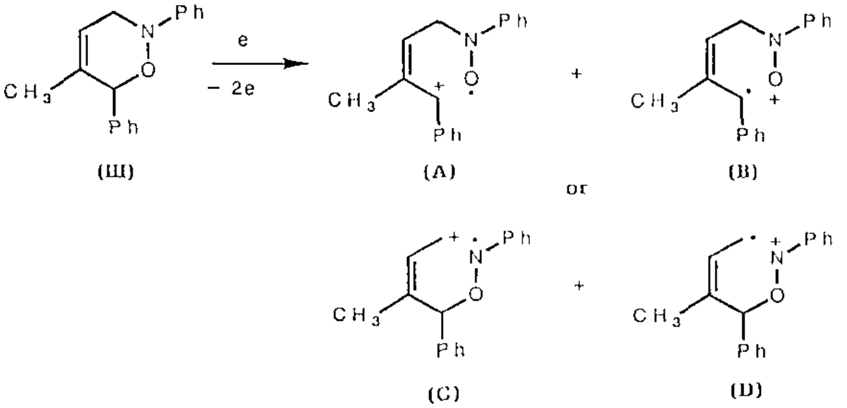
Scheme 8

The methyl 1,2-diphenylpyrrole-3-carboxylate derived from (VI) undergoes fragmentation resulting in the loss of the methoxy group as a radical and the formation of a stable acylium cation (21; Scheme 9).[13]

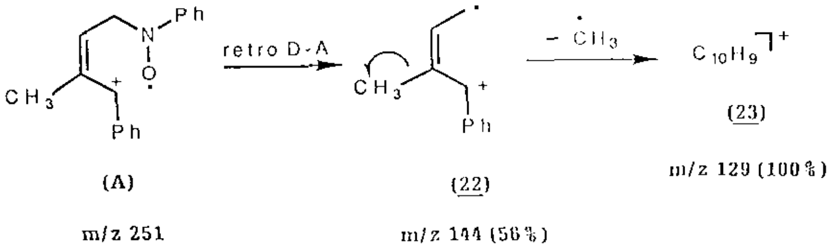


Scheme 9

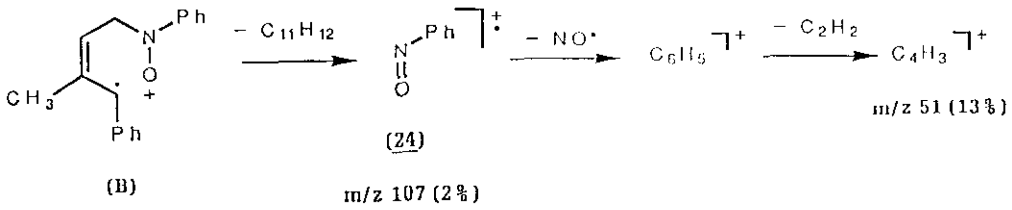
Retro Diels-Alder Fragmentations. The primary ionization of the 3,6-dihydro-1,2-oxazine molecule which is assumed to take place at the double bond, and which is followed by allylic cleavage, may lead to four possible molecular ions (A,B,C,D; Scheme 10). Since product A represents a secondary carbocation while product C is a primary carbocation, the formation of the former will correspond to the energetically more favored allylic cleavage path, leading to species A and B.[13,15,16] The next step in the fragmentation process is a retro Diels-Alder decomposition which results in the radical-cation (22) of a butadienyl system. Molecular ions bearing methyl or ethyl substituents may produce exceptionally stable cations (23) by loss of methyl or ethyl groups as radicals. Such cations correspond in many cases to the base peaks (III, V, X, XII, XIII, XIV, XVIII, XIX, XXI; Scheme 11a).



Scheme 10



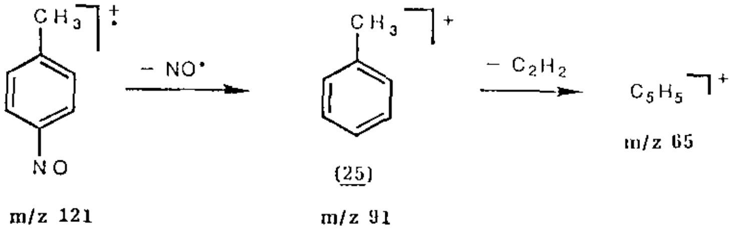
Scheme 11a



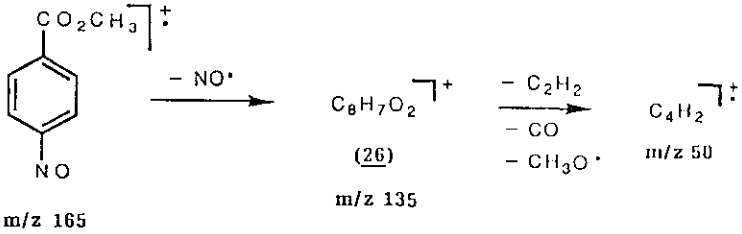
Scheme 11b

The second component of the retro Diels-Alder fragmentation, the nitroso compound which is observed in the mass spectra in negligible amount (2-4 %), is presumably due to the further fragmentation process of species B, which results in the radical-cation (24) and a neutral diene fragment ($C_{11}H_{12}$). The former undergoes sequential decomposition to smaller fragments. As was suggested previously,[13,17] nitrosobenzene may decompose by loss of nitric oxide to afford the phenyl cation which subsequently ejects an acetylene molecule to produce an ion of mass 51 (Scheme 11b). In the case of N-unsubstituted oxazines the retro Diels-Alder process affords only the butadienyl system. The nitroso compound is presumably lost as a nitric oxide (XVII, XVIII, XIX, XX, XXI, XXII, XXIII). The principal decomposition mode for p-nitrosotoluene might be analogous to that of nitrosobenzene. The elimination of nitric oxide would result in the tolyl cation (25). This cation which is observed in quite appreciable amounts (XI-18 %, XII-14 %), may undergo further decomposition by expulsion of an acetylene molecule to *yield a fragment of mass* 65 *(Scheme* 12*).*

Methyl p-nitrosobenzoate is assumed also to decompose by loss of nitric oxide to produce the rather unstable cation (26) which is observed in the mass spectra as a low intensity peak (XII-8 %, XIV-5 %, XV-6 %, XVI-8 %). Further decomposition of this cation is due to elimination of an acetylene molecule as well as the methylcarboxylate group. The latter is lost as carbon monoxide and a methoxy radical (Scheme 13).[12]

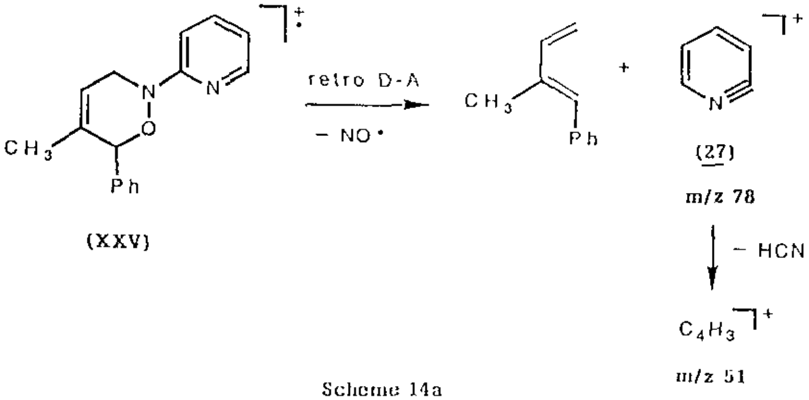


Scheme 12

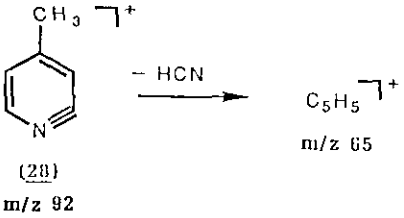


Scheme 13

Nitroso compounds which might arise from the retro Diels-Alder process for N-pyridyl substituted oxazines can be detected in the corresponding mass spectra as very low intensity peaks, usually of less than 1 % relative to the base peaks. The nitroso compound presumably decomposes to nitric oxide and a pyridine fragment ion (27). The latter appears in the mass spectra as a peak at m/z 78 for an oxazine bearing an unsubstituted pyridine moiety, or at m/z 92 when a C-methyl substituted pyridine group is present. Further degradation of the pyridine nucleus is facilitated by the electron attracting properties of the nitrogen atom. The most energetically favorable mode of fragmentation of the pyridine nucleus is assumed to involve bond scission followed by loss of hydrogen cyanide in a one-step process. For an unsubstituted pyridine system this is observed as the transformation m/z 78⟶51. In the case of a 2-methyl- or 4-methylpyridine moiety, the elimination of hydrogen cyanide leads to the formation of a fragment which is observed at m/z 65 (Schemes 14a and 14b).[18,19]



Scheme 14a



Scheme 14b

In conclusion, the electron impact induced fragmentation of 3,6-dihydro-1,2-oxazines proceeds by two principal pathways, namely, dehydration and retro Diels-Alder cycloaddition to give pyrrole and butadienyl cations, respectively. These initial fragments subsequently undergo further decomposition by processes which are characteristic of these systems. All alkyl substituted pyrroles consequently yield pyridinium cations. The preferred mode of fragmentation depends on the kind and the number of alkyl groups present in the pyrrole unit. The secondary allylic ions of a butadienyl system subsequently degrade to the most stable form by loss of alkyl groups.

EXPERIMENTAL

The 3,6-dihydro-1,2-oxazines used for the generation of these mass spectra were prepared either at the University of Science and Technology, Kumasi, Ghana,[2] or at Central Michigan University, Mount Pleasant, Michigan, USA.[3] Mass spectra were recorded using a Hewlett-Packard model 5995A gas chromatograph/mass spectrometer with programmed elution (90°-200°) through a 10 m x 0.32 mm id fused silica capillary column coated with poly(dimethylsiloxane) into the spectrometer inlet or by using a rapid ballastic elution from a direct insertion probe. In all instances, an ionizing potential of 70 electron volts was utilized.

Table 1. Principal peaks in the mass spectra of 3,6-dihydro-1,2-oxazines.

I.	237(100), 220(10), 219(59), 218(12), 217(6), 191(5), 131(8), 130(67), 129(36), 128(11), 116(10), 115(41), 107(20), 104(6), 102(7), 91(6), 89(8), 78(6), 77(36), 63(5), 51(17), 39(6).
II.	189(15), 187(7), 185(13), 184(7), 174(10), 172(16), 171(78), 170(100), 168(7), 167(5), 157(5), 156(22), 155(7), 154(12), 144(6), 143(5), 130(12), 129(15), 128(12), 127(6), 118(12), 117(10), 115(14), 107(13), 104(13), 103(6), 96(12), 95(8), 94(5), 93(13), 92(6), 91(7), 82(13), 81(9), 78(9), 77(70), 74(5), 67(36), 66(11), 65(18), 64(6), 63(8), 54(6), 53(15), 52(14), 51(50), 50(16), 43(8), 42(7), 41(27), 40(10), 39(47), 38(10), 37(5).
III.	251(48), 234(11), 233(62), 232(34), 158(6), 145(8), 144(56), 143(14), 130(15), 129(100), 128(25), 127(8), 122(7), 115(11), 104(8), 77(26), 51(13), 39(6).
IV.	251(100), 236(8), 234(8), 233(47), 232(32), 230(5), 192(7), 191(6), 189(8), 145(8), 144(62), 143(13), 130(8), 129(82), 128(80), 127(7), 115(20), 112(12), 104(11), 103(6), 102(8), 91(3), 83(7), 78(5), 77(33), 71(7), 51(11), 41(7), 39(6).
V.	265(63), 247(27), 233(8), 232(42), 230(5), 158(21), 143(5), 130(12), 129(100), 128(22), 127(6), 122(11), 115(7), 104(9), 91(6), 77(27), 51(10), 39(6).
VI.	295(100), 278(9), 277(42), 247(7), 246(39), 218(7), 217(10), 189(6), 188(23), 187(12), 180(5), 173(5), 130(12), 129(93), 128(27), 127(7), 115(12), 91(5), 77(23), 51(11).
VII.	203(40), 199(6), 188(9), 186(11), 185(73), 184(100), 171(6), 170(26), 169(5), 168(13), 167(6), 154(6), 144(5), 130(6), 129(10), 128(8), 118(9), 117(5), 115(5), 110(9), 109(11), 108(6), 107(6), 104(12), 97(88), 96(99), 95(15), 93(15), 91(7), 83(5), 82(6), 81(93), 79(9), 78(10), 77(65), 68(5), 67(15), 66(11), 65(14), 64(5), 63(6), 55(7), 53(12), 52(8), 51(37), 50(10), 44(23), 42(9), 41(24), 40(5), 39(34), 38(6).
VIII.	231(14), 214(5), 213(32), 212(7), 211(5), 199(16), 198(100), 196(12), 184(5), 183(6), 182(15), 168(7), 167(6), 124(26), 123(13), 118(5), 109(11), 104(7), 95(37), 93(8), 91(9), 81(7), 79(6), 78(7), 77(45), 67(9), 65(8), 55(7), 53(8), 52(5), 51(22), 44(5), 43(12), 41(16), 40(19), 39(18).
IX.	281(65), 265(13), 264(22), 263(97), 262(23), 249(10), 248(53), 220(6), 219(5), 218(6), 217(5), 204(8), 190(5), 188(7), 175(12), 174(100), 173(40), 171(7), 160(29), 159(89), 158(16), 145(8), 144(23), 143(25), 142(6), 131(9), 130(7), 129(8), 128(10), 127(5), 122(6), 117(5), 116(7), 114(15), 104(6), 91(10), 77(28), 65(5), 63(6), 51(12), 39(7).
X.	295(58), 278(16), 277(75), 263(18), 262(96), 231(12), 230(8), 218(8), 217(5), 202(9), 189(8), 188(46), 187(16), 174(22), 173(8), 160(12), 159(100), 145(8), 144(18), 143(5), 129(7), 128(7), 127(5), 122(10), 115(11), 104(9), 77(23), 65(5), 51(9), 41(5), 39(7).
XI.	295(63), 278(22), 277(100), 263(12), 262(60), 232(6), 218(6), 188(5), 175(8), 174(74), 173(28), 160(12), 159(63), 158(11), 145(5), 144(15), 143(21), 142(7), 131(6), 129(10), 128(7), 116(8), 115(11), 91(18), 77(7), 65(10), 63(5), 39(6).
XII.	309(76), 292(20), 291(88), 277(21), 276(100), 262(5), 261(5), 260(5), 246(6), 245(14), 244(7), 232(6), 231(5), 218(5), 217(5), 202(7), 189(9), 188(43), 187(14), 174(8), 173(6), 171(5), 160(11), 159(100), 157(8), 145(8), 144(14), 136(5), 129(8), 128(9), 118(6), 115(8), 91(14), 77(6), 65(10).
XIII.	309(90), 292(19), 291(78), 290(34), 278(15), 232(7), 231(5), 230(6), 217(5), 180(21), 145(10), 144(71), 143(15), 135(8), 130(17), 129(100), 128(28), 127(11), 120(5), 115(8), 104(10), 103(7), 91(5), 77(13), 76(7), 51(6).
XIV.	323(72), 306(16), 305(67), 292(14), 291(17), 290(78), 231(11), 230(13), 180(26), 162(5), 158(22), 157(5), 143(5), 135(5), 130(13), 129(100), 128(20), 127(6), 120(5), 115(8), 104(6), 103(5), 77(9), 76(5).
XV.	339(38), 322(21), 321(100), 308(9), 307(9), 306(33), 262(7), 218(7), 188(6), 180(5), 175(7), 174(62), 173(200), 160(22), 159(52), 145(5), 144(9), 143(13), 135(6), 129(5), 128(5), 120(5), 115(8), 103(5), 91(6), 77(7).
XVI.	353(43), 336(25), 335(100), 322(11), 321(25), 320(86), 304(5), 289(11), 288(5), 276(6), 261(7), 230(5), 217(7), 202(6), 189(6), 188(39), 187(13), 180(8), 174(26), 173(6), 160(9), 159(81), 157(6), 145(5), 144(12), 135(8), 129(6), 128(6), 120(6), 115(9), 103(6), 77(8).
XVII.	175(14), 160(11), 159(8), 158(51), 157(80), 156(100), 154(7), 144(21), 143(24), 141(6), 131(5), 130(14), 129(92), 128(63), 127(29), 126(5), 117(9), 116(12), 115(47), 105(8), 104(5), 103(10), 91(16), 89(10), 80(5), 79(5), 78(14), 77(33), 76(9), 75(7), 74(7), 65(13), 64(8), 63(17), 62(7), 52(9), 51(28), 50(12), 39(20), 38(5).

XVIII. 175(2), 158(14), 157(45), 156(65), 145(6), 144(45), 143(13), 141(5), 130(12), 129(100), 128(42), 127(12), 116(6), 115(23), 105(6), 104(6), 103(5), 102(6), 91(7), 89(6), 78(15), 77(19), 71(5), 65(8), 63(10), 60(5), 52(5), 51(16), 50(8), 42(5), 39(13).

XIX. 127(22), 112(34), 110(15), 109(51), 108(87), 107(9), 96(27), 95(20), 94(42), 93(14), 82(13), 81(100), 80(10), 79(21), 77(8), 70(8), 69(7), 68(12), 67(31), 66(9), 65(16), 63(6), 60(6), 56(7), 55(19), 54(11), 53(26), 52(10), 51(14), 50(9), 44(8), 43(58), 42(70), 41(65), 40(18), 39(76), 38(13).

XXa. 155(8), 138(6), 137(27), 136(7), 135(5), 126(5), 124(12), 123(16), 122(100), 120(19), 109(9), 108(11), 107(23), 106(6), 96(5), 95(27), 94(6), 93(8), 91(5), 82(5), 81(12), 79(8), 77(10), 68(5), 67(18), 65(6), 60(7), 57(5), 55(12), 53(10), 51(6), 43(12), 42(17), 41(18), 39(17).

XXb. 155(7), 138(14), 137(28), 124(7), 123(5), 122(14), 112(7), 110(15), 105(35), 108(100), 107(11), 106(10), 96(5), 95(25), 94(10), 93(28), 92(5), 82(11), 81(18), 80(13), 79(10), 77(10), 68(6), 67(24), 65(8), 55(16), 54(5), 53(15), 52(7), 51(8), 50(6), 43(13), 42(8), 41(25), 40(7), 39(28).

XXI. 189(4), 172(33), 171(54), 170(6), 168(5), 158(9), 157(39), 156(94), 154(10), 144(13), 143(9), 141(7), 130(13), 129(100), 128(51), 127(21), 117(5), 116(6), 115(22), 105(24), 104(6), 103(7), 102(7), 91(9), 89(7), 78(11), 77(37), 76(8), 75(5), 74(5), 64(7), 63(17), 62(5), 53(6), 52(9), 51(31), 50(13), 41(9), 39(24), 38(5).

XXII. 201(6), 189(11), 188(69), 187(95), 186(31), 174(20), 173(65), 172(100), 159(29), 158(11), 155(6), 145(14), 144(27), 143(22), 142(9), 135(29), 131(6), 129(7), 128(19), 127(12), 117(23), 116(19), 115(48), 104(5), 103(9), 102(9), 93(11), 92(12), 91(19), 90(7), 89(11), 78(7), 77(19), 76(6), 75(8), 74(8), 65(10), 64(10), 63(21), 62(9), 53(11), 52(19), 51(18), 50(13), 41(6), 39(20), 38(10).

XXIII. 201(63), 188(16), 187(58), 186(100), 171(11), 159(33), 156(12), 155(20), 154(12), 144(37), 143(14), 142(11), 135(13), 129(13), 128(19), 127(14), 117(11), 116(13), 115(33), 101(10), 92(11), 91(9), 89(9), 77(15), 65(11), 64(12), 63(14), 51(17), 50(10), 41(11), 39(17), 38(9).

XXIV. 190(89), 174(12), 173(86), 172(46), 171(38), 161(27), 160(6), 159(20), 158(14), 157(9), 147(13), 146(20), 145(22), 144(16), 133(8), 132(14), 131(8), 123(19), 121(8), 119(6), 117(5), 108(17), 107(5), 94(14), 93(87), 92(100), 81(10), 80(17), 67(5), 66(26), 65(60), 63(6), 55(5), 54(5), 53(18), 52(12), 51(12), 50(6), 41(16), 40(9), 39(43), 38(8).

XXV. 252(100), 235(22), 234(42), 233(41), 219(14), 218(5), 209(6), 159(9), 156(5), 145(7), 144(1 2), 143(9), 131(5), 130(10), 129(63), 128(25), 123(20), 115(9), 110(5), 105(5), 91(6), 79(9), 78(23), 77(10), 52(8), 51(16), 39(6).

XXVI. 266(100), 250(5), 249(22), 248(34), 247(35), 233(14), 159(9), 145(8), 144(17), 143(12), 137(11), 130(12), 129(83), 128(27), 127(10), 124(5), 114(11), 109(5), 108(7), 93(14), 92(21), 91(9), 77(13), 66(8), 65(24), 53(5), 52(5), 51(10), 39(15).

XXVII. 266(100), 249(16), 248(32), 247(31), 233(9), 223(11), 173(6), 159(12), 158(7), 144(20), 143(13), 137(13), 133(6), 132(5), 130(10), 129(97), 128(30), 127(9), 124(5), 114(13), 109(5), 108(12), 93(17), 92(24), 91(11), 77(14), 66(8), 65(30), 53(5), 51(10), 39(14).

XXVIII. 266(100), 249(17), 248(33), 247(7), 234(9), 233(43), 219(6), 209(7), 172(7), 157(9), 145(5), 143(8), 130(13), 129(99), 128(27), 127(9), 122(35), 119(9), 117(6), 116(6), 114(19), 109(10), 105(8), 95(6), 91(11), 79(10), 51(20), 41(9), 39(8).

XXIX. 296(100), 280(6), 279(29), 278(66), 277(35), 264(10), 263(29), 262(16), 235(6), 166(13), 174(19), 173(31), 172(6), 171(5), 161(5), 160(9), 159(62), 153(12), 144(15), 143(17), 142(5), 137(11), 134(5), 123(17), 121(9), 116(6), 114(10), 93(9), 92(17), 91(8), 77(7), 66(5), 65(15), 39(9).

Table 2. The ratio of pyrrole fragment ion to molecular ion for electron impact induced fragmentation of 3,6-dihydro-1,2-oxazines.

1,2-Oxazine	$\frac{[M-H_2O]^{+\cdot}}{[M]^{+\cdot}}$	1,2-Oxazine	$\frac{[M-H_2O]^{+\cdot}}{[M]^{+\cdot}}$
I.	0.59	XVI.	2.33
II.	3.08	XVII.	5.71
III.	1.29	XVIII.	22.50
IV.	0.47	XIX.	2.32
V.	0.43	XX.	3.38
VI.	0.42	XXI.	13.50
VII.	1.83	XXII.	95.00
VIII.	2.29	XXIII.	63.00
IX.	1.49	XXIV.	0.52
X.	1.29	XXV.	0.42
XI.	1.59	XXVI.	0.38
XII.	1.16	XXVII.	0.32
XIII.	0.87	XXVIII.	0.33
XIV.	0.93	XXIX.	0.66
XV.	2.63		

Table 3. The relative abundance of ions formed by loss of methyl or ethyl groups as radicals from the pyrrole nucleus.

Pyrrole (Pyr) Nucleus		$\%[Pyr]^{+\cdot}$	$\%[Pyr-15]^{+}$	$\%[Pyr-29]^{+}$
II.	2,3-dimethyl	78	22	---
III.	3-methyl	62	---	---
IV.	2-methyl	47	---	---
V.	3-ethyl	27	42	3
VII.	2,3,5-trimethyl	73	26	---
VIII.	3,5-diethyl-2-methyl	32	100	5
IX.	3-methyl	97	53	---
X.	3-ethyl	75	96	3
XI.	3-methyl	100	60	---
XII.	3-ethyl	88	100	5
XIII.	3-methyl	78	2	---
XIV.	3-ethyl	67	78	1
XV.	3-methyl	100	33	---
XVI.	3-ethyl	100	86	2
XVII.	3-methyl	80	3	---
XVIII.	2-methyl	45	2	---
XIX.	2,3,5-trimethyl	51	42	---
XX.	3,5-diethyl-2-methyl	27	100	11
XXI.	3-ethyl	54	94	3
XXII.	3-methyl	95	100	---
XXIII.	3-ethyl	63	100	---
XXIV.	3-methyl	46	9	---
XXV.	3-methyl	42	14	---
XXVI.	3-methyl	37	14	---
XXVII.	3-methyl	32	9	---
XXVIII.	3-ethyl	33	42	6
XXIX.	3-methyl	66	30	---

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