^{13}C NMR SPECTRA OF THE BASES AND CONJUGATE ACIDS OF 3- AND 5-FORMYL-, ACETYL-, AND CARBETHOXYPYRROLES

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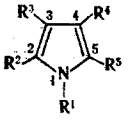
The effect of protonation of the oxygen atom of the carbonyl group and the carbon atom of the pyrrole ring on the ^{13}C chemical shifts in a series of 3- and 5-formyl-, 3-acetyl-, and 3-carbethoxypyrroles was studied. The structures of the conjugate acids of the 5-carbethoxypyrroles was established on the basis of measurement of the ^{1}H and ^{13}C NMR spectra. It is shown that protonation of the 5-carbethoxypyrroles occurs at the ring 5-C atom in 28-35 N H_2SO_4. The effect of structural factors and the acidity of the medium on the relative stabilities of the CH conjugate acids of the investigated compounds is examined.

Pyrrole and its derivatives are included in the composition of many biologically important compounds such as chromoproteides, porphyrins, prodigiosine, and vitamin B_{12}. Carbon-13 NMR spectroscopy is being used more and more intensively for the study of the structures of these compounds and the products of their biochemical transformations (e.g., see [1, 2]). In connection with the development of such research, the study of the structures and ^{13}C spectra of neutral and protonated forms of substituted pyrroles is a timely problem. These data are of important significance both for the solution of the complex problem of the assignment of the lines in the spectra of macromolecules that contain pyrrole rings and for the study of the structural aspects of the biotransformation of macromolecules associated with processes involved in the protonation and deprotonation of pyrrole fragments in biological systems.

We have previously studied the protonation of 3- and 5-formyl-, acetyl-, and carbethoxypyrroles by ^{1}H NMR and UV spectroscopy [3-6]. In the present research we investigated the ^{13}C NMR spectra of the bases and conjugate acids of compounds (1)-(10). The assignment of the signals in the spectra of the neutral molecules (Table 1) was made on the basis of the character of the multiplicity of the spectral lines in the absence of suppression of the $^{13}C-\{^{1}H\}$ spin–spin couplings (SSC) and the effects of substituents on the chemical shifts (CS) of the pyrrole ring [7]. The CS of the pyrrole ring calculated by an additive scheme with the use of the increments presented in [7] are in satisfactory agreement with the experimental values. The relative CS of the methyl groups follow the trend of the relative CS of the carbon atoms in the corresponding positions of the ring. The signals of the carbonyl carbon atoms of the formyl (175-185 ppm), acetyl (190-195 ppm), and carbethoxy (160-170 ppm) groups are identified distinctly from the characteristic range of their positions.



	R^1	R^2	R^3	R^4	R^5
(1)	C_2H_5	CH_3	CHO	H	CH_3
(2)	H	H	$COCH_3$	CH_3	H
(3)	H	CH_3	$COCH_3$	CH_3	H
(4)	H	CH_3	$COCH_3$	CH_3	CH_3
(5)	H	CH_3	$COCH_3$	CH_3	C_2H_5
(6)	H	CH_3	$COOC_2H_5$	CH_3	CH_3
(7)	H	CH_3	$COOC_2H_5$	CH_3	C_2H_5
(8)	H	H	CH_3	CH_3	CHO
(9)	H	CH_3	CH_3	CH_3	$COOC_2H_5$
(10)	CH_3	CH_3	CH_3	CH_3	$COOC_2H_5$

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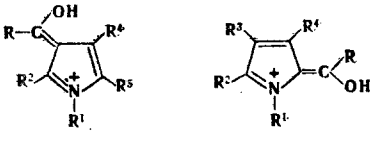
TABLE 1. ^{13}C Chemical Shifts (ppm) in the Spectra of the Bases and Conjugate Acids of Formyl-, Acetyl-, and Carbethoxypyrroles*

Compound	Charge	Protonation center	Pyrrole ring C atoms				Substituent C atoms									
							R^1		R^2	R^3			R^4	R^5		
			2-C	3-C	4-C	5-C	$-CH_2-$	$-CH_3$	$-CH_3$	C=O	$-CH_2-$	$-CH_3$	$-CH_3$	C=O	$-CH_2-$	$-CH_3$
(1)	0		137,1	121,6	106,4 (170)	129,2	38,2	10,3	15,5	185,0 (165)	—	—	—	—	—	12,0
	+	(C)=O	162,0	121,0	108,4	141,3	42,1	12,2	15,2	174,9	—	—	—	—	—	12,9
(2)	0		125,6 (184)	124,1	120,7	118,4 (184)	—	—	—	194,9	—	27,8	12,4	—	—	—
	+	(C)=O	141,5 (190)	121,3	125,6	124,3 (190)	—	—	—	200,5	—	24,0	13,3	—	—	—
(3)	0		135,9	121,5	121,5	115,8†	—	—	14,8	194,5	—	31,0	13,7	—	—	—
	+	(C)=O	155,2	118,6	126,5	122,1†	—	—	17,8	195,9	—	24,8	14,1	—	—	—
(4)	0		133,0	120,7	114,3	122,4	—	—	14,7	193,9	—	30,9	10,2	—	—	11,9
	+	(C)=O	154,6	119,5	120,4	131,4	—	—	18,1	194,1	—	24,9	10,7	—	—	12,6
(5)	0		133,3	120,7	113,6	128,8	—	—	14,8	194,1	—	30,9	11,7	—	18,0	14,8
	+	(C)=O	155,2	119,3	119,3	136,7	—	—	17,9	193,3	—	24,6	12,2	—	18,4	13,8
(6)	0		134,1	110,8	116,0	122,6	—	—	13,8	167,1	59,1	14,6	10,4	—	—	11,0
	+	5-C	184,8	126,5	165,5	71,6 (146)	—	—	16,0	190,0	66,5	19,0	13,8	—	—	14,3
(7)	0		133,8	110,2	111,8	128,5	—	—	13,6	166,8	58,9	14,2	10,6	—	18,4	14,3
	+	5-C	185,0	127,3	164,4	76,3 (141)	—	—	16,1	187,8	65,0	18,9	13,9	—	23,4	9,1
(8)	0		125,9 (182)	120,9	131,9	129,6	—	—	—	—	—	8,6	9,5	177,6 (173)	—	—
	+	(C)=O	151,6 (190)	131,8	152,3	129,9	—	—	—	—	—	10,0	10,5	161,3 (185)	—	—
(9)	0		130,1	116,3	127,0	116,6	—	—	11,3	—	—	8,7	10,7	162,6	59,7	14,6
	+	5-C	164,5	135,5	162,0	74,5 (146)	—	—	13,8	—	—	9,2	13,4	191,1	66,1	16,6
(10)	0		133,8	116,3	128,4	119,0	—	32,8	11,7	—	—	9,1	10,3	162,5	59,7	14,6
	+	5-C	165,3	137,2	160,1	81,1†	—	37,3	14,9	—	—	11,0	13,9	189,4	69,8	16,7

*The $^1I^{13}C^1H$ constants are presented in the parentheses.
†The $^{13}C^1H$ constants were not measured.

On the basis of a study of the ^1H NMR and UV spectra and the ionization constants [4, 5] it was shown that protonation of 3- and 5-formyl- and acetylpyrroles in aqueous solutions of sulfuric acid takes place at the oxygen atom of the carbonyl group (structure I and II). Similar results were obtained in a study of the IR spectra of the salts of these compounds [8, 9]. The measurement of the ^{13}C NMR spectra of the protonated forms of formyl- and acetylpyrroles (1)-(5) and (8) confirmed structures I and II. A signal of the carbon atom of the protonated carbonyl group (δ = 175-200 ppm) and four signals of the C atoms of the pyrrole ring (δ = 105-165 ppm) are observed in the region characteristic for sp^2 C atoms. The assignment of the signals in the spectra of the OH conjugate acids (Table 1) was based on their multiplicity and a comparison of the spectra of the investigated compounds. The changes in the spectra on passing from the bases to the conjugate acids are similar to the changes observed in the case of O-protonation of enamino ketones RC(O)=CH-NR'R" to



I II

give cations of the R-C(OH)=CH-CH=$\overset{+}{N}$R'R" type [10]. The 3-C signal in the spectra of the conjugate acids of 3-formyl and acetylpyrroles [(1^+)-(5^+)] is shifted 0.5-3.0 ppm to strong field, while the signals of the remaining ring C atoms are shifted to weak fields relative to the corresponding signals in the spectra of the bases. On the basis of a correlation with the calculated parameters of the electronic structure it is shown that the changes in the CS of the five-membered heterocycles on passing from the neutral to the charged forms are due to changes in the electron densities and the bond orders [11]. Conformity between these parameters and the $^{13}C\Delta\delta$ values is also observed in the case of protonation and quaternization of enamino ketones [10, 12]. An examination of the effects of

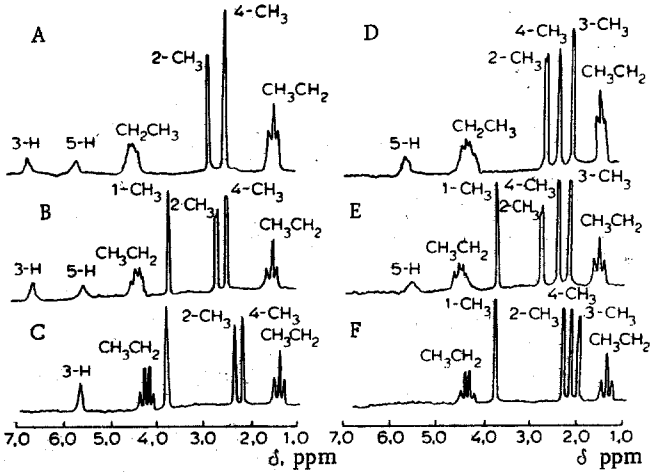
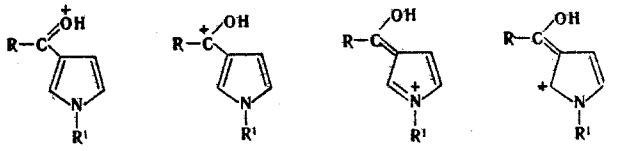


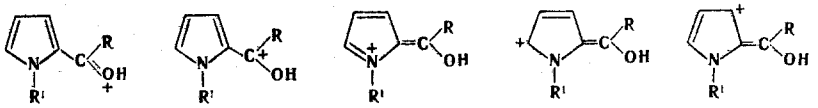
Fig. 1. ^{1}H NMR spectra of conjugate acids (in 31 N H_2SO_4) [2,4-dimethyl-5-carbethoxypyrrole (A) and 2,3,4-trimethyl-5-carbethoxypyrrole (D)], bases (in $CDCl_3$), and conjugate acids (in 18-22 N H_2SO_4) [1,2,4-trimethyl-5-carbethoxypyrrole (C, B) and 1,2,3,4-tetramethyl-5-carbethoxypyrrole (F, E)].

delocalization of the positive charge in the conjugate acids of the carbonyl derivatives of pyrrole (structures Ia-d and IIa-e) makes it possible to explain the relative changes in the



Ia Ib Ic Id

CS of the pyrrole ring and the carbonyl carbon in the case of protonation of the investigated compounds. Delocalization of the positive charge on 2-C is possible in the conjugate acids of 3-formyl- and acetylpyrroles, whereas 4-C and 5-C are less sensitive to this effect. In conformity with this, in the case of protonation of (1)-(5) the greatest deshielding effect is observed for 2-C ($\Delta\delta_2$ = 16-25 ppm), and the changes in the CS of 4-C and 5-C are substantially smaller ($\Delta\delta_4$ = 2-6 ppm; $\Delta\delta_5$ = 6-12 ppm). In the corresponding 5-derivatives the positive charge can be partially delocalized on 2-C and 4-C (IId, e). Protonation of 3,4-dimethyl-5-formylpyrrole (8) leads to a greater shift to weak field of the 2-C and 4-C signals ($\Delta\delta_2$ = 25.7 ppm; $\Delta\delta_4$ = 20.4 ppm) as compared with 3-C ($\Delta\delta_3$ = 10.9 ppm). A change in the order of the adjacent C=C and C-N bonds evidently has a substantial effect on the $\Delta\delta$ value of the ring C atom bonded to the carbonyl group.



IIa IIb IIc IId IIe

It may be assumed that localization of the charge on the carbonyl group (structures Ia, b and IIa, b) is associated with the effect of deshielding of the carbonyl carbon atom. The signal of the C^+ atom in hydroxy carbonium ions of the $R'R''C^+$-OH type (R' = N, R'' = CH_3, and R' = R'' = CH_3) is shifted to weak field (δ = 237.2 and 250.3 ppm) [13] relative to the signals of the carbonyl carbon atom in the spectra of acetaldehyde and acetone (200.5 and 204.1 ppm) [14]. Moreover, the shift of the signal of the C atom of the carbonyl group to strong field, as observed in the case of the O-protonation of enamino ketones [10], should correspond to charge delocalization in the ring and a decrease in the C=O bond order. The signal of the carbonyl carbon atom is shifted to strong field relative to the base in the spectrum of the conjugate acid of 3,4-dimethyl-5-formylpyrrole (8^+) ($\Delta\delta$ = −16.3 ppm). This is in agreement with the predominant contribution of structures that correspond to transfer of positive charge to the pyrrole ring (IIc, d). The relative contribution of such structures (Ic, d) is smaller in protonated 3-formyl- and acetylpyrroles, and consequently the effect of localization of the positive charge on the carbonyl group is greater than in the 5-derivatives. The differences in the changes in the CS of the carbonyl carbon atom aboserved in the case of protonation of (1)-(5) ($\Delta\delta$ = −10 to +6 ppm) as compared with (8) are probably associated with this. It should be noted that, as in the case of enamino ketones [10], in all of the investigated acetylpyrroles the signal of the methyl carbon atom of the CH_3CO groups is

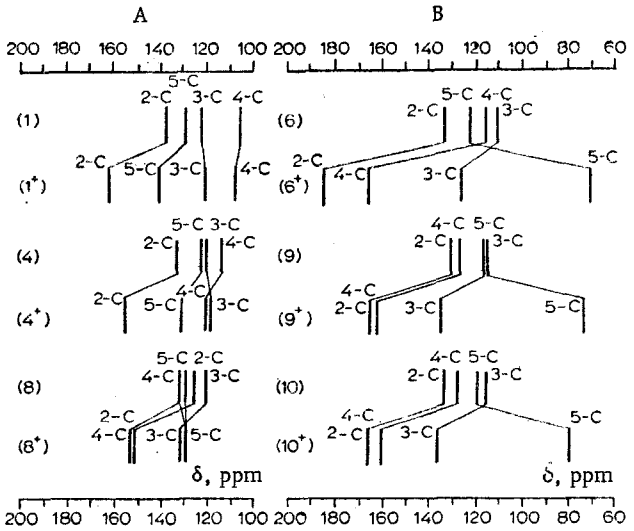
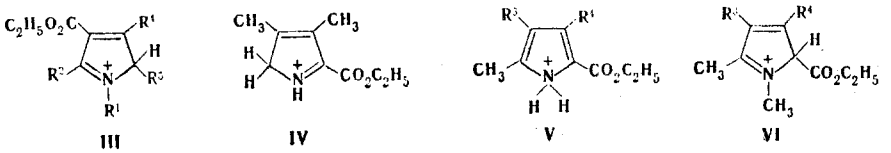


Fig. 2. Effect of protonation of the oxygen atom of the carbonyl group (A) and the 5-C atom (B) on the position of the signals of the pyrrole ring in the ^{13}C NMR spectra of formyl-, acetyl-, and carbethoxypyrroles.

shifted to strong field ($\Delta\delta$ = −3.8 to −6.3 ppm) on passing from the bases to the conjugate acids.

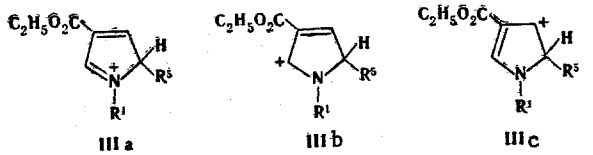
It was established by ^1H and UV spectroscopy that in aqueous solutions of sulfuric acid 3-carbethoxypyrroles are protonated at the ring 5-C atom (structure III). The protonation of 5-carbethoxypyrroles that are unsubstituted at the N atom under the same conditions proceeds through the formation of an intermediate form of the cation, which is converted after a few hours to the stable forms of the conjugate acids. The structures of the stable forms depend on the presence or absence of an alkyl substituent attached to 2-C. The stable form of the 3,4-dimethyl-5-carbethoxypyrrole cation has structure IV. N-Protonated form V is the stable form for 2-methyl derivatives of 5-carbethoxypyrroles. The formation of two structurally different conjugate acids IV and V proceeds through the same intermediate form.



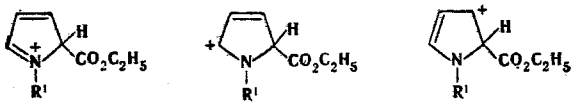
The studies of the ^1H NMR spectra conducted in the present research showed that a decrease in the rate of proton exchange as the H_2SO_4 concentration is increased to 28-35 N leads to a sharp decrease in the rate of conversion of the intermediate form to the stable forms of the conjugate acids. Under these conditions the spectra of the protonated 5-carbethoxypyrroles that are unsubstituted at the nitrogen atom proved to be similar to the spectra of the cations of the corresponding N-method derivatives (Fig. 1). Consequently, protonation of all of the examined 5-carbethoxypyrroles occurs initially at the same center. Moreover, in contrast to N-unsubstituted compounds, this form is stable for 1,2,4-trimethyl- and 1,2,3,4-tetramethyl-5-carbethoxypyrroles: When the H_2SO_4 concentration is reduced to 18 N, the appearance of signals corresponding to the formation of two protonated forms is not observed in the spectra of these compounds. A comparison of the spectra of 5-carbethoxypyrroles measured in 28-35 N H_2SO_4 with the previously described spectra of conjugate acids IV and V [3] makes it possible to exclude the 1-N, 2-C, 3-C, and 4-C atoms as possible centers of the addition of a proton under these conditions. In addition to this, the signal of the CH_3 group attached to 2-C is observed in the spectra of 2,3,4-trimethyl- and 1,2,3,4-tetramethyl-5-carbethoxypyrroles in the form of a doublet with an SSC constant of 2.4-3.0 Hz, which is close to the value of the homoallyl constant (3.3 Hz) in 5-C-protonated forms of alkylpyrroles [15]. These data and the results of a study of the UV spectra and ionization constants [3, 5] make it possible to assume that under conditions of slow proton exchange the protonation of 5-carbethoxypyrroles takes place at the 5-C atom bonded to the carbethoxy group (structure VI).

To prove structure VI we measured the ^{13}C NMR spectra of 3- and 5-carbethoxypyrroles (6), (7), (9), and (10) in 31 N H_2SO_4. A comparison of the spectra of the neutral and protonated forms of 3-formyl-, acetyl-, and carbethoxypyrroles (Table 1 and Fig. 2) showed that the formation of the OH and CH conjugate acids leads to substantially different changes in

the ^{13}C chemical shifts. In the case of protonation of 3-carbethoxypyrroles (6) and (7) at 5-C (structure III) the signal of the carbonyl carbon atom experiences a weak-field shift of 21-23 ppm. The 3-C, 3-C, and 4-C signals are also shifted significantly to weak field (δ = 126-185 ppm) relative to the spectra of the bases (δ = 110-134 ppm). It follows from an examination of the effects of delocalization of the positive charge in the conjugate acids (structures IIIa-c) that protonation of (6) and (7) should lead to greater deshielding of 2-C and 4-C as compared with 3-C. In conformity with this, the signals at weak fields at 184-185 and 164-166 ppm were assigned to 2-C and 4-C. The 5-C signal is shifted to strong field and appears at 70-80 ppm in the form of a doublet with $^1J^{13}C^1H$ = 141-146 Hz.



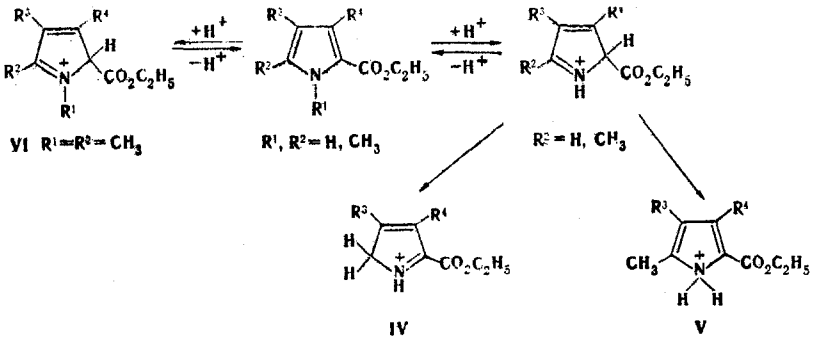
IIIa IIIb IIIc



VIa VIb VIc

Similar changes in the spectra are observed in the protonation of 5-carbethoxypyrroles (Table 1 and Fig. 2). In the spectrum of the conjugate acid of 2,3,4-trimethyl-5-carbethoxypyrrole (9) the signal of the carbonyl carbon atom (δ = 191.5 ppm) is shifted 28.5 ppm to weak field relative to the base. Three signals of the pyrrole ring (δ = 135-165 ppm) are observed in the region characteristic for the sp^2 carbon atoms. Since the effects of delocalization of the positive charge in the 5-C-protonated forms of 3- and 5-carbethoxypyrroles should be similar (structures IIIa-c and VIa-c), the assignment of the signals in the spectrum of (9^+) was made in analogy with the assignment for (6^+) and (7^+). A doublet with $^1J^{13}C^1H$ which should be assigned to 5-C, appears at strong field at 74.5 ppm. Similar changes in the spectrum on passing from the base to the conjugate acid are also observed for 1,2,3,4-tetramethyl-5-carbethoxypyrrole (10).

On the basis of these data and the results obtained during a study of the ^1H NMR and UV spectra [3] the protonation of 5-carbethoxypyrroles in aqueous solutions of sulfuric acid can be represented by the scheme



VI $R^1=R^2=CH_3$ $R^1, R^2=H, CH_3$ $R^2=H, CH_3$

IV V

Reversible addition of a proton to 5-C to give a stable form of conjugate acid VI is observed for N-methyl derivatives. The protonation of 5-carbethoxypyrroles that are unsubstituted at the nitrogen atom includes two steps: rapid reversible addition of a proton to 5-C and slow irreversible prototropic conversion of the unstable (for these compounds) form VI to stable forms of conjugate acids IV or V. The problem of the effect of structural factors on the relative stability of 5-CH-conjugate acids in the carbethoxypyrrole series can be examined on the basis of data on the ionization constants of these compounds [5] that are measured for the reversible steps of the protonation reaction and consequently characterize the basicity of 5-C. The ionization constants of 3-carbethoxypyrroles that form 5-CH acids lie in the pK_a range -2.1 to -3.5. The introduction of a $COOC_2H_5$ groups in the 5 position of the ring leads to a sharp decrease in the basicity of 5-C: The pK_a of 3,4-dimethyl-5-carbethoxypyrrole is -6.5. The basicity of 2-C should evidently increase simultaneously on passing from 2-methyl-3-carbethoxypyrroles to 3-methyl-5-carbethoxypyrroles. In the case of 3,4-dimethyl-

5-carbethoxypyrrole the 2-CH acid (IV) is therefore the stable form. The introduction of a CH_3 group in the 2 position lowers the basicity of 2-C by an order of magnitude and simultaneously increases the basicity of 5-C significantly. However, the ionization constants of 2,4-dimethyl- and 2,3,4-trimethyl-5-carbethoxypyrroles (pK_a = −4.7 and −3.6, respectively) still remain relatively low, and conversion of the 5-CH acids tothe more stable NH acids (V) is observed for these compounds. N-Methylation leads to a decrease in the basicity of the nitrogen atom and a further increase in the basicity of 5-C. The ionization constants of 1,2,4-trimethyl- and 1,2,3,4-tetramethyl-5-carbethoxypyrroles (pK_a = −3.1 and −1.6) become close to the average pK_a values for 3-carbethoxypyrroles that form thermodynamically stable forms of 5-CH acids. The effect of N-methylation on the basicity of 5-C in 5-carbethoxypyrroles is evidently due to a considerable extent to steric factors. An examination of molecular models showed that the bases and all of the theoretically possible forms of the conjugate acids of 1,2,4-trimethyl- and 1,2,3,4-tetramethyl-5-carbethoxypyrroles are more sterically hindered than the 5-CH acids.

EXPERIMENTAL

The ^{13}C NMR spectra of the investigated compounds were measured under pulse conditions with a Bruker Physik AG WP-60 spectrometer with an operating frequency with respect to ^{13}C of 15.08 MHz under conditions of total suppression of the spin–spin coupling with the protons. The method of switching off and switching on the radiating proton of the H_2 field, respectively, before and after collection of the data of the free induction signal (FIS), which gives the gain in sensitivity of compared with experiments with a switched-off H_2 field [16], was used in the measurement of the monoresonance spectra. The power of the FIS-exciting pulse was 50 W. The duration of the pulse varied from 0.5 to 5.5 μsec. The volume of the memory of the computer used for recording the FIS was 8000 bytes. The typical frequency range of the observations was 3750 Hz. The spectra of the neutral molecules were measured in $CDCl_3$ [the spectra of compounds (4) and (5) were measured in d_6-DMSO]. Stabilization of the resonance conditions was realized with respect to the ^2H signal of the solvent. The spectra of the protonated forms were measured in 31 N H_2SO_4, the resonance conditions were stabilized with respect to the ^2H signal, and the external standard was methanol (δ = 49.3 ppm). In addition to the spectra of compounds (1)-(10), we measured the spectra of the bases 2,4-dimethyl-5-formylpyrrole (11), 2,4-dimethyl-5-acetylpyrrole (12), 2,4-dimethyl-3-ethyl-5-acetylpyrrole (13), and 2,4-dimethyl-5-carbethoxypyrrole (14) in $CDCl_3$. The ^{13}C cehmical shifts of compound (11) were: 175.2 (C=O), 139.1 (2-C), 135.0 (4-C), 129.0 (5-C), 112.2 (3-C), 13.0 (2-CH_3), 10.6 (4-CH_3); compound (12): 186.6 (C=O), 135.2 (2-C), 129.1 (4-C), 129.1 (5-C), 112.7 (3-C), 27.9 (OCH_3), 14.4 (2-CH_3), 17.2 (4-CH_3); compound (13): 186.4 (C=O), 132.5 (2-C), 128.2 (4-C), 126.5 (5-C), 124.6 (3-C), 27.9 (OCH_3), 17.3, 15.4 (3-C_2H_5), 11.7 (2-CH_3), 11.1 (4-CH_3); compound (14): 162.2 (C=O), 133.0 (2-C), 128.8 (4-C), 117.2 (5-C), 111.2 (3-C), 59.8, 14.6 (OC_2H_5), 13.0 (2-CH_3), 13.0 (4-CH_3).

The ^1H NMR spectra of 1,2,4-trimethyl-5-carbethoxypyrrole (15) and 1,2,3,4-tetramethyl-5-carbethoxypyrrole (10) were measured in $CDCl_3$ and 18-35 N H_2SO_4 with a C-60 HL spectrometer. The internal standards were tetramethylsilane in $CDCl_3$ and 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) in H_2SO_4. The ^1H chemical shifts (δ, ppm) of compound (15) in $CDCl_3$ (15): $CDCl_3$ 5.70 (3-H), 3.70 (1-CH_3), 2.23 (2-CH_3), 2.12 (4-CH_3), 423, 1.29 (OCH_2CH_3); 18 N H_2SO_4: 6.70 (3-H), 5.50 (5-H), 3.67 (1-CH_3), 2.64 (2-CH_3), 2.37 (4-CH_3), 4.40, 1.36 (OCH_2CH_3); (10), $CDCl_3$: 3.70 (1-CH_3), 2.18 (2-CH_3), 2.08 (4-CH_3), 1.86 (3-CH_3), 4.23, 1.28 (OCH_2CH_3); 2.25 N H_2SO_4: 5.50 (5-H), 3.64 (1-CH_3), 2.58 (20CH_3), 2.24 (4-CH_3), 2.01 (3-CH_3), 4.37, 1.35 (OCH_2CH_3).

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NEW NUCLEOPHILIC SUBSTITUTION REACTIONS IN THE INDOLE SERIES*

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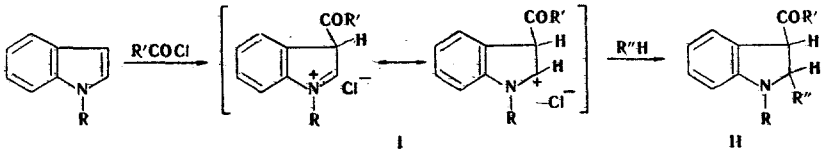
UDC 547.759.2

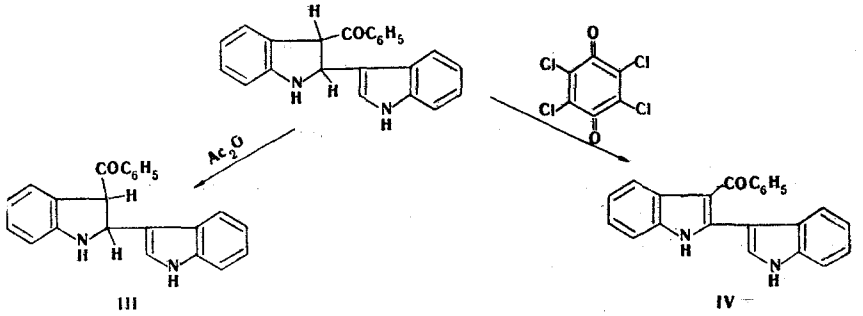
The direct incorporation of residues of π-surplus heterocycles, CH acids, and inorganic anions in the indole ring was accomplished by the reaction of indole with various nucleophilic organic compounds in the presence of acylating agents.

Indole is a π-surplus heterocycle [2] that readily undergoes various electropholic substitution reactions [3] but does not react with nucleophilic reagents. In the present paper we propose a method for the activation of indole in reactions with nucleophiles by converting it to the electrophilic 3-acylindoleninium cation by the action of acylating agents. It was found that indole reacts readily with various π-surplus heterocycles, CH acids, and other nucleophilic compounds in an inert solvent in the presence of acylating agents. In this case we assume the intermediate formation of 3-acylindoleninium cation I, which gives addition products II with various nucleophiles:



I II

The synthesized indolines II (when R = H) are readily acylated by, for example, refluxing in acetic anhydride to give 1-acetyl-3-acyl derivatives (III) and are dehydrogenated to the corresponding indoles IV by the action of chloranil or nitrobenzene; some of the resulting indoles (when R = H) have been described in the literature:



III IV

*See [1] for the preliminary communication.

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