Organic Mass Spectrometry, 1968, Vol. 1, pp. 703 to 712. Heyden & Son Limited. Printed in Northern Ireland

THE MASS SPECTRA OF SOME ALKYL AND ARYL IMIDAZOLINES

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(*Received* 19 *June* 1968; *accepted* 9 *July* 1968)

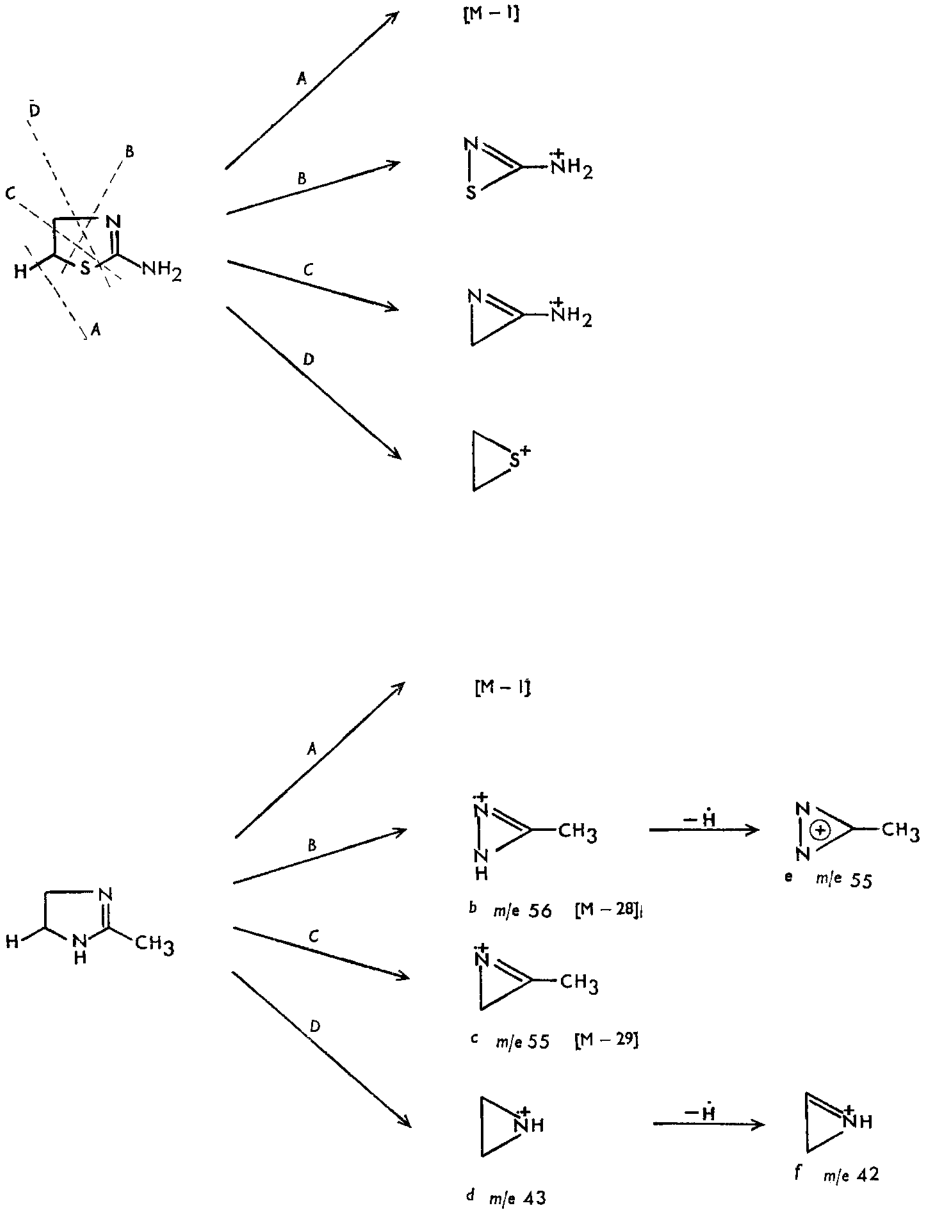
Abstract—The mass spectra of mono- and di-substituted alkyl and aryl imidazolines have been measured and the spectra analysed with the aid of deuterium labelling and high resolution techniques. In contrast to the fragmentation of thiazolines, all principal fragments of the imidazoline ring contain one nitrogen with or without hydrogen migration. In the case of 2,4-disubstituted imidazolines, the presence of two tautomeric molecular ions are suggested.

RECENTLY, Klayman and Milne investigated the mass spectra of some aminothiazolines[1] and proposed a general fragmentation of five-membered hetero-cyclics which contain one double bond in the ring. Since imidazolines have similar structures to thiazolines, only differing from the latter by the replacement of —S— with —NH—, their proposal was expected to be applicable to the fragmentation of the former under electron-impact. This paper deals with the mass spectra of some imidazolines in an attempt to detect any characteristic fragmentation due to the difference between these two atoms.

The spectra of 2-methylimidazoline (I) showed strong peaks at [M — 1], [M — 29] and [M — 42] (Table I). As with aminothiazolines the above three peaks were accounted for by fissions A, C and D respectively as shown in Scheme 1. Although no peak corresponding directly to the fragments of fission B or D was found in the spectra, the [M — 29] and [M — 42] peaks were considered to be possibly the fragments *e* and *f* originating from the resulted ions *b* and *d*, respectively.

From the above discussion it was assumed that the fragmentation of imidazolines was quite similar to that of thiazolines, and that in the case of the former a further elimination of hydrogen took place due to the presence of the second ring nitrogen.

Application of the above mentioned assumptions to 2-phenylimidazoline (III) reveals the characteristic fragmentation of 2-substituted imidazolines as follows. In the spectrum of 2-phenylimidazoline there is a strong peak at *m/e* 104 but no peak at *m/e* 42 (Fig. 1). Judging from its *m/e* value the *m/e* 104 fragment obviously retains the phenyl group and it is concluded that the [M — 42] peak does not originate from fission D but from another fragmentation which is not observed in the case of thiazolines.[1]



SCHEME 1

On exchanging NH for ND, the *m/e* 104 peak shifts by one mass unit showing that either fission D with a hydrogen migration or fission E without a hydrogen migration takes place in this process as shown in Scheme 2. Since fission E is a kind of inhibited cleavage,[1] only the former process is conceivable at this stage.

Further studies on an accurate mass measurement of the fragment at *m/e* 117 [M − 42] reveal that the ion *g* is due solely to C_8H_7N (observed *m/e* 117·0577,

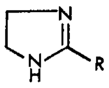
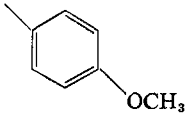
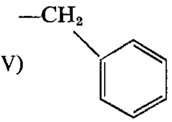
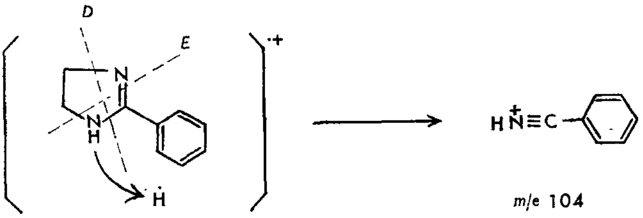


TABLE 1. MASS SPECTRA OF 2-SUBSTITUTED IMIDAZOLINES

No.	R	M$^{+\cdot}$	[M − 1]	[M − 29]	[M − 42]	Others							
(I)	—CH_3	*m/e* 84	83	55	42	41	43	54	73	85			
		% (36)	(17)	(100)	(40)	(11)	(25)	(33)	(5)	(4)			
(II)	—CH_2CH_3	98	97	69	56	38	39	40	41	42	43	44	52
		(50)	(31)	(100)	(20)	(10)	(25)	(28)	(52)	(41)	(21)	(16)	(13)
						53	54	55	57	58	67	68	70
						(9)	(73)	(22)	(12)	(8)	(10)	(20)	(14)
						81	82	83	95	96	99		
						(31)	(20)	(10)	(29)	(22)	(11)		
(IV)		176	175	147	134	41	42	63	64	77	78	89	90
		(81)	(53)	(100)	(15)	(7)	(10)	(10)	(7)	(34)	(9)	(7)	(8)
						91	102	103	104	105	117	119	131
						(8)	(6)	(6)	(8)	(5)	(8)	(8)	(9)
						132	133	148	158	159	174	177	
						(60)	(13)	(32)	(10)	(14)	(19)	(17)	
(V)		160	159	131	118	41	42	51	63	65	77	81	89
		(20)	(48)	(19)	(3)	(7)	(9)	(12)	(8)	(21)	(9)	(7)	(9)
						90	91	92	103	132			
						(6)	(100)	(11)	(7)	(6)			
(VII)	—$C_{17}H_{35}$	308	307	279	—	41	42	43	44	54	55	56	57
		(15)	(20)	(8)	—	(22)	(10)	(27)	(9)	(7)	(20)	(8)	(12)
						69	82	83	84	85	95	96	97
						(7)	(16)	(7)	(100)	(18)	(10)	(7)	(74)
						98	110	111	124	125	126	139	153
						(38)	(7)	(21)	(6)	(14)	(8)	(38)	(15)
						167	181	195	209	223			
						(11)	(9)	(10)	(8)	(7)			



SCHEME 2

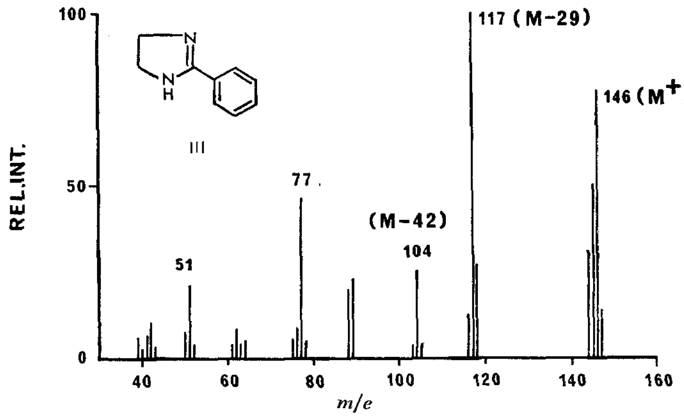
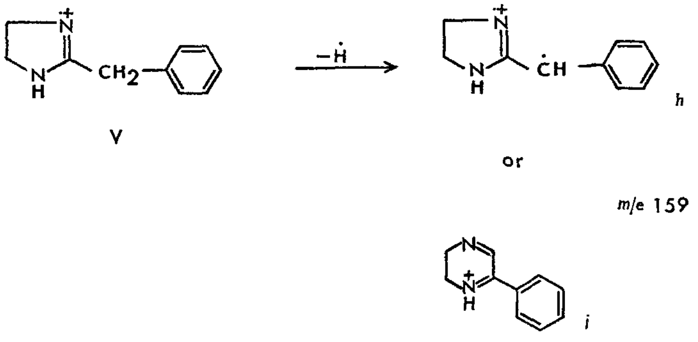


FIG. 1

calculated for C_8H_7N m/e 117·0578) and not due to the other conceivable ion $C_7H_5N_2$ (calculated for m/e 117·0453) which was thought at first to be the fragment resulting from fission B in accordance with the afore mentioned assumptions.

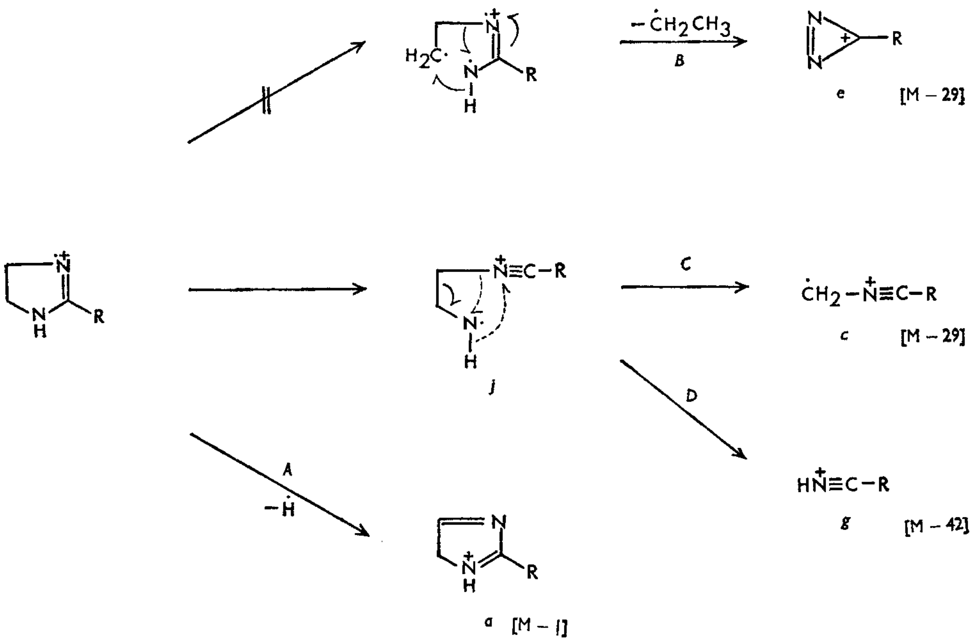
The principal peaks of the mass spectra of five 2-substituted imidazolines (I to V) are summarized in Table 1. Each has its base peak at [M − 29] and a characteristic peak at [M − 42] of 20 to 25% relative abundance except for the spectrum of 2-benzylimidazoline (V) showing a very strong base peak at m/e 91 (Tropylium cation) as well as a fairly strong [M − 1] peak which seems to be a resonance stabilized ion *h* or *i*[2] instead of the usual fragment through fission A (Scheme 3).



SCHEME 3

In case of 2-ethylimidazoline (II) and 2(4'-methoxy-phenyl) imidazoline (IV), strong peaks are present at [M — 43] (*m/e* 54 and 132, respectively). Although the appropriate metastable ions are not observed, these peaks seem to originate from loss of methyl radicals from the very abundant [M — 29] ions.

From the above mentioned facts and arguments the fragmentations of 2-substituted imidazolines can be summarized as in Scheme 4. That is, the fragmentations originate from homolysis of the C—N single bond to form an intermediate ion *j* from which further decompositions take place through processes C and D with or without hydrogen migration respectively. Fission A gives a [M — 1] fragment while fission C furnishes the [M — 29] (*c*) ion.



SCHEME 4. Fragmentation Scheme of 2-substituted imidazoline.

Another important fragment at *m/e* [M — 42] (*g*) is generated through fission D as mentioned above. The fact that the [M — 42] peak shifts by one mass unit on deuterium exchange makes it reasonable to regard fission D as a displacement rearrangement.[3]

In the case of long chain alkylsubstituted imidazolines such as 2-undecylimidazoline (VI) or 2-heptadecylimidazoline (VII), the base peaks in their spectra are present at *m/e* 84 which is well accounted for by the well known McLafferty rearrangement of the molecular ion to form ion *l* or *k* as shown in Scheme 5.[4] The composition of the *m/e* 97 fragment in the spectrum of 2-undecylimidazoline (Fig. 2) is determined as $C_5H_9N_2$ by the accurate mass measurement (found *m/e* 97·0803, calculated for $C_5H_9N_2$ *m/e* 97·0844) showing that the ion must contain the imidazoline moiety.

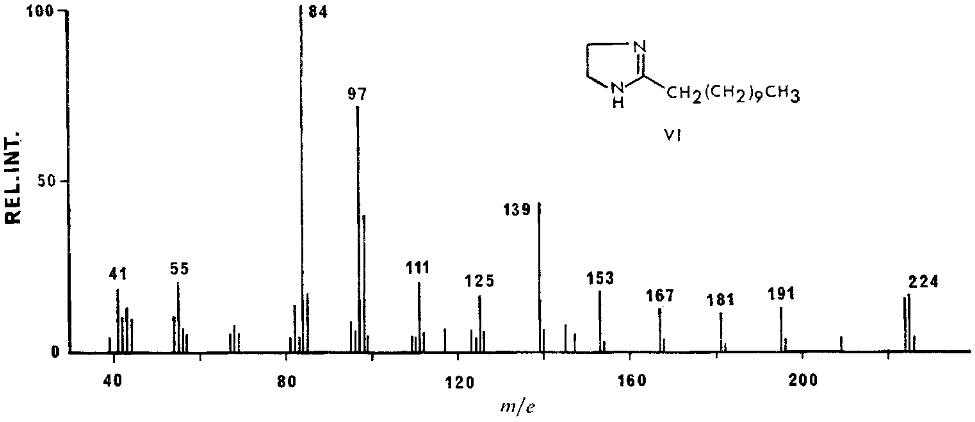
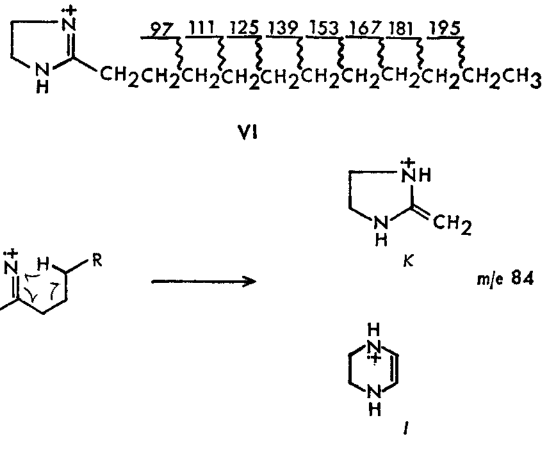


FIG. 2: Mass spectrum of 2-undecylimidazoline (VI)

Other peaks beside the above mentioned fragments are formulated in terms of well established fragmentations of alkylsubstituted heterocyclics[5] as summarized in Scheme 5.



SCHEME 5

The mass spectra of 2,4-disubstituted imidazolines are rather complex as shown in Fig. 3 which represents the spectrum of 2-phenyl-4-methylimidazoline (X). The principal peaks are elucidated through the fissions described hereafter.

Although the peaks at *m/e* 145, 131, and 104 are nicely formulated in accordance with the fissions established in the case of mono-substituted imidazolines, the base peak at *m/e* 117 seemed to correspond to a cleavage of the C=N double bond.

Accurate mass measurements of the peaks at *m/e* 131·0750 and *m/e* 117·0850 establish their compositions as C_9H_9N (calculated 131·0735) and C_8H_7N (calculated 117·0578), respectively. On deuterium exchange of NH for ND the peaks at *m/e* 145 and *m/e* 104 shifts by one mass unit and others remain unchanged.

Application of the fragmentation of mono-substituted imidazolines and consideration of the above experiments lead to a conclusion that the compound must consist of two species and that the apparent spectrum is the sum of two independent tautomeric forms of 2-phenyl-4-methylimidazoline (X).

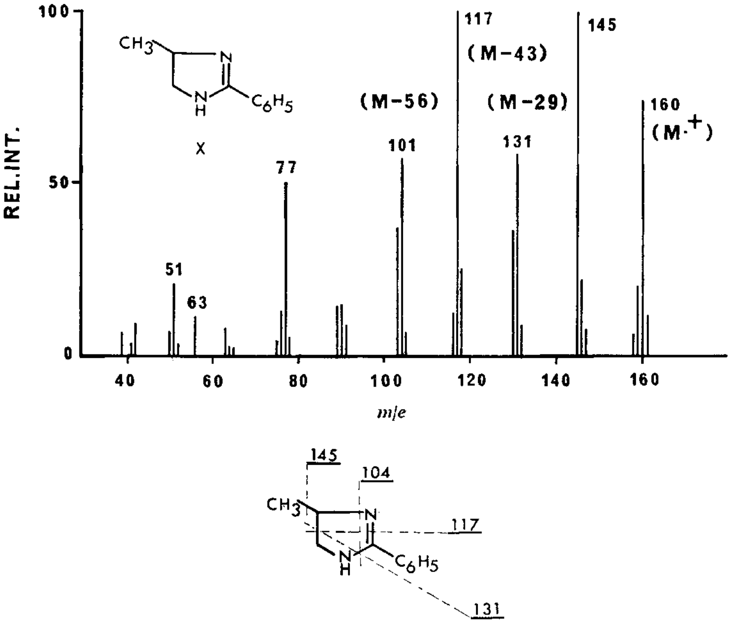


Fig. 3

Because of the absence of keto-enol tautomerism in fragment ions,[6] the above tautomerism must have taken place before electron-impact as in the case of β-keto-esters.[7]

Since the n.m.r. spectrum of X gives its methyl signal at δ^{CDCl_3} 1·20 ppm as a sharp doublet and those of 2-substituted imidazolines (I to V) show their ring methylene protons as sharp singlets, the rapid tautomerization must be present in the liquid state.

Although it is difficult to prove the presence of two tautomers in the vapour phase without isotope labelling on carbons or hydrogens attached to ring carbons, it is the most reasonable assumption to make at this stage.

The spectra of other 4-methyl-2-substituted imidazolines exhibit strong common peaks at *m/e* [M — 15], [M — 29], [M — 43] and [M — 56] as shown in Table 2. These fragmentations are explained similarly as in the case of 2-phenyl-4-methylimidazoline, i.e. the two molecular ions of their tautomers decompose independently

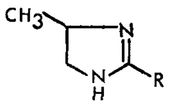
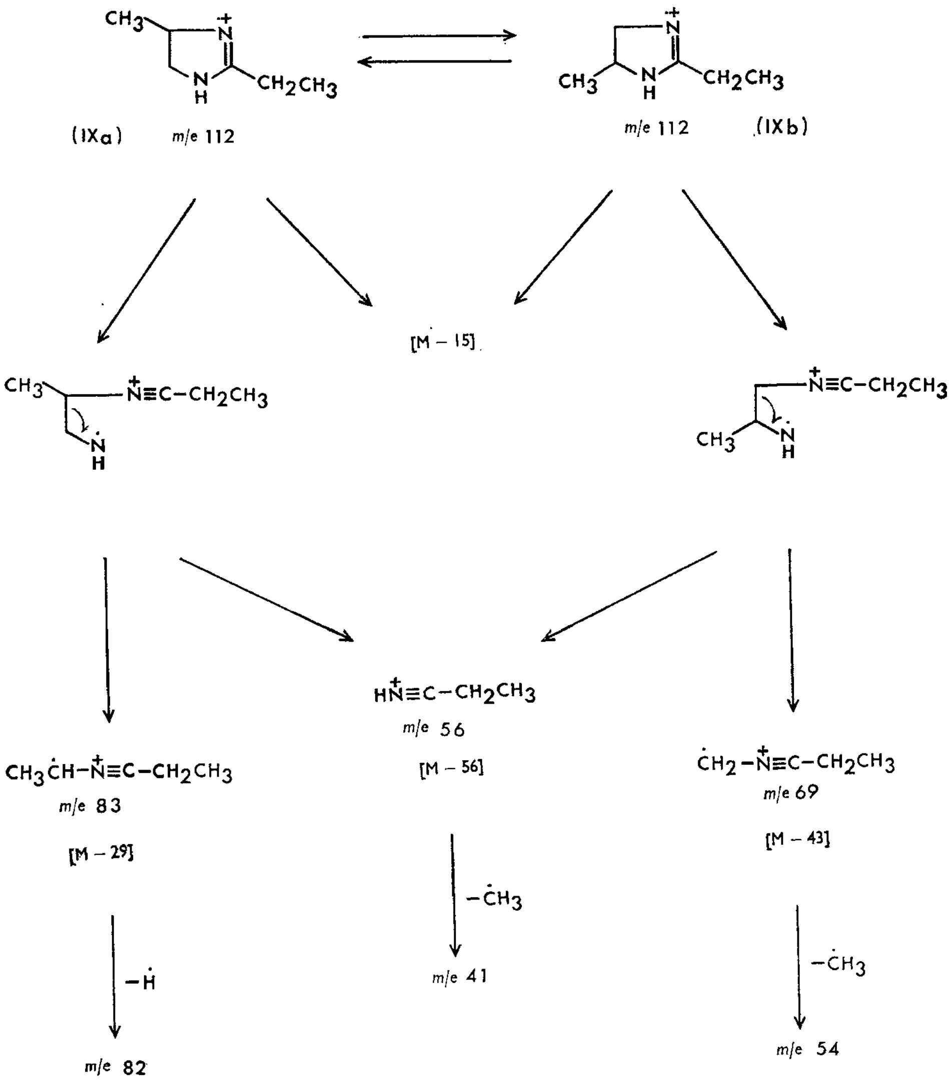


Table 2. Mass spectra of 2,4-disubstituted imidazolines

No.	R	M$^{+\cdot}$	[M − 15]	[M − 29]	[M − 43]	[M − 56]	Others					
(VIII)	—CH_3	*m/e* 98 % (78)	83 (100)	69 (70)	55 (88)	42 (76)	39 (8)	40 (8)	41 (20)	43 (10)	44 (13)	52 (6)
							53 (3)	54 (38)	56 (8)	68 (50)	82 (6)	84 (14)
							97 (25)	99 (8)				
(IX)	—CH_2CH_3	112 (89)	97 (98)	83 (78)	69 (100)	56 (54)	39 (15)	40 (7)	41 (38)	42 (32)	43 (7)	44 (7)
							54 (52)	55 (14)	57 (6)	68 (46)	70 (12)	81 (5)
							82 (63)	84 (8)	95 (9)	96 (7)	98 (9)	111 (32)
							113 (9)					

and the spectrum is the sum of each fragmentation as shown in Scheme 6, which formulates the fragmentation of 2-ethyl-4-methylimidazoline (IX) as a typical example.



Scheme 6

EXPERIMENTAL

Mass spectra were measured with a Hitachi RMU-7 high resolution mass spectrometer operating at 70 eV with an inlet temperature of *ca.* 200°. Exact mass measurements were carried out using a resolution of 24,000 (10% valley definition) with the appropriate hydrocarbon providing reference masses.

All samples were checked by nuclear magnetic resonance spectroscopy. The following compounds were commercial products: I, II, VI, VII, VIII, IX, X; the others, III, IV and V were synthesized by reported procedures:

2-Phenylimidazoline (III): This was synthesized from ethyl benzoate and ethylenediamine following the method of Morrill.[8] m.p. 99·5 to 100·5° (lit. 101°),[9] picrate m.p. 232·5° (lit. 233°), δ^{CDCl_3} in ppm 3·75 (s, 4H), 5·05 (bs, 1H), 7·3 to 7·9 (m, 5H).

2(4-Methoxyphenyl) imidazoline (IV) A mixture of *p*-anisonitrile and 2-aminoethylammonium *p*-toluenesulfonate was heated at 180° for 2·5 hours.[9] The product was dissolved in water, made alkaline to pH 8·5 with 5N-sodium hydroxide and extracted with chloroform. After removal of the solvent, the residue was recrystallized from EtOH-petroleum ether to afford yellow needles, m.p. 118·5 to 119·5°, $\nu_{max}^{CHCl_3}$ 3400, 1620, 1250, 1030 cm^{-1}, δ^{CDCl_3} in ppm 3·74 (s, 4H), 3·80 (s, 3H), 5·50 (bs, 1H), 6·85 and 7·74 (ABq, 4H, $J = 8$ cps).

2-Benzylimidazoline(V); This was synthesized from benzyl cyanide and 2-aminoethylammonium *p*-toluenesulfonate by the method of Oxley and Short.[9] m.p. 67·0 (lit. 66 to 68), picrate m.p. 148 (lit. 148 to 149). δ^{CDCl_3} in ppm 3·58 (s, 6H) 4·34 (bs, 1H), 7·2 to 7·3 (m, 5H).

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