CHEMISTRY OF INDOLE

XLI.* ORIENTING EFFECT OF SUBSTITUENTS DURING THE NITRATION OF PROTONATED INDOLES

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The nitration of indoles containing donor substituents in the 5- and 7-positions in strongly acidic media involves the protonated form and gives primarily compounds with a nitro group in the 6-position. The structures of the products were proved by PMR, UV, and mass spectrometry.

The orientation of the entry of substituents during electrophilic attack of the benzene ring of indole structures has been studied primarily in the case of the accessible 2-methyl-3-carbethoxy(acyl)indoles [2], which are relatively stable with respect to dimerization, oxidation, and addition to the C_2-C_3 double bond. If such compounds are protonated in strongly acidic media, namely, at the oxygen atom of the carbonyl group, no substantial change in the distribution of the electron density in the aromatic ring occurs [3]. Consequently, it might be assumed that the observed principles correspond to orientation of the substituents during attack of the unprotonated molecule. In addition, the presence itself of an electron-acceptor group in the pyrrole ring cannot reflect the distribution of the electron density and complicates an evaluation of the orienting effect of substituents in the benzene ring of the indole structures.

It is known that nitration of 2,3-dimethylindole [4] takes place in the 5-position, while nitration of 2-methyl-3-carbethoxyindole takes place in the 6- and 4-positions [2]. Initial protonation of the pyrrole ring (attack of a proton at C_3) has been established for 2,3-dimethylindole, and the substantial difference in the orientation therefore depends not only on substitution of the electron-donor CH_3 group by the electron-acceptor COOR group (with a corresponding change in the distribution of the electron density in the benzene ring), but, above all, on the difference in the structure of the indole ring itself undergoing attack (the protonated and unprotonated structures).

The fact that aminomethylation (which proceeds as electrophilic attack but not in acidic media) is, to a first approximation, subject to the same principles of orientation as nitration or bromination, serves as a confirmation of the above rationale. For example, the dialkylaminomethyl group attacking 2-methyl-3-carbethoxy-5-hydroxyindole preferably enters the 4-position [5]. If the indole molecule does not contain a 3-carbethoxy group, aminomethylation of 5-hydroxyindoles also takes place in the 4-position [6]. Under the same conditions, 7-hydroxyindoles are aminomethylated in the 6-position [6].

It thus becomes necessary to study the orienting effect of substituents of the benzene ring under conditions of known protonation of the pyrrole ring. As model structures, we selected 2-methylindoles that have electron-donor substituents (CH_3, OH, and CH_3O) in the 5- or 7-positions. If compounds of this type undergo nitration in the unprotonated form, attack on C_3, i.e., substitution in the pyrrole ring, is preferable. If the pyrrole-ring protonated form undergoes the reaction, the substituent should enter the benzene ring.

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*For Communication XL see [1].

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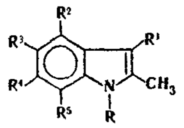
TABLE 1



Compound	R	R^1	R^2	R^3	R^4	R^5	mp, °C	Empirical formula	Found, %			Calc., %			UV spectrum (alcohol)		IR spectrum, NO_2 (NH), cm^{-1}	PMR spectrum, δ, ppm*							R_f	Yield, %
									C	H	N	C	H	N	λ_{max}, nm	lg ε		1-CH_3	2-CH_3	3-R^1	4-R^2	5-R^3	6-H	7-R^5		
IIc	H	CH_3	H	CH_3	NO_2	H	161—163 (alcohol)	$C_{11}H_{12}N_2O_2$	64,5	5,8	13,7	64,8	5,9	13,7	218 259 348 388	4,46 3,89 3,92 3,92	1560, 1300 (3300)		2,78b 2,96s†	1,73b 1,75d 4,51m	7,54b 7,68s 6,93s‡	2,56s 2,66s 2,54s		8,14s 8,35s 7,70s	0,5	38
IIa	H	CH_3	H	CH_3O	NO_2	H	179—180 (alcohol)	$C_{11}H_{12}N_2O_3$	59,7	5,5	13,0	60,0	5,5	12,8	222 268 374	4,44 3,92 4,04	1560, 1290 (3300)		2,82b	1,72 b	7,41b 6,84s‡	4,03s 3,59s		8,12s 7,52s	0,4	37
IIb	CH_3	H	H	CH_3O	NO_2	H	114—116 (benzene—heptane)	$C_{11}H_{12}N_2O_3$	59,8	5,5	13,2	60,0	5,5	12,8	215 266 363	4,80 3,98 3,98	1570, 1320	3,92s	2,78s	4,48m	7,47s	3,92s		8,16s	0,6	30
IV	CH_3	H	H	OH	NO_2	H	161—162 (alcohol)	$C_{10}H_{10}N_2O_3$	58,4	4,9	13,1	58,3	4,9	13,6	216 270 380	4,38 3,91 4,19	1530, 1310	3,99s	2,82s	4,48m	7,44s			8,34s	0,8	53
IVa	CH_3	H	NO_2	OH	H	H	155—157 (alcohol)	$C_{10}H_{10}N_2O_3$	58,0	5,0	13,0	58,3	4,9	13,6	215 250 410	4,43 4,12 4,06		4,04s	2,93s	5,17m			7,84s	7,43d	0,3	6
VI	H	CH_3	H	H	NO_2	CH_3O	174—176 (alcohol)	$C_{11}H_{12}N_2O_3$	60,6	5,8	13,0	60,0	5,5	12,8	219 256 405	4,63 4,00 3,86	1560, 1320 (3300)		2,78s	1,63b 4,84m	7,03d	8,21d		3,97s	0,4	32
VIa	CH_3	CH_3	H	H	NO_2	CH_3O	128—129 (benzene—petroleum ether)	$C_{12}H_{14}N_2O_3$	61,6	6,2	12,3	61,6	6,1	11,9	222 260 410	4,65 4,01 3,83	1560, 1300	4,14s	2,73s	1,55d 4,80m	7,21d	8,28d		4,03s	0,6	29

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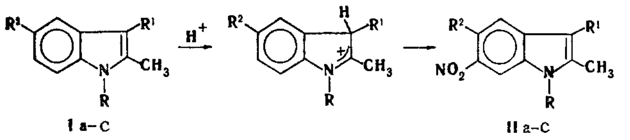
*The following abbreviations were adopted: s is singlet, d is doublet, m is multiplet, and b is broad singlet.

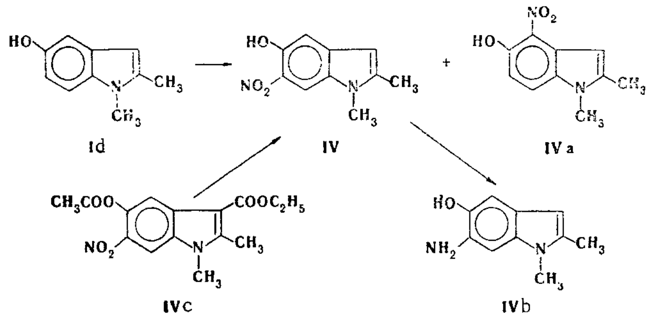
†In trifluoroacetic and sulfuric acids (10 : 1).

‡In acetone.

It was found that a complex mixture of deeply colored substances, from which nitration products could not be isolated, is formed by the action of a nitrating mixture or nitric acid solutions of various concentrations on 5-hydroxyindoles (Ia-c). However, if the hydroxyindoles and their O-substituted derivatives are carefully dissolved in concentrated sulfuric acid with cooling (to −10°) and the nitration is then carried out at −20 to −25°, primarily 6-nitroindoles are formed. Thin-layer chromatography (TLC) of the reaction mixture in the nitration of 1,2-dimethyl-5-methoxyindole (Ib) made it possible to detect a very small amount of the 4-nitro isomer, which, with respect to its chromatographic behavior in various systems, is identical to 1,2-dimethyl-4-nitro-5-methoxyindole (III), obtained by hydrolysis and decarboxylation of 1,2-dimethyl-3-carbethoxy-4-nitro-5-methoxyindole (IIIa) [7]. We were able to isolate 4-nitro isomer IVa preparatively in very low yield only from the products of nitration of 1,2-dimethyl-5-hydroxyindole (Id) (IV : IVa = 9 : 1).



I–II a R = H, R¹ = CH$_3$, R² = OCH$_3$; b R = CH$_3$, R¹ = H, R² = OCH$_3$; c R = H, R¹ = R² = CH$_3$



3-Nitroindoles were not detected in any of the experiments, and this excludes the possible nitration of the unprotonated form. The PMR spectra of the starting indoles, even in trifluoroacetic acid, indicate protonation of the C_3 atom (for IIb a singlet of two protons attached to C_3 and a shift of the signal of the 2-CH_3 protons to weak field are observed because of partial localization of the positive charge on C_2). When a nitro group is introduced, the basicity decreases, and the addition of sulfuric acid is required for complete protonation. In trifluoroacetic acid, these compounds give spectra with a broadened signal of 4-H protons and protons of the methyl groups in the 2- and 3-positions (IIa and IIc), apparently as a consequence of exchange with trifluoroacetic acid; in dimethyl sulfoxide (DMSO) or acetone, these signals are visible as sharp peaks. The same observations were also made for some other indoles. They correlate with direct measurements of the basicities of these substances. In fact, the spectrophotometric determination of the pK_a values of a number of the starting indoles and their nitro derivatives gave the following values, expressed on the Hinman scale [8] in sulfuric acid concentration (by weight), in which the indicator ratio log J = 0 (i.e., the ratio of the ionized form of indole to the nonionized form is 1):

	pK_a	H_2SO_4, %
Ia	−1,0±0,10	15,3
Ib	+0,8±0,30*	—
Ic	−1,0±0,15	15,4
IIa	−4,15±0,15	45,4
IIb	−2,25±0,15	28,3
IIc	−4,20±0,15	46,4

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* From the additive contribution of the substituents to the basicity of the compounds.

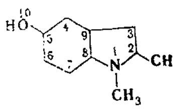
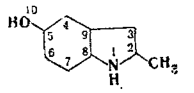
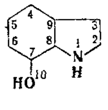
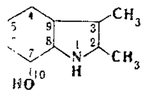
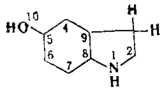
Thus, the introduction of a nitro group into the benzene ring substantially decreases the basicity of the indole structures (up to 3 units on the Hinman scale), which is one of the few numerical characteristics in the literature relative to the transmission of the effect of a substituent from the benzene ring to the pyrrole ring in indole structures.

The UV spectra make it possible to distinguish the 4- and 6-nitro-indoles, inasmuch as the former differ with respect to the shift of the long-wave maximum by 10-20 nm in the visible portion of the spectrum (Fig. 1). The structure of IV is confirmed by the PMR spectrum, which is identical to the spectrum of a sample obtained by hydrolysis and decarboxylation of IVc [7].

In the nitration of 7-methoxyindoles V and Va under similar conditions, the chief product is the 6-nitro isomer, although the presence of a small amount of a second isomer (apparently the 4-nitro compound) and of oxidation products was detected by chromatography.

The PMR spectra of nitroindoles VI and VIa contain two doublets of protons with a spin–spin splitting constant of 9 Hz in the aromatic region. The PMR spectrum does not give an unambiguous answer to the character of the substitution, inasmuch as the spectrum of the 4-isomer would give a similar pattern. Methylation of nitroindole VI with dimethyl sulfate in DMSO with sodium hydride gives nitro compound VIa, and the methyl group attached to the nitrogen atom of the indole ring, consequently, does not affect the orientation.

TABLE 2. Results of Calculation by the Pariser–Parr–Pople Method for 5- and 7-Hydroxyindoles

Indole	Atom No.	Total charge	Charge density in the boundary orbital	Bond multiplicity	
1	2	3	4	5	
	1	+0,370	0,256	$N=C_2$	0,490
	2	+0,080	0,033	$C_2=C_3$	0,787
	3	−0,110	0,317	$C_3=C_9$	0,500
	4	−0,078	0,544	$C_9=C_4$	0,547
	5	+0,008	0,286	$C_4=C_5$	0.689
	6	−0,060	0,003	$C_5=O_{10}$	0,345
	7	−0,036	0,273	$C_5=C_6$	0,550
	8	−0,091	0,066	$C_6=C_7$	0,743
	9	−0,041	0,018	$C_7=C_8$	0,548
	10	+0,119	0,212	$C_8=C_9$	0,576
	1	+0.349*	0,235	$N=C_2$	0,500
	2	+0,022	0,075	$C_2=C_3$	0,787
	3	−0,171	0,404	$C_3=C_9$	0,491
	4	−0,083	0,562	$C_9=C_4$	0,552
	5	+0,008	0,234	$C_4=C_5$	0,693
	6	−0,068	0,011	$C_5=O_{10}$	0,344
	7	−0,362	0,274	$C_5=C_6$	0,556
	8	−0,104	0,024	$C_6=C_7$	0,736
	9	−0,035	0,005	$C_7=C_8$	0,558
	10	+0,118	0,173	$C_8=C_9$	0,577
	1	+0,368	0,201	$N=C_2$	0,489
	2	−0,083	0,091	$C_2=C_3$	0,787
	3	−0,103	0,286	$C_3=C_9$	0,502
	4	−0,036	0,471	$C_9=C_4$	0,534
	5	−0,015	0,111	$C_4=C_5$	0,743
	6	−0,087	0,289	$C_5=C_6$	0,589
	7	−0,007	0,338	$C_6=C_7$	0,869
	8	−0,111	0,013	$C_7=O_{10}$	0,338
	9	−0,048	0,003	$C_7=C_8$	0,516
	10	+0,117	0,200	$C_8=C_9$	0,587
	1	+0,342*	0,193	$N=C_2$	0,475
	2	−0,043	0,202	$C_2=C_3$	0,789
	3	−0,066	0,406	$C_3=C_9$	0,503
	4	−0,042	0,416	$C_9=C_4$	0,533
	5	−0,019	0,083	$C_4=C_5$	0,743
	6	−0,093	0,286	$C_5=C_6$	0,589
	7	−0,008	0,268	$C_6=C_7$	0,696
	8	−0,123	0,003	$C_7=O_{10}$	0,231
	9	−0,064	0,013	$C_7=C_8$	0,520
	10	+0,116	0,144	$C_8=C_9$	0,582
	1	+0,588	0,0007	$N=C_2$	0,826
	2	+0,245	0,222	$C_9=C_4$	0,719
	4	+0,028	0,310	$C_4=C_5$	0,579
	5	+0,116	0,299	$C_5=C_6$	0,576
	6	−0,024	0,289	$C_5=O_{10}$	0,436
	7	+0,037	0,017	$C_6=C_7$	0,723
	8	−0.136	0,457	$C_7=C_8$	0,574
	9	+0,025	0,016	$C_8=C_9$	0,577
	10	+0,176	0,193		

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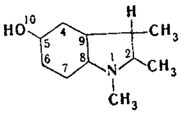
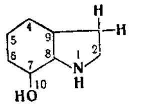
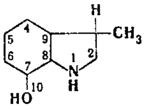
*The inductive effect of the methyl groups was taken into account.

TABLE 2 (continued)

1	2	3	4	5	
	1	+0,534*	0,006	$N=C_2$	0,819
	2	+0,368	0,164	$C_9=C_4$	0,708
	4	−0,031	0,312	$C_4=C_5$	0,588
	5	+0,100	0,314	$C_5=O_{10}$	0,422
	6	−0,026	0,294	$C_5=C_6$	0,587
	7	+0,025	0,023	$C_6=C_7$	0,711
	8	−0,143	0,460	$C_7=C_8$	0,595
	9	+0,007	0,022	$C_8=C_9$	0,696
	10	+0,167	0,404		
	1	+0,583	0,0004	$N=C_2$	0,826
	2	+0,252	0,101	$C_9=C_4$	0,716
	4	+0,016	0,504	$C_4=C_5$	0,614
	5	+0,097	0,032	$C_5=C_6$	0,691
	6	−0,023	0,274	$C_6=C_7$	0,615
	7	+0,068	0,364	$C_7=O_{10}$	0,346
	8	−0,157	0,202	$C_7=C_8$	0,558
	9	+0,013	0,202	$C_8=C_9$	0,571
	10	+0,152	0,326		
	1	+0,525*	0,004	$N=C_2$	0,817
	2	+0,373	0,080	$C_9=C_4$	0,705
	4	+0,011	0,504	$C_4=C_5$	0,624
	5	+0,082	0,040	$C_5=C_6$	0,689
	6	−0,023	0,259	$C_6=C_7$	0,615
	7	+0,054	0,378	$C_7=O_{10}$	0,382
	8	−0,165	0,226	$C_7=C_8$	0,576
	9	−0,001	0,171	$C_8=C_9$	0,591
	10	+0,143	0,338		

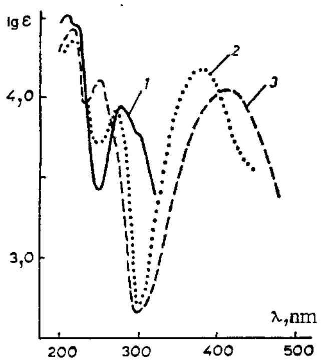
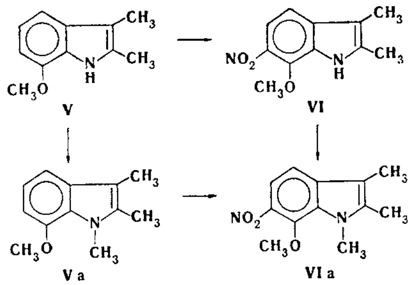
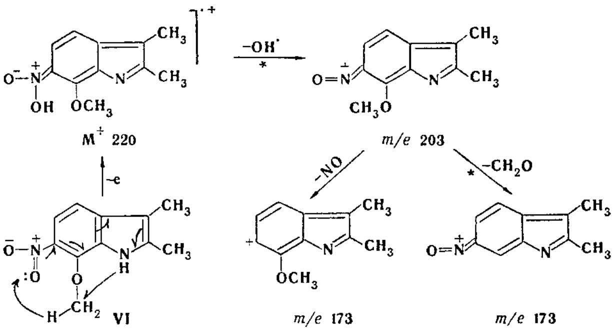


Fig. 1. UV spectra of nitroindoles (alcohol): 1) 1,2-dimethyl-5-hydroxyindole (Id); 2) 1,2-dimethyl-5-hydroxy-6-nitroindole (IV); 3) 1,2,dimethyl-4-nitro-5-hydroxyindole (IVa).

The mass spectrum of VI, in addition to an intense molecular ion, contains two intense ions with m/e 203 and 173,



which are formed, respectively, by loss by the molecular ion of 17 and, subsequently, 30 amu, which is confirmed by peaks of metastable ions with m/e 187.3 and 147.2. This type of disintegration is characteristic



for aromatic nitro compounds with an ortho group that includes a hydrogen atom [9]. Consequently, the structure of the 6-isomer can be assigned to VI.

We have previously observed the presence of an M-17(OH) ion in an analysis of the mass spectra of 1,2,5- and 1,2,7-trimethyl-3-carbethoxy-6-nitroindoles [1], and we ascribed it to splitting out of OH from the neighboring nitro and methoxy groups. Peaks formed by the loss by the molecular ion of 17 and, subsequently, 30 units were also observed in the mass spectrum of o-nitroanisole, while the most characteristic process for p-nitroanisole was loss of 16 amu or even the fragmentation characteristic for aromatic nitro compounds (successive loss of NO and CO).

The appearance of a maximum characteristic for 6-nitroindoles is observed in the UV spectra of indoles VI and VIa in the 400-nm region.

Nitroindoles IIc, IV, and VI were reduced to the corresponding amines (IVb, VII, and VIIa) (Table 1).

Calculation of the electron density by the LCAO MO method within the Pariser–Parr–Pople approximation* for 1,2-dimethyl-5-hydroxyindole Id and its protonated form (Table 2) does not make it possible to form a preference for nitration in the 6- or 4-positions both with respect to the overall electron density and with respect to the charge density in the upper occupied orbital (the boundary orbital).

Substantial deviations in orientation were revealed for 7-substituted indoles. It is known that the chief product of nitration in sulfuric acid of 2,3-dimethyl-1,7-trimethyleneindole (in which the trimethylene bridge can be considered to be a 1,7-dialkyl grouping) is the 5-isomer (up to 90%) with a small admixture of the 6-nitro derivative [10]. In our case, the 7-methoxy group oriented nitration primarily in the 6-position under the similar conditions. The total charge on C_6 for 7-hydroxyindoles is higher than the total charge on C_4 for the protonated form, and this is in agreement with the experimental results.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with an IKS-22 spectrometer. The UV spectra of alcohol solutions were recorded with a Cary-15 spectrophotometer. The PMR spectra of trifluoroacetic acid solutions were recorded with a Varian S-60T spectrometer with hexamethyldisiloxane (HMDS) as the external standard. The mass spectrum of VI was recorded with an MKh-1303 spectrometer with a system for the introduction of the sample directly into the ion source (50 eV, 110-120°). The reactions were monitored by means of thin-layer chromatography (TLC) on activity II (Brockmann classification) aluminum oxide in the following systems: benzene–ethyl acetate–heptane (4 : 1 : 3) for IIa-c and VII, benzene–ethyl acetate (3 : 1) for Ib, IV, and IVa, and benzene–petroleum ether (10 : 3) for 7-methoxyindoles VI and VIa.

General Method for the Preparation of 6-Nitro- and 5- and 7-Substituted Indoles. A 5-mmole sample of the indole was dissolved in 20 ml of 96% sulfuric acid (–10°), after which the solution was cooled to –25°, and a solution of 0.32 g (5 mmole) of nitric acid (sp. gr. 1.5) in 10 ml of 96% sulfuric acid was added. The mixture was stirred at this temperature for 1-2 h (with chromatographic monitoring), after which it was poured over ice. The resulting precipitate was removed by filtration, washed with water, dried, and recrystallized (Table 1).

6- and 4-Nitro-1,2-dimethyl-5-hydroxyindoles (IV and IVa). The mixture of isomers formed after nitration of 1,2-dimethyl-5-hydroxyindole (Id) by the method described above was passed through a column containing activity II aluminum oxide with elution with benzene–ethyl acetate (3 : 1). The first (dark) fraction yielded 6-nitroindole IV, after which 4-nitroindole IVa was isolated (Table 1).

1,2-Dimethyl-5-hydroxy-6-aminoindole (IVb). A 0.824-g (4 mmole) sample of 1,2-dimethyl-5-hydroxy-6-nitroindole (IV) was suspended in 80 ml of ethanol, and a small amount of Raney nickel and hydrazine hydrate (8 ml) (dropwise) were added until all of the nitro compound had dissolved (~40 min). The mixture was then heated on a boiling-water bath until the solution had decolorized (30 min). The hot solution was filtered and vacuum evaporated to dryness, and the residue was recrystallized from dioxane to give 0.36 g (51%) of aminoindole IV with mp ~200° (dec.). Found: C 68.4; H 7.1%. $C_{10}H_{12}N_2O$. Calculated: C 68.2; H 6.9%. UV spectrum (2 N solution in H_2SO_4), λ_{max}, nm (log ε): 223 (4.03) and 294 (4.00).

2,3,5-Trimethyl-6-aminoindole (VII). As in the preparation of IVb, 0.816 g (4 mmole) of 1,2,5-trimethyl-6-nitroindole IIc gave, after recrystallization from aqueous alcohol, 0.613 g (72%) of aminoindole VII with mp 163-164° and R_f 0.2. Found: C 75.9; H 8.1%. $C_{11}H_{14}N_2$. Calculated: C 75.7; H 8.2%. IR spectrum: 3100-3350 cm^{-1} (NH). UV spectrum (alcohol), λ_{max}, nm (log ε): 233 (4.53), 274 (3.78), and 308 (3.85).

2,3-Dimethyl-6-acetamido-7-methoxyindole (VIII). The reduction of 0.88 g (4 mmole) of 1,2-dimethyl-6-nitro-7-methoxyindole VI was carried out as in the case of IVb. At the end of the reduction, 10 ml of acetic anhydride was added to the mixture, and it was refluxed for ~15 min. The hot solution was filtered, the solvent was vacuum evaporated, and the residue was poured into cold water. The resulting

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*The calculations were performed by V. I. Minkin (Rostov State University).

precipitate was removed by filtration, washed with water, air dried, and recrystallized from aqueous ethanol to give 0.896 g (85%) of acetamidoindole VIII with mp 194-195° and R_f 0.3 [chloroform – methanol (25 : 1)]. Found: C 67.7; H 7.1%. $C_{13}H_{16}N_2O_2$. Calculated: C 67.3; H 6.9%. IR spectrum: 3200 (NH) and 1685 (CO) cm^{-1}. UV spectrum (alcohol), λ_{max}, nm (log ε): 229 (4.79), 280 (3.99), and 377 (1.85).

1,2-Dimethyl-4-nitro-5-methoxyindole (III). A 1.46-g (5 mmole) sample of 1,2-dimethyl-3-carbethoxy-4-nitro-5-methoxyindole (IVc) was suspended in 40 ml of glacial acetic acid containing 2 ml of 96% sulfuric acid, and the mixture was refluxed for 10 min, cooled, and neutralized with 2 NaOH. The resulting precipitate was removed by filtration, washed with water, dried, and recrystallized successively from benzene – petroleum ether (2 : 1) and methanol to give 0.46 g (42%) of III with mp 139-140° and R_f 0.66. Found: C 60.3; H 5.6; N 13.3%. $C_{11}H_{12}N_2O_3$. Calculated: C 60.0; H 5.5; N 12.8%. IR spectrum: 1500 and 1330 cm^{-1} (NO_2). UV spectrum (alcohol), λ_{max}, nm (log ε): 216 (4.57) and 383 (3.80).

1,2,3-Trimethyl-7-methoxyindole (Va). A 1.75-g (10 mmole) sample of 2,3-dimethyl-7-methoxyindole (V) was dissolved in 17 ml of dry DMSO, and 0.5 g (20 mmole) of dry dimethyl sulfate was added in small portions with stirring. The reaction mixture heated by spontaneously to 50-60°. It was stirred for 2-3 h (with chromatographic monitoring) and poured into water. The precipitate was removed by filtration, washed with water, air dried, and recrystallized from aqueous methanol (with activated charcoal) to give 1.7 g of Va. An analytical sample was purified by elution with benzene in a column filled with aluminum oxide. The yield of Va with mp 74-75° and R_f 0.8 was 1.55 g (82%). Found: C 76.7; H 8.0, N 7.8%. $C_{12}H_{15}NO$. Calculated: C 76.3; H 8.0; N 7.4%. UV spectrum (alcohol), λ_{max}, nm (log ε): 280 (4.69), 276 (3.84), 285 (3.83), and 296 (3.79).

1,2,3-Trimethyl-6-nitro-7-methoxyindole (VIa). The procedure used to obtain Va was used to obtain this compound by methylation of 2.2 g (10 mmole) of 2,3-dimethyl-6-nitro-7-methoxyindole (VI). The yield of nitroindole VIa was 2.2 g (90%); with respect to its melting point and IR spectra, the product was identical to the nitroindole obtained by nitration of Va.

LITERATURE CITED

1. A. N. Kost, L. G. Yudin, E. Ya. Zinchenko, A. B. Belikov, and O. A. Solov'ev, Khim. Geterotsikl. Soedin., 375 (1974).
2. L. G. Yudin, A. I. Pavlyuchenko, V. A. Budylin, V. I. Minkin, and A. N. Kost, Khim. Geterotsikl. Soedin., 1506 (1971).
3. V. A. Budylin, A. N. Kost, E. D. Matveeva, and V. I. Minkin, Khim. Geterotsikl. Soedin., 68 (1972).
4. W. Noland, H. Smith, and D. Johnson, J. Org. Chem., 28, 2534 (1962).
5. S. A. Monti and W. O. Johnson, Tetrahedron, 26, 3685 (1970).
6. F. Troxler, G. Borman, and F. Seeman, Helv. Chim. Acta, 51, 1203 (1968).
7. E. Ya. Zinchenko, L. G. Yudin, and A. N. Kost, Khim. Geterotsikl. Soedin., 1646 (1973).
8. R. L. Hinman and I. Lang, J. Amer. Chem. Soc., 86, 3796 (1964).
9. S. Meyerson, I. Puskas, and E. K. Fields, J. Amer. Chem. Soc., 88, 4974 (1966).
10. A. N. Kost, L. G. Yudin, and V. A. Budylin, Khim. Geterotsikl. Soedin., 39 (1966).