Mass Spectra of Some Di- and Triazaindenes

WILLIAM W. PAUDLER, JAMES E. KUDER, AND LARRY S. HELMICK

Department of Chemistry, Ohio University, Athens, Ohio

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The mass spectra of imidazo[1,2-*a*]pyridine (I), imidazo[1,5-*a*]pyridine (II), imidazo[1,2-*a*]pyrimidine (III), and various methyl derivatives are reported and analyzed. The parent compounds lose HCN and C_2H_2N. In the methyl derivatives, analogous fragmentations occur. In addition, the loss of a hydrogen atom from the methyl group results in possible ring-expanded products which subsequently lose HCN as well as C_4H_4. The major fragmentations of the parent ion radicals are in agreement with the ion-radical bond orders.

As part of our continuing studies of the chemistry of polyazaindenes,[1] we now wish to report and analyze the mass spectral cleavage patterns of some imidazo-[1,2-*a*]pyridines (I), imidazo[1,5-*a*]pyridines (II), and imidazo[1,2-*a*]pyrimidines (III).

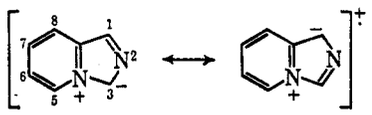
The major fragmentations of aromatic nitrogen heterocyclic systems that have been described to date can be outlined as shown in Chart I.

Thus, the loss of HCN (*m/e* 27) appears to be the major fragmentation path in pyridines,[2] quinolines,[3] naphthyridines,[4] quinoxalines,[4] quinazolines,[4] indoles,[2] and pyrazines.[2,5] The methyl derivatives of these heterocyclic systems either lose a hydrogen or a methyl radical to afford species **2** or **4**, respectively. Species **2**, a presumed ring-expanded ion, loses HCN when structurally possible.

The presence of a nitrogen atom at the bridgehead of the polyazaindenes, under study in our laboratories, represents a structural variation of considerable interest in terms of its influence upon the fragmentations of these compounds.

Scheme I outlines the paths which are common to the ring systems studied. The facile one-step loss of HCN (*m/e* 27) is typical of these compounds and is substantiated by metastable ions. The 3-methylimidazo-[1,5-*a*]pyridine loses CH_3CN to a much greater extent (Σ_{37} 8.9%) than it loses HCN (Σ_{37} 2.82%). Thus, bonds 1–2[6] and 3–4 are cleaved more readily than the 1–9 and 2–3 bonds.

The simultaneous cleavage of bonds 1–9 and 3–4 in these compounds to yield the species **6** or **6′** is confirmed by suitable metastable transitions. That we are in fact dealing with the cleavage of bonds 1–9 and 3–4, and not some other bonds, is shown by deuterium labeling. The *m/e* 78 peak in the 3-deuteroimidazo-[1,2-*a*]pyridine is not shifted to *m/e* 79. On the other hand the *m/e* 79 peak (**6**) in the 5-deuteroimidazo-[1,2-*a*]pyrimidine is, in fact, shifted to *m/e* 80. Similarly the 3-deuteroimidazo[1,5-*a*]pyrimidine affords the *m/e* 78 peak only and no *m/e* 79 peak.



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The bond orders (Table I) calculated for the polyazaindenes described in the foregoing discussion are in agreement with the observed fragmentation patterns.

TABLE I

BOND ORDERS OF SOME POLYAZAINDENES

Compd	Bond order (p_{AB}) for bond AB: $p_{1,2}$ Ground state	$p_{1,2}$ Ion radical	$p_{2,3}$ Ground state	$p_{2,3}$ Ion radical	$p_{3,4}$ Ground state	$p_{3,4}$ Ion radical	$p_{1,9}$ Ground state	$p_{1,9}$ Ion radical
	0.644	0.753	0.632	0.487	0.474	0.484	0.495	0.463
	0.592	0.573	0.677	0.696	0.536	0.585	0.656	0.459
	0.673	0.819	0.527	0.272	0.486	0.507	0.468	0.365

The loss of HCN from the imidazo[1,2-*a*]pyridine (I) and from the imidazo[1,2-*a*]pyrimidine (III) might be predicted from the lengths of the 1–9 and 2–3 bonds in the ion radicals of these two compounds. These bonds possess much more single-bond character than the clearly doubly bonded atoms 1 and 2.

The cleavage of bonds 1–9 and 3–4 to afford the ion radical **6** (Scheme I) is also predicted by the length of the 3–4 bond (*cf.* Table I), which has a considerable amount of single-bond character.

In the case of the imidazo[1,5-*a*]pyridine (II), one can envision loss of HCN to occur by either cleavage of bonds 1–9 and 2–3 or by rupture of bonds 1–2 and 3–4. Since we have now shown that the latter process predominates, we would expect that the 2–3 bond possess much more double-bond character than the 1–2 bond. Table I clearly shows this to be the case.

(1) W. W. Paudler and L. S. Helmick, *Chem. Commun.*, 377 (1967); W. W. Paudler and J. E. Kuder, *J. Org. Chem.*, **32**, 2430 (1967).

(2) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra," Holden-Day, Inc., San Francisco, Calif., 1964, pp 225–258.

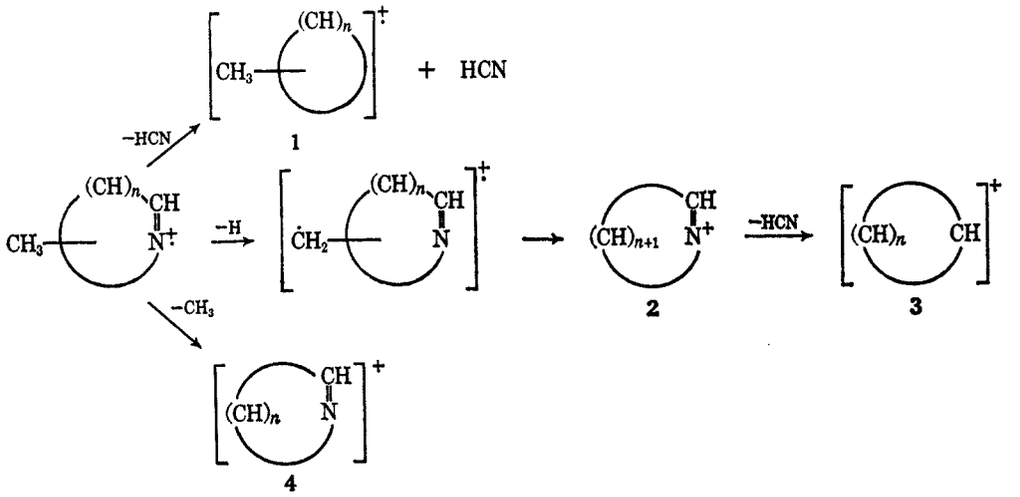
(3) S. D. Sample, D. A. Lightner, O. Buchart, and C. Djerassi, *J. Org. Chem.*, **32**, 997 (1967).

(4) W. W. Paudler and T. J. Kress, presented at the 1st International Congress of Heterocyclic Chemistry, Albuquerque, N. M., June 1967; *J. Heterocycl. Chem.*, **4**, 547 (1967).

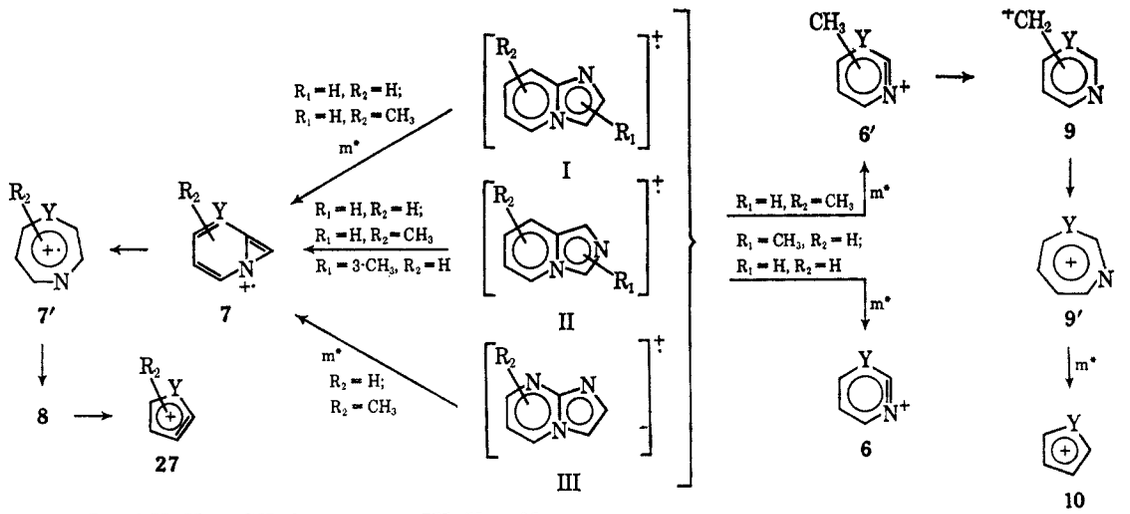
(5) A. L. Jennings, Jr., and J. E. Boggs, *J. Org. Chem.*, **29**, 2065 (1964).

(6) For the sake of clarity in the discussion, all compounds are numbered as shown in structures **5**.

CHART I



SCHEME I[a]



[a] For structures I and II, Y = CH; for structure III, Y = N.

The fragment **7** loses HCN to yield the species **8**. This process can be envisioned to occur *via* the ring-expanded ion radical **7′**.

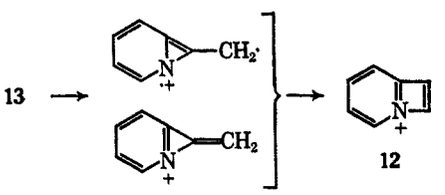
If such a ring expansion occurs, prior to HCN loss, we would anticipate the species **8** to appear with equal intensity at *m/e* 64 and 65 in the 3-deuteroimidazo-[1,2-*a*]pyridine. This has, in fact, been shown to be the case.

Ions **6** and **6′** fragment further by processes identical with those observed in the mass spectra of 2-halopyridines and of 2-halopyrimidines (loss of either CN or C_2H_2, etc.).

The ion **6′** can rearrange to **9′** prior to loss of HCN to form the ion **10**. The formation of **9′** is strongly supported by the fact that ion **6′** obtained from the 5-methyl compounds loses HCN to the same extent as all of the other monomethyl compounds with the methyl groups substituted in the six-membered ring. Also, the ratios of species **9** to **10** is essentially constant within a given series of compounds. Thus, the formation of the ring-expanded ion **9′** is strongly implied.

Fragmentations Typical of Methyl-Substituted Compounds. A. Methyl Groups Substituted on the Five-Membered Ring.—The generally most pronounced process typical of polyazaindenes substituted in the five-membered ring with a methyl group involves the loss of a hydrogen atom to form the species **11** (*cf.* Scheme II). These ions can ring expand to form the bicyclic systems represented by **11′**. The loss of HCN from these ions affords the species **12** (substantiated by a metastable transition). This ion fragments further by loss of C_2H_2 to afford the pyridyne ion **6**. Thus, this ion is formed by two different paths (*cf.* Scheme I also), both of which are substantiated by metastable ion peaks.

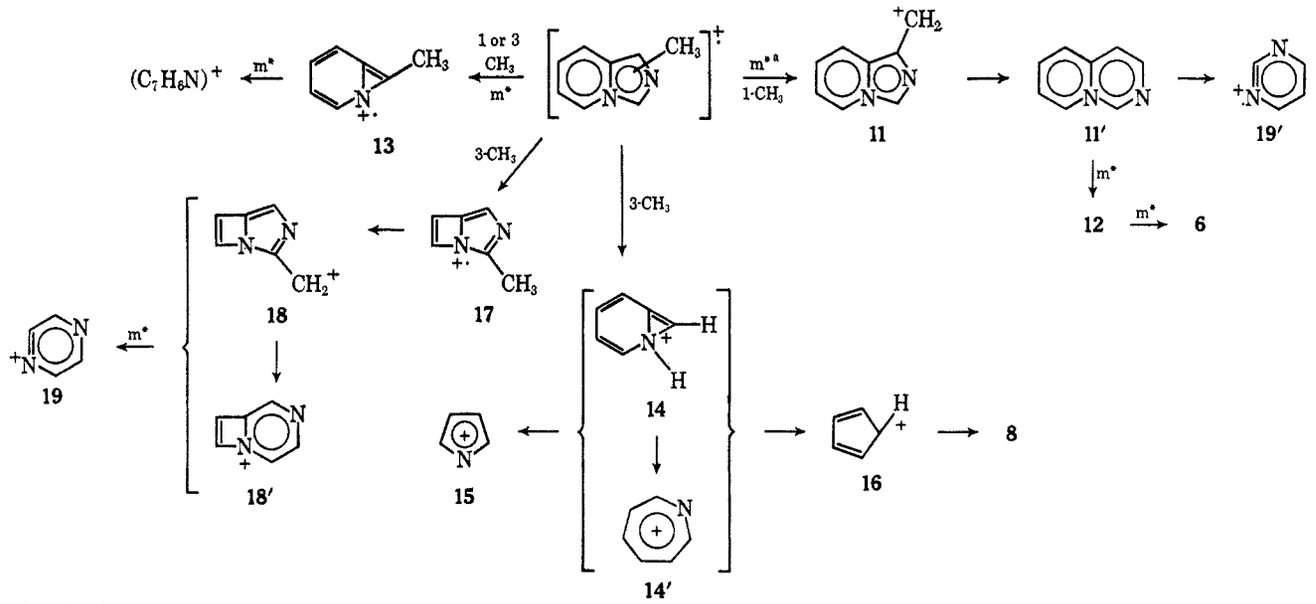
Depending upon the ring system, the loss of HCN, described in Scheme I, can also occur in these methyl derivatives. The ion radical **13** (*m/e* 105) is indeed observed in the cases studied (*cf.* Scheme II). This ion loses a hydrogen atom (supported by a metastable ion peak) to afford the species $(C_7H_6N)^+$. This may well have the structure **12**, if **13** undergoes the transformation in eq 1.



(1)

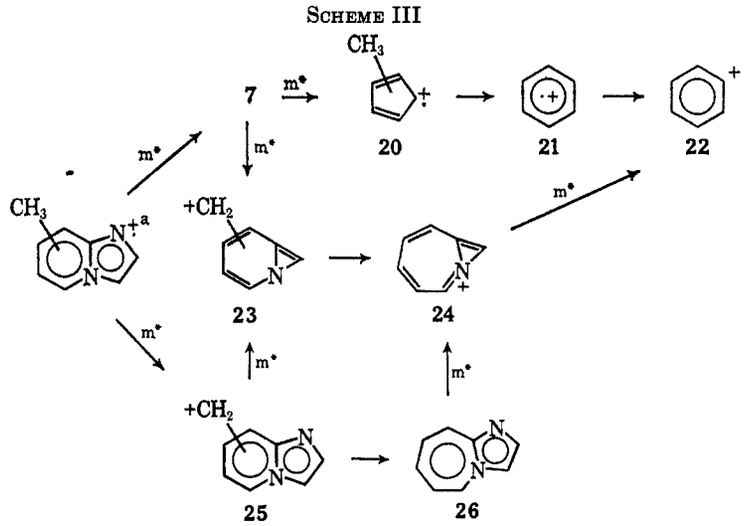
The *m/e* 105 ion radical **13** could, potentially, lose CH_3CN to afford a *m/e* 64 ion **8**. However, among the monomethyl compounds with the substituent in the

SCHEME II



[a] Similar fragmentations occur in the 3-methylimidazo[1,2-a]pyridine as well as in the 3-methylimidazo[1,5-a]pyridine.

SCHEME III



[a] The six-membered ring methyl derivatives of the imidazo[1,2-a]pyridines and pyrimidines fragment similarly.

five-membered ring, this species is only present in the mass spectrum of the 3-methylimidazo[1,5-a]pyridine. Consequently, it must arise from another path which is specific for this compound.

In fact, the 3-methylimidazo[1,5-a]pyridine undergoes two fragmentation paths which are not observed in the other methylpolyazaindenes described in this paper.

The formation of the *m/e* 92 ion **14** (or **14'**) must result from a hydrogen migration from the methyl group to either the bridgehead nitrogen atom or the carbon atom at position 5 (only the former alternative is shown in Scheme II). This species can ring expand to form the azatropylium ion **14'** which in turn can lose C_2H_2 and HCN to form the ions *m/e* 66 (**15**) and *m/e* 65 (**16**), respectively. The latter can stabilize itself somewhat by loss of a hydrogen atom to form the cyclopentadienyl ion radical **8**.

The second fragmentation path typical of the 3-methylimidazo[1,5-a]pyridine involves the loss of C_2H_2 from the parent ion radical to afford the bicyclic system **17** which in turn loses a hydrogen atom to afford **18**. This species may well ring expand to afford the ion **18'** which then loses C_2H_2 to afford the pyridyne ion **19**. The latter step is substantiated by the presence of a metastable transition.

B. Methyl Groups Substituted on the Six-Membered Ring.—During the discussion of the fragmentations described in Scheme I, we pointed out that the loss of HCN is the most pronounced process that occurs in these electron-impact reactions. The presence of methyl groups in the six-membered ring opens some additional avenues for fragmentation(s). Thus, ion **20** forms what we believe to be the ring-expanded ion radical **21**. This ion radical loses a hydrogen atom to form the species **22**. The loss of a hydrogen atom from **7** to afford the ion **23** is substantiated by a metastable transition. This ion can be envisioned to undergo a ring expansion to afford the bicyclic system **24**, which loses HCN to yield the ion **22**, Scheme III. This process is again substantiated by a metastable transition.

Species **25** results from loss of a hydrogen atom from the parent ion radical. This species then loses HCN to afford the ion **24** possibly *via* the ring-expanded

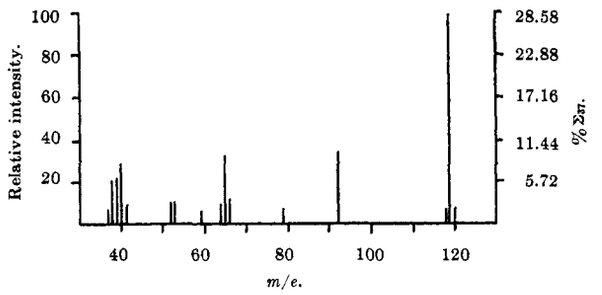


Figure 1.—Mass spectrum of imidazo[1,2-*a*]pyrimidine.

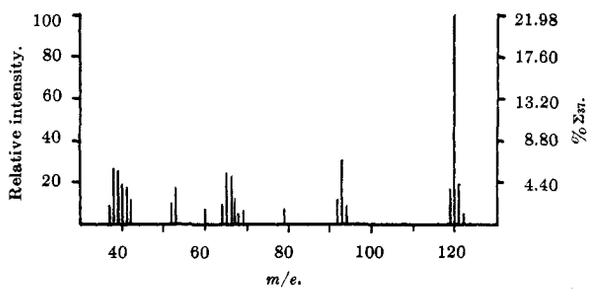


Figure 2.—Mass spectrum of 3-deuterioimidazo[1,2-*a*]pyrimidine.

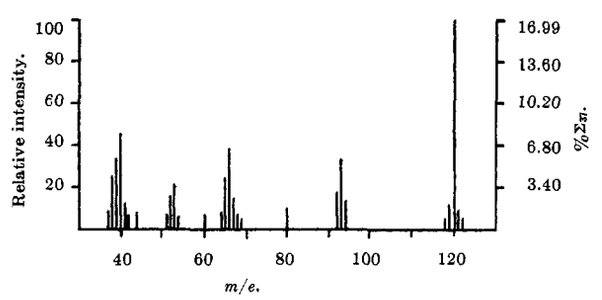


Figure 3.—Mass spectrum of 5-deuterioimidazo[1,2-*a*]pyrimidine.

species **26**. Alternately, the sequence **25** → **23** → **24** is also feasible.

It is of interest to note that the loss of any of the methyl groups in the monomethylpolyazaindenes discussed in this paper is essentially nil. This is in contrast to the relatively facile loss of methyl groups in the various methylpyridines and methylquinolines during electron bombardment, and might be interpreted as being due to the large contribution of resonance structures such as **5**. These contributions would tend to facilitate loss of a hydrogen atom from the methyl group, rather than loss of the methyl group itself.

Experimental Section[7]

The experimental portion of this paper is described in tabular form (Tables II–V) in the following section. Only peaks representing 1% or more of the total ion current are generally listed. The masss pectra of imidazo[1,2-*a*]pyrimidine, 3-deuterioimidazo[1,2-*a*]pyrimidine, and 5-deuterioimidazo[1,2-*a*]pyrimidine are represented in Figures 1, 2, and 3, respectively.

(7) All compounds described in this paper have been prepared by known methods (ref 1 and 2, and papers cited therein). The mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E mass spectrometer. The ionization potential used was 80 eV and the inlet system temperature was set at 180°.

TABLE II

PARENT COMPOUNDS

	Imidazo[1,2-*a*]-pyridine		Imidazo[1,5-*a*]-pyridine		Imidazo[1,2-*a*]-pyrimidine	
m/e	% Σ_{37}	Species[a]	% Σ_{37}	Species[a]	% Σ_{37}	Species[a]
120					2.19	
119	3.05		2.68		28.58	III
118	35.08	I	29.88	II	2.06	
118	1.46		0.81			
93					1.30	
92	2.81		0.85		10.09	**7**
91	8.66	**7**	10.16	**7**	1.18	
90	1.59		1.93			
79	1.10				2.10	**6**
78	11.23	**6**	5.49	**6**		
68					1.26	
66					3.32	
65	1.83		2.44		9.25	**8**
64	5.61	**8**	10.77	**8**	2.52	**27**
63	4.09	**27**	7.12	**27**	0.55	
62	1.46		2.24			
61			1.02			
59.5					1.68	P^{2+}
59	1.59	P^{2+}	1.52	P^{2+}		
53			1.42		2.86	
52	2.81		2.44		2.77	
51	3.66		2.03		1.26	
50	1.46		1.22			
41	2.07		2.13		2.61	
40	1.83		1.22		8.20	
39	3.48		3.86		5.88	
38	3.17		4.27		6.09	
37	1.95		2.03		1.98	

[a] See Schemes I, II, and III.

TABLE III

FIVE-MEMBERED RING METHYL COMPOUNDS

	5-Methylimidazo-[1,2-*a*]pyridine		1-Methylimidazo-[1,5-*a*]pyridine		3-Methylimidazo-[1,5-*a*]pyridine	
m/e	% Σ_3	Species[a]	% Σ_{37}	Species[a]	% Σ_{37}	Species[a]
133	1.64		1.86		1.15	
132	15.36	I	19.59	II	11.99	II
131	19.95	**11, 11′**	12.06	**11, 11′**	7.82	**11, 11′**
106					4.04	**17**
105	1.20	**13**	5.77	**13**	2.82	**13, 18, 18′**
104	1.40	**12**	13.61	**12**	1.69	**12**
92					2.92	**14, 14′**
91					8.92	**7,7′**
79	4.39	**19′**	9.28	**19′**	3.78	**19**
78	6.98	**6**	5.57	**6**	2.22	**6**
77	1.00		2.27		1.82	
76			1.44			
66	2.79	P^{2+}	1.34	P^{2+}	7.25	**15**, P^{2+}
65					5.42	**16**
64	1.40		0.62		4.17	**8**
63	1.60		1.44		4.74	**27**
62					1.88	
52	3.39		4.54		2.48	
51	4.40		5.98		3.34	
50	1.60		3.09		1.88	
41	2.19		0.52		1.56	
40	1.80				3.00	
39	5.00		2.16		6.93	
38	2.59		1.44		3.28	
37	1.40		0.82		1.43	

[a] See Schemes I, II, and III.

TABLE IV
SIX-MEMBERED RING METHYL COMPOUNDS

	5-Methylimidazo-[1,2-*a*]pyridine[a]		5-Methylimidazo-[1,5-*a*]pyridine		7-Methylimidazo-[1,2-*a*]pyrimidine	
m/e	% Σ_{37}	Species[b]	% Σ_{37}	Species[b]	% Σ_{37}	Species[b]
134					2.19	
133	2.68		2.70		25.86	III
132	25.48	I	26.97	II	3.43	**25, 26**
131	14.27	**25, 26**	4.42	**25, 26**		
130	1.02					
118					1.84	
107					1.34	
106	1.02				2.93	**7, 7′**
105	1.53	**7, 7′**	3.76	**7, 7′**	2.39	**23, 24**
104	3.82	**23, 24**	7.63	**23, 24**		
94					1.24	
93					1.69	**6′, 9, 9**
92	1.02	**6′, 9, 9′**	2.87	**6′, 9, 9′**	3.00	*m/e* 93 − H′
91	2.55	*m/e* 92−H	1.66	*m/e* 92−H	0.75	
80					2.19	
79	1.53		2.65		4.97	**8, 20, 21**
78	2.55	**8, 20, 21**	6.32	**8, 20, 21**	1.39	**22**
77	3.06	**22**	4.11	**22**		
76	1.27		1.50			
67					1.79	
66.5					1.24	P^{2+}
66	2.55	P^{2+}	2.21	P^{2+}	2.29	**10**
65	2.21	**10**	2.61	**10**	2.69	
64	1.78		1.90		1.04	
63	2.04		3.45			
62	0.76		1.50			
53	2.04		1.06		3.88	
52	3.31		3.89		5.47	
51	3.57		4.53		3.23	
50	2.04		2.78		1.50	
42	1.27		1.00		1.00	
41	1.27		1.00		1.59	
40	1.78		1.00		3.18	
39	4.33		4.53		4.28	
38	2.04		2.76		1.50	
37	1.27		1.24		0.75	

[a] 6-Methyl, 7-methyl, and 8-methyl are very similar. [b] See Schemes I, II, and III.

Registry No.—I, 274-76-0; I, 3-CH_3, 5857-45-4; I, 5-CH_3, 933-69-7; I, 6-CH_3, 874-38-4; I, 7-CH_3, 874-39-5; I, 8-CH_3, 874-10-2; II, 274-47-5; II, 1-CH_3, 6558-62-9; II, 3-CH_3, 6558-63-0; II, 5-CH_3, 6558-64-1; III, 274-95-3; III, 7-CH_3, 6558-66-3; III, 3-deuterio, 15823-28-6; III, 5-deuterio, 15823-29-7.

TABLE V
METASTABLE IONS

	m* (experimental)	m* (theoretical)	m_1	m_2
Parent Compounds				
Imidazo[1,2-*a*]pyridine	70.1	70.18	118	91
	51.6	51.56	118	78
	45.0	45.01	91	64
Imidazo[1,5-*a*]pyridine	70.1	70.18	118	91
	51.6	51.56	118	78
	45.0	45.01	91	64
Imidazo[1,2-*a*]pyrimidine	71.1	71.12	119	92
	45.9	45.92	92	65
Five-Membered Ring Methyl Compounds				
3-Methylimidazo[1,2-*a*]pyridine	130.0	130.01	132	131
	103.0	103.01	105	104
	83.5	83.52	132	105
	82.6	82.56	131	104
1-Methylimidazo[1,5-*a*]pyridine	130.0	130.01	132	131
	103.0	103.01	105	104
	83.6	83.52	132	105
	82.6	82.56	131	104
	59.5	59.44	105	79
	58.5	58.50	104	78
3-Methylimidazo[1,5-*a*]pyridine	130.0	130.01	132	131
	103.0	103.01	105	104
	82.6	82.56	131	104
Six-Membered Ring Methyl Compounds				
5-Methylimidazo[1,2-*a*]pyridine	130.0	130.01	132	131
	103.0	103.01	105	104
	82.6	82.56	131	104
6-Methylimidazo[1,2-*a*]pyridine	130.0	130.01	132	131
	103.0	103.01	105	104
7-Methylimidazo[1,2-*a*]pyridine	130.0	130.01	132	131
	82.5	82.56	131	104
8-Methylimidazo[1,2-*a*]pyridine	130.0	130.01	132	131
5-Methylimidazo[1,5-*a*]pyridine	130.0	130.01	132	131
	103.0	103.01	105	104
	83.5	83.52	132	105
	82.6	82.56	131	104
	58.0	57.94	105	78
	57.0	57.01	104	77
	46.0	45.92	92	65
7-Methylimidazo[1,2-*a*]pyrimidine	131.0	131.01	133	132
	105.0	104.69	133	118
	84.5	84.48	133	106
	83.5	83.52	132	105
	59.0	58.88	106	79
	47.0	46.84	93	66
	45.9	45.92	92	65