Spectroscopic Analysis of Imidazolidines. Part I : Electron Impact Mass Spectrometry

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The electron impact mass spectral fragmentation pathways for a series of 1,3-di- and 1,2,3-trisubstituted imidazolidines were investigated. The data show remarkable differences depending on the location and identity of substituents. The atypical 1,2,2,3-tetrasubstituted imidazolidine, 2-cyano-1-methyl-3-(*p*-nitrophenyl)-2-phenylimidazolidine, was also investigated.

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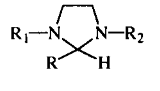
Imidazolidines are of great biological interest because they may act as carriers of either pharmacologically active ethylenediamines [1,2] or carbonyl compounds [3,4]. They are also closely related to the coenzyme N^5,N^{10}-methylenetetrahydrofolic acid, which participate in single carbon transfer at the oxidation level of formaldehyde [5].

A brief electron impact (EI) mass spectral analysis of some polyfluoro-1,3-dimethylimidazolidines was reported for structural confirmation [6]. Also, the literature describes the mass spectral properties of certain 2-aryl-1,3-dimethylimidazolidines [7] in order to explain substituent effects in free radical reactions of imidazolidines. However, no systematic study of the EI fragmentation patterns of imidazolidines has yet been reported.

Owing to their biological interest, and in connection with research on the characterization of nitrogen heterocycles by mass spectrometry [8-10], we have focused our attention on mass spectral analysis of imidazolidines, with special regard to the influence of substituents on nitrogen atoms (R_1 and R_2) and on C_2 (R).

Table I



Imidazolidines **1a-l**

Comp.	R	R_1	R_2
1a	H	C_6H_5	C_6H_5
1b	H	*p*-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$
1c	H	*P*-ClC_6H_4	*p*-ClC_6H_4
1d	H	*p*-$C_2H_5OC_6H_4$	*p*-$C_2H_5OC_6H_4$
1e	CH_3	C_6H_5	C_6H_5
1f	C_6H_5	C_6H_5	C_6H_5
1g	C_6H_5	C_6H_5	CH_3
1h	C_6H_5	*p*-$CH_3C_6H_4$	CH_3
1i	C_6H_5	*p*-$CH_3OC_6H_4$	CH_3
1j	C_6H_5	*p*-$NO_2C_6H_4$	CH_3
1k	H	*p*-ClC_6H_4	$C_6H_5CH_2$
1l	H	*p*-$NO_2C_6H_4$	$C_6H_5CH_2$

In this study, the mass spectral fragmentation patterns under EI were examined for a series of 1,3-diarylimidazolidines (**1a-d**), 2-substituted 1,3-diphenylimidazolidines (**1e,f**), 1,2-diaryl-3-methylimidazolidines (**1g-j**) and 1-aryl-3-benzylimidazolidines (**1k,l**) (Table I). A recently obtained 1,2,2,3-tetrasubstituted imidazolidine, namely 2-cyano-1-methyl-3-(*p*-nitrophenyl)-2-phenylimidazolidine (**1m**) [11], was also analyzed. Results were correlated with those reported in the literature for related compounds. On examining recorded spectra, ring fission fragmentations were more commonly observed than so called "simple" ones such as aryl substituent loss or fragmentation.

Results and Discussion.

On the basis of previous work on mass spectrometry of 2-aryl-1,3-dimethylimidazolidines [7], the most significant fragmentations expected for imidazolidines **1a-m** are shown in Scheme I and included: i) loss of R_1 and R_2 by homolytic C-N fission in the molecular ion with hydrogen migration, leading to stabilized imidazolinium ions $[M-R_1]^+$ and $[M-R_2]^+$ respectively (Routes 1 and 2); ii) loss of either R (Route 3) or H (Route 4) due to homolytic fission on C_2 in the molecular ion, generating the imidazolinium ions $[M-R]^+$ and $[M-1]^+$ respectively; iii) fragmentation of ions $[M-R]^+$ and $[M-1]^+$ following Route A

Table II

Select Fragments in the El Mass Spectra of Compounds **1a-d**
[m/z (% relative abundance)]

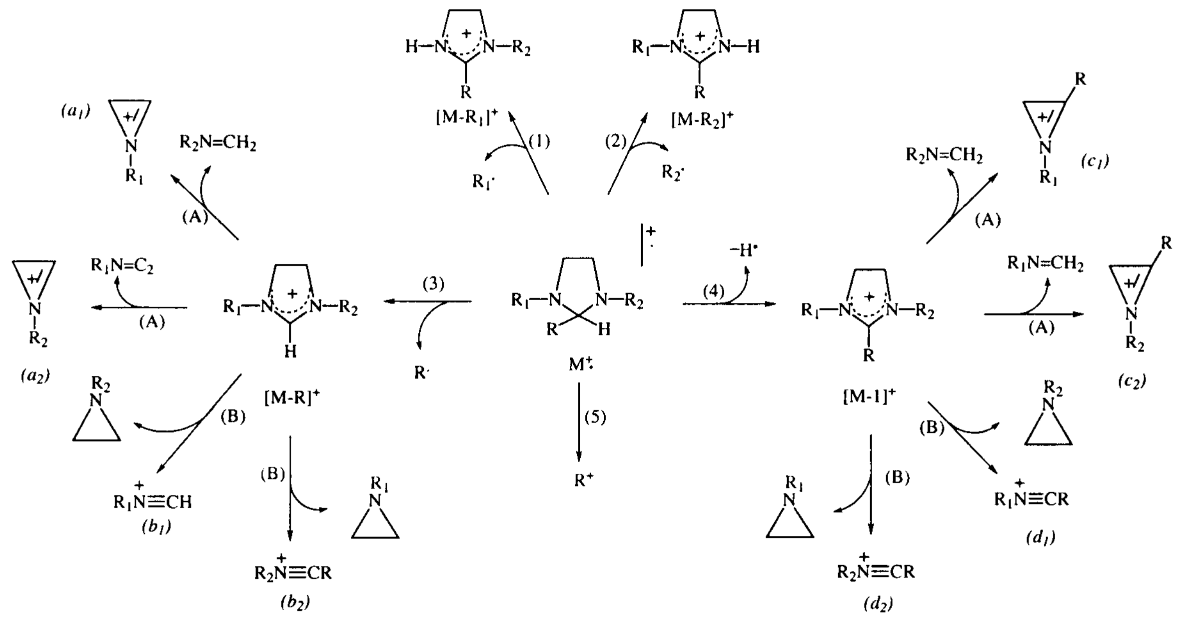
Ion	**1a**	**1b**	**1c**	**1d**
M^+	224(47,3)	252(63,5)	293(35,6)	312(89,6)
$[M-1]^+$	223(77,2)	251 (89,6)	292(34,4)	311(78,3)
$[M-R_1]^+=[M-R_2]^+$	147(2,2)	161(3,1)	181(2,5)	191(2,3)
$R_1N^+=R_2N^+$	91(100)	105(100)	125(100)	135(100)
c [a]	118(7,2)	132(-)	152(-)	162 (-) [c]
d [b]	104(13,6)	118(15,6)	138(27,2)	148(11,1)
e	42(3,4)	42(3,6)	42(8,5)	42(9,7)
g	119(45,3)	133(59,6)	153(65,3)	163(89,3)

[a] In this case, where R=H, *c*=*a*. [b] In this case where R=H, *d*=*b*. [c] [*c*-C_2H_4]$^+$=134 (6,7%)

(which in our compounds would be expected to originate ions a_1, a_2, c_1 and c_2 through loss of an imine unit), and Route B (which in our case would produce the ions b_1, b_2, d_1, and d_2 through loss of an aziridine unit); and iv) C_2-R fission (Route 5) leading to R^+ ions.

On examining the recorded spectra of compounds **1a-m**, and bearing in mind the fragmentation pathways described above, the results are as follows.

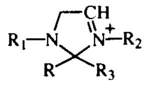
Scheme I



1,3-Diarylimidazolidines **1a-d** (Table II).

The molecular ion $M^{+\cdot}$ is generally intense (35-89%), as well as the $[M-1]^+$ ion originating by the loss of hydrogen from $M^{+\cdot}$ (Route 4, Scheme I). Ions $[M-1]^+$ may be the origin of ions *d* (R=H), through fragmentation by Route B. In contrast, the loss of imine (Route A) seems less significant since the abundance of ions *c* (R=H) is low or even nil [12].

The possibility that the $[M-1]^+$ ion arises by the loss of a hydrogen atom from the methylene chain producing ion A (shown below), should not be ruled out. However, the 1,3-diarylimidazolinium ion stability [13] and results previously reported for the dioxolane series [14] (where structures like A are excluded due to the absence of $[M-1]^+$ ions in ethyleneketals) support the proposed structures.



Ion A

Fragments assigned to $[M-R_1]^+$ and $[M-R_2]^+$ ions (Scheme I), having the same structure in the case of compounds **1a-d** (Routes 1 and 2), appear in the spectra with low relative intensity in all cases. The *e* fragment, that presumably originates from the $[M-R_1]^+$ and $[M-R_2]^+$ by cleavage similar to that described for the $[M-R]^+$ or $[M-1]^+$ ions (Scheme II) appears with intensities of 3-9% [15].

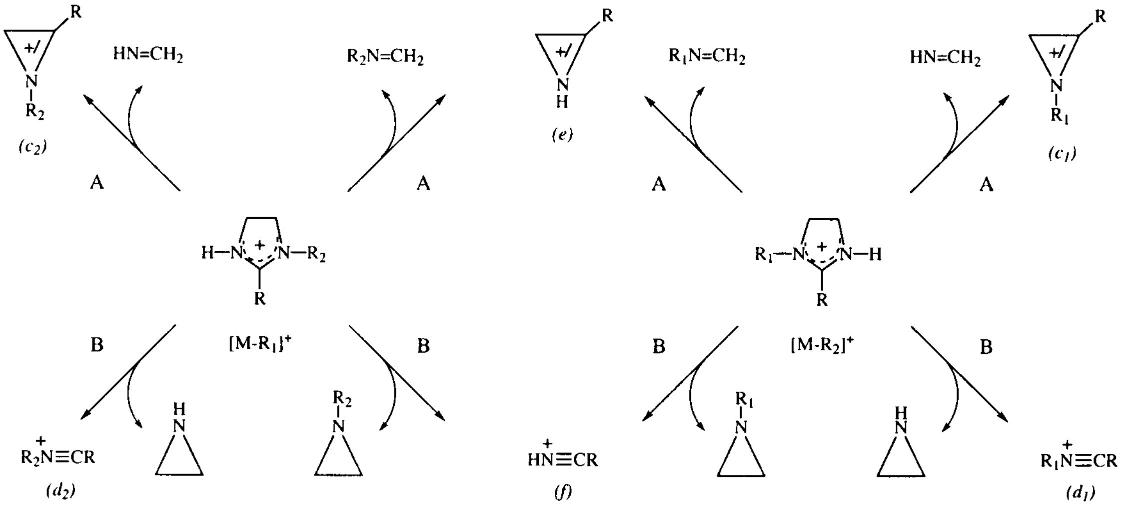
Fragmentation pathways proposed in the literature for related compounds, however, do not account for the presence of the base peaks in our 2-unsubstituted imidazolidines **1a-d**. Thus, we proposed an alternative fragmentation route (Route 6, Scheme III), involving initial ring

Table III
Select Fragments in the EI Mass Spectra of Compounds **1e,f**
[m/z (% relative abundance)]

Ion	**1e**	**1f**
$M^{+\cdot}$	238(22,4)	300(22,2)
$[M-R]^+$	223(100)	223(100)
$[M-1]^+$	237(2,5)	299(4,4)
$R_1N^{+\cdot}=R_2N^{+\cdot}$	91(31,3)	91 (25,4) [a]
a	118(7,7)	118 (4,7) [b]
b	104(15,5)	104 (19,7) [c]
c	132(31,6)	194(72,4)
d	118(7,7)	180(10,3)
g	119(8,7)	119(2,6)

[a] Ion m/z 91 is due to the contribution of two isobaric ions that have been resolved by high resolution mass spectrometry; one correspond to $C_7H_7^+$ (experimental exact mass: 91.0548, calculated: 91.0547 and the other to $C_6H_5N^{+\cdot}$ (experimental exact mass: 91.0425, calculated: 91.0422). [b] In this case ion *e*, which could originate from $[M-R_1]^+$, has the same m/z. [c] In this case ion *f*, which could originate from $[M-R_1]^+$, has the same m/z.

Scheme II



cleavage of $M^{+\cdot}$ through homolytic C_2-N fission, followed by successive elimination of an imine and ethylene, generating $R_1N^{+\cdot}=R_2N^{+\cdot}$ ions, which correspond to the base peaks for compounds **1a-d**. High resolution experiments performed on compound **1b** showed that C_7H_7N is the formula for the ion of m/z 105 (experimental exact mass 105.0584, calculated 105.0579). As far as we have been able to ascertain, this ion has not been described in the literature for aniline derivatives; however, we found it to be a significant fragment ion in 1,2-diarylimidazolines [9].

2-Substituted 1,3-Diarylimidazolidines **1e-f** (Table III).

Molecular ions of 1,3-diphenyl-2-methylimidazolidine (**1e**) and 1,2,3-triphenylimidazolidine (**1f**) are significant in these compounds (22%), although less than in 2-unsubstituted imidazolidines **1a-d**. In contrast, $[M-1]^+$ ions, appear with very low intensity (2-4%).

The base peak for compounds **1e,f** corresponds, as in the 2-aryl-1,3-dimethylimidazolidines [7], to ion $[M-R]^+$, originated from the loss of the substituent on C_2.

The loss of nitrogen substituents, ion $[M-C_6H_5]^+$ is not observed for compound **1e**, implying that fragment ion $[M-77]^+$, present in the **1f** spectrum, results from the loss of the phenyl substituent on C_2 ($[M-R]^+$), verifying the base peak ion as that described above.

The ions of m/z 132 (**1e**) and m/z 194 (**1f**) correspond to azirinium ions *c*, and originate from $[M-1]^+$ following Route A. This was demonstrated by means of a parent ion scan for compound **1e**, showing that the ion of m/z 132 is a secondary fragment of the ion corresponding to m/z 237 exclusively. The greater abundance of the m/z 194 ion (72.4%) *versus* the m/z 132 ion (31.6%) may be related to the presence of the aryl group on C_2 of the azirinium ion, that is capable of stabilizing the endocyclic double bond [7].

As in the previous series, Route 6 is an important fragmentation pathway as shown by the abundance of ions $C_6H_5N^{+\cdot}$ and the presence of ions *g* (Scheme III).

1,2-Diaryl-3-methylimidazolidines **1g-j** (Table IV).

Spectra of these compounds show ions corresponding to all of the fragmentation pathways proposed. The relative abundance of ions $M^{+\cdot}$ and $[M-1]^+$ is similar to that of 1,2,3-trisubstituted compounds **1e,f**. Loss of substituents on nitrogen atoms leading to $[M-R_1]^+$ and $[M-R_2]^+$ ions are observed in low abundance. On the other hand, the fragment ions corresponding to $[M-R]^+$ appear with relatively high intensity (~40-80%), though not the base peak as in compounds **1e,f**. This may be explained by the greater stability of the 1,3-diaryl ion compared to that of the 1-aryl-3-methylimidazolinium ion. This is due to the marked conjugation in the planar 1,3-diaryl amidinium system [13].

Scheme III

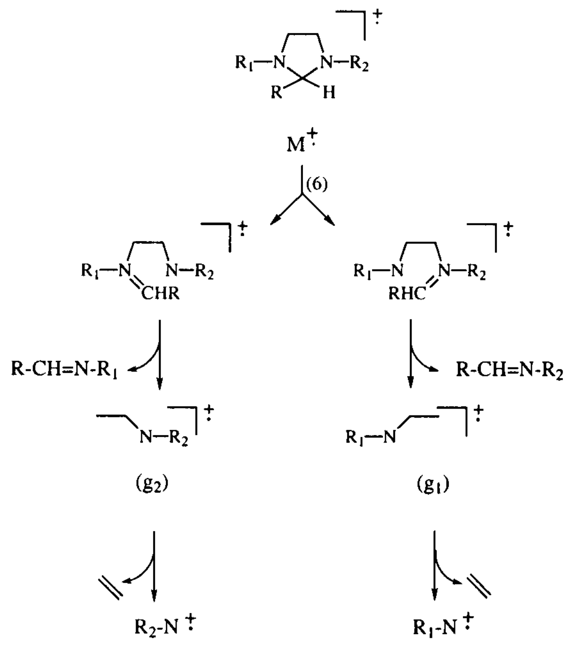


Table IV

Select Fragments in the EI Mass Spectra of Compounds **1g-j**
[m/z (% relative abundance)]

Ion	**1g**	**1h**	**1i**	**1j**
$M^{+\cdot}$	238 (26,4)	252 (23,5)	268 (27,2)	283 (19.9)
$[M-R]^+$	161 (83,2) [a]	175 (47,5)	119 (44,4)	206 (51,4)
$[M-1]^+$	237 (8,3)	251 (6,3)	267 (3,6)	282 (3,4)
$[M-R_1]^+$	161 (83,2) [a]	161 (3,6)	161 (2,5)	161 (1,3)
$[M-R_2]^+$	223 (-)	237 (-)	253 (1.9) [b]	268 (-)
$R_1N^{+\cdot}$	91 (25,4) [c]	105 (6,4)	121 (3,9)	136 (-)
a_1	118 (11,5) [d]	132 (100) [e]	148 (1,8)	163 (-)
a_2	56 (2,5)	56 (2,6)	56 (2,2)	56 (2,4)
b_1	104 (6,6) [f]	118 (18.9) [g]	134 (10,9)	141 (2,6)
b_2	42 (9,4)	42 (10,5)	42 (8,5)	42 (9,9)
c_1	194 (7,6)	208 (3,3)	224 (2,7)	239 (2,6)
c_2	132 (100)	132 (100) [e]	132 (100)	132 (100)
d_1	180 (4,6)	194 (2,4)	210 (1,6)	225 (-)
d_2	118 (11,5) [d]	118 (18,9) [g]	118 (7,8) [h]	118 (10,4) [h]
g_1	119 (4,5)	133 (13,3)	149 (3,5)	164 (1,9)
g_2	57 (2,4)	57 (2,2)	57 (2,5)	57 (2,6)
f	104 (6,6) [f]	104 (-)	104 (1,2)	104 (2,6)
e	118 (11,5) [d]	118 (18,9) [g]	118 (7,8) [h]	118 (10,4) [h]
$C_7H_7^+$	91 (25,4) [c]	91 (23,8)	91 (14,5)	91 (21,3)
$C_5H_5^+$ [i]	65 (4,5)	65 (9,2)	65 (3,9)	65 (3,8)

[a] In this case ions $[M-R]^+$ and $[M-R_1]^+$ have the same m/z. [b] Probably originates from CH_3-O bond fission of molecular ion. [c] In this case $R_1N^{+\cdot}$ and tropylium are isobaric ions. [d] Ions a_1, d_2 and e have the same m/z. [e] Ions a_1 and c_2 have the same m/z. [f] Ions b_1 and f have the same m/z. [g] Ions d_2, b_1 and e have the same m/z. [h] Ions d_2 and e have the same m/z. [i] Probably cyclopentadienyl ion originated from tropylium.

The intensity of ions obtained through secondary fragmentations (Routes A and B) does not allow conclusions to be drawn with regard to the primary fragmentation since many of such ions can have a double or triple origin. The base peak for all these compounds appears on the spectrum at m/z 132 and corresponds to the azirinium ion c_2, which is stabilized by both the phenyl group on C_2 and the methyl linked to the nitrogen. It has considerable analytical value for the characterization of this series of compounds, and may originate either from decomposition of ion $[M-1]^+$ followed by Route A, or alternatively from fragmentation of ion $[M-R_1]^+$. However, results obtained for compound **1e** lead us to conclude that the former is the preferred fragmentation pathway.

The tropylium ion (m/z 91) is observed in the spectra of compounds **1g-j** as in that of 1,3-dimethyl-2-phenylimidazolidine [7]. The high relative abundance, observed in all cases, correlates structurally with the presence of the phenyl group on C_2.

1-Aryl-3-benzylimidazolidines **1k,l** (Table V).

With respect to the previous compounds, an increase is observed in the abundance of ions $[M-R_2]^+$ ($[M\text{-benzyl}]^+$, 12-16%), as is expected given the high stability of the benzyl radical. This ion may originate by Route A (Scheme II). The base peak observed for each of these compounds (m/z 42) corresponds to the unsubstituted azirinium ion e (R=H) (Scheme II).

Table V

Select Fragments in the EI Mass Spectra of Compounds **1k,l**
[m/z (% relative abundance)]

Ion	**1k**	**1l**
$M^{+\cdot}$	272(24.2)	283(9.0)
$[M-R]^+=[M-H]^+$	271(42.2)	282(15.9)
$[M-R_1]^+$	161(-)	161(-)
$[M-R_2]^+$	181(12.5)	192(16.3)
$R_1N^{+\cdot}$	125(17.2)	136(4.5)
$R_2N^{+\cdot}$	105(3.7)	105(4.2)
a_1 [a]	152(-)	163(-)
a_2 [b]	132(24.7)	132(9.2)
b_1 [c]	138(5.0)	149(1.8)
b_2 [d]	118(4.5)	118(3.2)
g_1	153(7.4)	164(2.4)
g_2	133(26.4)	133(9.7)
e	42(100)	42(100)
$C_7H_7^+$	91(85.7)	91(98.5)
$C_5H_5^+$	65(19.5)	65(35.8)

[a] In this case where R=H, $a_1=c_1$. [b] In this case where R=H, $a_2=c_2$. [c] In this case where R=H, $b_1=d_1$. [d] In this case where R=H, $b_2=d_2$.

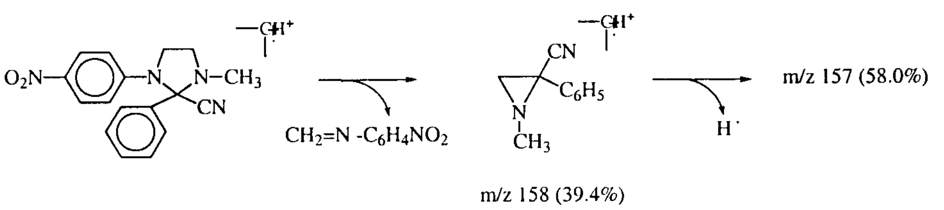
The lability of the *N*-benzyl group under EI conditions also allows the heterolytic cleavage of the N-R_2 bond with formation of tropylium ion giving rise to the peak at m/z 91 (85-98%) and to the $C_5H_5^+$ ion (m/z 65, 19-33%) [16].

2-Cyano-1-methyl-3-(*p*-nitrophenyl)-2-phenylimidazolidine (**1m**).

Since mass spectrometry operates in the gas phase under a high vacuum, it allows the study of intrinsic properties of a given molecule free from solvating or hydration effects [17]. Therefore, it was of interest to study the behavior of the recently synthesized compound **1m**, whose properties have been shown to depend markedly on the solvent [18].

Fragments obtained [19] correspond to a compound with a covalent bond (cyclic α,α-diaminonitrile) rather than an ionic bond (imidazolinium cyanide) [9]. Molecular ion is highly stable, being the base peak. Ions are observed that correspond to the routes proposed for compounds **1a-l**: $[M\text{-}CN]^+$ (m/z 282, 14.8%), $[M\text{-}CH_3]^+$ (m/z 293, 10.5%), $[M\text{-}C_6H_5]^+$ (m/z 231, 7.8%) and $R_1\text{-}N^{+\cdot}$ (m/z 136, 18.8%). Two major peaks, m/z 158 (39.4%) and 157 (58.0%), cannot be explained by such routes. Instead, their presence may be justified by considering that ion $M^{+\cdot}$ undergoes a fragmentation similar to the one proposed by Rendell for 2,2-difluoroimidazolidines [6] (Scheme IV).

Scheme IV



Conclusions.

Data obtained show remarkable differences depending on the substitution pattern: 1. In all the imidazolidines analyzed, ions corresponding to R_1N^+ are detected. This fragment ion is especially important when the loss of the group on C_2 or on the nitrogen atoms is not favored. 2. In 2-substituted 1,3-diarylimidazolidines, the loss of the substituent on C_2 ($[M\text{-}R]^+$) is favored with respect to the loss of hydrogen. 3. In 1,2,3-trisubstituted compounds, azirinium ions *c* generated through Route A are abundant, especially when there is an aryl group on C_2 which stabilizes the endocyclic double bond. 4. 2-Phenylimidazolidines characteristically fragment to form the ions of m/z 91 ($C_7H_7^+$, tropylium) and m/z 65 ($C_5H_5^+$, cyclopentadienyl ion). 5. 1-Aryl-3-benzylimidazolidines readily lose benzyl groups as radical or cation, which is shown by the presence of ions [M-benzyl]$^+$, m/z 42 (unsubstituted azirinium *e*), m/z 91 ($C_7H_7^+$) and m/z 65 ($C_5H_5^+$).

EXPERIMENTAL

Melting points were taken on a Büchi capillary apparatus and are uncorrected. The ^1H nmr spectra were obtained on a Bruker MSL 300 MHz spectrometer using deuteriochloroform as solvent. Chemical shifts are reported in parts per million (δ) downfield from an internal TMS reference. Signals are quoted as: s (singlet), d (doublet), t (triplet) and m (multiplet). The presence of exchangeable protons was confirmed by use of deuterium oxide. Mass spectra were recorded on a MS Shimadzu QP-1000 instrument at 70 eV. High resolution mass spectra and parent ion scan experiments were performed on a VG ZAB-SEQ (VG Analytical, Manchester, UK) hybrid tandem mass spectrometer of BEqQ geometry (where B is a magnetic sector, E an electric sector, q a r.f. only quadrupole and Q a quadrupole mass analyzer), equipped with an electron impact ion source. The electron impact mass spectrometry (EIMS) experiments were carried out using 70 eV ionization energy with direct sample introduction. For EI mass spectrometry/mass spectrometry (MS/MS), the pertinent precursor ions generated by bombarding the analyte with the electron beam, were mass selected with BE, which was operated at resolution 100, and analyzed by a second spectrometer (Q) at unit resolution. The MS/MS spectrum was acquired by scanning the mass range m/z 120-300 at a rate of 2 s per scan, and was obtained by fixing the second spectrometer (Q) and scanning the first (BE). Analytical tlc was carried out on Silica Gel 60 F_{254}. Column chromatography was carried out on Silica Gel 60 (70-325 mesh).

Reagents, solvents and starting materials were purchased from standard sources and purified according to literature procedures.

Imidazolidines **1a-m**.

Compounds **1a,b,d** [13], **1c** [20], **1e** [21], **1f-i** [22], **1j** [23] and **1m** [11] were prepared following literature procedures. Purity was ascertained by tlc experiments employing five different solvent mixtures.

New compounds **1k,l** were synthesized from formaldehyde (0.4 mmole, aqueous solution) and the corresponding *N,N'*-disubstituted ethylenediamine [24] (0.1 mmole) in ethanol (10 ml).

1-Benzyl-3-(*p*-chlorophenyl)imidazolidine (**1k**).

This compound has an mp of 88° (ethanol); ^1H nmr: δ 3.00 (t, 2H, $CH_2\text{-}NCH_2C_6H_5$), 3.40 (t, 2H, $CH_2\text{-}NC_6H_4Cl$), 3.70 (s, 2H, $N\text{-}CH_2\text{-}C_6H_5$), 4.00 (s, 2H, $N\text{-}CH_2\text{-}N$), 6.45 (d, 2H, ClC_6H_4, 2 *ortho* H), 7.17 (d, 2H, ClC_6H_4, 2 *meta* H) and 7.40 (m, 5H, C_6H_5).

Anal. Calcd. for $C_{16}H_{17}ClN_2$: C, 70.45; H, 6.28; N, 10.27. Found: C, 70.57; H, 6.38; N, 10.20.

1-Benzyl-3-(*p*-nitrophenyl)imidazolidine (**11**).

This compound was obtained as an oil and was purified by column chromatography eluting with benzene-methanol (9:1); ^{1}H nmr: δ 3.10 (t, 2H, CH_2-$NCH_2C_6H_5$), 3.41 (t, 2H, CH_2-$NC_6H_4NO_2$), 3.73 (s, 2H, N-CH_2-C_6H_5), 4.02 (s, 2H, N-CH_2-N), 6.50 (d, 2H, $NO_2C_6H_4$, 2 *ortho* H), 7.42 (m, 5H, C_6H_5) and 8.10 (d, 2H, $NO_2C_6H_4$, 2 *meta* H).

Anal. Calcd. for $C_{16}H_{17}N_3O_2$: C, 67.81; H, 6.05; N, 14.84. Found: C, 67.73; H, 6.12; N, 14.79.

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