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MASS-SPECTROMETRIC STUDY OF 6-METHYL-2-ARYL-7-BENZYLINDOLIZINES

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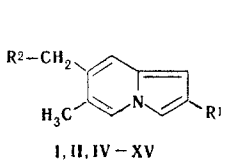
The mass-spectral behavior of 15 compounds from the 6-methyl-2-aryl-7-benzylindolizine series was investigated, and it was shown that the peculiarities of their dissociative ionization are due to the formation of stable resonance-stabilized ions that contain a quaternized nitrogen atom in the heteroring.

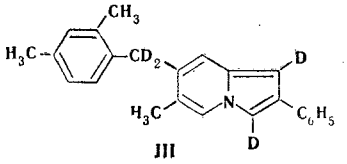
In contrast to the isomeric indoles [1], little study has been devoted to the dissociative ionization of indolizines. Only three reports have been devoted to a systematic study of the fragmentation of compounds of this series [2-4], whereas this problem is deserving of serious attention.

The nitrogen atom in the indolizine ring is found simultaneously in the pyridine and pyrrole rings. This position of the nitrogen atom in the fragmentation of indolizines may lead to the formation of resonance-stabilized ions that contain a quaternized nitrogen atom. The hypothetical electronic effect of the indolizine ring should be similar to the effect of electron-donor substituents of the OH, OR, NH_2, OCH_3, and $N(CH_3)_2$ type in the ortho or para positions of aromatic and heteroaromatic rings [5, 6]. It is known that these substituents markedly change the character of fragmentation under the influence of electron impact of the atomic groups included in the aromatic or heteroaromatic ring. Consequently one might also expect anomalous mass-spectrometric behavior for indolizine derivatives.

In the present research we studied the dissociative ionization of 6-methyl-2-aryl-7-benzylindolizines I-XV in order to establish the chief principles of their fragmentation and to verify the assumption indicated above.



I, II, IV – XV



III

I $R^1=C_6H_5$, $R^2=C_6H_5$; II $R^1=C_6H_5$, $R^2=2,4\text{-}(CH_3)_2C_6H_3$; IV $R^1=C_6H_5$, $R^2=3,4\text{-}(CH_3)_2C_6H_3$; V $R^1=4\text{-}CH_3C_6H_4$, $R^2=3,4\text{-}(CH_3)_2C_6H_3$; VI $R^1=C_6H_5$, $R^2=2,4,5\text{-}(CH_3)_3C_6H_2$; VII $R^1=4\text{-}CH_3C_6H_4$, $R^2=4\text{-}C_2H_5C_6H_4$; VIII $R^1=4\text{-}CH_3C_6H_4$, $R^2=2,4,5\text{-}(CH_3)_3C_6H_2$; IX $R^1=4\text{-}OCH_3C_6H_4$; $R^2=2,4,5\text{-}(CH_3)_3C_6H_2$; X $R^1=4\text{-}BrC_6H_4$, $R^2=C_6H_5$; XI $R^1=4\text{-}BrC_6H_4$, $R^2=4\text{-}C_2H_5C_6H_4$; XII $R^1=4\text{-}BrC_6H_4$, $R^2=2,4,5\text{-}(CH_3)_3C_6H_2$; XIII $R^1=C_6H_5$, $R^2=4\text{-}NO_2C_6H_4$; XIV $R^1=4\text{-}NO_2C_6H_4$, $R^2=C_6H_5$; XV $R^1=4\text{-}NO_2C_6H_4$, $R^2=4\text{-}NO_2C_6H_4$

The molecular-ion peaks (M^+) are the most intense peaks in the mass spectra of I-XV (Table 1). The stabilities of indolizines with respect to electron impact (W_M, Table 2) are approximately equal to the stabilities of the M^+ ions of 6-methyl-2,7-diarylindolizines [4]. The W_M value changes only slightly when the electron-donor substituents CH_3, C_2H_5, OCH_3, and Br are present in 7-benzylindolizines I-XII (Table 2) but decreases appreciably (by a factor of 1.5-2) in the case of XIII-XV, which contain an electron-acceptor NO_2 group.

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TABLE 1. Mass Spectra of 6-Methyl-2-phenyl-7-benzyl-substituted Indolizines

Compound	m/z values (relative intensities of the ion peaks in percent relative to the maximum peak)*
1	2
6-Methyl-2-phenyl-7-benzylindolizine (I)	297 (100), 296 (10,8), 295 (4,5), 294 (3,4), 293 (2,3), 292 (2,0), 282 (3,7), 281 (3,7), 280 (3,7), 221 (3,7), 220 (18,3), 219 (2,3), 218 (4,5), 205 (2,3), 204 (4,5), 178 (2,3), 141 (3,4), 126 (2,3), 115 (3,4), 102 (2,3), 91 (2,3), 77 (2,3)
6-Methyl-2-phenyl-7-(2,4-dimethylbenzyl)-indolizine (II)	325 (100), 324 (7,4), 310 (4,3), 309 (2,0), 308 (2,0), 294 (2,6), 221 (2,6), 220 (16,1), 218 (2,6), 208 (3,8), 207 (18,4), 206 (2,1), 204 (2,6), 155 (2,6), 140 (2,6), 119 (4,1), 117 (2,6), 116 (9,2), 115 (4,6), 105 (2,6), 97 (2,6), 91 (4,1), 87 (3,1), 85 (2,1), 83 (3,1), 82 (2,1), 81 (3,1), 77 (3,1), 73 (3,6), 71 (5,6), 70 (6,8), 69 (6,9), 68 (3,1), 67 (3,1), 60 (6,9), 57 (8,2), 56 (5,1), 55 (10,3), 54 (2,6), 53 (2,6)
Deutero analog of indolizine II (III)	329 (100), 328 (7,1), 327 (13,0), 315 (2,0), 314 (4,0), 313 (4,0), 298 (2,5), 297 (3,0), 296 (2,0), 225 (4,0), 224 (15,9), 223 (11,0), 222 (5,5), 210 (6,5), 209 (28,0), 195 (3,0), 175 (4,0)
6-Methyl-2-phenyl-7-(3,4-dimethylbenzyl)-indolizine (IV)	325 (100), 324 (7,0), 323 (4,4), 322 (5,6), 321 (3,3), 310 (6,6), 309 (4,4), 294 (4,4), 251 (2,2), 250 (5,6), 222 (6,7), 221 (10,0), 220 (26,0), 219 (4,4), 218 (5,6), 208 (3,3), 207 (6,5), 206 (2,2), 181 (4,4), 180 (5,5), 179 (3,3), 178 (4,4), 166 (6,7), 164 (2,2), 153 (6,7), 152 (6,7), 142 (2,2), 141 (4,4), 140 (2,2), 105 (68,9), 104 (5,6), 91 (15,6), 77 (33,3)
6-Methyl-2-(4-methylphenyl)-7-3,4-dimethylbenzyl)indolizine (V)	339 (100), 338 (6,3), 337 (2,2), 324 (9,0), 309 (3,2), 308 (4,8), 234 (13,0), 233 (4,0), 221 (7,0), 142 (3,2), 141 (7,9), 129 (2,4), 115 (3,2), 85 (3,2), 83 (3,2), 81 (3,2), 71 (3,2), 69 (5,6), 60 (3,2), 57 (4,0), 55 (4,0)
6-Methyl-2-phenyl-7-(2,4,5-trimethylbenzyl)indolizine (VI)	339 (100), 338 (6,0), 325 (2,7), 324 (7,0), 323 (2,8), 322 (3,3), 309 (3,5), 308 (4,4), 307 (2,0), 294 (2,2), 221 (2,4), 220 (6,9), 219 (2,5), 218 (2,4), 208 (3,2), 207 (7,3), 204 (2,7), 115 (2,2), 91 (2,0), 77 (2,0)
6-Methyl-2-(4-methylphenyl)-7-(4-ethylbenzyl)indolizine (VII)	339 (100), 338 (6,7), 324 (3,8), 322 (2,0), 311 (4,6), 310 (5,1), 309 (3,6), 308 (4,1), 307 (2,0), 295 (2,0), 294 (3,1), 235 (3,1), 234 (12,2), 233 (2,0), 222 (3,1), 221 (9,4), 220 (2,0), 162 (3,1), 141 (2,0), 115 (2,0), 91 (2,6), 83 (2,6), 57 (3,1), 55 (3,1)
6-Methyl-2-(4-methylphenyl)-7-(2,4,5-trimethylbenzyl)indolizine (VIII)	353 (100), 352 (6,0), 339 (4,4), 338 (5,0), 337 (2,4), 336 (2,9), 323 (2,9), 322 (3,9), 235 (4,9), 234 (10,8), 222 (3,1), 221 (16,3), 220 (2,0), 169 (3,1), 141 (4,9), 119 (5,3), 105 (2,6), 97 (3,9), 91 (4,9), 85 (3,1), 83 (3,9), 69 (5,3)
6-Methyl-2-(4-methoxyphenyl)-7-(2,4,5-trimethylbenzyl)indolizine (IX)	369 (100), 368 (3,7), 355 (4,6), 354 (5,2), 352 (2,9), 338 (2,3), 324 (2,9), 250 (5,2), 238 (2,9), 237 (8,4), 222 (2,9), 207 (2,9), 177 (3,5), 169 (2,5), 155 (3,5), 141 (7,0), 69 (2,9), 57 (2,9)
6-Methyl-(4-bromophenyl)-7-benzyl-2-indolizine (X)	377 (96,6), 376 (30,8), 375 (100), 374 (9,0), 362 (3,8), 360 (4,1), 300 (13,3), 299 (3,8), 298 (14,3), 297 (5,6), 296 (6,8), 295 (3,4), 294 (3,8), 280 (3,0), 279 (2,3), 219 (4,5), 218 (7,5), 204 (4,5), 203 (2,3), 149 (3,0), 147 (2,3), 141 (5,3), 140 (3,8), 139 (3,8), 85 (3,0), 84 (2,3), 83 (5,3), 82 (3,0), 81 (5,3), 73 (3,8), 71 (4,5), 70 (3,0), 69 (10,5), 67 (3,0), 60 (3,0), 57 (6,3), 56 (3,0), 55 (7,5)
6-Methyl-2-(4-bromophenyl)-7-(4-ethylbenzyl)indolizine (XI)	405 (96,2), 404 (37,8), 403 (100), 402 (5,3), 401 (4,7), 391 (4,7), 390 (4,0), 388 (4,3), 376 (6,6), 374 (7,6), 373 (4,7), 324 (7,6), 300 (11,8), 298 (12,1), 294 (3,8), 287 (10,4), 285 (10,8), 219 (5,7), 218 (7,5), 204 (5,7), 191 (3,8), 169 (3,8), 155 (7,5), 149 (5,6), 147 (5,6), 141 (12,3), 139 (4,7), 137 (3,7), 127 (4,7), 123 (4,7), 119 (4,7), 115 (4,7), 113 (4,7), 111 (5,7), 99 (5,7), 98 (4,7), 97 (7,5), 95 (6,7), 85 (13,2), 84 (5,7), 83 (9,4), 82 (5,7), 81 (13,2), 73 (5,7), 71 (17,0), 70 (7,6), 69 (24,6), 68 (4,7), 67 (5,7), 60 (5,7), 57 (20,8), 56 (5,7)
6-Methyl-2-(4-bromophenyl)-7-(2,4,5-trimethylbenzyl)indolizine (XII)	419 (96,4), 418 (33,3), 417 (100), 416 (8,5), 404 (10,7), 402 (11,1), 396 (33,3), 389 (5,6), 387 (11,1), 338 (5,6), 300 (11,1), 298 (13,3), 287 (20,2), 285 (21,7), 239 (22,2), 213 (22,2), 211 (22,2), 157 (38,9), 155 (44,4), 141 (11,1), 133 (33,3), 119 (27,8), 104 (16,7), 76 (27,8)
6-Methyl-2-phenyl-7-(4-nitrobenzyl)indolizine (XIII)	342 (100), 341 (2,4), 327 (2,4), 313 (11,3), 312 (40,5), 311 (10,1), 310 (3,4), 297 (10,1), 296 (21,4), 295 (5,6), 280 (4,5), 279 (2,2), 268 (2,2), 221 (4,5), 220 (26,4), 219 (4,5), 204 (4,5), 191 (2,2), 156 (4,5), 155 (3,4), 142 (2,2), 141 (5,6), 140 (2,8), 84 (2,2), 83 (3,9), 71 (2,8), 69 (5,6), 57 (6,8), 55 (6,2)

TABLE 1. (continued)

1	2
6-Methyl-2-(4-nitrophenyl)-7-benzylindolizine (XIV)	342 (100), 341 (3,5), 327 (2,9), 326 (6,1), 325 (12,1), 313 (21,1), 312 (78,8), 311 (12,1), 297 (9,1), 296 (27,3), 295 (9,1), 294 (5,3), 280 (4,5), 279 (3,0), 266 (3,0), 265 (6,4), 256 (3,0), 252 (2,0), 236 (3,8), 235 (12,1), 234 (2,6), 220 (5,3), 219 (9,9), 218 (8,8), 217 (3,8), 205 (4,5), 204 (5,3), 142 (3,0), 140 (3,0), 139 (3,8), 98 (3,8), 97 (6,1), 96 (3,8), 95 (4,5), 84 (3,8), 83 (6,8), 82 (3,0), 81 (4,5), 69 (9,1), 56 (4,5), 55 (9,8), 54 (2,3)
6-Methyl-2-(4-nitrophenyl)-7-(4-nitrobenzyl)indolizine (XV)	387 (100), 358 (12,7), 357 (45,0), 356 (4,2), 342 (7,8), 341 (23,1), 328 (7,0), 327 (22,3), 326 (5,6), 312 (4,9), 311 (9,9), 310 (4,2), 296 (4,2), 295 (11,3), 294 (4,2), 278 (3,5), 265 (6,5), 235 (7,0), 219 (7,7), 218 (5,6), 155 (5,6), 141 (7,0), 139 (3,5), 129 (3,5), 127 (2,8), 111 (3,5), 98 (4,2), 97 (5,6), 96 (2,8), 95 (4,2), 85 (4,2), 84 (4,2), 83 (5,6), 81 (4,2), 72 (4,9)

*The ion peaks with intensities $\geqslant 2\%$ of the maximum intensity are presented. The $[M+1]^+$ and $[M+2]^+$ ions are not presented.

TABLE 2. Intensities of the Peaks of the Principal Characteristic Fragments* in the Mass Spectra of 6-Methyl-2-aryl-7-benzylindolizines and Stabilities of Their Molecular Ions (W_M)

Compound	M^+	W_{M^+} (%)	M^{2+}	$[M-H]^+$	$[M-CH_3]^+$	$[M-R^2]^+$	$[M-CHR^2]^+$
I	297	44,3	2,3	10,8	3,7	18,3	1,3
II	325	41,0	6,4	7,4	4,3	16,1	18,4
III	329	42,0	6,3	7,1	4,0	15,9	18,0
IV	325	41,0	6,6	7,0	6,6	26,0	6,5
V	339	48,9	3,2	6,3	9,0	13,0	7,0
VI	339	47,0	2,6	6,0	7,0	6,9	7,3
VII	339	45,1	1,5	6,7	3,8	12,2	9,4
VIII	353	30,5	4,9	6,0	5,0	10,8	16,3
IX	369	48,5	3,5	3,7	5,2	5,2	8,4
X	376	41,1	2,3	9,0	4,1	14,3	0,9
XI	404	38,4	1,9	5,3	4,3	12,1	10,8
XII	418	36,2	5,9	8,5	11,1	13,3	21,7
XIII	342	28,0	2,6	2,4	2,4	26,4	—
XIV	312	20,4	4,5	3,5	2,9	6,4	2,0
XV	387	23,7	7,1	1,6	1,3	6,5	—

*The intensities of the ion peaks are given in percent relative to the maximum peak. The intensities of the fragments that contain the ^{79}Br isotope are presented for X-XII.

Double charged M^{2+} ions with appreciable intensities are observed in the mass spectra of I-XV (Table 2), and this confirms the condensed character of the molecular ions [7], i.e., the indolizine ring is retained during ionization of the molecule.

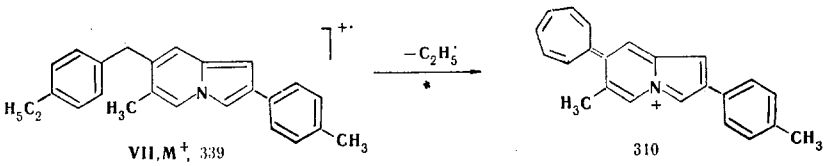
The fragmentation of the benzyl derivztives of indolizine produces $[M - H]^+$ ions, the peaks of which have significant intensities. The presence of methoxy and nitro groups in the benzyl or aryl fragment of the molecule decreases the intensity of the peak of $[M - H]^+$ ions appreciably. These groups have a similar effect on the formation of $[M - nH]^+$ ions, for which n = 2-5.

Peaks of $[M - CH_3]^+$ ions, which have somewhat higher intensities as compared with the mass spectra of 6-methyl-2,7-diarylindolizines [4], appear in the mass spectra of 7-benzyl-substituted indolizines I-XV. In contrast to 2,7-diarylindolizines, the intensities of the peaks of the $[M - CH_3]^+$ fragments in the mass spectra of I-XV remain virtually unchanged as the number of methyl groups is increased but decrease appreciably when there is a nitro group in the R^1 and (or) R^2 substituents.

The anomalous behavior of this series of substances is displayed by the absence of an intense $[M - CH^3]^+$ ion peak in the mass spectra of p-ethylbenzyl-substituted indolizines VII and XI. The low probability of cleavage of the β bond in the ethyl substituent for these compounds (Table 2) distinguishes indolizines from alkylbenzenes [8] with respect to their mass-spectral behavior. Cleavage of the α bond in the fragmentation of indolizines VII and XI leads to the formation of $[M - C_2H_5]^+$ ions, which have the same intensity as the $[M - CH_3]^+$

fragments. The increased proability of detachmemt of an ethyl radical can be explained by the development of a resonance-stabilized ion (Scheme 1) with a quaternized nitrogen atom, which is associated with expansion (evidently at the moment of ejection of a C_2H_5 radical) of the phenyl ring to a tropylium ring due to the inclusion of the methylene group of the benzyl substituent.

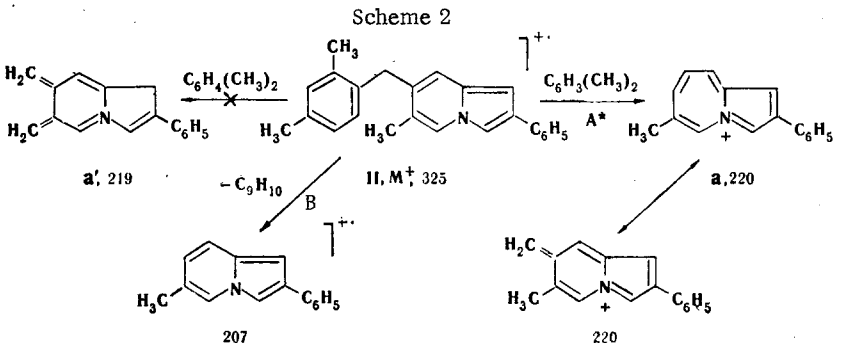
Scheme 1



Assuming that the formation of a tropylium ring from the benzyl grouping in the investigated series of substances occurs only via the indicated mechanism (Scheme 1), it is easy to explain the very low intensity of the peak of the $[M - CH_3]^+$ fragments in the mass spectra of VII and XI. In these cases the elimination of a CH_3 radidal from the ethyl substituent is not accompanied by expansion of the phenyl ring to a tropylium ring by inclusion in it of the methylene group of the substituent (as in alkylbenzenes), and the process becomes energically unfavorable.

Another peculiarity of the dissociative ionization of I-XV is the absence of an "ortho effect" of the benzyl and methyl radicals, which leads to the formation of an intense peak of a rearranged $[M - C_6H_6]^+$ ion in the mass spectra of o-benzyl-substituted toluene [9] and 2.5-dimethyl-4-benzylpyridine [10]. In this case an $[M - R^2]^+$ fragment is formed as a result of cleavage of the C—C bond between the phenyl ring and the methylene group in the benzyl substituent (Scheme 2, pathway A). The indicated process is confirmed by the 4-amu shift in the mass spectrum of deutero analog III and the shifts of 14 (V, VII, and VIII), 30 (IX), 45 (XIV), and 78/80 amu (X-XII) in the mass spectra of the other derivatives, as well as by the absence of a similar shift in the mass spectra of indolizines I, II, IV, VI, and XIII. In the case of II (Scheme 2, pathway A) it is apparent that the absence of an "ortho effect" of the methyl and benzyl groups is evidently due to the fact that the resulting rearranged a' ion, in contrast to fragment ion a, cannot be represented in a resonance form that assumes the maximum valence of the carbon atoms. Consequently, the indicated process is energically unfavorable due to the position of the CH_3 and $CH_2C_6H_3(CH_3)_2$ groups in the indolizine ring relative to the nitrogen atom. A similar pattern was observed in the fragmentation of other heteroaromatic systems [11], in which the relative position of the heteroatom and the substituent completely determined the possibility of the elimination of the latter as a function of the stability of the resulting ion.

Scheme 2

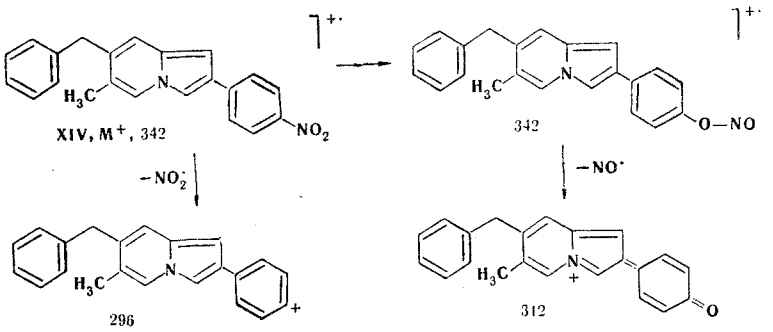


A characteristic feature of the dissociative ionization of 7-benzylindolizines I-XV is the formation of a rearranged $[M - CHR^2]^+$ fragment (Scheme 2, pathway B), which is associated with splitting out of a benzyl radical that is accompanied by the migration of a hydrogen atom from the substituent to the indolizine ring. A similar process was previously observed for carbalkoxy-substituted indolizines [2]. The 2-amu shift of the peak of this fragment in the mass spectrum of deutero analog III to the high-mass region constitutes evidence that hydrogen atoms of the methylene group of the benzyl grouping do not migrate to the indolizine ring. The 14 (V, VII, and VIII), 30 (IX), 45 (XIV, XV), and 78/80 amu (X-XII) shifts of the

*Here and subsequently, the numbers that characterize the ions are the mass-to-charge (m/z) ratios.

$[M - CHR^2]^+$ ions* in the mass spectra of the investigated substances confirm the proposed pathway for their formation. The indicated process has a low probability when two and three methyl groups or an ethyl substituent are present in the benzyl group; however, the presence of a nitro group completely excludes the formation of an $[M - CHR^2]^+$ fragment in the fragmentation (XIII-XV).

Scheme 3



The dissociative ionization of nitro derivatives of 7-benzylindolizines XIII-XV is accompanied by nitro-nitrite rearrangement (Scheme 3), the probability of which ($z = I_{[M-NO]^+}/I_M^+$) depends on the position of the NO_2 group. When the nitro group is in the para position of the phenyl ring (XIV), z is 0.78, which exceeds by a factor of almost two the z value for nitro derivative XIII (0.46), in which the nitro group is located in the benzyl substituent. This fact can be explained by the appearance in the mass spectrum of indolizine XIV (in contrast to the mass spectrum of XIII) of an $[M - NO]^+$ fragment, which has a stable quinoid structure with a quaternized nitrogen atom. In the case of dinitro-substituted XV one might have expected that the probability of nitro-nitrite rearrangement is primarily determined by the nitro group in the phenyl substituent, since the ejection of an NO particle in this case leads to the formation of a resonance-stabilized ion. However, z is 0.46 in the mass spectrum of indolizine XV, i.e., it coincides with the z value for XIII. The apparent contradiction is eliminated if one takes into account the subsequent fragmentation of the $[M - NO]^+$ ion that is observed for all three nitro derivatives XIII-XV. The z' values calculated as the ratios of the sums of the peaks of the M^+ ions are 0.50, 0.92, and 0.78, respectively, for these compounds. It is apparent from the data obtained that the probability of nitro-nitrite rearrangement of dinitro derivative XV is primarily determined by the NO_2 group in the para position of the phenyl substituent.

Thus a study of the dissociative ionization of 6-methyl-2-aryl-7-benzylindolizines showed that the mass-spectral behavior of this series of compounds under the influence of electron impact is determined by their ability to form stable resonance-stabilized ions that contain a quaternized nitrogen atom in the indolizine ring, i.e., in the final analysis, by the site of localization of the positive charge in the indolizine ring.

EXPERIMENTAL

The mass spectra of I-XV were recorded with an MKh-1303 spectrometer equipped with a system for the direct introduction of samples into the ion source at an ionizing voltage of 70 V and recording temperatures of 40-105°C. The substances were synthesized previously by the method in [12]. Deutero derivative III was obtained by deuteration of the corresponding imide with a 30% solution of CF_3COOD in $CDCl_3$ and conversion of the deuterated ylid to an indolizine by heating. The purity and individuality of the compounds were monitored by thin-layer chromatography and the IR, UV, and PMR spectra.

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*The designation of the ion s is arbitrary, since the methylene hydrogen atom does not participate in the rearrangement.

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SYNTHESIS OF 2,3,4,6-TETRA-O-ACETYL-β-D-GLUCOPYRANOSYL ESTERS OF ACIDS WITH PHYTOHORMONAL ACTIVITY. NEW MODIFICATION OF THE KOENIGS—KNORR METHOD

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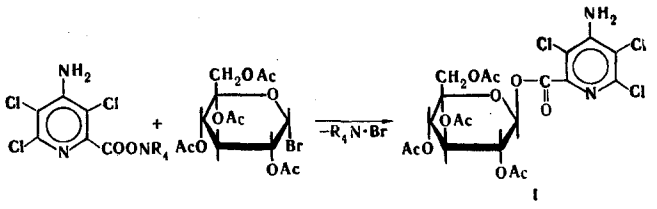
2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl esters were synthesized by the reaction of tetralkylammonium salts of 4-amino-3,5,7-trichloropicolinic, 2,4-dichlorophenoxyacetic, and β-indolylacetic acids with 2,3,4,6-tetra-O-acetyl-α-D-glucopyranosyl bromide. According to the PMR spectral data, substitution occurs stereospecifically to give the β anomers.

Glucopyranosyl esters of acids with phytohormonal activity are attracting attention as metabolites of phytohormones [1].

Glucopyranosyl esters can be obtained by the Koenigs—Knorr method [2, 3] or modifications of it based on the reaction of acetobromoglucose with silver [4], mercury [5], or amine [6] salts of acids. However, these methods are not universal and are often accompanied by low yields and the formation of mixtures of anomers that are difficult to separate [7].

Our attempts to synthesize a previously unknown ester of aminopicolinic acid (I) by the Koenigs—Knorr method and some of its modifications were unsuccessful. For the synthesis of this compound we propose a new modification of the Koenigs—Knorr method based on the reaction of acetobromoglucose with the tetraalkylammonium salt of 4-amino-3,5,6-trichloropicolinic acid:



R=CH3, C4H9

According to the PMR spectral data, the reaction proceeds stereoselectively to give the β anomer. The signal of the anomeric proton in the PMR spectra appears at 6.25 ppm in the form of a doublet with splitting constant J = 8 Hz. A similar splitting constant of an ano-

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