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MASS SPECTROMETRY OF NITROGEN HETEROCYCLES.
4.* MASS SPECTRAL BEHAVIOR OF TRIAZOLO[1,5-a]PYRIDO[2,3-d]PYRIMIDINES

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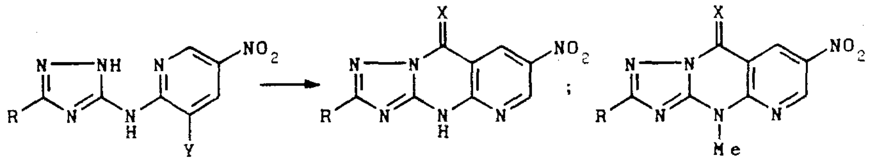
and V. L. Rusinov**

The electron impact mass spectra of substituted 9-imino- and 9-oxotriazolo[1,5-a]pyrido[2,3-d]pyrimidines were studied. The mass spectral data obtained permitted us to determine the order of the fusion of the triazole, pyrimidine, and pyridine rings as well as the position of the hydrogen atoms at the heteroatoms. Compounds labelled with ^{15}N *and* ^{13}C *atoms were used to check the assignments made.*

The thermal intramolecular cyclization of 2-triazolylamino-3-Y-5-nitropyridines I [1] and the closure of heteroaryl systems by the action of bases such as KOH [2] lead to the formation of triazolo[1,5-a]pyrido[2,3-a]pyrimidines (IIa)-(IIf). These processes are accompanied by the elimination of neutral molecules. Ethanol, ammonia, and hydrogen sulfide are lost when Y = $CO_2C_2H_5$, $CONH_2$, and $CSNH_2$, respectively.



I IIa-f III g-j

II, III a R=H, X=NH; b R=CH_3, c R-CF_3, X=NH; d R=H, X=O; e R=CH_3, X=O; f R=SCH_3, X=O; g R=H, X=NH; h R=CF_3, X=NH; i R=H, X=O; j R=CH_3, X=O; Y=$COOC_2H_5$, $CONH_2$, $CSNH_2$

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*For Communication 3, see [1].

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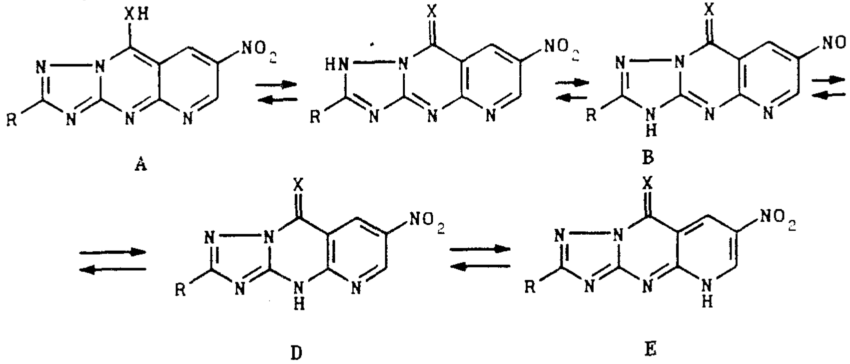
In principle, IIa-IIf may exist in one or several tautomeric forms A-E.



Optical and NMR spectroscopy did not permit us to determine the predominance of a specific form. Furthermore, there are often technical limitations, which complicate the use of these methods in analyzing IIa-IIf due to their poor solubility. In order to reveal the analytical features characterizing this new heterocyclic system and determine the position of the hydrogen atom at the exo- and endocyclic heteroatoms of forms A-E, we examined the electron impact mass spectra of 7-nitro-1,2,4-triazolo[1,5-a]pyrido[2,3-d]pyrimidines IIa-IIf and compounds with fixed structure 4-methyl-7-nitro-1,2,4-triazolo[1,5-a]pyrido[2,3-d]pyrimidines IIg-IIj (see Table 1).

Upon evaporation of the sample in the ion source under direct inlet conditions, the molecular ion (M^+), as a rule, retains the structure of the original molecule [3]. The possibility of the existence of II as tautomeric forms A-E presupposes obvious differences in the fragmentation of each of these forms. The elucidation of these differences would permit us to establish the predominance of IIa-IIj in a specific tautomeric form.

The electron impact mass spectra of IIa-IIj have a number of features characterizing the structure of this complicated heterocyclic system (Table 1). The finding that M^+ has the greatest intensity with the exception of the case of IIf suggests extensive conjugation in IIa-IIj. The composition of the molecular ions was established by high-resolution mass spectra for IIb and IIe ($\Delta M = 0.1$-0.8 ppm), while the sequence of formation of the daughter ions was determined by taking the mass spectra of the metastable ions in the DADI mode for IIa-IIc, IIe, and IIf.

The existence of peaks for the $[M - NO]^+$ and $[M - NO_2]^+$ ions (Φ_1) in the spectra of IIa-IIj is attributed to the presence of the nitro group in the starting molecules [4]. Formation of the $[\Phi - CX]^+$ ion, where X = NH and O, is related to elimination of NCH (IIa-c, IIg, and IIh) or CO (IId-IIf, IIi, and IIj) directly from the central pyrimidine ring.

This conclusion is in accord with the finding that the appearance of these ions is independent of the nature of substituent R and occurs in the mass spectra of all II along with the $[\Phi_1 - RCN]^+$ ion. When X = NH and R = H, the elimination of HCN from the triazole part of the molecule and from the central pyrimidine ring coincide and give peaks with the same mass numbers. Furthermore, evidence for contraction of the pyrimidine ring due to the loss of HCN or CO from $C_{(9)}$ in II may

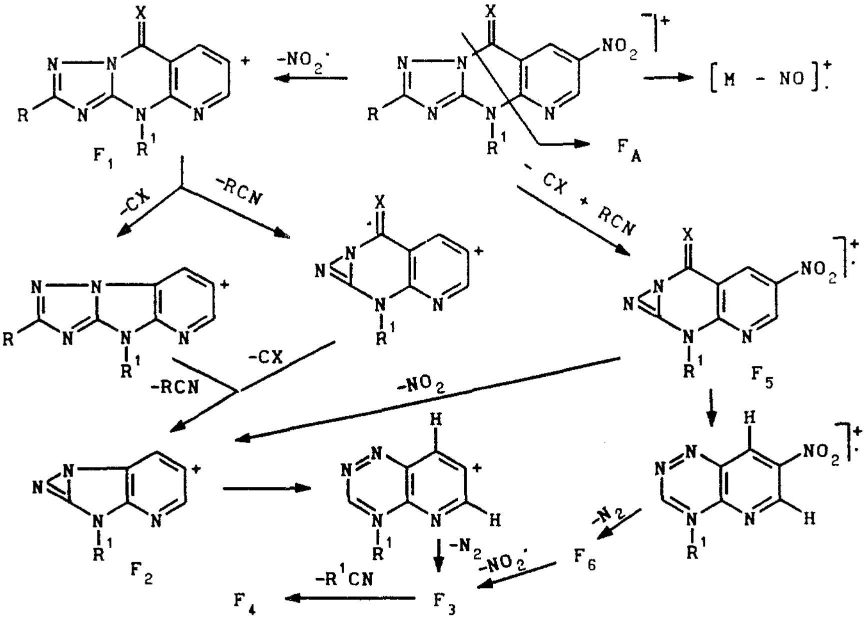


TABLE 1. Mass Spectra of Triazolo[1,5-a]pyrido[2,3-d]pyrimidines IIa-IIj and III, m/z (%)

Compound	M^+	$[M-NO]^+$	$[M-NO_2]^+$ Φ_1	Φ_A	$[\Phi_1-CX]^+$	$[\Phi_1-RCN]^+$	$[M-(CX+RCN)]^+$, Φ_5	$[\Phi_1-(CX+RCN)]^+$, Φ_2	$[\Phi_2-N_2]^+$, Φ_3	$[\Phi_5-N_2]^+$, Φ_6	$[\Phi-R^1CN]^+$, Φ_4	Other fragments $J \geq 10\%$
IIa	231 (100)	201 (10)	185 (45)	149 (22)	158 (22)	158 (22)	—	131 (13)	103 (33)	149 (22)	76 (40)	140 (10), 102 (16), 69 (17), 68 (13), 64 (18)
IIb	245 (100)	215 (25)	199 (38)	149 (34)	172 (8)	158 (2)	—	131 (4)	103 (22)	149 (34)	76 (25)	102 (12), 85 (12), 83 (15), 71 (24), 69 (20), 64 (10)
IIc	299 (100)	269 (9)	153 (44)	149 (28)	226 (18)	158 (5)	—	131 (7)	103 (17)	149 (28)	76 (34)	280 (12), 233 (11), 102 (15), 91 (10), 64 (17)
IId	232 (100)	202 (3)	186 (18)	150 (8)	158 (7)	159 (8)	—	131 (9)	103 (19)	149 (13)	76 (25)	104 (10), 77 (15), 75 (12), 71 (18)
IIe	246 (100)	216 (3)	200 (41)	150 (15)	172 (12)	159 (5)	177 (3)	131 (7)	103 (22)	149 (41)	76 (55)	104 (19), 83 (18), 77 (21), 75 (25), 64 (19)
IIf	278 (92)	248 (7)	232 (100)	150 (9)	204 (4)	159 (6)	177 (8)	131 (6)	103 (10)	149 (17)	76 (35)	245 (13), 235 (11), 233 (12), 231 (13), 207 (14), 190 (21), 189 (25), 187 (47), 171 (11), 145 (150), 119 (11), 105 (11), 104 (16), 91 (12), 85 (28), 77 (26), 75 (20), 71 (11), 68 (11), 67 (10), 64 (19), 63 (10)
IIg	245 (100)	215 (2)	199 (25)	149 (10)	172 (7)	172 (7)	199 (25)	145 (8)	117 (7)	163 (1)	76 (17)	103 (59)
IIh	313 (100)	—	267 (85)	149 (9)	240 (12)	172 (5)	199 (8)	145 (25)	117 (18)	—	76 (47)	294 (17), 268 (22), 258 (18), 227 (15), 212 (10), 177 (18), 165 (88), 163 (10), 143 (13), 131 (13), 118 (14), 105 (10), 104 (11), 103 (25), 102 (18), 91 (10), 90 (14), 78 (11), 77 (15), 75 (12), 69 (18), 67 (15), 64 (13)
IIi	246 (100)	216 (4)	200 (16)	150 (8)	172 (6)	173 (8)	191 (21)	145 (14)	117 (26)	163 (12)	76 (23)	199 (21), 105 (14), 104 (13), 90 (12), 77 (14), 75 (13), 74 (20)
IIj	260 (100)	230 (2)	214 (19)	150 (5)	186 (3)	173 (3)	191 (3)	145 (6)	117 (24)	163 (24)	76 (16)	104 (16), 85 (12), 83 (23), 77 (13), 74 (34), 73 (12), 71 (16), 69 (13), 60 (12)
III	248 (100)	218 (4)	202 (17)	152 (4)	174 (16)	175 (8)	193 (19)	147 (15)	199 (30)	165 (14)	78 (31)	

be found in the analogous processes observed in 9-oxo- and 9-thioacridines [5]. This process presupposes the predominance of the imino and oxo forms for IIa-IIj in the gas phase. Thus, form A is excluded from consideration, especially since there is tendency for a shift in the equilibrium toward enol, amine, and mercapto forms in the gas phase.

The mass spectra of the metastable ions indicate the formation of Φ_A ions (m/z 149 or 150 depending on X) directly from M^+. The high-resolution mass spectra indicate the chemical formulas of these ions. We should note that this process is possible only for forms B-D, which excludes tautomeric form E from further consideration.

The loss of CX proceeds in parallel to the loss of the RCN fragment from the triazole part of II, which leads to the formation of fragmentation ion Φ_2 (Scheme). The subsequent decrease in the mass of fragmentation ion Φ_2 by 28 units indicates the loss of an N_2 molecule, which is characteristic for rings with an aza bond. On this basis, the present process involves the rearrangement of ion Φ_2 into a 1,2,4-triazinopyridine structure followed by the elimination of N_2 [6] with formation of fragmentation ion Φ_3, whose chemical formula was supported by high-resolution mass spectroscopy. Such fragmentation would be impossible if the hydrogen atom were located at position 1 or 3 of the triazole ring. This permits us to exclude tautomeric forms B and C in the gas phase. Hence, we may conclude the predominance of pyrimidines IIa-IIf in tautomeric form D.

The mass spectra of IIj-IIk, which have a methyl group at $N_{(4)}$ need not differ significantly from the spectra of IIa-IIf. The existence of an additional methyl group is seen in the shift of the masses of all the fragmentation ions by 14 a. m. u. An increase in ion mass is not seen only in the step involving formation of fragmentation ion Φ_4, which suggests the location of the methyl group at the nitrogen atom of the pyrimidine ring. Such a structure for IIg-IIj was supported by ^{13}C NMR spectroscopy [7]. The conversion of fragmentation ion Φ_3 into Φ_4 is the usual fragmentation for nitrogen heterocycles and is related to the loss of R^1CN [6].

In order to confirm the order of fusion of the heterocycles in the heterocyclic system and the proposed scheme for its decomposition, we synthesized an analog of triazolo[1,5-a]pyrido[2,3-d]pyrimidine (Py) having isotope labels: ^{13}C at position 4a and ^{15}N at position 5 (III). The presence of the labelled atoms (enrichment: 65% ^{13}C and 80% ^{15}N) [7] is seen in all the fragmentation ions (increase in m/z by 2 a. m. u.) with the exception of Φ_4, which is in complete accord with the proposed decomposition scheme with consecutive destruction of the triazole and pyrimidine rings, assuming linear fusion.

Thus, the use of high-resolution mass spectrometry, isotope labelling, and recording of metastable ions permitted us to establish the fusion of the heterocycles in this complex polynitrogen system and the predominant position of the hydrogen atom in this system.

EXPERIMENTAL

The mass spectra were taken on a Varian MAT 311A mass spectrometer. Standard conditions were used: 3 kV accelerating voltage, 70 eV ionizing electron energy, 1 mA cathode emission current. The high-resolution mass spectra were taken under the same conditions with resolution $M/\Delta M = 10{,}000$. The mass spectra of the metastable ions were taken using the DADI mode according to our previous procedure [8]. Products IIg-IIj and triazolo[1,5-a]pyrido[2,3-d]pyrimidine III having ^{13}C and ^{15}N isotope labels were synthesized according to our procedures [7].

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