Mass Spectra of Some Imidazo[1,2-*b*]pyridazines

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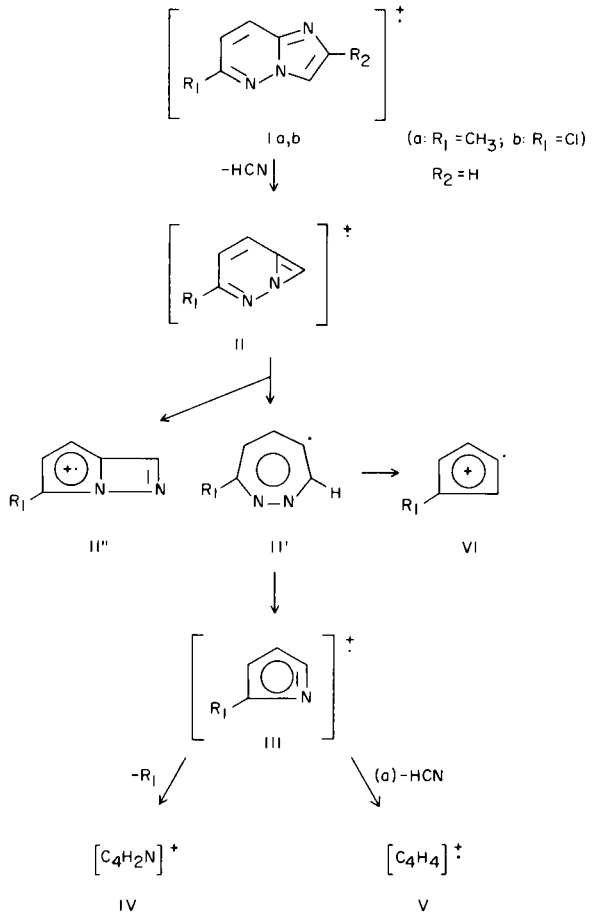
Recent publications from the laboratories of the authors describe the syntheses of some imidazo[1,2-*b*]pyridazines (1,2,3) and the mass spectra of some imidazo[1,2-*a*] and [1,5-*a*]pyridines and imidazo[1,2-*a*]pyrimidines (4), respectively. The parents of these ring systems lose HCN and C_2H_2N, with similar species being formed during fragmentation of the methyl derivatives. In addition, the loss of a hydrogen atom from the methyl group results in possible ring-expanded ions which subsequently lose HCN as well as C_4H_4.

Scheme I

Fragmentations Typical of the 5-Membered Rings



It became of interest to compare these fragmentations with those of several imidazo[1,2-*b*]pyridazines, particularly in view of the presence of a *N-N* bond in these compounds. Table I records the major fragment ions observed for these substances.

In those instances where R_2 (see Scheme I) is hydrogen, the major fragmentation that is observed involves the loss of HCN. The resulting ion-radical II might rearrange to the diazepine system II'. This ring expanded ion is similar to that shown to be formed in the mass spectra of the imidazopyridines and imidazopyrimidines (4). An alternate process that could occur involves the formation of the bicyclic system II''. While no deuterium studies are possible in this system, to establish the intermediacy of the ring expanded ion II' we might suggest, by analogy, that it is the diazepine system that is formed after HCN loss from the parent

Scheme II

Fragmentations Typical of the 6-Membered Ring

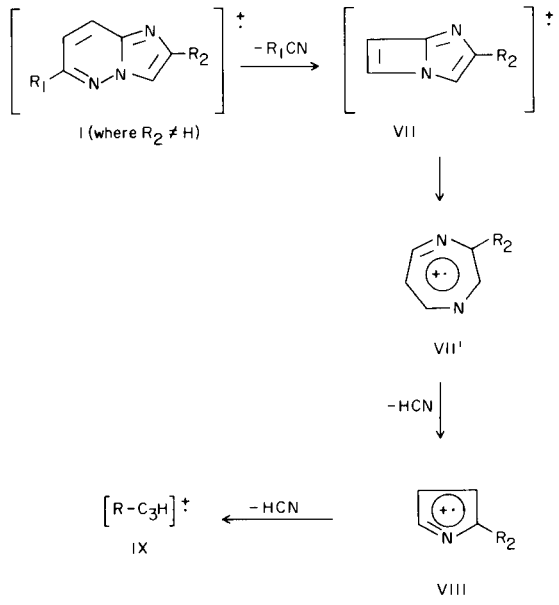


TABLE I

Mass Spectral Data of Some Imidazo[1,2-*b*]pyridazines

6-Methyl			6-Chloro			2-Methyl			2,6-Dimethyl		
m/e	% rel. int.	Species	m/e	% rel. int.	Species	m/e	% rel. int.	Species	m/e	% rel. int.	Species
			155	17							
			153	51	P^+						
									147	72	P^+
									146	38	P^+-1 (XIII) (X)
133	100	P^+				133	100	P^+			
132	30	P^+-1 (XIII)				132	48	P^+-1 (X)			
			128	11							
			126	31	II						
									120	9	
									119	19	XII
106	12	II				106	20	VII	106	10	VII, II
105	12	XIV				105	13	XII	105	17	XI, XIV
			101	8							
			99	17	III						
									93	10	XV
92	4	VII									
						80	6		80	9	
79	33	III				79	23	VIII, XV	79	52	VIII, III
78	13	VI				78	5		78	29	VI
		(XIV-HCN?)				66	5		66	12	
65	7	VIII				65	7	III	65	11	
64	8	IV	64	44	IV	64	19	VI	64	9	IV
			63	14							
						55	7				
						54	16		54	22	
53	9					53	9		53	45	
52	33	V	52	13		52	22	IX	52	100	IX, V
51	15		51	11		51	8		51	47	
50	8								50	18	
			44	8		44	7		44	7	
42	5					42	6		42	43	
41	10								41	24	
40	10		40	100					40	21	
39	12		39	11		39	20		39	67	
38	4		38	15		38	22		38	50	
37	7		37	21		37	7		37	17	

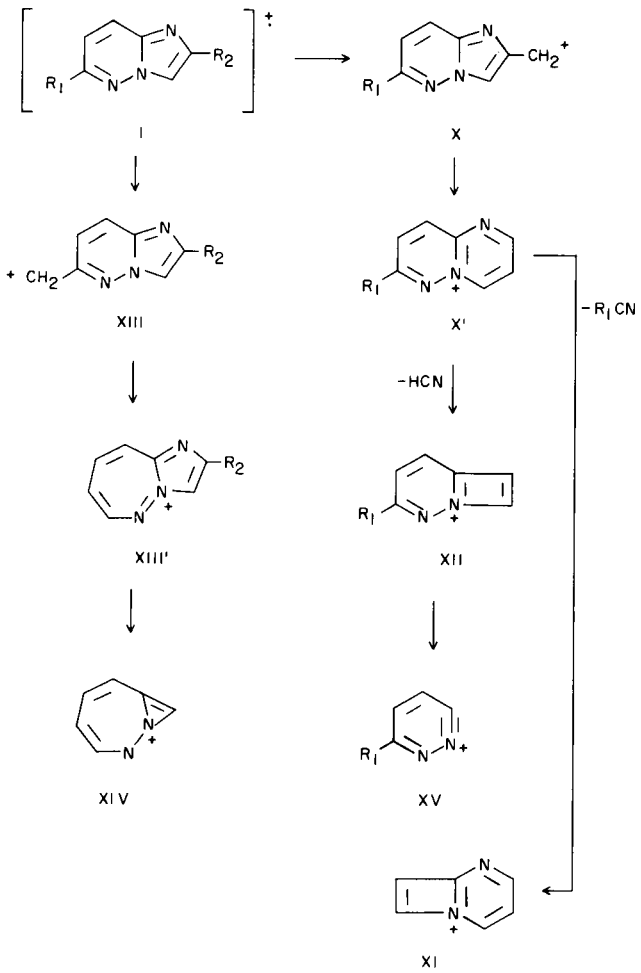
molecular ion. If this ring expanded species is indeed formed, it would be expected to lose N_2. The presence of a peak at m/e 78 (species VI) in the 6-methyl and in the 2,6-dimethyl and the m/e 64 peak in the 2-methyl derivatives is indicative that this process does, in fact, occur.

The loss of a second molecule of HCN from the species II (or II′) affords the ion III with some ease. The ion radical III loses HCN when R is not halogen to afford an ion radical $C_4H_4^{\cdot+}$ (V). The chloro derivative of the ion radical III, on the other hand, loses $Cl^{\cdot}$ instead of HCN to afford the ion IV.

Scheme II details the fragmentations which are typical of the six-member ring is this system. The major cleavage that occurs, when R_2 is *not* hydrogen (compounds I c and I d), involves the loss of R_1CN to yield the ion radical VII.

Scheme III

Fragmentations Caused by the Presence of Methyl Groups



This type of fragmentation would result in the formation of a m/e 92 species from the 6-methyl and the 6-chloro compounds. The low intensity of the m/e 92 (species VII) fragment ion from compound Ia shows, again, that the loss of HCN occurs with greater facility than the loss of CH_3CN. The facile loss of HCN from the ion-radical VII suggests that a ring-expanded species (VII′) may be involved. The loss of HCN from this fragment, which is substantiated by the presence of an appropriate metastable peak, affords an ion-radical which can be represented by the structure VIII. Since this ion-radical loses HCN to form the m/e 52 ion (species IX), its monocyclic nature is strongly indicated. A similar process occurs, as indicated earlier, in those compounds where R_2 = H.

The remaining paths to be considered involve fragmentations that are due to the presence of the C-methyl groups. Neither the 2-methyl nor the 6-methyl group is cleaved from the parent ion-radical. The loss of a proton from the methyl groups is, however, a significant process which affords the ions X and XIII, from the 2-methyl and the 6-methyl groups, respectively (see Scheme III). These ions can then ring-expand to the X′ and XIII′ ions, which, in turn, form the species XI, XII and XIV by loss of R_1CN. Thus, the 2-methyl and the 2,6-dimethylimidazo[1,2-*b*]-pyridazines can afford the species XI and XII, while the 6-methyl and the 2,6-dimethyl derivatives form the ion XIV by this process. The formation of the ion XI is, however, not very probable, in view of the necessity of cleaving a *N-N* bond, when, in fact, the ion XII is formed by a much more facile process. The presence of a m/e 93 peak in the mass spectrum of the 2,6-dimethyl compound can be explained by the transformation XII → XV. This fragmentation would give rise to a m/e 79 peak in the 2-methyl compound. A fragment of the same unit mass, species VIII, is, however, also formed from a different route (see Scheme II); consequently, this peak represents *two different* species in the 2-methyl compound.

The results of the studies described in this note are in agreement with, and further corroborate the previously described fragmentation processes of various polyazaindenes.

EXPERIMENTAL

The compounds used for these mass spectral investigations were prepared previously (1,2,3).

All mass spectra were measured with a Hitachi-Perkin-Elmer RMV-6E mass spectrometer operating at an ionization potential of 80 eV and with an inlet and source temperature of 180° (150° for compound Id).

REFERENCES

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