(3.4%) of XIX with mp 107-109° was obtained by crystallization from hexane. Found, %: C 87.2; H 8.5; N 4.1. M 343. $C_{25}H_{29}N$. Calculated, %: C 87.4; H 8.5; N 4.1. M 343. Crystallization of the residue from the mother liquors from ligroin gave 0.34 g (11.5%) of XVII with R_f 0.19 and mp 113-114°. UV spectrum, λ_{max} (log ε): 203 (4.62), 220 (4.12), 262 (2.68), 266 (2.74), 269 (2.85), and 279 nm (2.80). Found, %: C 86.4; H 9.2; N 3.7. M 347. $C_{25}H_{33}N$. Calculated, %: C 86.4; H 9.5; N 4.0. M 347.

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MASS SPECTRA OF 2,3,4,5-TETRAHYDROPYRIMIDO[3,4-a]INDOLES

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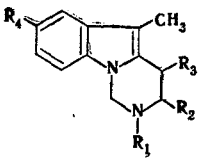
The dissociative ionization of protected 2,3,4,5-tetrahydropyrimido[3,4-a]indoles of the general formula



I-XI

under the influence of electron impact proceeds via two pathways. The first process is elimination of an R_1NCHR_2 group when $R_1 = CH_3$. The second process, which is characteristic for compounds with a formyl substituent (R_1 = CHO) or without a substituent (R_1 = H) attached to the amino nitrogen atom, is detachment of a CH_2NCHR_2 group with migration of a hydrogen atom of the amino group to the fragment ion; this is confirmed by the spectrum of the deuterium-labeled compound. The principal ion peaks (the fragment and rearranged ions) in combination with the molecular ion in the mass spectra constitute 55.0-70.0% of the total ion current. Ion peaks that characterize a methoxy group and a chloro substituent in the indole portion of the molecule are present in the mass spectra. The compositions of the ions were confirmed by the high-resolution mass spectra.

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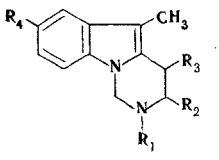
It is known [1] that tryptamines undergo "β cleavage" with elimination of the CH_2NH_2 group under the influence of electron impact. In addition, a rearrangement process with the loss of a CH_3N residue is characteristic for them. The mass spectral fragmentation of indoles containing a β-aminoethyl group in the 2 position of the pyrrole ring of indole has not been described in the literature. We have studied the dissociative ionization of a series of cyclic analogs of compounds of this type (I-XI):



I-XI

I $R_1=R_2=R_3=R_4=H$; II $R_1=R_2=R_3=H$, $R_4=CH_3$; III $R_1=R_2=R_3=H$, $R_4=OCH_3$; IV $R_2=R_3=H$, $R_1=CHO$, $R_4=CH_3$; V $R_2=R_3=R_4=H$, $R_1=CH_3$; VI $R_2=R_3=H$, $R_1=R_4=CH_3$; VII $R_2=R_3=H$, $R_1=CH_3$, $R_4=Cl$; VIII $R_2=R_3=H$, $R_1=CH_3$, $R_4=OCH_3$; IX $R_2=H$, $R_1=R_3=R_4=CH_3$; X $R_3=R_4=H$, $R_1=R_2=CH_3$; XI $R_2=R_3=R_4=H$, $R_1=D$

The mass spectra obtained from these compounds and the stabilities (W_M) of their molecular ions with respect to fragmentation are presented in Table 2, and the intensities and compositions of the principal characteristic ions are given in Table 1. It is apparent from an analysis of the data in Table 2 and the literature data [2-4] that I-X have high stabilities with respect to electron impact: this is probably explained by the "cyclic" structure of their β-aminoethyl chain. It should be noted that substituents in the benzene ring of the indole have practically no effect on the W_M values. However, replacement of the hydrogen atom of the amino group (IV-X) somewhat increases the stability of the molecule. Acylation of the amino group (IV) has the greatest stabilizing effect on the molecular ion, while introduction of a methyl group in the α position relative to the amino nitrogen atom leads to destabilization of the X molecule. All of these facts make it possible to assert that the positive charge in the molecular ions of I-X is localized on the amino nitrogen atom. In fact, it is easy to note that fragmentation pathways that characterize the indole system (the $[M-H]^+$ ions characteristic for methyl- and alkylindoles) or a substituent contained in the molecule (the $[M-Cl]^+$ ions in the mass spectrum of VII and the $[M-CH_3]^+$ and $[M-CH_2O]^+$ ions in the mass spectra of III and VIII) are absent in the spectra of these compounds or are expressed extremely weakly. The principal dissociative ionization process of the investigated group of compounds consists in the formation of two types of ions – fragment F_1 and rearranged F_2 ions the compositions of these and other fragments are confirmed by the metastable ions and the high-resolution mass spectra (see the scheme below). In fact, the F_1 and F_2 ions in combination with the molecular ions in the mass spectra of the compounds constitute 55.0-70.0% of the total ion current. In the mass spectra of I-IV, in which there is no substituent (or a formyl group is present) in the 3 position, the maximum peak is that of rearranged ion F_2. An analysis of the mass spectrum of labeled XI showed that transfer of a hydrogen atom only of the amino group to the fragment ion occurs during the formation of the F_2 ion. The "labile" hydrogen atom of the formyl group is evidently transferred during the fragmentation of

TABLE 1. Intensities and Compositions of the Principal Characteristic Ions

Compound	F_1				F_2			
	I*	mass observed	mass calc.	elementary composition	I	mass observed	mass calc.	elementary composition
I	11,13	157,0906	157,0891	$C_{11}H_{11}N$	44,00	144,0806	144,0813	$C_{10}H_{10}N$
II	9,18	171,1042	171,1048	$C_{12}H_{13}N$	27,00	158,0969	158,0969	$C_{11}H_{12}N$
III	8,91	187,1020	187,0997	$C_{12}H_{13}NO$	27,00	174,0903	174,0918	$C_{11}H_{12}NO$
IV	14,57	171,1054	171,1048	$C_{12}H_{13}N$	21,00	158,0977	158,0969	$C_{11}H_{12}N$
V	46,00	157,0908	157,0891	$C_{11}H_{11}N$	1,37	144,0826	144,0813	$C_{10}H_{10}N$
VI	45,00	171,1038	171,1048	$C_{12}H_{13}N$	1,53	158,0964	158,0969	$C_{11}H_{12}N$
VII	38,00				0,78			
VIII	40,00	187,1022	187,0997	$C_{12}H_{13}NO$	1,10	174,0945	174,0918	$C_{11}H_{12}NO$
IX	51,00	185,1195	185,1204	$C_{13}H_{15}N$				
X	42,00				1,39			

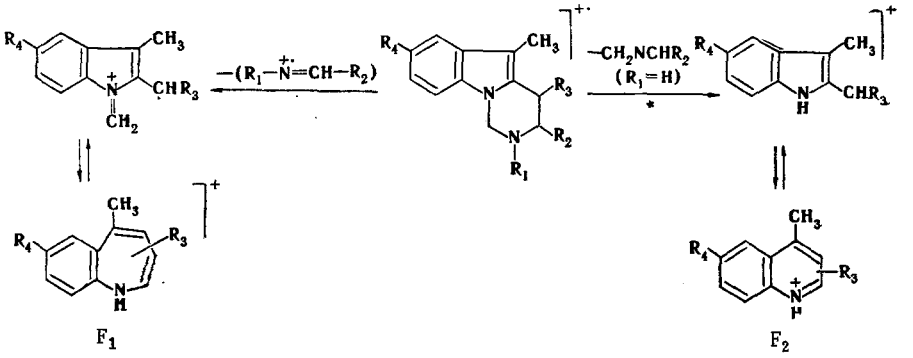
*The I values are the intensities of the peaks in percent with respect to the total ion current.

TABLE 2. Mass Spectra of I-XI*

Compound	m/e (intensities of the peaks in percent relative to the maximum peak)	W_M
I	42 (8,0) 77 (4,5) 115 (3,3) 143 (8,7) 144 (100,0) 145 (6,8) 156 (5,8) 157 (25,3) 186 (32,2) 187 (4,2)	14,1
II	42 (5,6) 43 (3,6) 115 (4,6) 143 (7,8) 156 (6,6) 157 (6,8) 158 (100,0) 159 (10,2) 170 (5,6) 171 (34,0) 200 (36,0) 201 (5,0)	14,0
III	42 (5,8) 77 (3,6) 108 (3,0) 115 (4,6) 130 (6,2) 131 (13,8) 143 (7,4) 144 (6,8) 158 (5,7) 159 (8,7) 160 (3,6) 172 (8,1) 173 (4,2) 174 (100,0) 175 (14,0) 186 (6,2) 187 (33,0) 188 (7,5) 215 (5,2) 216 (52,5) 217 (9,1)	14,2
IV	42 (17,1) 43 (18,4) 55 (8,8) 57 (13,4) 60 (4,5) 69 (17,1) 71 (6,2) 73 (4,2) 81 (5,7) 83 (3,3) 115 (5,3) 143 (6,5) 156 (6,1) 157 (4,8) 158 (100,0) 159 (4,9) 170 (8,3) 171 (70,2) 172 (4,5) 186 (8,3) 228 (93,0) 229 (6,7)	19,5
V	42 (8,5) 130 (3,8) 156 (21,1) 157 (100,0) 158 (9,5) 200 (37,2) 201 (5,3)	17,1
VI	42 (5,9) 156 (9,2) 158 (3,4) 170 (19,6) 171 (100,0) 172 (10,6) 214 (35,0) 215 (5,2)	15,7
VII	42 (8,7) 57 (3,1) 156 (21,3) 190 (10,7) 191 (100,0) 192 (12,1) 193 (26,6) 234 (36,8) 235 (5,0) 236 (9,7) 237 (1,2)	15,0
VIII	42 (6,0) 115 (4,4) 144 (6,3) 157 (3,4) 158 (3,0) 172 (22,0) 186 (13,0) 187 (100,0) 188 (10,5) 230 (40,0) 231 (3,8)	16,0
IX	158 (5,2) 170 (3,2) 184 (23,9) 185 (100,0) 186 (8,4) 228 (31,8) 229 (2,3)	16,2
X	42 (3,4) 56 (3,1) 77 (3,5) 107 (3,2) 115 (4,1) 128 (4,9) 129 (4,4) 130 (7,2) 142 (5,5) 144 (3,3) 154 (3,5) 156 (13,5) 157 (100,0) 158 (12,6) 214 (28,3) 215 (6,5)	12,9
XI	42 (8,8) 77 (8,1) 115 (6,3) 128 (7,2) 130 (5,0) 143 (8,7) 144 (64,6) 145 (100,0) 146 (11,8) 156 (10,0) 157 (56,3) 158 (9,1) 186 (24,4) 187 (53,5) 188 (7,0)	

*The peaks with intensities higher than 3% are presented.

IV. The introduction of a methyl group at the amino nitrogen atom leads to a change in the principal pathway of fragmentation of the molecular ion, and the F_1 ion, which possibly has a benzazepine structure, becomes the maximum ion in the spectrum.



The subsequent fragmentation of the F_1 and F_2 ions occurs via successive elimination of H, CH_3, HCN, or CH_2N and leads to $C_{10}H_8$ (m/e 128) and C_9H_7 (m/e 115) hydrocarbon ions; this is confirmed by the high-resolution mass spectra. Low-intensity peaks of $[M - H]^+$, $[(M - H) - CH_3]^+$, and $[M - CH_2O]^+$ ions are observed in the mass spectra of methoxy-substituted III and VIII. An extremely intense peak with m/e 156, which corresponds to the loss of chlorine by the F_2 ion, is observed in the spectrum of chloro-substituted VII.

The lack of data on the conformation of I-X makes it impossible to draw a confident conclusion regarding its effect on the fragmentation in this case. However, an analysis of Dreiding and Stuart–Briegleb models of the structure of IV provides evidence that it should have a half-chair conformation with an axially oriented formyl group. In this case, in the conformation most favorable for the orientation of the >C=O group the aldehyde hydrogen atom should actually be situated near the nitrogen atom of the pyrrole ring, and its rearrangement will be facilitated. Definitive conclusions regarding the correctness of this interpretation of the observed facts can be obtained only after recording of the PMR spectra of IV at various temperatures.

EXPERIMENTAL

The mass spectra of the investigated compounds were recorded with an MKh-1303 spectrometer with a system for introduction of the samples directly into the ion source at an ionizing-electron energy of 70 eV and 80-100°. The high-resolution mass spectra were recorded with a JEOL JMS-10SG2 spectrometer with recording on a photographic plate and subsequent processing with a microphotometer—JEC-6 computer system.

Compound XI was obtained by refluxing (three times) I in CH_3OD, which made it possible to achieve 70% deuteration.

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RESEARCH ON FIVE-MEMBERED HETEROCYCLES.

I. SYNTHESIS OF NITROCHLOROIMIDAZOLES

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Nitrochloroimidazoles were synthesized by replacement of the nitro group in dinitroimidazoles by chlorine by the action of $POCl_3$. It is shown that in the case of 4,5-dinitroimidazoles substitution takes place when both dimethylformamide (DMF) and pyridine are used as the solvents, while only DMF is suitable for 2,4-dinitroimidazoles. The location of the halogen in the synthesized nitrochloroimidazoles was confirmed by alternative synthesis.

Very little information on nitrochloroimidazoles is available in the literature. The synthesis of 1-alkyl-, (1,2-dialkyl)-4-nitro-5-chloro-, 1-alkyl-, and (1,2-dialkyl)-5-nitro-4-chloroimidazoles [1] and 2-chloro-4(5)-nitro-5(4)-chloroimidazole, to which the isomeric 4(5)-nitro-5(4)-chloroimidazole structure was incorrectly assigned [2], has been described. Chloronitroimidazoles are of definite interest as subjects for biological studies [2] and as intermediates for the preparation of amino- [3] and mercaptoimidazoles [4] and heterocyclic compounds containing an imidazole fragment.

In the present research we investigated the possibility of the synthesis of the previously undescribed nitrochloroimidazoles IIIa-c and IVa,b by reaction of dinitroimidazoles Ia-c and IIa,b with $POCl_3$ in dimethylformamide (DMF) or pyridine.

We have shown that the ease of replacement of a nitro group by chlorine in Ia-c and IIa-b depends on the nature of the solvent and the structure of the dinitroimidazoles. Thus similar substitution occurs in 4,5-dinitroimidazoles Ia-c under the influence of $POCl_3$ in DMF at 80-85°C (method A) or in pyridine at 90-95° (method B). 2,4-Dinitroimidazoles (IIa,b) form the corresponding chloronitroimidazoles IVa,b only via method A. Despite variations in

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