MASS SPECTRAL BEHAVIOR OF ALKYL- AND AMINO-5-AZACINNOLINES

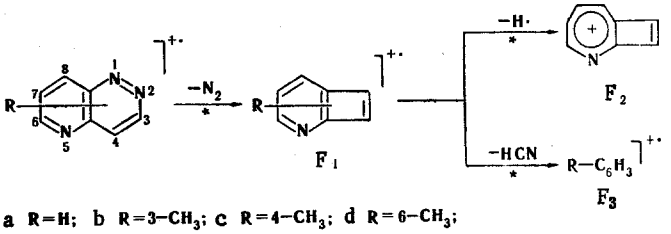
P. B. Terent'ev, V. G. Kartsev, and M. F. Budyka

UDC 543.51;547.3'852

Characteristic features of the processes of dissociative ionization of alkylarenes or alkylheteroarenes are the splitting of the "benzyl" C–H or C–C bonds with formation of stable fragments to which in a number of cases is ascribed a tropylium or heterotropylium cation structure [1-5]. Splitting of the heterocyclic ring itself usually occurs at more deep-seated stages of the breakdown. On the other hand, for mass spectrometric decomposition of aryl- or heteroarylamines the primary processes of "amine" fragmentation are a characteristic feature [6].

By exploiting the methods of preparing and studying the properties of derivatives of 5-azacinnoline [7] and 4-amino-5-azacinnoline [8, 9], we have studied their mass spectrometric behavior, which showed that the coupling of two electron-deficient rings (pyridine and pyridazine) results in the development of specific paths of dissociative ionization of the molecules. Thus in the mass spectra of all the studied alkyl-5-azacinnolines (Ia-g, Table 1), in contrast to the mass spectra of the alkylcinnolines [10], ion peaks due to "benzyl" type fragmentation are completely absent, and the primary process is characterized by elimination of a nitrogen molecule (Scheme 1). The fragment F_1 which is formed loses a further hydrogen atom (F_2) or ejects a molecule of hydrocyanic acid (F_3). This successive fragmentation is confirmed by the metastable ions. The three indicated ions, together with the molecular ion, as a rule constitute from 60 to 85% (Table 2) of all the ions, which points to a high selectivity of such a breakdown path (the compositions of the F_1-F_3 ions were confirmed by the high-resolution mass spectra):

Scheme



a R=H; b R=3-CH_3; c R=4-CH_3; d R=6-CH_3; e R=7-CH_3; f R=7-C_2H_5; g R=8-CH_3

A similar fragmentation was also characteristic of the mass spectrum of 7-methyl-8-azacinnoline (II).

In the mass spectrum of compound If the ion $(M - CH_3)^+$, which is characteristic for β-ethylpyridines [6], is completely absent and the ion F_1, according to the high-resolution mass spectra, is a compound ion and is formed through elimination from the molecular ion of both a nitrogen molecule (59%) and an ethylene molecule (41%). We stress that in the mass spectra of all the azacinnolines I ion peaks due to $(M - R)^+$ were not detected.

M. V. Lomonosov Moscow State University, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1124-1127, August, 1979. Original article submitted December 5, 1978.

 0009-3122/79/1508-0922$07.50

TABLE 1. Mass Spectra of Alkyl-5-azacinnolines

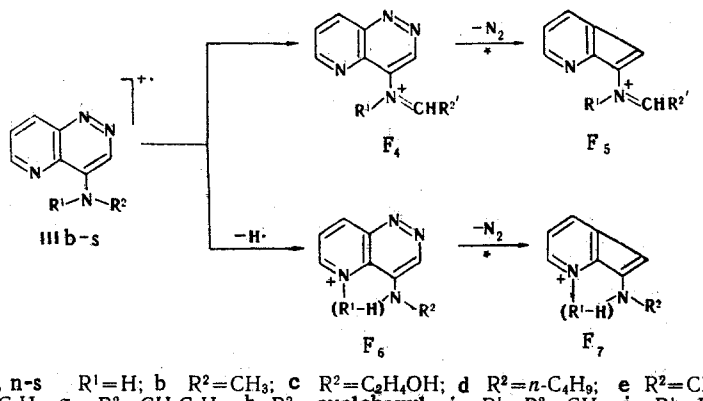
Compound	m/e (relative intensity, %)*
Ia	131 (100), 103 (32), 77 (16), 76 (90), 65 (3), 64 (3), 52 (11), 51 (10), 50 (30)
Ib	145 (100), 117 (12), 116 (12), 91 (9), 90 (62), 89 (54), 77 (4), 74 (13), 63 (26)
Ic	145 (100), 117 (6), 116 (8), 91 (4), 90 (33), 89 (35), 77 (6), 64 (6), 63 (9)
Id	145 (100), 117 (8), 116 (20), 90 (50), 89 (40), 77 (8), 76 (20), 64 (11), 63 (11)
Ie	145 (100), 117 (8), 116 (20), 91 (8), 90 (48), 89 (39), 78 (7), 64 (11), 63 (13)
If	159 (100), 131 (17), 130 (17), 116 (19), 103 (5), 89 (6), 78 (4), 77 (3), 64 (5)
Ig	145 (100), 116 (8), 104 (8), 93 (4), 91 (4), 90 (18), 89 (15), 64 (4), 63 (4)
II	145 (100), 117 (4), 116 (11), 91 (2), 90 (21), 89 (22), 76 (5), 64 (5), 63 (5)

*The molecular ion and the eight strongest peaks are given.

TABLE 2. Peak Intensities of the Characteristic Ions of Alkyl-5-azacinnolines (% Σ_{39})

Compound	W_M	F_1	F_2	F_3	F_2–HCN
Ia	40,0	12,8	—	36,0	—
Ib	31,7	3,8	4,0	19,6	17,1
Ic	47,0	2,8	3,6	15,7	16,5
Id	44,6	3,6	8,9	22,3	17,9
Ie	37,9	3,0	7,6	18,2	15,0
If	60,2	1,0	10,5	1,3	3,1
Ig	56,5	1,4	4,2	10,1	8,5
II	64,0	2,3	7,1	13,6	14,0

Scheme 2



III b-h, n-s R^1=H; b R^2=CH_3; c R^2=C_2H_4OH; d R^2=n-C_4H_9; e R^2=$CH(CH_3)_2$; f R^2=s-C_4H_9; g R^2=$CH_2C_6H_5$; h R^2=cyclohexyl; i R^1=R^2=CH_3; j R^1=R^2=C_2H_5; k R^1+R^2=$(CH_2)_4$; l R^1+R^2=$(CH_2)_5$; m R^1+R^2=$(CH_2)_2O(CH_2)_2$; n R^2=C_6H_5; o R^2=4-$CH_3C_6H_4$; p R^2=4-$CH_3OC_6H_4$; q R^2=4-ClC_6H_4; r R^2 = pyridyl-3; s R^2 = naphthyl-1; t R^1=D, R^2=CH_3; u R^1=D, R^2=n-C_4H_9

In contrast to the arylamines as well as 4-aminonaphthyridine-1,5 [11] and 4-aminocinnoline [12], the molecular ion of 4-aminoazacinnoline (IIIa) does not eliminate a HCN molecule in the primary breakdown stage. The mass spectrum of this compound (Table 3) is characterized by a molecular ion of high stability, which, as for compound I, loses first of all a nitrogen molecule and only then HCN. These three ions constitute more than half of all the ions in the spectrum. Substitution of the amino group by an alkyl radical markedly reduces the stability of the molecular ion, and the presence at the amino nitrogen atom of the aromatic nucleus raises the value of W_M (Table 4).

TABLE 3. Mass Spectra of 4-Amino-5-azacinnolines

Compound	m/e (relative intensity, %) *
IIIa	146 (100), 118 (8), 117 (7), 92 (8), 91 (47), 78 (15), 65 (13), 64 (34), 63 (11)
IIIb	160 (100), 159 (6), 132 (6), 131 (6), 105 (5), 104 (14), 103 (15), 98 (8), 91 (6)
IIIc	190 (24), 173 (11), 172 (17), 159 (100), 104 (17), 103 (10), 102 (14), 91 (4), 77 (8)
IIId	202 (23), 173 (14), 159 (100), 146 (14), 104 (20), 103 (19), 102 (17), 91 (11), 77 (17)
IIIe	188 (46), 173 (100), 159 (19), 147 (10), 118 (21), 117 (17), 103 (17), 91 (21), 58 (29)
IIIf	202 (20), 137 (4), 173 (100), 146 (2), 118 (2), 117 (2), 102 (3), 91 (4), 76 (3)
IIIg	236 (76), 235 (4), 106 (55), 105 (13), 104 (11), 103 (14), 91 (100), 77 (13), 65 (18)
IIIh	238 (45), 185 (43), 171 (66), 158 (44), 157 (45), 147 (31), 146 (100), 103 (47), 91 (48)
IIIi	174 (81), 159 (68), 146 (100), 131 (9), 121 (29), 103 (20), 90 (15), 77 (12), 76 (16)
IIIj	202 (3), 174 (100), 173 (28), 159 (85), 146 (32), 131 (10), 104 (14), 103 (23), 91 (19)
IIIk	200 (100), 172 (33), 171 (19), 158 (50), 144 (26), 117 (19), 103 (96), 76 (33), 70 (92)
IIIl	214 (48), 171 (17), 159 (17), 158 (18), 157 (15), 146 (16), 103 (64), 84 (100), 76 (19)
IIIm	216 (89), 198 (78), 173 (35), 159 (53), 158 (32), 157 (33), 145 (31), 103 (100), 78 (50)
IIIn	222 (100), 221 (37), 194 (15), 193 (34), 192 (14), 167 (17), 91 (36), 90 (14), 77 (55)
IIIo	236 (100), 235 (31), 103 (10), 91 (49), 90 (10), 81 (30), 79 (13), 78 (14), 77 (28)
IIIp	252 (100), 251 (55), 237 (69), 236 (22), 209 (13), 181 (18), 102 (30), 91 (21), 77 (18)
IIIq	258 (36), 257 (20), 256 (100), 255 (26), 193 (18), 192 (38), 111 (25), 102 (12), 91 (44)
IIIr	223 (93), 222 (100), 145 (22), 117 (37), 91 (44), 81 (48), 79 (20), 78 (39), 76 (35)
IIIs	272 (100), 271 (20), 244 (25), 243 (25), 126 (25), 98 (23), 97 (20), 84 (30) 81 (23)

*The molecular ion peak and the eight strongest peaks are given.

However the nature of the disintegration of the N-substituted 4-amino-5-azacinnolines IIIb-s (Scheme 2) markedly differed from the fragmentation of the unsubstituted amine IIIa primarily in the negligible probability of breakdown of the pyridazine ring in the primary process. The main course of dissociative ionization of the alkylamines IIIb-n (Scheme 2) is splitting of the radical R with formation of the stable ion F_4. In the case of the arylamines IIIj-s the main initial breakdown process is the loss of a hydrogen atom (probably from the aromatic ring) with stabilization of the ion F_6 due to the free electron pair of the pyridine nucleus. Elimination of a nitrogen molecule was observed only in the secondary stage of fragmentation of the F_4 and F_6 ions (ions F_5 and F_7 respectively). Finally when a substituent such as a methoxyl group or a halogen is present in the arylamino group the processes which are characterized by a splitting off of the methyl group or the chlorine respectively become marked, with subsequent fragmentation according to the scheme detailed above (loss of H and N_2). All the indicated breakdown paths were confirmed by the metastable ions, and analysis of the mass spectra of the alkylamines IIIt and IIIu possessing a deuterium atom on the nitrogen showed that the latter does not participate in all the conversions already mentioned.

The features which have been noted for the dissociative ionization of substituted 5-azacinnolines suggests that in their molecular ions the positive charge is predominantly localized on the pyridazine ring (alkyl-5-azacinnolines) or on the nitrogen atom of the amino group in position 4 (4-amino-5-azacinnolines). This enables conclusions to be made from the mass spectra concerning the character and structure of the substituents on the pyridazine nucleus, but does not make it possible to characterize substituents on the pyridine nucleus.

EXPERIMENTAL

The syntheses of compounds Ia-g and II are described in [7] and of compounds IIIa-s in [8, 9]. Synthesis of the deuterated compounds IIIt and IIIu was accomplished by three

TABLE 4. Peak Intensities of the Principal Characteristic Ions in the Mass Spectra of 4-Amino-5-azacinnolines (% Σ_{51})

Compound	W_M	F_4	F_5	F_6	F_7	Compound	W_M	F_4	F_5	F_6	F_7
IIIa	32,8	—	—	—	—	IIIk	13,7	2; 4c	1,0	0,4	2,4
IIIb	29,1	1,8	1,1	1,8	1,8	III1	7,6	1,2 d	2,1	0,6	1,2
IIIc	7,4	30,6	0,3	—	—	IIIm	6,2	1,2 c	1,9	3,5	0,4
IIId	7,2	21,5	1,1	0,2	3,0	IIIn	20,6	—	—	7,6	7,0
IIIe	7,0	15,3	—	0,1	2,4	IIIo	18,9	—	—	5,9	4,7
IIIf	11,7	61,2	—	—	61,2a	IIIp	14,5	11,8d	2,4	10,2	—
IIIg	19,2	1,3	1,5	0,9	0,2	IIIq	16,4	—	—	4,3	1,3
IIIh	3,5	2,8b	2,9	—	—	IIIr	13,5	—	—	14,5	1,3
IIIi	14,4	0,4	18,3	0,4	18,3	IIIs	19,3	—	—	3,9	4,8
IIIj	0,7	0,5	20,3	0,1	6,6						

[a] Most probably the $(M-C_2H_5)^+$ ion, but not $(M-H-N_2)^+$. [b] The $(M-C_3H_7)^+$ ion due to breakdown of the cyclic radical [c] The $(M-C_2H_5)^+$ ion due to breakdown of the cyclic radical. [d] The $(M-CH_3)^+$ ion due to the CH_3 group.

recrystallizations of the compounds IIIb,d from CH_3OD, the degree of enrichment achieved being 70-80%. Mass spectra were recorded on the MKh-1303 mass spectrometer with introduction of the substance into the ionization region at an electron ionization energy of 50 eV. High-resolution mass spectra were obtained on the JEOL JMS-01-SG-2 instrument at an electron ionization energy of 75 eV with automatic treatment of the data.

LITERATURE CITED

1. P. M. Draper and D. B. MacLean, Canad. J. Chem., 46, 1487 (1968).
2. S. D. Sample, D. A. Lightner, O. Buchart, and C. Djerassi, J. Org. Chem., 32, 997 (1967).
3. P. M. Draper and D. B. MacLean, Canad. J. Chem., 48, 738 (1970).
4. P. M. Draper and D. B. MacLean, Canad. J. Chem., 48, 746 (1970).
5. P. B. Terent'ev, A. N. Kost, A. A. Polyakova, and R. A. Khmel'nitskii, Dokl. Akad. Nauk SSSR, 167, 1066 (1966).
6. H. Budzikiewicz, C. Djerassi, and D. H. Williams, Mass Spectrometry of Organic Compounds, Holden Day (1967).
7. P. B. Terent'ev, V. G. Kartsev, and A. N. Kost, Khim. Geterotsikl. Soedin., No. 7, 976 (1976).
8. M. F. Budyka, P. B. Terent'ev, and A. N. Kost, Khim. Geterotsikl. Soedin., No. 11, 1154 (1977).
9. M. F. Budyka, P. B. Terent'ev, and A. N. Kost, Khim. Geterotsikl. Soedin., No. 6, 809 (1978).
10. M. H. Palmer, E. R. R. Russel, and W. A. Wolstenholme, Org. Mass Spectrom., 2, 1265 (1969).
11. E. V. Brown, A. C. Plasz, and S. R. Mitchel, J. Heterocycl. Chem., 7, 661 (1970).
12. J. R. Elkins and E. V. Brown, J. Heterocycl. Chem., 5, 639 (1968).