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ACETALS OF LACTAMS AND ACID AMIDES.

66.* SYNTHESIS AND SPECTRAL STUDIES OF 4(AND 6)-AMINO-5-HYDROXYINDOLE DERIVATIVES

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A method has been developed for the selective N-alkylation of derivatives of 4-amino-5-hydroxy- and 6-amino-5-hydroxyindoles, based on the preliminary closure of the oxazolone ring by reaction with sodium cyanate and alkylation of the resulting oxazolo[4,5-e]- and oxazolo[5,4-f]-indole derivatives in an alkaline medium. The latter, on heating in an alkali, convert into 5-hydroxy-6-methylaminoindoles, while the former give substituted N-methyl-N-indolylurethanes under these conditions. The reaction of amino-hydroxyindoles with DMFA diethylacetal and certain reactions of the resulting amidines were studied.

Compounds having hydroxy and substituted amino groups in the ortho positions of the aromatic ring are known to be promising in the search for antitumorigenic agents, protein synthesis inhibitors, and antiviral compounds [2]. The synthesis of systems of this type are complicated in view of the possible occurrence of processes at two reaction centers (amino and hydroxy groups) and specific methods are required for carrying out selective reactions. We chose 4-amino-5-hydroxy-6-bromo- [3] and 5-hydroxy-6-amino-1,2-dimethyl-3-ethoxycarbonylindoles (I, II) as starting compounds in the present work. Compound II was obtained by the reduction of the corresponding nitro derivative [4].

At the first stage, we studied the possibility of the selective preparation of N-alkyl derivatives in the two series of compounds. The reaction of aminophenols I, II with sodium cyanate in an acid medium proceeds similarly, and as a result oxazoloindoles III, IV, respectively, are obtained. Heating of compound I with urea in acetic acid also leads to the formation of the tricyclic compound III, while when hydrochloric acid is used, the ureido derivative V is obtained. Alkylation of tricyclic compounds III, IV proceeds smoothly, and N-methyl derivatives VI, VII are formed in satisfactory yields.

However, substantial differences were revealed at the stage of hydrolytic splitting of the oxazolone ring in compounds VI and VII, which are probably due to the steric interaction of the substituent at the 4-position (in the series of 4-aminoindole I derivatives) and the ethoxycarbonyl group at the 3-position. Thus, while the alkaline hydrolysis of oxazolo[5,4-f]indole VII proceeds as usual with the formation of 6-methylamino-5-hydroxy derivative VIII, a similar treatment of oxazolo[4,5-e]indole VI leads to urethanes IXa, b, which are very stable with respect to alkalies: we were unable to split off the N-alkoxycarbonyl fragments without the destruction of the molecule. This anomalous stability of compounds (IXa, b) required a reliable confirmation of their structure by means of PMR spectroscopy (Table 1), and especially ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of compounds IXa, b and 5-O-acetyl derivative X under the conditions of a complete uncoupling from protons, contain a double set of signals, whereby the

*For communication 65, see [1].

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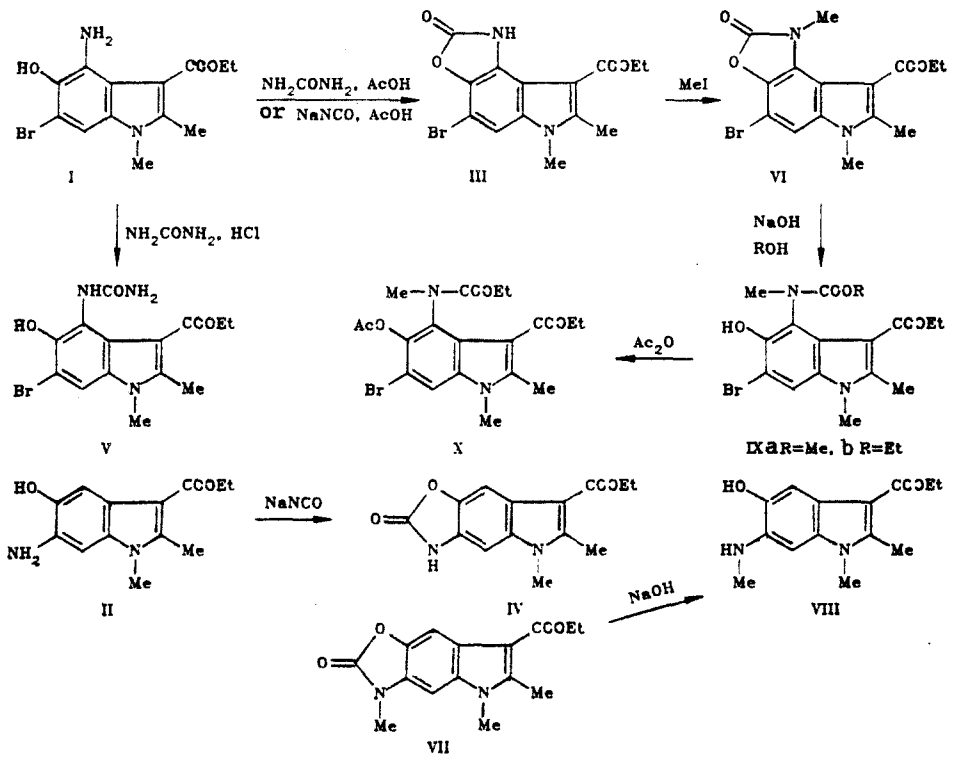


signals of the corresponding carbon atoms have similar chemical shifts, but differ in intensity. The use of spectra taken under conditions of the absence of suppression of the interaction with protons for an unequivocal confirmation of the structure of compounds IXa, b, X is difficult because of the appearance of complex nonanalyzable multiplets. We therefore used the ^{13}C NMR spectra, taken under conditions of selective heteronuclear resonance with subsequent suppression of the interaction with the methyl group protons at the 1,2-positions and the N-methyl group protons at the 4-position. During the suppression of the interaction with the 1-CH_3 group protons, the structure of the paired signals (using compound IXb as an example) at 131.8 and 131.7, 145.4 and 145.3, 145.2 and 144.9 ppm, was substantially simplified. The first two signals convert into two doublets with different intensities with splitting of J = 1.8 Hz. The character of the splitting indicates that these signals can be assigned to the $C_{(7a)}$ atoms (the reasons for the existence of the compounds studied in two forms are discussed below). The splitting into doublets is possibly due to the interaction with the 7-H proton. A similar pattern is observed for the halogen-substituted benzenes [5]. The second pair of signals (145.4 and 145.3 ppm) in this experiment also converts into two doublets of different intensities, which split with the same constant J ≈ 7.5 Hz, each component of which additionally splits with J ≃ 1 Hz, while the latter splitting disappears when deuteromethanol is added. Hence, it follows that these signals belong to the $C_{(5)}$ atoms, while the splitting corresponds to the interaction with a proton at the 7-position and the 5-OH group proton. The signals at 145.2 and 144.9 ppm were assigned to the $C_{(2)}$ atom, since they convert into quartets with J = 2.5 Hz, which is due to the interaction with the protons of the 2-CH_3 group. It should be noted that these signals react to the suppression of the interaction with the 2-CH_3 group protons by converting into quartets which split with a lower (J ≃ 1 Hz) constant due to the interaction with the protons of the more distant 1-methyl substituent. In the same experiment (suppression of the interaction with the 2-CH_3 group protons), the quartets at 103.5 and 103.3 ppm convert into singlets, which make it possible to assign them unequivocally to the $C_{(3)}$ atom. In the selective heteronuclear resonance spectrum (the 4-NMe group), the structure of the multiplets at 122.6 and 121.8 ppm changes considerably — they convert into triplets (J ≃ 2 Hz), while in the spectrum taken in CD_3OD — into doublets (J ≃ 2 Hz). This successive change in the splitting gives grounds for assigning these signals to the $C_{(4)}$ atom, and explaining the splitting by the interaction with the 7-H and OH group protons. The assignment of the remaining signals was based on concepts of the influence of electronegativity of the neighboring groups on the chemical shifts and the character of multiplicity of the signals: 122.3 and 122.5 (J = 6 Hz) — $C_{(3a)}$; 113.0 and 112.9 ppm (J = 160 Hz) — $C_{(7)}$; the carbonyl carbon atoms of the 2-COOEt and 4-N(Me)COOEt groups have signals at 164.6, 164.4 and 155.0 and 154.8 ppm,

TABLE 1. Characteristics of Compounds VIII, IXa, IXb, XIV, XV, XVII

Compound	mp, °C*	4-H, s	PMR spectrum, δ, ppm**						Yield %
			7-H, s	1-CH_3, s	2-CH_3	4-NCH_3, s	3-$COOCH_2CH_3$	OH, NH, NH_2	
VIII	210...211	6,43	7,29	3,61	2,77 br.	2,62	1,34t; 4,22 q	8,99	18
IXa	226...228	—	7,43; 7,42	3,65; 3,63	2,67s; 2,64 s	3,20; 3,20; 3,61 / 3,83 } OCH_3	1,37t; 4,38 m	5,82 s; 5,96 s	86
IXb	205...206	—	7,44; 7,42	3,61; 3,63	2,67s; 2,65 s	3,22; 3,22	1,37t; 4,38 m	5,70s; 6,02 s	89
XIV	216...218	—	7,35	3,62	2,66 s	—	1,44t; 4,42 q	13,68 br.s; 9,88s; 8,27 s	99
XV	194...196	—	7,67	3,72	2,72 s	2,03 (Ac); 2,33 (OAc)	1,33t; 4,30 m	9,51	76
XVII***	163...165	7,77; 7,73	—	3,74	2,75 s	2,21 / 2,24 } Ac	1,38t; 4,30 q	—	80

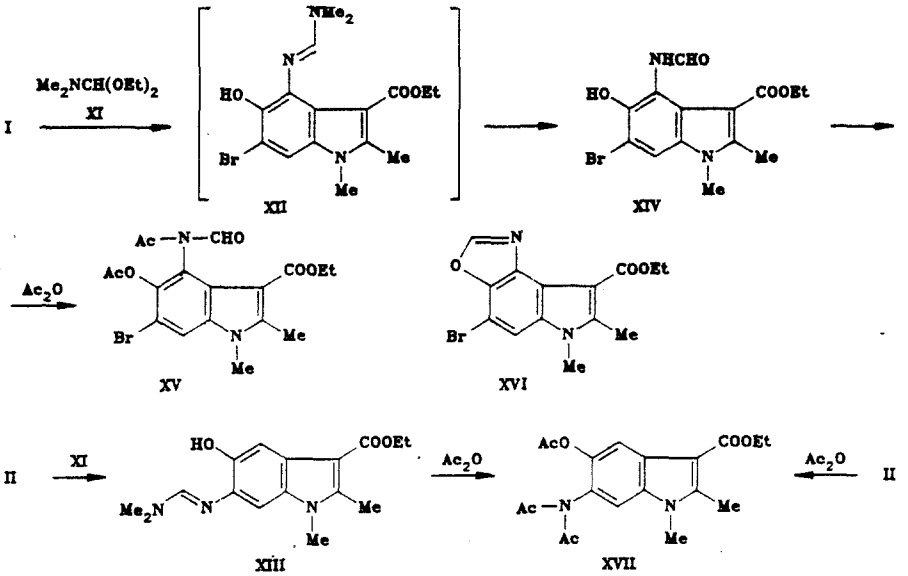
*Compound VIII was recyrstallized from a 1:1 hexane—acetone mixture, compounds IXa, b, XIV — from acetone, compounds XV, XVII — from alcohol.

**The spectra of compounds VIII and XVII were taken in DMSO-D_6, of compounds IXa, b, XIV, and XV in $CDCl_3$.

***The amount of the minor isomer does not exceed 5%.

respectively. Thus, a detailed analysis of splitting of the signals in the ^{13}C NMR spectrum of compound IXb unequivocally confirms its structure. The same conclusion can be made when considering the spectra of compounds IXa, X.

The presence of paired signals in the spectra of the compounds under consideration and the complete identity of the structure of these signals indicate that the double set of signals is due to the inhibited rotation with respect to either the N—CO bond of the urethane fragment (the amide isomerism) or the N—$C_{(4)}$ bond. The data enabling the assignment to this of the other type of the inhibited rotation may be presented in the following way: in the spectrum of compound IXa, the most substantial difference in the chemical shifts between the paired components is observed for signals of hydroxyl groups (~0.14 ppm) and the N—COOMe groups (0.22 ppm), while for other signals this difference does not exceed 0.04 ppm (Table 1). This feature, as well as the nonequivalency of the CH_2 groups in the urethane fragment of compound IXb, can be explained by taking into account the above two types of isomerism. Hoever, the nonequivalency of the CH_2 groups of the ethoxycarbonyl substituents at the 3-position of the indole ring in compounds IXa, b, X, and XV (see below) observed in the PMR spectra can only be explained by the inhibited rotation with respect to the N—$C_{(4)}$ bond. The molecules of these compounds possibly exist in the form of two steric isomers with a high interconversion barrier, due to the steric proximity of the substituents in the 3- and 4-positions. This creates the diastereotopic environment of the methylene units of the 3-COOEt groups (as, for example, in biphenyls [6]). These concepts are supported by the fact that when temperature of taking the spectrum is increased to 95°C, no broadening or change in the chemical shifts of the signals prior to their coalescence is observed (which should take place if amide isomerism was involved),* and also the nonequivalency of the methylene group protons of the ethoxycarbonyl groups at the 3-position is retained.



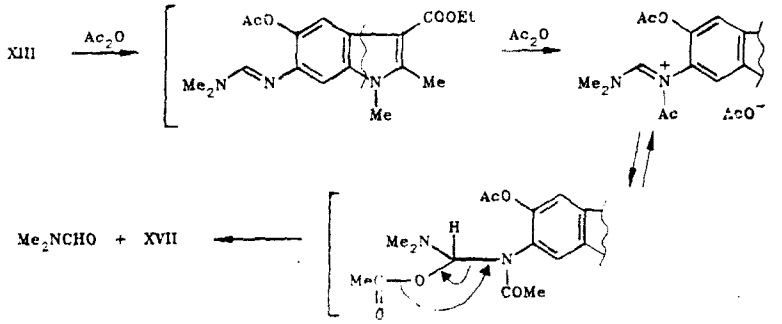
Thus, the selective N-alkylation of amino-hydroxyindoles I, II is possible by successive closure of the oxazolone ring, which serves as protection for the phenolic hydroxyl group. The possible path of protection of the primary amino group — the formation of amidines — was also used in the present work. In the reaction of compounds I and II with DMFA diethylacetal XI, we expected to obtain the corresponding dimethylaminomethylene derivatives XII and XIII, to protect the hydroxy group by acylation, and to subsequently carry out the reactions with nucleophilic reagents at the amidine fragment.

However, in carrying out these processes, we were confronted with unexpected results. Thus, while the reaction of amino-hydroxyindole II with acetal XI proceeds smoothly with the formation of amidine XIII, the reaction of compound I and acetal XI is accompanied by rapid hydrolysis of the amide fragment and gives the formylamino derivative XIV. Such a ready hydrolysis is probably due to the fact that in amidine XII there is a strong steric interaction with

*It is known [7] that for urethanes the coalescence of the signals of the amide isomers is observed even at low temperatures (0-10°C).

the 3-ethoxycarbonyl group and the conversion of the amidine fragment into the formylamino group with a smaller volume is energetically favorable. The acceleration of the hydrolytic splitting is probably also due to the participation of the neighboring phenolic hydroxyl ensuring the protonation of the amidine grouping.

The acetylation of the formyl derivative XIV proceeds both at the phenolic hydroxyl and at the amide group NH with the formation of the N,O-diacetyl derivative XV. It is interesting that the successive treatment of amino-hydroxyindole I by acetal XI and acetic anhydride leads to a tricyclic oxazoloindole XVI. Contrary to this, the reaction of amidine XIII with acetic anhydride has an unexpected result — the triacetyl derivative XVII was separated, which was also obtained by a countersynthesis from indole II. This unusual splitting of the indole fragment may be due to attack of acetic anhydride at the iminic nitrogen atom, based on the (N → O)-acyl migration:



This scheme was confirmed to some extent by the formation of DMFA in this process, which was detected in the reaction mixture by GLC.

EXPERIMENTAL

The NMR spectra were run on a Varian XL 200 spectrometer, using TMS as internal standard; the IR spectra were recorded in mineral oil on a Perkin—Elmer 599 spectrophotometer; the mass spectra were measured on a Varian MAT 112 spectrometer at an energy of 70 eV, with direct introduction of the material into the ionic source. The course of the reaction and the purity of the compounds were monitored chromatographically on Silufol UV-254 plates in benzene—methanol (9:1) and chloroform systems with development in UV light.

The elemental analysis data correspond to the calculated values.

1,2-Dimethyl-3-ethoxycarbonyl-5-hydroxy-6-aminoindole (II, $C_{13}H_{16}N_2O_3$). A 2 g portion of Raney nickel (W-7) was added to a suspension of 14 g (44 mmoles) of 1,2-dimethyl-3-ethoxycarbonyl-5-acetoxy-6-nitroindole in 600 ml of ethanol, the mixture was heated to boiling, and approximately 80 ml of hydrazine hydrate was added dropwise up to decoloration of the reaction mixture (~1 h). The hot solution was filtered, the solvent was evaporated to 1/3 of its volume, and the precipitate obtained was filtered off, washed with alcohol, and dried. Yield 8.3 g (76%) of compound II, mp 203-204°C (from ethanol). IR spectrum: 3460 (5-OH), 3380, 3300, 3210 cm^{-1} (6-NH_2).

2-Oxo-4-bromo-6,7-dimethyl-8-ethoxycarbonyloxazolo[4,5-e]indole (III, $C_{14}H_{13}BrN_2O_4$). **A.** A 2.6 g portion (40 mmoles) of sodium cyanate was added in the course of 20 min to a boiling solution of 3.3 g (10 mmoles) of indole I in 50 ml of acetic acid. The mixture was boiled for 10 min and diluted with 150 ml of water. The precipitate that separated out was filtered off, washed with water, and dried. Yield 3.3 g (94%) of compound III, mp 254-256°C (from an alcohol—dioxane mixture).

B. A mixture of 0.33 g (1 mmole) of indole I and 0.1 g (1.7 mmole) of urea in 15 ml of acetic acid was boiled for 2 h, and then was diluted with 100 ml of water. The precipitate was filtered, washed with water, and dried. Yield 0.2 g (57%) of compound III.

A mixed sample of compounds obtained by the different methods showed no depression of the melting point.

PMR spectrum ($CDCl_3$), ppm: 7.10 (s, 5-H), 3.67 (s, 6-CH_3), 2.71 (s, 7-CH_3); 1.44 t, 4.41 q (8-$COOCH_2CH_3$); 9.45 (s, 1-H).

2-Oxo-5,6-dimethyl-7-ethoxycarbonyloxazolo[5,4-f]indole (IV, $C_{14}H_{14}N_2O_4$). Sodium cyanate (6 g, 100 mmoles) was added in small portions to a solution of 6 g (24 mmoles) of indole II in 90 ml of acetic acid, and the mixture was boiled for 4 h. The reaction mixture was cooled to 10°C. The precipitate that separated out was filtered off and washed with methanol. Yield 3.6 g (55%) of compound IV, mp 270-271°C (from an acetone—DMFA mixture). IR spectrum: 3160 (3-NH), 1775 (2-CO), 1660 cm^{-1} (7-$COOC_2H_5$).

1,2-Dimethyl-3-ethoxycarbonyl-4-ureido-5-hydroxy-6-bromoindole (V, $C_{14}H_{16}BrN_3O_4$). A mixture of 3.3 g (10 mmoles) of indole I, 0.72 g (12 mmoles) of urea, and 0.45 g (12 mmoles) of concentrated HCl was heated on an oil bath at 120°C for 5 h. The powder that formed was washed with water and recrystallized from dichloroethane. Yield 1.9 g (51%) of compound V, mp 223-226°C; M^+ 369.

1,6,7-Trimethyl-2-oxo-4-bromo-8-ethoxycarbonyloxazolo[4,5-e]indole (VI, $C_{15}H_{15}BrN_2O_4$). A 0.9 ml portion of a 42% solution of NaOH was added to a boiling suspension of 2.2 g (6 mmoles) of indole III in 200 ml of acetone, the mixture was boiled for 30 min, and then 1.7 g (12 mmoles) of methyl iodide was added. The mixture was boiled for 7 h, the solvent was evaporated to 30 ml volume, the precipitate was filtered off, washed with water, cold acetone, and dried. Yield 2.1 g (98%) of compound VI, mp 206-208°C (from acetone). PMR spectrum ($CDCl_3$), ppm: 7.17 (s, 5-H), 3.68 (s, 6-CH_3), 2.64 (s, 7-CH_3), 3.58 (s, 1-CH_3); 1.40 t, 4.38 q (8-$COOCH_2CH_3$).

2-Oxo-3,5,6-trimethyl-7-ethoxycarbonyloxazolo[5,4-f]indole (VII, $C_{15}H_{16}N_2O_4$). A 6.5 g portion of a 1.5 N NaOH solution was added dropwise at 20°C to a suspension of 2.3 g (8.4 mmoles) of compound IV in 20 ml of acetone, and then 1.22 g (9.7 mmoles) of dimethyl sulfate was added. The reaction mixture was stirred for 1 h, the precipitate that separated out was filtered off, washed with water and methanol, and recrystallized from acetone. Yield 1.5 g (62%) of compound VII, mp 225-226°C. IR spectrum: 1755 (2-CO), 1680 cm^{-1} (7-$COOC_2H_5$). PMR spectrum (DMSO-D_6), ppm: 7.48 (d, 8H, J = 0.6 Hz), 7.75 (d, 4H, J = 0.6 Hz), 3.75 (s, 5-NCH_3), 2.73 (s, 6-CH_3), 3.39 (s, 3-NCH_3); 1.36 t, 4.39 q (7-$COOCH_2CH_3$).

1,2-Dimethyl-3-ethoxycarbonyl-5-hydroxy-6-methylaminoindole (VIII, $C_{14}H_{18}N_2O_3$). A 0.5 g portion (1.75 mmoles) of compound VII was added to a solution of 0.4 g (10 mmoles) of NaOH in 5 ml of ethanol, and the mixture was boiled for 1 h. The alcohol was evaporated, the residue was dissolved in 50 ml of water, and the solution was acidified with acetic acid to a neutral reaction. The precipitate that separated out was washed with water, dried, and recrystallized from a hexane—acetone (1:1) mixture. Yield 0.08 g of compound VIII. IR spectrum: 3610 (5-OH), 3460 (6-NH), 1690 cm^{-1} (3-$COOC_2H_5$).

1,2-Dimethyl-3-ethoxycarbonyl-4-(N-methyl-N-methoxycarbonyl)amino-5-hydroxy-6-bromoindole (IXa, $C_{16}H_{19}BrN_2O_5$). A 1.3 g portion (3.5 mmoles) of compound VI was added to a solution of 0.42 g (11 mmoles) of NaOH in 5 ml of methanol, and the mixture was boiled for 1 h. It was then cooled to 10°C, neutralized with acetic acid, the precipitate was filtered off, washed with water, and dried. Yield 1.2 g of compound IXa.

1,2-Dimethyl-3-ethoxycarbonyl-4-(N-methyl-N-ethoxycarbonyl)amino-5-hydroxy-6-bromoindole (IXb, $C_{17}H_{21}BrN_2O_5$) was prepared in a similar way from 0.65 g (16 mmoles) of NaOH, 60 ml of ethanol, and 2 g (5.5 mmoles) of compound VI. Yield 2 g of compound IXb.

1,2-Dimethyl-3-ethoxycarbonyl-4-(N-methyl-N-ethoxycarbonyl)amino-5-acetoxy-6-bromoindole (X, $C_{19}H_{23}BrN_2O_6$). A mixture of 1 g (2.4 mmoles) of compound IXa, 10 ml of acetic anhydride, and a catalytic amount of sulfuric acid was shaken for 3-5 min. The solution formed was diluted by a double amount of water. The precipitate that separated out was filtered off, washed with water, and dried. Yield 0.9 g (90%) of compound X, mp 120-121°C (from petroleum ether); M^+ 454.

1,2-Dimethyl-3-ethoxycarbonyl-5-hydroxy-6-dimethylaminomethyleneaminoindole (XIII, $C_{16}H_{21}N_2O_3$). A 0.96 g portion (6.6 mmoles) of DMFA diethylacetal was added at 60°C to a solution of 1.5 g (6 mmoles) of compound II in 140 ml of dioxane. The reaction mixture was allowed to stand for 1 h at this temperature, dioxane was evaporated, and the residue was recrystallized twice from a hexane—acetone (1:1) mixture. Yield 0.5 g (27%) of compound XIII, mp 162-164°C. IR spectrum: 3330 (5-OH), 1680 cm^{-1} (3-$COOC_2H_5$).

1,2-Dimethyl-3-ethoxycarbonyl-4-formylamino-5-hydroxy-6-bromoindole (XIV, $C_{14}H_{15}BrN_2O_4$). **A.** A 3.3 g portion (23 mmoles) of DMFA diethylacetal was added at 20°C to a solution of 5 g (15 mmoles) of indole in 500 ml of chloroform. The mixture was allowed to stand for 30 min, the solvent was evaporated, and the residue was recrystallized from acetone. Yield 4 g (74%) of compound XIV.

B. A 0.15 g portion (1 mmole) of DMFA diethylacetal was added to a solution of 0.33 g (1 mmole) of I in 10 ml of DMFA, the mixture was shaken for 3-5 min and diluted with 50 ml of water. The precipitate that separated out was filtered off, washed with water, and dried. Yield 0.35 g (99%) of compound XIV.

A mixed sample of the compounds obtained by the different methods did not show a depression of the melting point.

1,2-Dimethyl-3-ethoxycarbonyl-4-(N-formyl-N-acetyl)amino-5-acetoxy-6-bromoindole (XV, $C_{18}H_{19}BrN_2O_6$). A mixture of 0.5 g (1.4 mmoles) of indole XIV, 30 ml of acetic anhydride, and a catalytic amount of triethylamine was

boiled for 3 h, and then diluted with a double volume of water. The precipitate that separated out was filtered off, washed with water, and dried. Yield 0.47 g of compound XV.

4-Bromo-6,7-dimethyl-8-ethoxycarbonyloxazolo[4,5-e]indole (XVI, $C_{14}H_{13}BrN_2O_3$). A 0.16 g portion (1 mmole) of DMFA diethylacetal was added to a solution of 0.33 g (1 mmole) of indole I in 80 ml of absolute benzene. The mixture was shaken for 3 min, and after adding 0.1 g (1 mmole) of acetic anhyride, was boiled for 4 h. It was then boiled for another 2-3 min in the presence of silica gel, filtered, the benzene mother liquor was evaporated, and the residue was recrystallized from alcohol. Yield 0.2 g (59%) of compound XVI, mp 179-181°C (from alcohol); M^+ 336.

1,2-Dimethyl-3-ethoxycarbonyl-5-acetoxy-6-diacetylaminoindole (XVII, $C_{19}H_{22}N_2O_6$). A. A solution of 0.5 g (1.6 mmoles) of indole XIII in 5 ml of acetic anhydride was boiled for 1 h, diluted with 50 ml of water, and sodium carbonate was added to pH 8. The precipitate that separated out was filtered off, washed with water, and dried. Yield 0.35 g (58%) of compound XVII.

B. A solution of 0.5 g (2 mmoles) of indole II in 15 ml of acetic anhydride was boiled for 2 h, then was diluted with 50 ml of water, the precipitate that separated out was filtered off, washed with water, and dried. Yield 0.6 g (80%) of compound XVII.

A mixed sample of the compounds obtained by methods A and B did not show a depression of the melting point.

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