of TLC [Silufol, benzene—acetone (4:1), spraying with a solution with p-dimethylaminobenzaldehyde] a decrease in the concentration of the initial hydrazine (R_f 0.75, orange coloration), the formation and participation in the reaction of the 4-benzyloxyphenylhydrazone of γ-phthalimidoburyraldehyde (R_f 0.7, yellow coloration), and the formation of 5-benzyloxy-N-phthalyltryptamine (R_f 0.55, blue coloration) were observed. The mass was diluted with water and extracted with chloroform, the solvent was evaporated off, and the residue was triturated with 10 ml of ethanol to give 1.37 g (74%) of cream-colored crystals of 5-benzyloxy-N-phthalyltryptamine, mp 181-183°C; according to the literature [12], mp 179-181°C.

LITERATURE CITED

1. N. N. Suvorov, L. Kh. Vinograd, K. F. Turchin, G. N. Il'ina, M. M. Vigdorchik, and G. Ya. Filipenko, Khim. Geterotsikl. Soedin., No. 8, 1093 (1984).
2. L. Kh. Vinograd and N. N. Suvorov, USSR Inventors' Certificate No. 992, 513; Byull. Izobret., No. 4, 108 (1983).
3. V. I. Shvedov, N. B. Galstukhova, O. A. Fedotova, and A. N. Grinev, USSR Inventors' Certificate No. 642,300; Byull. Izobret., No. 2, 97 (1979).
4. K. Balenovič, I. Jambrešič, and I. Furič, J. Org. Chem., 17, 1459 (1952).
5. N. N. Suvorov, G. A. Chernov, L. Kh. Vinograd, M. M. Vigdorchuk, G. N. Il'ina, and N. I. Lisina, Fifth All-Union Colloquium on the Chemistry, Biochemistry, and Pharmacology of Indole Derivatives [in Russian], Izd. Tbil. Univ., Tbilisi (1981), p. 110.
6. S. Gabriel and J. Colman, Chem. Ber., 41, 513 (1908).
7. R. Mozingo, Organic Syntheses [Russian translation], IL, Moscow, Vol. 4 (1953), p. 409.
8. E. B. Hershberg and J. Cason, Org. Synth., 21, 84 (1941).
9. G. H. Nefkens, G. I. Tesser, and R. J. Nivard, Recl. Trav. Chim., 79, 688 (1960).
10. V. B. Del'nik, S. Sh. Kagna, V. V. Kashina, M. G. Katsnel'son, and G. N. Mishenkova, Zh. Prakt. Khim., 51, 1912 (1978).
11. S. Sato, Nippon Kagaku Zasshi, 90, 404 (1969); Chem. Abstr., 71, 21828 (1969).
12. British Patent No. 841,521; Chem. Abstr., 56, 1431 (1962).

REACTIONS OF 2-ACETYLINDOLE-3-CARBOXYLIC ACIDS

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UDC 547.757+547.756

Information is given on the synthesis and establishment of the structures of previously unreported 2-acetyl-3-bromoindoles formed by the action of bromine on 2-acetylindole-3-carboxylic acids. The reduction of the latter with sodium tetrahydroborate leads to the formation of 2-(1-hydroxyethyl)indole-3-carboxylic acids.

2-Acetylindole-3-carboxylic acids (I) [1, 2] are convenient compounds for the synthesis of previously unknown or difficultly accessible indole derivatives. For example, the synthesis of 5H-pyridazo[4,5-b]indol-1-ones (II) by the condensation of the acids (I) with hydrazine has been described [3]. An acetyl group in a pyrrole ring promotes ready decarboxylation, which has enabled a convenient synthesis of the 2-acetylindoles (III) to be developed [4].

When solutions of compounds (I) in DMFA were treated with elementary bromine, decarboxylation products containing one atom of bromine in the molecule were formed. The UV spectra of these compounds showed three absorption maxima of different intensities in the 208-214, 240-246, and 310-313 nm regions, which are characteristic for 2-acetylindoles [4]. In the IR spectra there were signals in the 1630-1650 cm^{-1} region that could be assigned to a carbonyl group conjugated with an indole nucleus, and the band of a NH group in the 3290-3300 cm^{-1}

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TABLE 1. 2-Acetyl-3-bromoindoles (IV)

Compound	R¹	R²	mp, °C	IR spectrum, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	Found, %				Empirical formula	Calculated, %				Yield, %
						C	H	N	Br(Cl)		C	H	N	Br(Cl)	
IVb	CH_3	H	180—181	1635, 3330	210 (4,33), 242 (4,13), 313 (4,31)	52,2	3,7	5,2	31,5	$C_{11}H_{10}BrNO$	52,4	4,0	5,6	31,7	31,7
IVc	H	CH_3	158	1655, 3320	208 (4,33), 246 (4,26), 311 (4,30)	52,1	4,3	5,8	31,8	$C_{11}H_{10}BrNO$	52,4	4,0	5,6	31,7	61,5
IVd	Br	H	225	1655, 3320	214 (4,40), 244 (4,25), 311 (4,30)	38,0	2,4	4,3	50,0	$C_{10}H_7Br_2NO$	37,9	2,2	4,4	50,4	72,5
IVe	Cl	H	201—203	1655, 3320	214 (4,37), 242 (4,27), 311 (4,31)	44,2	3,0	5,4	(42,7)	$C_{10}H_7BrClNO$	44,1	2,6	5,1	(42,3)	66,5

TABLE 2. Spectral Characteristics of 2-(1-Hydroxyethyl)indole-3-carboxylic Acids (V)

Compound	R¹	R²	IR spectrum, cm^{-1}		UV spectrum, λ_{max}, nm (log ε)
			CO	OH, NH	
Va*	H	H	1655	3510, 3270, 3240, 3000—2500	215 (4,57); 227 (4,34); 282 (4,05); 288 (4,04)
Vb	CH_3	H	1630	3210, 3000—2580	217 (4,55); 233 (4,30); 288 (4,05); 294 (4,02)
Vc*	H	CH_3	1690	3510, 3220, 3000—2500	214 (4,56); 231 (4,36); 285 (4,05)
Vd	Br	H	1635	3465, 3240, 3210, 3000—2540	220 (4,59); 289 (4,03); 296 (4,00)
Ve	Cl	H	1635	3465, 3250, 3210, 3000—2500	222 (4,58); 289 (4,02); 296 (3,98)

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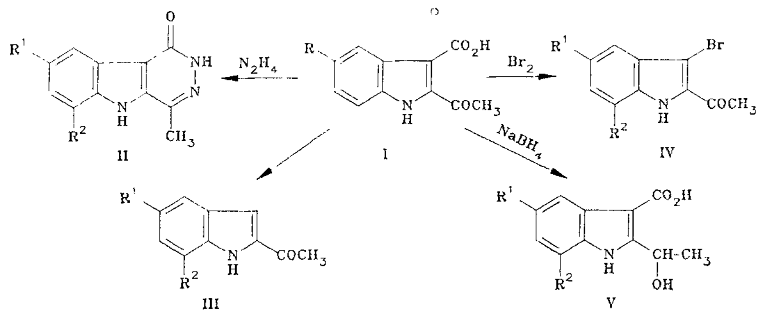
*The synthesis and physicochemical characteristics of these compounds have been given previously [2].



region. The introduction of a methyl group or a halogen atom into the benzene ring did not cause appreciable changes in the UV and IR spectra.

The PMR spectra of the bromination products each contained a three-proton singlet of the protons of the acetyl group at 2.68 ppm, a group of signals of aromatic protons, and the singlets of the methyl groups in positions 7 and 5 at 2.53 and 2.6 ppm, respectively. On the basis of the spectroscopic results, we assigned the structure of 2-acetyl-3-bromoindoles (IV) to the compounds obtained. The introduction of a bromine atom into the pyrrole ring stabilizes the 2-acetylindole molecule. The stability of the 2-acetyl-3-bromoindoles (IV) under the action of bases, acids, and oxidizing agents considerably exceeded the stability of the 2-acetylindoles (III) in relation to these factors — they did not change under the action of dilute ethanolic solutions of hydrogen chloride or caustic potash and could be stored for a long time in the light and in the air.

The action of sodium tetrahydroborate on the acids (I) in DMFA at room temperature formed the 2-(1-hydroxyethyl)indole-3-carboxylic acids (V) [2], colorless crystalline substances stable under the action of aqueous solutions of alkalis, light, and atmospheric oxygen. The IR spectra of compounds (V) each had a group of weak bands in the 2500-3000 cm^{-1} region that are characteristic for dimers of carboxylic acids, and the band of the stretching vibrations of the carbonyl group were present in the 1610-1690 cm^{-1} region. The stretching vibrations of the NH group and of the alcoholic OH group appeared in the form of three or two bands of different intensities in the 3210-3510 cm^{-1} region for the assignment of which we do not possess the necessary information [in the spectrum of the 5-methyl derivative (Vb) only one strong band was detected, at 3210 cm^{-1}]. In the spectrum of the sodium salt of the hydroxy acid (Va), the NH group appeared in the form of a narrow intense band at 3240 cm^{-1} against a background of a broad band in the 3200-3500 cm^{-1} region due to the stretching vibrations of an alcoholic hydroxy bound by an intramolecular hydrogen bond.

To obtain additional information on the structure of the hydroxy acids (V) the IR spectra of the methyl ester (Va) were recorded in paraffin oil and in fluorinated hydrocarbons: the signal of the carbonyl group split into narrow peaks (1660 and 1670 cm^{-1}), and the hydroxy and NH groups appeared in the form of three narrow peaks at 3240, 3350, and 3430 cm^{-1}.

EXPERIMENTAL

The melting points of the compounds synthesized were determined on a Boëtius instrument and are not corrected. IR spectra were taken on a UR-20 spectrometer in the form of mulls in fluorinated hydrocarbons, UV spectra on a Specord UV-vis instrument, and PMR spectra on a Tesla BS-467 instrument (60 MHz) in acetone-D_6.

2-Acetyl-3-bromoindoles (IVa). Over 15 min, with vigorous stirring and cooling with ice water, 0.25 ml (0.8 g, 5 mmole) of bromine was added to a solution of 1.01 g (5 mmole) of 2-acetylindole-3-carboxylic acid in 25 ml of DMFA. The mixture was stirred for 30 min and then the cooling was removed and the reaction mixture was allowed to warm up to room temperature. After 1 h 30 min, the mixture was poured into 100 ml of cold water, the mixture was made alkaline with a solution of sodium bicarbonate, and the resulting precipitate was filtered off, dried in the air, and crystallized from a mixture of benzene and acetone. Yield 0.7 g (58%), mp 152-153°C. IR spectrum, cm^{-1}: 3325 (NH), 1645 (CO). UV spectrum, λ_{max}, nm (log ε): 208 (4.29), 240 (4.14), 310 (4.29). Found, %: C 50.1, H 3.2, N 5.8, Br 33.5. $C_{10}H_8BrNO$. Calculated, %: C 50.5, H 3.4, N 5.9, Br 33.6.

2-Acetyl-3-bromoindoles with substituents in the benzene ring were obtained by a similar procedure (see Table 1).

2-(1-Hydroxyethyl)-5-methylindole-3-carboxylic Acid (Va). In one portion, 0.2 g (2.7 mmole) of sodium tetrahydroborate was added to a solution of 1.09 g (5 mmole) of 2-acetyl-5-methylindole-3-carboxylic acid in 25 ml of DMFA, and the mixture was stirred for 30 min. Then it was poured into water, impurities were removed by extraction with ether, the aqueous solution was acidified with 5% sulfuric acid, the oil that separated out was extracted with ether (14 × 100 ml), the extract was dried with anhydrous sodium sulfate and was evaporated, and the residue was crystallized from a mixture of benzene and acetone. Yield 0.76 g (69%), mp 189-190°C. Found, %: C 66.0, H 6.2, H 6.2. $C_{12}H_{11}NO_3$. Calculated, %: C 65.7, H 6.0, N 6.4.

5-Bromo-2-(1-hydroxyethyl)indole-3-carboxylic Acid (Vd). This was obtained in a similar manner to (Va). Yield 75%, mp 243°C. Found, % C 46.8, H 3.6, N 4.8, Br 28.0. $C_{11}H_{10}BrNO_3$. Calculated, % C 46.5, H 3.5, N 4.9, Br 28.1.

5-Chloro-2-(1-hydroxyethyl)indole-3-carboxylic Acid (Ve). This was obtained by a similar procedure. Yield 67%, mp 203°C. Found, %: C 55.4, H 4.4, N 5.7, Cl 15.0. $C_{11}H_{10}ClNO_3$. Calculated, %: C 55.1, H 4.2, N 5.8, Cl 14.8.

LITERATURE CITED

1. M. A. Rekhter, V. I. Gorgos, L. M. Zorin, and G. I. Zhungietu, USSR Inventors' Certificate No. 696,016; Byull. Izobret., No. 41, 91 (1979).
2. G. I. Zhungietu, L. M. Zorin, and M. A. Rekhter, Izv. Akad. Nauk MSSR, Ser. Biol. Khim. Nauk, No. 2, 57 (1981).
3. G. I. Zhungietu, L. M. Zorin, V. I. Gorgos, and M. A. Rekhter, Khim. Geterotsikl. Soedin., No. 8, 1064 (1982).
4. L. M. Zorin, G. I. Zhungietu, and M. A. Rekhter, USSR Inventors' Certificate No. 810,686; Byull. Izobret., No. 9, 90 (1981).

THE DUAL REACTIVITY OF 1,2-DISUBSTITUTED DIHYDRO-N-HETEROAROMATIC SYSTEMS.

5.* A CASE OF AN UNUSUALLY EASY HETEROLYSIS OF THE INTERNUCLEAR BOND IN 2-(INDOL-3-YL)-1-METHYL-1,2-DIHYDROQUINOLINE AND ITS ANALOGS†

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The reaction of the 1-methylquinolinium cation with the indole anion has given a crystalline adduct of saltlike structure forming an ion pair in polar solvents and 2-(indol-3-yl)-1-methyl-1,2-dihydroquinoline in nonpolar solvents.

The aromatization of substituted dihydroheteroaromatic compounds takes place with the loss of the hydride-mobile hydrogen atom or of a substituent in the form of a carbanion as the result of the heterolysis of C–H or C–C bonds under the action of electrophiles. An alternative is a stepwise process of the one-electron oxidation of the dihydro derivatives to the corresponding radical cations with the subsequent splitting out of hydrogen or a substituent in the form of a radical [3-5]. Other mechanisms of bimolecular aromatization reactions are also widely discussed [1, 3-5]. A hypothesis has recently been put forward of the possibility of monomolecular aromatization reactions if, in polar solvents, they are preceded by a heterolytic dissociation of dihydroheteroatomic compounds with the formation of ion pairs [5]. This apparently explains the appearance of spontaneous aromatization and also of transhetarylation reactions [6], the nucleophilic alkylation of dihydroheteroaromatic compounds [7], and other reactions [5]. Examples of such dissociation are known. For instance, in

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*For communication 4, see [1].
†For a preliminary communication on this, see [2].

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