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MASS SPECTRA AND STRUCTURES OF SUBSTITUTED CARBAZOLES

R. A. Khmel'nitskii, P. B. Terent'ev, and O. A. Solov'ev

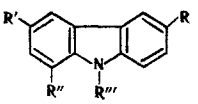
UDC 543.51:547.752.32

The anomalous character of the dependence of the stability with respect to electron impact on the size of the alkyl group in alkylacetylcarbazoles leads to the conclusion that the molecular ion undergoes profound rearrangement prior to detachment of the first neutral particle, during which the effect of the functional group on this process is manifested weakly. The functional group is not always the determining factor in the formation of the primary fragment ions, particularly if the processes involving the participation of the alkyl group lead to more stable ions than the processes involving the participation of a labile functional group.

Research on carbazoles by a number of investigators [1-3] has led to the conclusion that polycyclic condensed systems containing a carbazole fragment and alkylcarbazoles have anomalously high stabilities with respect to electron impact (W_M). The assumption of profound rearrangement of the molecular ion leading to specific fragmentation of these systems was advanced in a study of 9-alkylcarbazoles [3].

It seemed of interest to examine the effect of electron-donor groups on the W_M values and pathways of fragmentation of substituted carbazoles.

In the present research we studied the mass spectra of the following substituted carbazoles:



	R	R′	R″	R‴		R	R′	R″	R‴
I	NO_2	H	H	H	VIII	CH_3CO	CH_3CO	H	CH_3
II	NO_2	NO_2	H	H	IX	CH_3CO	CH_3CO	H	C_2H_5
III	NO_2	H	NO_2	H	X	CH_3CO	CH_3CO	H	C_3H_7
IV	CH_3CO	H	H	CH_3	XI	CH_3CO	CH_3CO	H	i-C_3H_7
V	CH_3CO	H	H	i-C_3H_7	XII	CH_3CO	CH_3CO	H	C_4H_9
VI	CH_3CO	H	H	C_4H_9	XIII	CH_3CO	CH_3CO	H	C_5H_{11}
VII	CH_3CO	H	H	C_5H_{11}	XIV	CH_3CO	CH_3CO	H	i-C_5H_{11}

The mass spectra of the investigated compounds were obtained with a modified MKh-1303 mass spectrometer with direct introduction of the substances into the ion source at various ionizing-electron ener-

M. V. Lomonosov Moscow State University, Moscow 117234. K. A. Timiryazev Moscow Agricultural Academy, Moscow 127434.

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TABLE 1. Mass Spectra of Carbazoles I-XIV

Compound	Mass spectra
I	39 (3,2), 41 (11,2), 43 (18,5), 55 (13,4), 57 (17,3), 60 (4,1), 63 (3,0), 69 (25,5), 70 (3,2), 71 (7,6), 73 (4,4), 81 (7,4), 82 (3,0), 83 (8,8), 84 (3,0), 85 (4,0), 97 (5,5), 138 (3,6), 139 (36,5), 140 (7,9), 154 (4,2), 164 (4,5), 165 (3,9), 166 (66,6), 167 (5,3), 182 (9,4), 212 (100,0), 213 (8,8), W_M=23,1, $S_{1/2}$=6
II	28 (16,6), 29 (8,0), 39 (4,4), 41 (15,8), 42 (5,3), 43 (26,6), 44 (25,8), 45 (3,3), 55 (15,8), 56 (4,7), 57 (15,5), 60 (4,4), 61 (4,2), 69 (12,5), 70 (3,0), 71 (6,7), 73 (4,7), 77 (3,0), 81 (4,7), 83 (6,1), 84 (5,5), 85 (3,9), 95 (3,3), 97 (5,0), 98 (4,4), 111 (3,3), 137 (4,2), 138 (9,1), 153 (5,8), 164 (61,4), 165 (59,1), 181 (34,9), 211 (31,6), 227 (34,1), 257 (100,0), 258 (7,2), W_M=17,5, $S_{1/2}$=7
III	39 (6,4), 41 (33,6), 42 (10,4), 43 (57,9), 54 (3,8), 55 (37,0), 56 (9,0), 57 (40,0), 60 (7,9), 67 (9,0), 68 (5,3), 69 (25,7), 70 (6,4), 71 (14,8), 73 (7,1), 81 (9,7), 82 (5,3), 83 (15,8), 84 (8,4), 85 (6,9), 95 (6,7), 96 (4,6), 97 (11,2), 98 (6,4), 111 (4,3), 138 (4,1), 152 (3,1), 153 (3,5), 164 (21,2), 165 (16,3), 181 (12,2), 184 (4,1), 211 (36,8), 226 (4,1), 227 (26,2), 257 (100,0), 258 (8,6), W_M=16,0, $S_{1/2}$=9
IV	41 (3,9), 43 (6,7), 55 (3,6), 57 (3,7), 69 (5,2), 90 (3,3), 104 (8,0), 151 (6,7), 152 (19,8), 153 (4,2), 178 (5,2), 179 (6,3), 180 (33,3), 181 (3,9), 208 (100,0), 209 (22,2), 223 (77,8), 224 (9,7), W_M=22,2, $S_{1/2}$=3
V	41 (25,0), 43 (14,0), 44 (5,7), 45 (31,0), 55 (15,0), 57 (20,0), 60 (17,0), 69 (39,0), 71 (7,4), 73 (8,1), 81 (12,0), 83 (4,7), 85 (3,6), 97 (3,1), 139 (11,5), 165 (5,4), 166 (28,0), 167 (16,0), 193 (16,0), 194 (52,0), 236 (98,0), 237 (23,0), 251 (100,0), 252 (17,0), W_M=21,8, $S_{1/2}$=6
VI	43 (11,3), 165 (3,9), 166 (3,8), 178 (8,8), 179 (42,3), 180 (14,8), 222 (100,0), 223 (29,6), 250 (46,5), 251 (5,5), 265 (83,1), 266 (15,8), W_M=23,9, $S_{1/2}$=3
VII	43 (10,3), 178 (3,4), 179 (20,2), 180 (7,2), 222 (100,0), 223 (15,7), 264 (18,5), 279 (50,9), 280 (6,9), W_M=21,4, $S_{1/2}$=3
VIII	41 (6,7), 43 (12,3), 44 (14,6), 45 (4,0), 55 (7,9), 56 (3,3), 57 (7,9), 60 (3,6), 67 (3,1), 69 (7,6), 71 (4,5), 73 (3,0), 81 (4,4), 83 (4,6), 89,5 (3,3), 95 (3,3), 97 (4,0), 111 (3,3), 149 (4,5), 151 (5,0), 152 (6,7), 164 (4,1), 177 (3,5), 178 (7,9), 179 (9,2), 193 (3,7), 207 (31,6), 208 (6,1), 222 (4,7), 236 (3,6), 250 (100,0), 251 (21,1), 265 (57,9), 266 (11,9), W_M=12,8, $S_{1/2}$=12
IX	41 (5,1), 43 (5,2), 44 (5,2), 55 (5,2), 56 (3,1), 57 (5,1), 60 (3,0), 67 (3,4), 69 (5,2), 71 (4,0), 73 (3,3), 81 (5,0), 83 (4,4), 95 (3,5), 97 (3,7), 98 (3,7), 124,5 (4,4), 164 (3,2), 178 (3,7), 221 (14,7), 222 (4,2), 264 (100,0), 265 (32,7), 279 (57,7), 280 (19,6), W_M=21,4, $S_{1/2}$=6
X	41 (7,8), 43 (25,7), 44 (14,5), 45 (7,6), 55 (5,0), 57 (7,3), 69 (4,1), 78 (5,2), 131,5 (7,8), 164 (4,8), 178 (10,6), 179 (4,5), 192 (3,0), 193 (4,7), 220 (3,3), 221 (31,3), 222 (6,3), 235 (4,8), 264 (100,0), 265 (15,3), 278 (91,7), 279 (13,8), 293 (79,2), 294 (13,4), W_M=16,9, $S_{1/2}$=3
XI	41 (28,4), 42 (5,0), 44 (14,1), 55 (35,6), 56 (11,8), 57 (78,8), 67 (9,9), 68 (4,7), 69 (40,2), 70 (9,5), 71 (43,3), 81 (17,0), 82 (6,8), 83 (21,7), 84 (5,8), 85 (24,2), 95 (13,0), 96 (4,8), 97 (18,1), 98 (3,7), 99 (5,4), 109 (7,2), 111 (9,0), 113 (14,1), 123 (5,0), 125 (3,6), 137 (4,1), 164 (6,4), 165 (6,0), 192 (3,5), 193 (14,4), 194 (10,0), 235 (11,0), 236 (26,0), 237 (14,0), 250 (12,0), 251 (27,0), 252 (17,0), 274 (4,4), 278 (100,0), 279 (10,8), 293 (45,5), 294 (17,0), W_M=12,7, $S_{1/2}$=6
XII	41 (12,7), 43 (38,6), 44 (12,7), 45 (23,8), 55 (10,8), 57 (11,9), 69 (7,5), 83 (4,8), 97 (3,8), 139 (15,9), 151 (3,5), 164 (4,9), 165 (3,5), 175 (3,5), 178 (12,9), 179 (6,5), 192 (4,6), 193 (8,3), 220 (5,4), 221 (35,2), 222 (9,8), 249 (3,3), 264 (94,0), 265 (30,6), 292 (90,8), 293 (100,0), 294 (10,4), 306 (6,9), 307 (100,0), 308 (28,4), W_M=16,3, $S_{1/2}$=5
XIII	28 (76,8), 32 (14,1), 41 (6,1), 43 (25,4), 45 (5,4), 55 (3,3), 57 (4,0), 146 (3,6), 178 (6,1), 193 (3,6), 221 (23,9), 222 (3,6), 264 (100,0), 265 (14,4), 306 (54,5), 307 (7,6), 321 (57,6), 322 (9,7), W_M=14,4, $S_{1/2}$=5
XIV	41 (3,3), 43 (17,9), 146 (3,4), 178 (5,8), 193 (3,9), 221 (24,0), 222 (5,8), 264 (100,0), 265 (18,5), 306 (63,6), 307 (12,0), 321 (80,0), 322 (14,9), W_M=24,7, $S_{1/2}$=3

gies. The elementary compositions of the characteristic ions in the mass spectra of IV, VI, XII, and XIII were determined with a JEOL JMS-01-SG-2 high-resolution mass spectrometer (Japan).

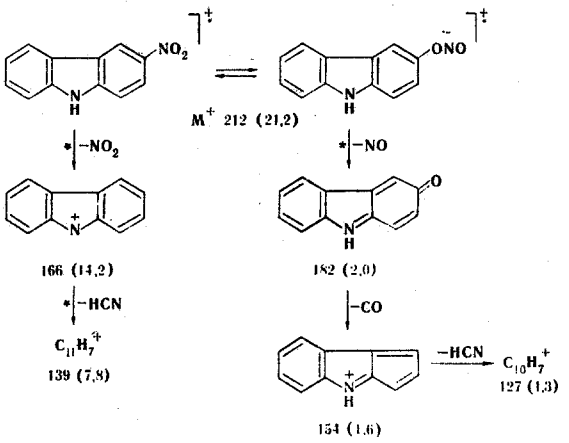
The mass spectra obtained at an ionizing-electron energy of 50 eV (>3% of the maximum peak), the W_M values, and the fragmentation selectivities ($S_{1/2}$) are presented in Table 1. The intensities of the peaks in the schemes are expressed in percent of the total ion current; the fragmentation pathways in the schemes are confirmed by the corresponding metastable peaks.

As expected, the introduction of a nitro group in the carbazole molecule lowers the W_M value, but, as before, this value remains very high.

The fragmentation of I proceeds via the pathways characteristic for nitro-substituted heterocyclic compounds. The fragmentation selectivity is quite high ($S_{1/2}$ = 6), and the fraction of ions depicted in the scheme

constitutes 45% of the total ion current. The probability of nitro–nitrite rearrangement, which is determined by the $I(M-NO)^+/I(M-NO_2)^+$ ratio, is 0.141 at an ionizing-electron energy of 50 eV. When the ionizing voltage is lowered to 15 eV, the probability increases to 1.9, i.e., the isomerized form of the molecular ion predominates.

The introduction of a second nitro group decreases the stability with respect to electron impact by 25 rel. %, and the position of the second substituent has little effect on the W_M value. This fact is probably a consequence of the absence of an additional pathway for



fragmentation of the $(M-OH)^+$ ion in the case of 3,8-dinitrocarbazole, although one might have assumed the existence of this process in analogy with some 8-nitrohydroxyindoles.

The presence of two nitro groups in the molecule may lead to the existence of at least three forms of molecular ion, even if one takes into account the positionally nonidentical character of the second nitro group. However, an examination of the scheme leads to the conclusion that the simultaneous nitro–nitrite isomerization of both nitro groups is only slightly possible and the relative weight of form C is very small. In addition, the presence of a second nitro group in the molecule considerably increases the isomerization of one of the groups: thus the $I(M-NO)^+/I(M-NO_2)^+$ ratio for III is 0.72 and the ratio for II is even 1.1. In other words, in the second case the probability of the elimination of NO exceeds the probability of detachment of NO_2. The probability of rearrangements increases as the ionizing-electron energy decreases, and the corresponding ratios are 2.3 and 6.0. Thus the spectrum with few lines is determined primarily by fragmentation of the B form of the molecular ion.

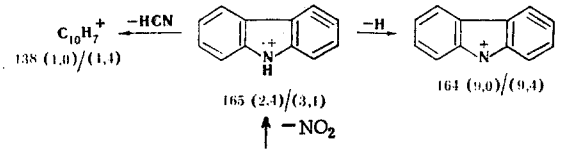
Returning to fragmentation at the usual ionizing-electron energy, one should note that secondary fragment ions are formed in the elimination of only an NO_2 particle from the primary ions, and the third step of the dissociative ionization is represented primarily by ions formed by dehydrogenation and cleavage with removal of HCN from the ions with mass 165.

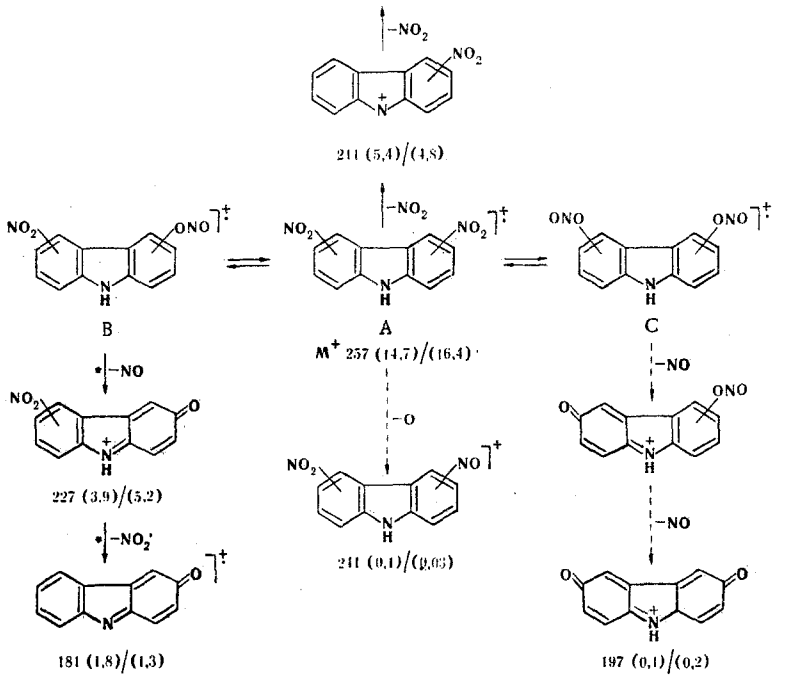
The detachment of an oxygen atom in both the first and subsequent steps is a process with a very low probability.

A comparison of the data from this research with the data in [3] makes it possible to conclude that the introduction of an electron-acceptor acetyl group in the 9-alkylcarbazole molecule does not decrease but rather increases the W_M values. This unprecedented fact confirms the previous assumption of isomerization of the molecular ion prior to detachment of the first particle to give a stable system. The extremely high selectivity of the fragmentation of acetylcarbazoles leads to the same conclusion.

The fragmentation of IV is followed quite distinctly by means of the metastable ions and data from high-resolution mass spectrometry.

The maximum peak in the spectrum corresponds to a unique primary ion (if one disregards the acetyl ion with mass 43), which is formed by elimination of a methyl radical from the acetyl group. The subsequent

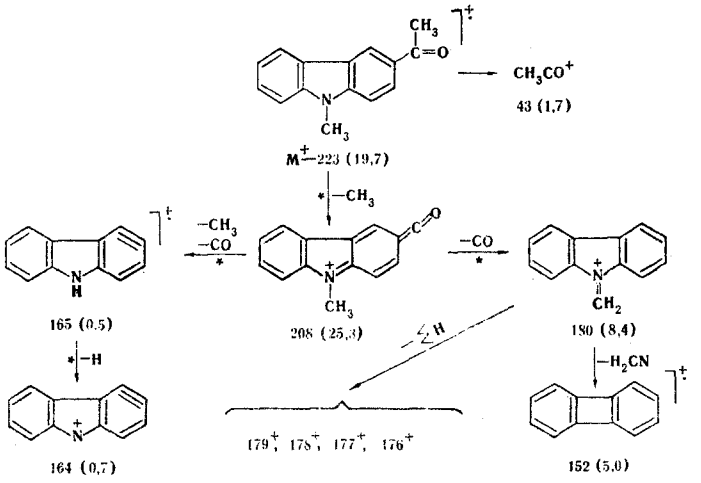




fragmentation steps and an examination of the mass spectra of homologs of this compound, in which the $(M-15)^+$ ion peak is also intense, provide evidence that cleavage of the N–C bond does not occur.

The second most intense fragment peak in the spectrum corresponds to removal of CO from the $(M-15)^+$ ion and the formation of an ion with mass 180. The intensities of the peaks of the above-indicated ions and the molecular ion peak constitute 53.4% of the total current. The secondary ion with mass 180 undergoes fragmentation via two pathways. One of them involves elimination of H_2CN and the formation of an ion with mass 152, which probably has a diphenylene structure (with an intensity of 5.0% of the total current). The second pathway is provided by dehydrogenation with removal of one, two, three, and four hydrogen atoms; the sum of the intensities of the peaks of these ions is ~3.0% of the total current. In all likelihood, the structures of the ions formed are associated with expansion of the central ring of the carbazole system to a six-membered ring. According to the high-resolution mass spectra, all of these ions contain nitrogen.

On passing to 9-alkyl derivatives of 3-acetylcarbazole, two competitive processes corresponding to elimination of a methyl group and cleavage of the β bond of the alkyl group develop in the first step of dissociative ionization. The subsequent process predominates overwhelmingly at both the usual ionizing-electron energy and at low energies, and this makes it possible to assume expansion of the pyrrole ring of the carbazole system during the formation of the primary $(M-R')^+$ fragment ions.

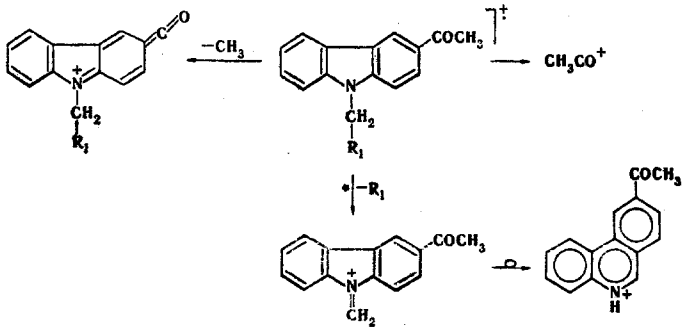


The ion with mass 222 also undergoes subsequent fragmentation via two competitive pathways: with detachment of an acetyl group and the formation of a pseudomolecular ion with mass 179 or with elimination of a

TABLE 2. Intensities of the Characteristic Ions in the Mass Spectra of 3,6-Diacetyl-9-alkylcarbazoles (in percent relative to the total current)

Ions	Compounds						
	VIII	IX	X	XI	XII	XIII	XIV
M—CH_3 (A)	18,4	21,6	16,6	14,7	11,5	11,6	16,6
A—CH_2CO	0,2	0,4	0,3	1,4	2,0	—	—
A—CH_3CO	5,8	3,1	0,8	3,8	—	—	—
A—CH_3CO—CO	1,7	0,5	—	—	—	—	—
A—CH_3CO—H	1,5	0,4	—	—	—	—	—
A—CH_3CO—HCN	1,2	—	—	—	—	—	—
M—R′ (B)	—	—	18,1	—	11,9	21,4	26,1
B—CH_3CO	—	—	5,7	—	4,5	5,1	6,3
B—CH_3CO—CH_3CO	—	—	1,9	—	1,6	1,3	1,5

neutral particle, probably in the form of ketene, and formation of an immonium ion with mass 180. At both the usual and low ionizing-electron energies the first process is much more likely.



In the dissociative ionization of diacetyl derivatives one's attention is primarily drawn to the strange relationship between the change in W_M and the number of carbon atoms in the alkyl group.

A comparison of the W_M values of the indicated compounds with the W_M values of alkylcarbazoles does not yet yield to any unambiguous explanation. The introduction of two labile groups in the molecule should have led to a sharp decrease in W_M due to the sharp increase in the fragmentation pathways, but this does not occur. In addition, the data obtained in this study attest to the absence of any interaction between the acetyl groups and the ring, since otherwise W_M should have decreased sharply due to destabilization of the molecular ion caused by the introduction of two electron-acceptor groups.

The similar trends in the changes in W_M for alkyl- and acylalkylcarbazoles within the limits of an increase in the size of the group from methyl to butyl indicate that the chief reason for the anomalous increase in W_M lies in the behavior of the alkylcarbazole system itself and evidently should again be drawn upon for the explanation of the hypothesis of profound rearrangement of the molecular ion prior to detachment of the first neutral particle [2]. However, as in the case of alkylcarbazoles, this hypothesis cannot explain the effect of even and odd numbers of carbon atoms in the alkyl group on the W_M value.

As in the case of the corresponding monoacetyl derivatives, the primary ions in the fragmentation of VIII are formed by detachment of the methyl group from the acetyl grouping. The resulting $(M-CH_3)^+$ ion undergoes subsequent fragmentation via three pathways, but the principal pathway involves elimination of CH_3CO; the formation of ions with removal of ketene from the primary $(M-CH_3)^+$ ion is unlikely. The probability of the processes does not change on passing to the low-voltage mass spectra.

An increase in the length of the alkyl group leads to the appearance of a new fragmentation pathway involving cleavage of the β bond with respect to the aromatic system; this process competes successfully with detachment of a methyl group and formation of an acetyl ion (Table 2).

The ratio of the peaks of ions with structures A and B cannot be determined in the case of the ethyl group without the use of carbon-labeled compounds: the ratio in the case of the n-propyl group is 0.92, as compared with 0.97, 0.54, and 0.64, respectively, for XII, XIII, and XIV. In the case of ionization by low-energy electrons these values undergo little change and are, respectively, 0.90, 0.87, 0.48, and 0.52.

Thus the data obtained in this study completely unambiguously attest to the unexpectedly small effect of two acetyl groups on the probability of the primary ions. Cleavage of the alkyl chain at the β-carbon–carbon bond to give the corresponding immonium ion turns out to be more favorable energically than detachment of the methyl group adjacent to the carbonyl group and formation of an acylium ion.

The subsequent fragmentation of ions A and B involves elimination of an acetyl group. The removal of ketene is only slightly probable in the case of ions A and is practically unrealizable in the case of ions B.

The formation of an ion with mass 43, evidently corresponding to the $CH_2=C=\overset{+}{O}H$ or CH_3CO^+ structure, is characteristic for all of the examined compounds. The intensity of the peak of this ion is almost identical and does not exceed 5.5% of the total current. The ion with mass 43 has the primary composition C_3H_7 only in the case of XI. This process requires considerable energy expenditure and is not observed when the ionizing-electron energy is lowered.

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PYRROLOINDOLES

I. SYNTHESIS OF 1H,6H-PYRROLO[2,3-e]INDOLE

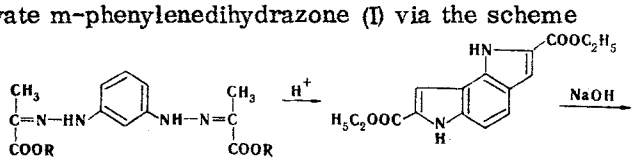
Sh. A. Samsoniya, N. L. Targamadze, L. G. Tret'yakova, T. K. Efimova, K. F. Turchin, I. M. Gverdtsiteli, and N. N. Suvorov

UDC 547.759.3'5.07:541.63:543.422.25.4.6

1H,6H-Pyrrolo[2,3-e]indole was obtained by Fischer cyclization of the m-phenylenedihydrazone of ethyl pyruvate. The structure of the product was proved by analysis of the PMR spectra and mass spectrum. Bands characteristic for the corresponding spectra of indole were observed in the absorption, luminescence, and IR spectra of the pyrroloindole. The geometrical isomers of ethyl pyruvate m-phenylenedihydrazone were isolated.

Despite the fact that pyrroloindoles are the closest analogs of indole, this class of compounds remains practically uninvestigated. The synthesis of pyrroloindole derivatives has been reported in individual studies [1-4], but up until now no one has been able to obtain even enough of the unsubstituted heterocycle to investigate its physicochemical properties.

To obtain 1H,6H-pyrrolo[2,3-e]indole we used Fischer cyclization of pyruvic acid m-phenylenedihydrazone (II) and ethyl pyruvate m-phenylenedihydrazone (I) via the scheme



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D. I. Mendeleev Moscow Chemical-Engineering Institute, Moscow 125047.

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