Enamine Chemistry. Part XV.[1] Mass Spectra of Dienamines

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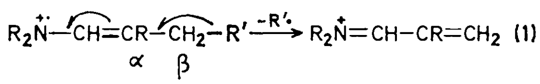
The mass spectra of dienamines derived from αβ-unsaturated aldehydes and ketones have been studied. The presence of the additional double bond considerably complicates the fragmentation, compared with that of simple enamines, and cleavage α to the double bond (vinylic cleavage) or rearrangement and complex fission processes may predominate over the allylic or β-fission processes observed in simple enamines. The fragmentation of the cyclic dienamines studied is dominated by aromatisation of the unsaturated six-membered ring.

THE mass spectra of acyclic enamines have previously been shown [2] to be relatively simple, the principle mode of fragmentation of the molecular ion involving β-fission [process (1)]. This process results in the form-



$$R_2\overset{+\cdot}{N}-\underset{\alpha}{CH}=CR-\underset{\beta}{CH_2}-R' \xrightarrow{-R'\cdot} R_2\overset{+}{N}=CH-CR=CH_2 \quad (1)$$

ation of stable eniminium ions which often form the base peak and which carry a high percentage of the total ion current.[2] We have examined the mass spectra of a series of linear and cross-conjugated acyclic and cyclic dienamines, available from previous work,[3,4] and find that the presence of the second double bond completely alters the mode of fragmentation. It appears that vinylic fission or fission of the terminal double bond may play a more important role than simple allylic or β-fission. The reasons for this are discussed below.

6-Methyl-4-morpholinonona-3,5-diene [(Ia); one stereoisomer shown] gives peaks at *m/e* 208 and 194 (Figure 1) formed by allylic or β-fission, and elimination of methyl and ethyl radicals respectively, but the base peak (*m/e* 180) corresponds to loss of a propyl radical. Loss of the terminal propyl group from the molecular ion (II) would involve vinylic fission of the C(d)–C(e) bond (numbering as in Scheme 1) and would normally be less favourable than allylic or β-fission, which could be expected to lead to stable conjugated eniminium ions such as (III) and (IV) (Scheme 1). It was therefore necessary to consider the possibility that the base peak was formed by fission of the C(a)–C(b) bond of the molecular ion, with hydrogen transfer, leading to loss of a propyl group by a concerted process as shown in Scheme 2.

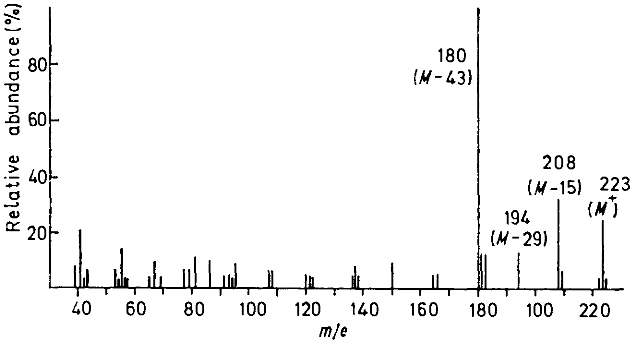
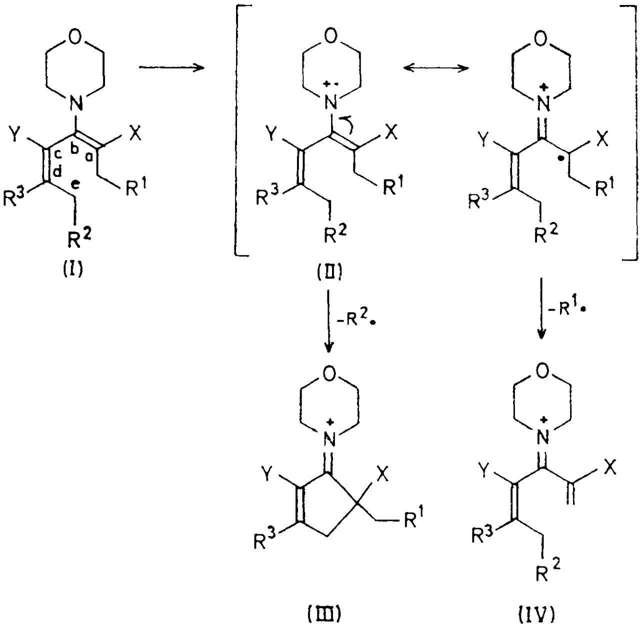


FIGURE 1 Mass spectrum of compound (Ia)



a; $R^1 = R^3 = $ Me, $R^2 = $ Et, $X = Y = H$
b; $R^1 = R^3 = $ Me, $R^2 = $ Et, $X = D$, $Y = H$
c; $R^1 = R^3 = $ Me, $R^2 = $ Et, $X = Y = D$
d; $R^2 = R^3 = $ Me, $R^1 = X = Y = H$

SCHEME 1

In order to ascertain unambiguously from which end of the carbon chain the propyl group was lost, attempts were made to prepare the monodeuteriated enamine (Ib). However it was not possible to accomplish this without also incorporating deuterium at C(c). The best deuteriated sample obtained (see Experimental section) consisted of a mixture of non-deuteriated (Ia) (41%), monodeuteriated (Ib) (40%), dideuteriated (Ic) (17%), and trideuteriated dienamine (2%). The mass spectrum of this mixture (Figure 2) showed fragment ions at *m/e* 180,

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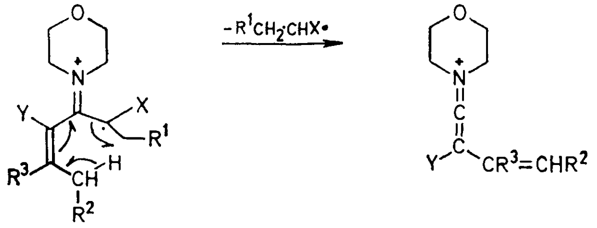
[1] Part XIV, P. W. Hickmott and G. Sheppard, *J.C.S. Perkin I*, 1972, 1938.

[2] H. J. Jakobsen, S.-O. Lawesson, J. T. B. Marshall, G. Schroll, and D. H. Williams, *J. Chem. Soc.* (*B*), 1966, 940.

[3] (*a*) N. F. Firrell and P. W. Hickmott, *J. Chem. Soc.* (*B*), 1969, 293; *J. Chem. Soc.* (*C*), 1970, 716; N. F. Firrell, P. W. Hickmott, and B. J. Hopkins, *ibid.*, p. 1477; (*b*) N. F. Firrell, P. W. Hickmott, and B. J. Hopkins, *J. Chem. Soc.* (*B*), 1971, 351.

[4] P. W. Hickmott, B. J. Hopkins, and C. T. Yoxall, *J. Chem. Soc.* (*B*), 1971, 205.

181, and 182, which had virtually the same relative abundance ratios (1·96 : 2·05 : 1) as the corresponding molecular ions ($[M]^{+\cdot} : [M + 1]^{+\cdot} : [M + 2]^{+\cdot} = 1{\cdot}86 : 2{\cdot}22 : 1$). The ratio of the total ion current carried by the fragment ions at *m/e* 180, 181, and 182 to that carried by the molecular ions at *m/e* 223, 224, and 225 in the deuteriated sample (4 : 1) was the same as that in the non-deuteriated dienamine (Table I). If the neutral fragment lost does *not* contain deuterium then the ratio of the relative abundances of the fragment ions at *m/e* 180, 181, and 182, should remain the same as that for the molecular ions ($[M]^{+\cdot} : [M + 1]^{+\cdot} : [M + 2]^{+\cdot}$). If however the neutral fragment lost contains deuterium (as in Scheme 2, X = D) then the intensity of the peak at *m/e* 180 should increase relative to that at 181 and there should be no ion corresponding to *m/e* 182. Since the relative abundance ratios of the fragment ions and molecular ions are in such close agreement, we conclude that formation of the base peak occurs by fission of the C(d)–C(e) bond. Similarly in the case of 6-methyl-4-pyrrolidinonona-3,5-diene (Table 2) the $[M - \mathrm{Pr}]^+$ ion forms the base peak at *m/e* 164, whereas the $[M - 15]^+$ ion, formed by β-fission of a methyl radical, and the $[M - 29]^+$ ion, formed by allylic fission of an ethyl group, are considerably less abundant. Formation of base peaks by fission of the C(d)–C(e) bond also occurs in the fragmentation of 5-methyl-3-morpholinohepta-2,4-diene (Id) and 3,5-dimethyl-2-morpholinohexa-1,3-diene (V) to give an $[M - \mathrm{Et}]^+$ ion at *m/e* 166 and an $[M -$



SCHEME 2

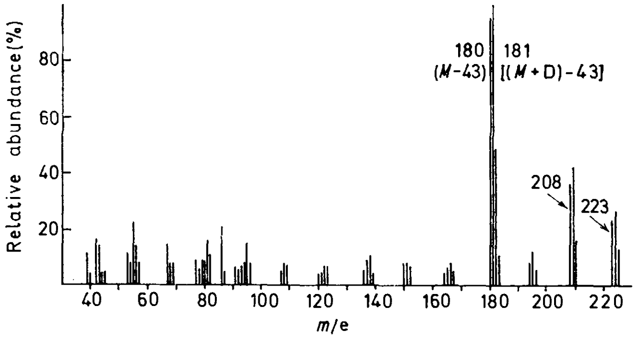


FIGURE 2 Mass spectrum of the mixture (Ia) and its mono-, di-, and tri-deuteriated isomers

TABLE 1

Percentage of the total ion current (Σ_{30}) carried by some prominent ions of 6-methyl-4-morpholinonona-3,5-diene (Ia) and the deuteriated mixture (Ia—c) [a]

	m/e (Σ_{30})
Compound (Ia)	224 (0·9), 223 (5·3), 222 (0·9), 208 (9·2), 194 (2·8), 181 (2·8), 180 (22·0)
Mixture (Ia—c)	225 (1·4), 224 (3·1), 223 (2·6), 222 (0·3), 210 (1·8), 209 (4·8), 208 (4·0), 195 (1·4), 194 (0·9), 183 (1·3), 182 (5·6), 181 (11·5), 180 (11·0)

[a] Samples introduced through a heated inlet system at 220°.

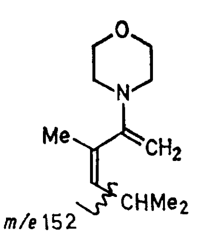
TABLE 2

Mass spectral data of acyclic cross-conjugated dienamines [a]

5-Methyl-3-morpholinohepta-2,4-diene (Id) (M.W. 195) [b]	
m/e (%)	196 (6), 195 (33), 194 (9), 180 * (35), 167 (13), 166 * (100), 150 (9), 138 (7), 137 (7), 136 (21), 126 (7), 122 (17), 109 (12), 108 (15), 107 (6), 97 (9), 95 (9), 93 (15), 91 (8), 86 (14)
3,5-Dimethyl-2-morpholinohexa-1,3-diene (V) (M.W. 195)	
m/e (%)	196 (8), 195 (23), 194 (6), 182 (19), 180 (10), 170 (8), 168 (15), 166 (12), 154 (19), 153 (14), 152 * (100), 150 (8), 140 (15), 138 (12), 137 (8), 136 (12), 128 (14), 126 (12), 125 (10), 124 (12), 123 (10), 122 (29), 121 (6), 114 (23), 112 (8), 111 (27), 110 (15), 109 (19), 108 (15), 107 (9), 106 (6), 100 (12), 99 (6), 98 (12), 97 (15), 96 (15), 95 (19), 94 (17), 93 (19), 91 (15), 88 (6), 87 (19), 86 (31), 85 (14), 84 (10), 83 (25), 82 (14), 81 (23), 80 (8)
6-Methyl-4-pyrrolidinonona-3,5-diene (M.W. 207) [b]	
m/e (%)	208 (5), 207 (19), 193 (8), 192 (38), 178 (19), 165 (13), 164 (100), 162 (6), 154 (8), 150 (10), 148 (8), 136 (10), 134 (6), 124 (6), 122 (10), 120 (6), 111 (54), 110 (6), 98 (6), 96 (6), 95 (10), 93 (6), 91 (10), 83 (8), 82 (6), 81 (15), 79 (10), 77 (10), 71 (46), 70 (54), 69 (15)
H.R. [c]	207·1990 ($C_{14}H_{25}N$), 111·0812 ($C_7H_{11}O$),[d] 70·0658 (C_4H_8N)

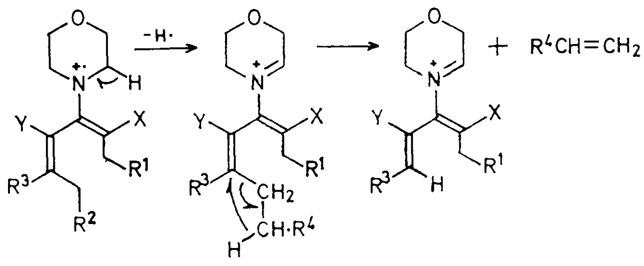
[a] Abundances as percentages of base peak. Values <5% are not quoted. [b] Sample introduced through a heated inlet system at 220°. [c] High resolution mass measurements. [d] Attributed to the $\mathrm{Me[CH_2]_2CMe{:}CH{\cdot}CO^+}$ ion derived from the ketone produced by hydrolysis of the dienamine in the inlet system.

* Metastable peaks support the following transitions in compound (Id): *m/e* 195 → 180 $M - \mathrm{Me}$; *m/e* 195 → 166 $M - \mathrm{Et}$; and compound (V): *m/e* 195 → 152 $M - \mathrm{Pr}$.



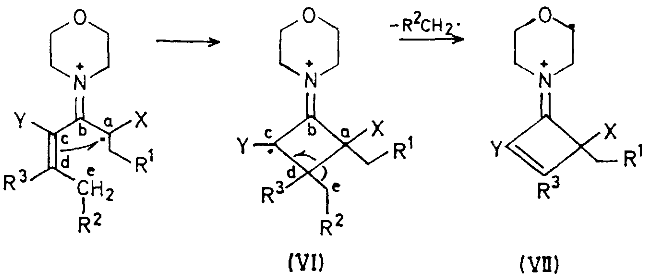
(V)

Pr^{i}]$^{+}$ ion at *m/e* 152 respectively. Both transitions are supported by metastable peaks, at *m/e* 141·5 and 118·3 respectively, and this makes it unlikely that the base peaks are formed from $[M - 1]^{+}$ ions as shown in Scheme 3.* The low intensity of the $[M - 15]^{+}$ ion in the dienamine (V) (Table 2) relative to that of the $[M - 43]^{+}$ ion also serves to provide further evidence against Scheme 2.



SCHEME 3

The explanation which we offer for the preferential fission of the C(d)–C(e) bond in all the acyclic cross-conjugated dienamines [(Ia—d) and (V)] which we have examined is shown in Scheme 4. Bond formation between C(a) and C(d) in the molecular ion is postulated to give the cyclic valence isomer (VI). Loss of the larger of the two radicals ($R^{3}\cdot$ or $R^{2}CH_{2}\cdot$) then occurs to give the observed base peak. This fragmentation is favoured over loss of $R^{1}CH_{2}\cdot$, $X\cdot$, or $Y\cdot$, since a conjugated eniminium ion (VII) is formed in which the stability may be further enhanced by transannular 1,3 π-bonding interactions.[5]



SCHEME 4

In contrast to the cross-conjugated dienamines, the acyclic linear conjugated dienamines (VIII) investigated (Table 3) produce prominent molecular ions (IX) which are, in fact, the base peaks in two of the three examples studied. The enhanced stability of the molecular ions (IX) can be attributed to the fact that the steric interactions which cause the cross-conjugated dienamines to be non-planar[4] are absent from the linear dienamines. The planarity of the conjugated system therefore allows extensive delocalisation in the radical ion [(IXa) ↔ (IXb) ↔ *etc.*). In the case of 3-methyl-1-morpholinobuta-1,3-diene (Figure 3) the base peak is formed by loss of the methyl radical to give the conjugated eniminium ion (X), typical of simple enamine fragmentation. Further fragmentation is complicated. The ions at *m/e* 94 and 95, for example, are due to $C_6H_8N^+$ and $C_6H_9N^{+\cdot}$ (high resolution) and presumably arise by partial fission of the morpholine ring and cyclisation onto the terminal position of the diene chain to give structures such as

TABLE 3

Mass spectral data of acyclic linear conjugated dienamines [a]

1-Morpholinobuta-1,3-diene (VIIIa) (M.W. 139)

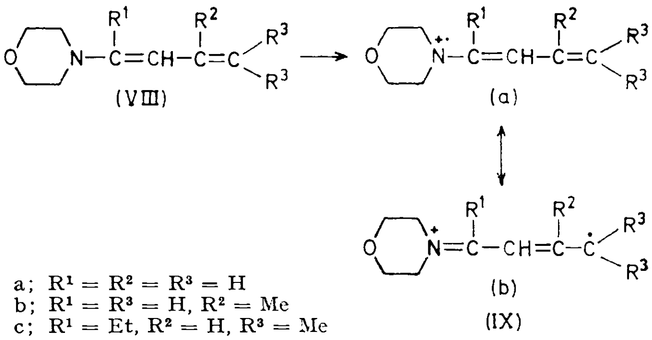
m/e (%) 140 (9·7), 139 (100), 138 (9), 126 (7), 124 (25), 115 (5), 110 (7), 109 (18), 108 (19), 95 (6), 94 (30), 87 (15), 86 (8), 82 (24), 81 (79), 80 (76), 79 (7), 69 (12), 68 (10), 67 (13)

2-Methyl-5-morpholinohepta-2,4-diene (VIIIc) (M.W. 195)

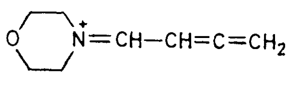
m/e (%) 196 (23), 195 (100), 194 (20), 182 (5), 181 (7), 180 * (16), 170 (19), 166 * (21), 154 (9), 153 (9), 152 * (68), 150 (12), 143 (6), 140 (21), 138 (7), 136 (10), 128 (26), 126 (13), 125 (14), 124 (8), 123 (6), 122 (29), 114 (18), 113 (9), 110 (5), 109 (111), 108 (14), 107 (7), 100 (14), 99 (10), 97 (7), 96 (13), 95 (11), 94 (11), 93 (12), 91 (8), 87 (7), 86 (21), (85 (10)

[a] Abundances as percentages of base peak. Values <5% are not quoted.

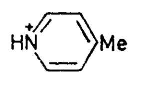
* Metastable peaks support the following transitions in compound (VIIIc): *m/e* 195 → 180 *M* − Me; *m/e* 195 → 166 *M* − Et; *m/e* 195 → 152 *M* − Pr.



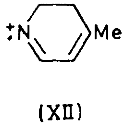
a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^3 = H, R^2 = Me$
c; $R^1 = Et, R^2 = H, R^3 = Me$



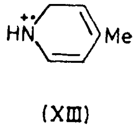
(X)



(XI)



(XII)



(XIII)

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* Suggested by a referee.

[5] T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, 1964, **86**, 1600.

(XI) and (XII) or (XIII). The most surprising feature of the mass spectrum of 2-methyl-5-morpholinohepta-2,4-diene (VIIIc) is the prominent peak at *m/e* 152 (Σ_{30} 7·0). This is formed by direct loss of an isopropyl radical from the molecular ion (m^* 118·3) and involves

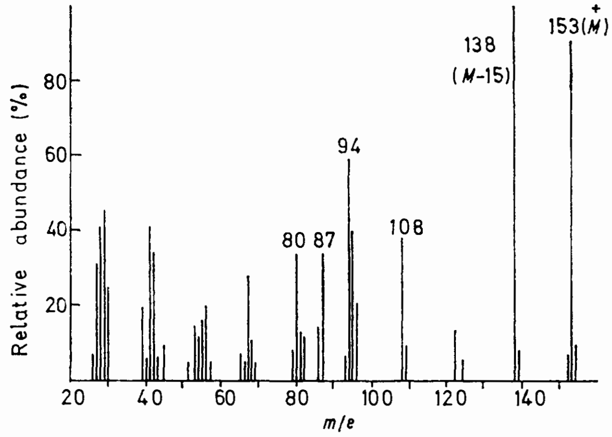
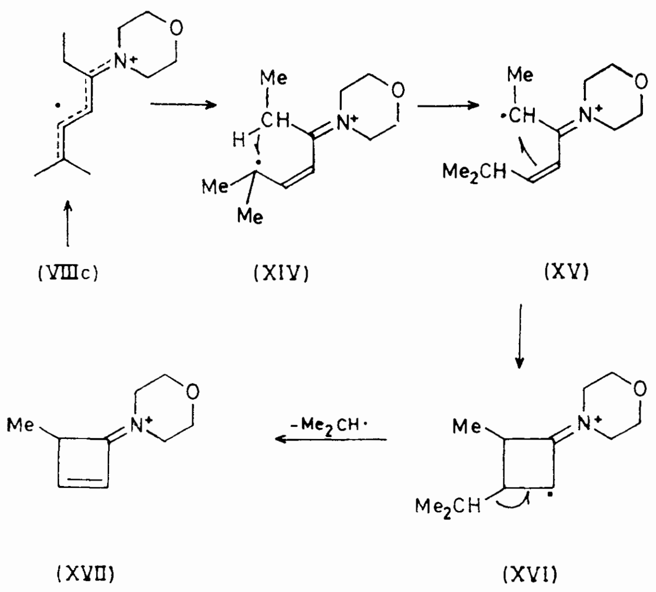


FIGURE 3 Mass spectrum of 3-methyl-1-morpholinobuta-1,3-diene

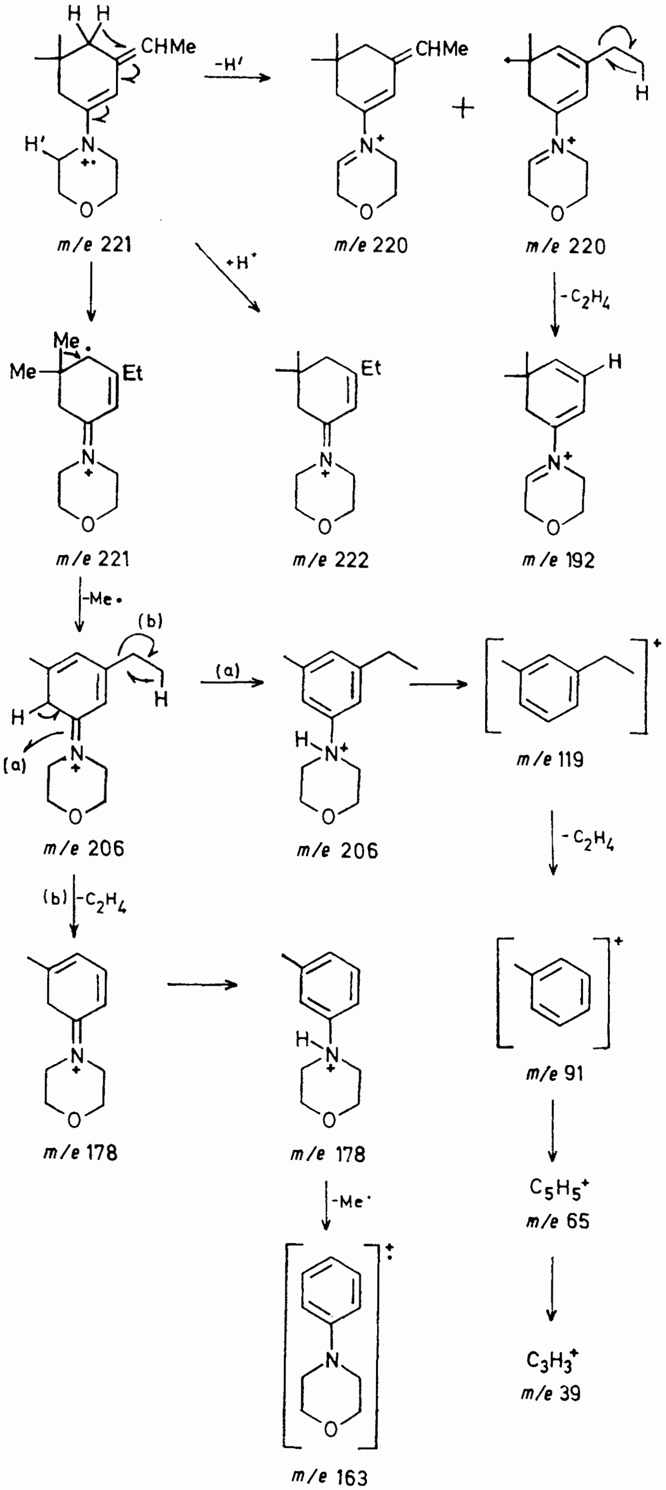
fission of the terminal double bond with hydrogen transfer. This can be rationalised as in Scheme 5.



SCHEME 5

Hydrogen transfer in the radical ion (XIV) generates a second radical ion (XV) which can then give a cyclic valence isomer (XVI) similar to that postulated previously [(VI); Scheme 4]. Loss of the isopropyl radical then generates an analogous cyclic eniminium ion (XVII) (*m/e* 152).

The cyclic dienamines examined (Table 4) were derived from 3-alkyl-5,5-dimethylcyclohex-2-en-1-ones and generally show strong $[M]^{+\cdot}$, $[M + 1]^+$ and $[M - 1]^+$



SCHEME 6

peaks. The most striking feature, however, is the very strong $[M - 15]^+$ ion, which generally forms the base peak, and which must arise by loss of one of the geminal methyl groups since in the case of 5,5-dimethyl-3-methylene-1-pyrrolidinocyclohex-1-ene (Table 4), where there are no other methyl groups, the $[M - \mathrm{Me}]^+$ ion still forms a base peak. Similar behaviour has been observed in the fragmentation of cyclohexanone enamines.[2,6] Most of the remaining fragmentation can readily be accounted for on this basis, as shown for 3-ethylidene-5,5-dimethyl-1-morpholinocyclohex-1-ene (Figure 4; Scheme 6). A peak at *m*/*e* 41 is often very prominent in the spectra of all the dienamines examined and is due to $C_3H_5^+$ (high resolution) mainly, with some contribution from $C_2H_3N^{+\bullet}$.

TABLE 4

Mass spectral data of cyclic dienamines [a]

5,5-Dimethyl-3-methylene-1-pyrrolidinocyclohex-1-ene (M.W. 191)	
m/*e* (%)	192 (19), 191 (100), 190 (21), 177 (43), 176 (100), 175 (13), 174 (30), 162 (16), 161 (55), 160 (30), 148 (17), 136 (16), 134 (16), 133 (7), 132 (7), 121 (10), 120 (9), 119 (11), 118 (7), 108 (7), 107 (17), 106 (19), 105 (30), 103 (7), 94 (6), 93 (10), 92 (7), 91 (40), 88 (8), 83 (6), 82 (7), 80 (7), 79 (25), 78 (10), 77 (32), 70 (30), 69 (6)
3-Isopropylidene-5,5-dimethyl-1-morpholinocyclohex-1-ene (M.W. 235)	
m/*e* (%)	236 (29), 235 (100), 234 (50), 221 (21), 220 (100), 206 (11), 194 (8), 192 (11), 190 (7), 178 (25), 177 (25), 176 (8), 160 (6), 149 (7), 148 (7), 147 (6), 146 (13), 139 (6), 135 (9), 134 (21), 133 (16), 132 (14), 131 (9), 121 (10), 120 (9), 119 (21), 118 (12), 117 (12), 115 (7), 108 (6), 107 (21), 106 (11), 105 (27), 94 (7), 93 (19), 92 (8), 91 (50)
3-Isopropylidene-5,5-dimethyl-1-pyrrolidinocyclohex-1-ene (M.W. 219)	
m/*e* (%)	220 (17), 219 (11), 218 (65), 217 (11), 205 (20), 204 (100), 203 (6), 202 (17), 190 (15), 188 (9), 178 (11), 176 (15), 175 (9), 174 (11), 162 (43), 161 (20), 160 (23), 149 (20), 148 (17), 147 (9), 146 (11), 136 (9), 135 (9), 134 (15), 133 (9), 132 (9), 131 (9), 121 (9), 120 (15), 119 (14), 118 (9), 117 (14), 115 (9), 110 (9), 109 (14), 108 (11), 107 (17), 106 (11), 105 (23), 96 (14), 95 (14), 94 (11), 93 (17), 92 (9), 91 (47), 83 (15), 82 (9), 81 (17), 80 (14), 79 (31), 78 (14), 77 (37), 71 (9), 70 (37), 69 (23)
5,5-Dimethyl-1-pyrrolidino-3-t-butylcyclohexa-1,3-diene (M.W. 233) [b]	
m/*e* (%)	234 (6), 233 (36), 232 (7), 219 (17), 218 (100), 163 (8), 162 (69), 161 (5), 160 (7), 120 (5), 91 (7), 57 (17), 41 (11), 29 (5)

[a] Abundances <5% are not quoted. [b] Sample introduced through a heated inlet system at 220°.

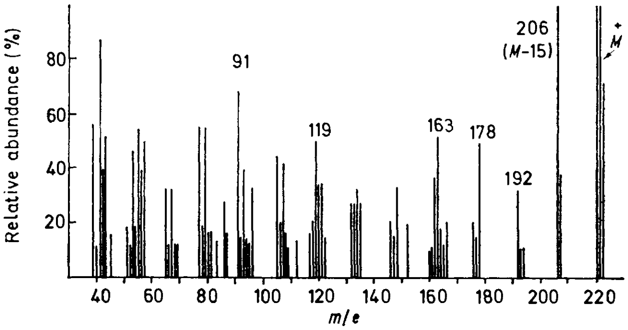


FIGURE 4 Mass spectrum of 3-ethylidene-5,5-dimethyl-1-morpholinocyclohex-1-ene

EXPERIMENTAL

Mass spectra were obtained on an A.E.I. MS12 mass spectrometer operating at 70 eV. Samples were introduced by means of a direct insertion probe in the temperature range 150—200°, unless stated otherwise. High-resolution measurements were carried out by the Physico-Chemical Measurements Unit, Harwell, with a resolving power of 10,000.

The preparation of the acyclic [3b,4] and cyclic [3a] dienamines has been reported previously.

Deuteriation of 6-*Methyl*-4-*morpholinonona*-3,5-*diene*.—Deuteriotrifluoroacetic acid (2·3 g, 0·02 mol) was added dropwise to a stirred solution of 6-methyl-4-morpholinonona-3,5-diene (2·23 g, 0·01 mol) in dry ether (20 ml). The deuteriated eniminium salt separated as an oil and after stirring for 2 h at ambient temperature the ether was decanted off and the residual oil was washed, by decantation, with dry ether. The oil was then suspended in dry ether (10 ml) and stirred with dry triethylamine (2·02 g, 0·02 mol) for 1 h at ambient temperature. No precipitate formed and the ether was evaporated *in vacuo* to give a liquid which separated into two layers. The top layer of dienamine was removed by means of a pipette and the whole process repeated twice to give the partially deuteriated dienamine mixture (see Discussion section).

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[1/1969 *Received*, 25*th October*, 1971]

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[6] P. P. Lynch, *Gazzetta*, 1969, 787.