

tion, washed with alcohol and water, and dried to give 0.05 g (40.6%) of VI with mp 355°C (from alcohol). Found: C 74.0; H 6.6; N 9.1%; M 308 (by mass spectrometry). $C_{19}H_{20}N_2O_2$. Calculated: C 74.0; H 6.5; N 9.1%; M 308.

trans-3a-Methyl-1,2,3,4,5,6,6a,8,9,9a-decahydro-7H-indeno[5,4-h][9H-pyrido[3,4-b]indole]-1,7-dione (VII). Workup of the filtrate yielded 0.042 g (32.6%) of a mixture, which, according to the PMR spectrum, contained 85% isomer VII and 15% isomer VI. Crystallization of the mixture from alcohol yielded VII with mp 325°C. Found: C 73.8; H 6.5; N 9.1%; M 308 (by mass spectrometry). $C_{19}H_{20}N_2O_2$. Calculated: C 74.0; H 6.5; N 9.1%; M 308.

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RESEARCH ON 1-AZA TWO-RING SYSTEMS

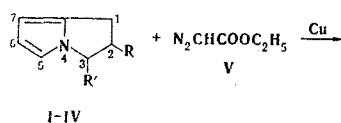
XVI.* SYNTHESIS OF 5-, 6-, AND 7-CARBETHOXYMETHYL-1,2-DIHYDROPYRROLIZINES AND METHOD FOR THE ISOLATION OF 5-CARBETHOXYMETHYL-1,2-DIHYDROPYRROLIZINES FROM MIXTURES WITH OTHER ISOMERS

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Mixtures of isomeric 5-, 6-, and 7-carbethoxymethyl-1,2-dihydropyrrolizines were obtained by reaction of 1,2-dihydropyrrolizines with ethyl diazoacetate. The effect of the position of the alkyl groups in the two-membered ring on the ratio of isomers in the reaction products is demonstrated. A method for the isolation of 5-carbethoxymethyl-1,2-dihydropyrrolizines from the mixtures of isomers based on the difference in their reactivities in diazo coupling is described. The preferred conformations of the two-membered rings in the 5-carbethoxymethyl-1,2-dihydropyrrolizines are judged from the PMR spectral data.

We have previously demonstrated that mixtures of compounds with a carbethoxymethyl group in the 5 and 7 positions are obtained as a result of the reaction of 1,2-dihydropyrrolizines with ethyl diazoacetate (in contrast to the analogous reaction of the simplest pyrroles, which leads to products of substitution of the α -carbon atoms [2]) [3]. In the present paper we describe the results of further studies of the products of the reaction of 1,2-dihydropyrrolizines (I-IV) with ethyl diazoacetate (V) and present new data on the preparation of 6-carbethoxymethyl-1,2-dihydropyrrolizines (XIV-XVII) in addition to 5- (VI-IX) and 7-carbethoxymethyl (X-XIII) derivatives:



* See [1] for communication XV.

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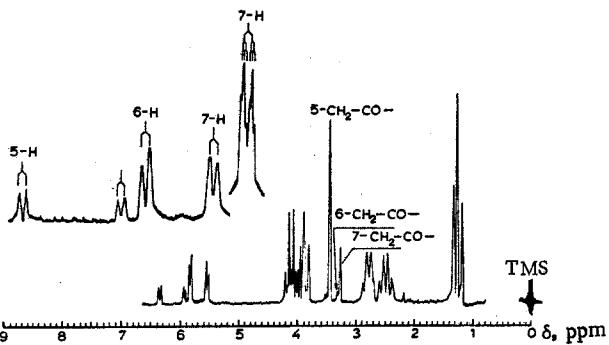
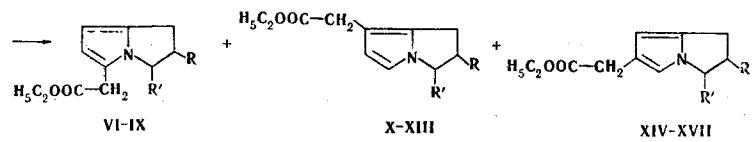


Fig. 1. PMR spectrum of a solution of the mixture including 72% VI, 25% X, and 3% XIV in CCl_4 .



I, VI, X, XIV $\text{R}=\text{R}'=\text{H}$; II, VII, XI, XV $\text{R}=\text{CH}_3$, $\text{R}'=\text{H}$; III, VIII, XII, XVI $\text{R}=\text{H}$, $\text{R}'=\text{CH}_3$; IV, IX, XIII, XVII $\text{R}=\text{C}_2\text{H}_5$, $\text{R}'=\text{H}$

The reaction was carried out with a copper catalyst [4]. In order to avoid the formation of a fumaric acid ester and to reduce the fraction of polysubstituted products, we carried out the process at a molar ratio of reagents I-IV and V of $\sim 2:1$. After removal of the starting 1,2-dihydropyrrolizines and heavy fractions, the results of elementary analysis of the three-component mixture [according to gas-liquid chromatography (GLC)] were in agreement with products of the addition of one carbethoxycarbene particle to one molecule of one or another 1,2-dihydropyrrolizine. Their structures were established by IR and NMR spectroscopy.

An examination of the IR spectra of the mixtures provides evidence for the presence of compounds of the pyrrole type that contain an ester group. The characteristic $\nu_{\text{C}-\text{H}}$ absorption of the pyrrole ring is observed at $3100-3125 \text{ cm}^{-1}$ [5, 6]. Retention of the dihydropyrrolizine structure in the transformation products is confirmed by the presence in the spectra of all of the mixtures of three bands of weak and medium intensity at $1500-1600 \text{ cm}^{-1}$, which are associated with the stretching vibrations of the pyrrole ring [6-8], and strong absorption at 1300 cm^{-1} , which is peculiar to N-alkyl-substituted pyrroles [6, 9]. Complex absorption consisting of two distinct and one unresolved peak is observed in the low-frequency region of the spectra of the investigated mixtures at $700-780 \text{ cm}^{-1}$. In analogy with simpler pyrrole compounds, these bands probably should be assigned to the out-of-plane deformation vibrations of the C-H bonds of the pyrrole ring [6]. The strong doublet of a carbonyl group centered at $1732-1740 \text{ cm}^{-1}$ and the characteristic $\nu_{\text{C}-\text{O}}$ absorption consisting of two bands (~ 1265 and 1040 cm^{-1}) constitute evidence for the presence of an ester group in the investigated compounds.

The PMR spectra of the investigated mixtures are of the same type in all four cases; the spectrum of the mixture of isomers VI, and X, and XIV is presented in Fig. 1 as an example. The assignment of the signals of the pyrrole protons was made in analogy with the assignment described for mixtures of isomeric 5- and 7-(β -hydroxyethyl)-1,2-dihydropyrrolizines [11] and 5-hydroxymethyl-1,2-dihydropyrrolizines [12]. It follows from the data from the analysis of the spectra (Table 1) that two compounds, the foundation of which is a dihydropyrrolizine system with a substituent in the 5 position of the pyrrole portion of the two-ring system in one case and in the 7 position in the other, predominate in the mixtures of the products of the reaction of 1,2-dihydropyrrolizines I-IV with reagent V. The singlets with chemical shifts of $3.34-3.40 \text{ ppm}$ were assigned to the CH_2-CO group of isomers VI-IX (the analogous methylene protons in the related monocyclic 1-methyl-2,5-dicarbethoxymethylpyrrole analog show up in the PMR spectrum as a singlet at 3.49 ppm [13]), whereas the signals with chemical shifts of $3.17-3.24 \text{ ppm}$ were assigned to the same group in X-XIII, since it is known that in the spectra of the isomeric methylpyrroles the signals of the substituents in the α position are located at weaker field than the signals of the substituents attached to the β -carbon atoms of the ring [14, 15].

In addition to the 5- and 7-carbethoxymethyl-1,2-dihydropyrrolizines, a third component of the mixtures is clearly observed in each case on the chromatograms. It was assumed that these three compounds are 6-carbethoxymethyl-1,2-dihydropyrrolizines (XIV-XVII). In conformity with their structures, one should have expected the appearance of another two multiplets in the PMR spectrum in the region of pyrrole protons and

TABLE 1. PMR Spectra of 5-, 6-, and 7-Carbethoxymethyl-1,2-dihydropyrrolizines (VI-XVII)*

Com- ound	δ , ppm †				$ J_{H,H} $, Hz ‡	
	5-H	6-H	7-H	$-\text{CH}_2-\text{CO}-$	6,7	5,6
VI	—	<i>5.81</i>	<i>5.52</i>	<i>3.40</i>	3.3	—
	—	<i>5.81</i>	<i>5.52</i>	<i>3.40</i>	3.4	—
VII	—	<i>5.78</i>	<i>5.49</i>	<i>3.38</i>	3.3	—
	—	<i>5.79</i>	<i>5.49</i>	<i>3.39</i>	3.3	—
VIII	—	<i>5.81</i>	<i>5.49</i>	<i>3.46</i>	3.3	—
	—	<i>5.72</i>	<i>5.44</i>	<i>3.39</i>	3.0	—
IX	—	<i>5.76</i>	<i>5.47</i>	<i>3.34</i>	3.3	—
X	<i>6.34</i>	<i>5.91</i>	—	3.24	—	2.7
XI	<i>6.30</i>	<i>5.89</i>	—	3.22	—	2.7
XII	<i>6.22</i>	<i>5.84</i>	—	3.17	—	2.4
XIII	<i>6.26</i>	<i>5.87</i>	—	3.20	—	2.7
XIV	—	—	—	3.29	—	—
XV	—	—	—	3.26	—	—
XVI	<i>6.28</i>	—	<i>5.50</i>	<i>3.25</i>	—	—
	—	—	—	3.21	—	—
XVII	—	—	—	3.24	—	—

* The values taken from the spectra of the individual compounds are given in italics. The remaining numerical values were obtained from the spectra of mixtures of the isomers.

† Chemical shifts of the identified signals of the other protons of the compounds (ppm): VI ($\text{O}-\text{CH}_2$ 4.04, 3- CH_2 3.82, 1- CH_2 2.73, 2- CH_2 2.43); VII ($\text{O}-\text{CH}_2$ 4.04, 3- H_A 3.98, 3- H_B 3.40, 1- CH_2 2.91, 2-CH 2.39); VIII ($\text{O}-\text{CH}_2$ 4.07, 3-H 4.35, 1- CH_2 ~2.7, 2- H_B 2.04); XVI ($\text{O}-\text{CH}_2$ 3.98). Here and subsequently, subscript A indicates a trans orientation of the proton and the methyl group, and subscript B indicates a cis orientation.

‡ Absolute values of the other spin-spin coupling constants of the protons of VI-VIII (Hz): VI ($^4J_{7-\text{H}, 1-\text{H}} = 0.9$); VII ($^4J_{7-\text{H}, 1-\text{H}} = 0.8$; $^2J_{3-\text{H}_A, 3-\text{H}_B} = 9.4$; $^3J_{3-\text{H}_A, 2-\text{H}_A} = 7.0$; $^3J_{3-\text{H}_B, 2-\text{H}_A} = 6.2$); VIII ($^4J_{7-\text{H}, 1-\text{H}} = 0.9$).

singlets of a CH_2-CO group at 3.2 ppm. However, the low percentage of this isomer in the investigated mixtures (3-12%, according to GLC data) makes it difficult to identify the signals of its pyrrole protons, whereas weak singlets of the CH_2-CO group of XIV-XVII are clearly seen and have chemical shifts ranging from 3.21 to 3.29 ppm.

We established the nature of the third component in the case of 3-methyl-6-carbethoxymethyl-1,2-dihydropyrrolizine (XVI), which was isolated by preparative GLC from the mixture with isomers VIII and XII. Broad signals at 6.28 and 5.50 ppm, which were assigned to the 5-H and 7-H protons, are observed in the PMR spectrum of XVI in the region of pyrrole protons. The expected AB quartet splitting with $^4J_{5-\text{H}, 7-\text{H}} \approx 1.1$ Hz [16] is not observed because of the fact that it is masked by the subsequent splitting due to the long-range spin-spin coupling of the 5-H proton with the 6- CH_2 group and of the 7-H proton with the 1- CH_2 group. An intense singlet of the CH_2-CO group is observed at 3.25 ppm (in the mixture of the three isomers its chemical shift is 3.21 ppm).

The physical constants of the mixtures of isomers, the results of analysis, and the yields based on the converted 1,2-dihydropyrrolizines are presented in Table 2. The yields based on ethyl diazoacetate are lower because of side transformations of the carbethoxycarbene.

An important characteristic of the transformation under consideration is the ratio of the 5-, 6-, and 7-carbethoxymethyl-1,2-dihydropyrrolizines. This ratio was determined for the crude reaction product, since a certain change in the isomeric composition because of the difference in the boiling points of the components of the mixture is inevitable in the mixtures of isomers obtained after distillation. The crude reaction products were analyzed by GLC (Table 3); the assignment of the peaks on the chromatograms was made by prior comparison of the data from GLC and the PMR spectra of the mixtures of isomers, from which all of the accompanying impurities were removed. The isomers emerged in the following order in all cases on the stationary phase (polyethylene glycol 20,000): 5-, 7-, and 6-carbethoxymethyl-1,2-dihydropyrrolizines. According to the data in Table 3, considerable similarity is observed in the isomeric composition of the products of the reaction of I,

TABLE 2. 5-, 6-, and 7-Carbethoxymethyl-1,2-dihydropyrrolizines (VI-XVII)

Compound or mixture (component %)	bp, °C (1 mm) *	d_{4}^{20}	n_D^{20}	MR_D		Found, %			Empirical formula	Calc., %			Yield, %
				found	calc.	C	H	N		C	H	N	
VI (72), X (25), XIV (3)	113—118	1,0840	1,5103	53,34	53,26	68,8	7,9	7,7	$C_{11}H_{15}NO_2$	68,4	7,8	7,2	44
VI	100,5—103	1,0858	1,5090	53,14	53,26	68,0	8,0	7,6	$C_{11}H_{15}NO_2$	68,4	7,8	7,2	33
VII (65), XI (27), XV (8)	107—109	1,0524	1,4982	57,75	57,88	69,3	8,3	6,9	$C_{12}H_{17}NO_2$	69,5	8,3	6,8	36
VII	104—106	1,0557	1,5009	57,84	57,88	69,2	8,2	7,0	$C_{12}H_{17}NO_2$	69,5	8,3	6,8	45
VIII (52), XII (36), XVI (12)	116—120	1,0570	1,5030	57,96	57,88	69,1	8,4	7,1	$C_{12}H_{17}NO_2$	69,5	8,3	6,8	46
VIII	128,5—129	1,0633	1,5033	57,66	57,88	69,4	8,7	6,9	$C_{12}H_{17}NO_2$	69,5	8,3	6,8	52
IX (67), XIII (28), XVII (5)	119—126	1,0389	1,4960	62,22	62,45	70,8	8,9	6,5	$C_{13}H_{19}NO_2$	70,6	8,7	6,3	38

* In the case of VIII the figure given is the boiling point at 3.5 mm.

TABLE 3. Distribution of the Isomers with the Carbethoxymethyl Group in Various Positions in the Products of the Reaction of 1,2-Dihydropyrrolizines and Ethyl Diazoacetate

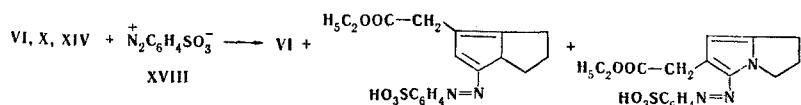
Starting compound	Percentage of positional isomer		
	5	6	7
I	59	8	33
II	62	7	31
IV	63	9	28
III	49	9	42

II, and IV with ethyl diazoacetate. This observation can be explained by the fact that the alkyl groups in the 2 position have too weak an effect on the order of substitution because of their considerable remoteness from the reaction centers. The fraction of the isomer with a carbethoxymethyl group in the 5 position is substantially lower in the mixture obtained as a result of the reaction of III and V than in the preceding cases. In analogy with the known influence of the steric effects of alkyl groups on the course of the reactions of aromatic systems with carbethoxycarbene [17], we suppose that the result of the reaction of III with V is due to partial shielding of the 5 position of the two-ring system by the $3-CH_3$ group.

The character of the quantitative distribution of the isomers in the products of transformation of 1,2-dihydropyrrolizines I, II, and V is evidently dependent on the electron densities in the 5, 6, and 7 positions. The 5 position in 1,2-dihydropyrrolizines, which corresponds to the 2 position in pyrroles, has a higher electron density than the 6 and 7 positions. The preferableness of the formation of 7-carbethoxy-1,2-dihydropyrrolizines as compared with the corresponding 6 isomers is in all likelihood due to the electronic effect of the $1-CH_2$ group.

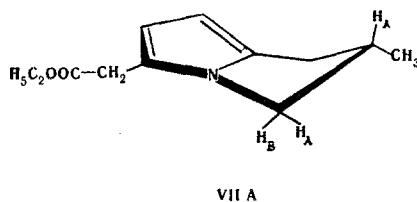
Separation of the 5-, 6-, and 7-carbethoxymethyl-1,2-dihydropyrrolizines by fractional distillation was found to be inefficient because of the closeness of their boiling points. During a search for a method for the isolation of the 5-carbethoxymethyl-1,2-dihydropyrrolizines from their mixtures with other isomers we proceeded from the possibility of separation of the α - and β -substituted pyrroles on the basis of the different reactivities of the α and β positions of the pyrroles in diazo coupling [18] and data [19, 20] on the reaction of

compounds of the pyrrole series with various diazonium salts. The use of azobenzenesulfonic acid (XVIII) as the azo component provided the desired result during treatment of the mixtures of isomers. The essential points of the method are illustrated in the case of the reaction of the mixture of isomeric VI, X, and XIV with XVIII:



In the experiments on the diazo coupling 1.6-2.5 moles of p-aminobenzenesulfonic acid, converted to XVIII, were used per mole (overall) of 6- and 7-carbethoxymethyl-1,2-dihydropyrrolizines. Under the conditions that we selected, ion XVIII first attacks the free 5 position of the dihydropyrrolizine system, and the 6 and 7 positions are involved to a lesser extent; this ensures the acceptable yields (33-55%) of VI-VIII. The purity of the isolated VI-VIII was monitored by GLC and NMR spectroscopy. Their physical constants are summarized in Table 2.

An examination of the PMR spectra of VI and VII makes it possible to obtain data on the splitting of the signals of the protons attached to C_2 to C_3 . The spectrum of VI indicates magnetic equivalence of the protons within the 1-, 2-, and 3- CH_2 groups. The primary conformation of the two-ring system of VII was determined on the basis of a comparison of the experimentally found vicinal spin-spin coupling constants in the 3- CH_3 -2- CH fragment (see the note to Table 1) with the values calculated for the three conformations - the planar conformation ($J_1 = 8-12$ Hz, $J_2 = 2.7-4.1$ Hz), and envelope conformations with a pseudoequatorial ($J_1 = 5.1-9.0$ Hz, $J_2 = 8.9-14.3$ Hz) and a pseudoaxial ($J_1 = 5.8-10.7$ Hz, $J_2 = 0-1.6$ Hz) 2- CH_3 group. The constants were estimated as in [21] for the various possible values of the coefficients in the Karplus equations and the dihedral angles measured for models. The values obtained from the spectra lie within the limits of the calculated values only for the VIIA conformation with a pseudoequatorial methyl group.



In the PMR spectrum of VIII the 3- H_A signal with a chemical shift of 4.35 ppm has the form of an indistinctly resolved multiplet, from which it is difficult to extract the spin-spin coupling constants. However, in analogy with 3-methyl-5-hydroxymethyl-1,2-dihydropyrrolizine [12], it can be assumed that the $\text{C}_1\text{C}_2\text{C}_3\text{N}_8$ ring has an envelope conformation, whereas the 3- CH_3 group occupies a pseudoaxial position. The multiplet centered at 2.69 ppm, the intensity of which corresponds to three protons, is the superimposition of the signals of the protons of the 1- CH_2 group and the 2- H_A proton, which lies in the deshielding region of the C_3-CH_3 bond and is found at lower field than the signal of the 2- H_B proton, which forms a multiplet with a chemical shift of 2.04 ppm and, as can be seen in the case of models, is located in the zone of shielding of the same bond.

The chemical shifts and the spin-spin coupling constants of the protons of VI-VIII are presented in Table 1 and in the notes to it.

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EXPERIMENTAL

The IR spectra of thin layers of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of CCl_4 solutions of the compounds (~25% by volume) were recorded with Varian HA-100D (100 MHz) and RS-60 (60 MHz) spectrometers with tetramethylsilane (TMS) and hexamethyldisiloxane as the internal standards. The chemical shifts are presented relative to TMS on the δ scale.

The chromatographic analysis of the mixtures of isomeric 5-, 6-, and 7-carbethoxymethyl-1,2-dihydropyrrolizines and of individual VI-VIII was accomplished with an LKhM-8M chromatograph with a thermal-conductivity detector. The column (2.9 m long with an inner diameter of 3 mm) was filled with 8% polyethylene glycol 20,000 on Sferokhrom-1 (0.30-0.35 mm); the thermostat temperatures were 190, 185, and 179°C at the corresponding carrier-gas (hydrogen) flow rates of 33, 46, and 54 ml/min. The 6-carbethoxymethyl-1,2-dihy-

dropyrrolizines, which had the highest retention times in the series of isomers, were satisfactorily separated from the 5 and 7 isomers, but the separation of the latter was incomplete. Various methods for the calculation of the chromatograms [22] were checked with standard mixtures, the compositions of which were established from the PMR spectral data. The best results were obtained by calculation with the first method described in [22] (the half-width of the peak was measured at 0.607 of the height), which we used to calculate the ratios of the isomers in the untreated reaction products.

Preliminary isolation of XVI was accomplished with a model 105 Pye chromatograph. A glass column (2.1 m by 4 mm) filled with 10% polyethylene glycol adipate on Chromosorb W_{aw} (100-120 mesh) was used. The column temperature was 185°C, and the carrier-gas (nitrogen) flow rate was 120 ml/min. A 1.4-g sample of a mixture of 93% (VIII+XII) and 7% XVI was introduced into the column in 5-10- μ l portions; 0.08 g of XVI was obtained.

5- (VI), 7- (X), and 6-Carbethoxymethyl-1,2-dihdropyrrolizine (XIV). A 40.2-g (0.38 mole) sample of 1,2-dihdropyrrolizine I was stirred with 2 g of finely ground copper bronze [4] in a 250-ml three-necked flask equipped with a dropping funnel, a stirrer, and a gas-inlet tube. The air was displaced from the flask with nitrogen, and the mixture was heated on a boiling-water bath as 19.5 g (0.17 mole) of freshly prepared ester V [23] was added in the course of 1 h. After the addition was complete, the mixture was heated with stirring for another 30 min, after which it was cooled and filtered to remove the catalyst. The filtrate was then allowed to stand for 12-14 h, after which it was subjected to fractional distillation to give 26.2 g of unchanged I and 11.1 g of a mixture of VI (72%), X (25%), and XIV (3%) (according to GLC data).

A similar procedure was used to obtain mixtures of isomeric (VII, XI, XV) VIII, XII, XIV and IX, XIII, XVII, the properties of which are presented in Table 2.

Isolation of 5-Carbethoxymethyl-1,2-dihdropyrrolizine (VI) from the Mixture with Isomers X and XIV. A 4.34-g sample of a mixture of isomers VI (72%), X (25%), and XIV (3%) was added with constant stirring at 10°C to an aqueous suspension of azobenzenesulfonic acid (XVIII), obtained by the usual method from 2.6 g (0.015 mole) of sulfanilic acid. At the end of the addition of the isomers, the mixture was stirred at 10°C for 10 min and at room temperature for another 20 min. The reaction product was extracted with five 15-20-ml portions of ether, and the extracts were washed twice with 5% aqueous potassium carbonate solution and water until the aqueous layer became colorless. The experiment was repeated seven times. The combined ether extracts were dried over calcium chloride and subjected to distillation to give 7.2 g (33% based on isomer VI present in the mixture of isomers) of VI.

A similar procedure was used to obtain VII and VIII. The properties of VI-VIII are presented in Table 2.

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POLAROGRAPHIC REDUCTION OF

2-(4-PYRIDYL)INDANE-1,3-DIONES IN DIMETHYLFORMAMIDE

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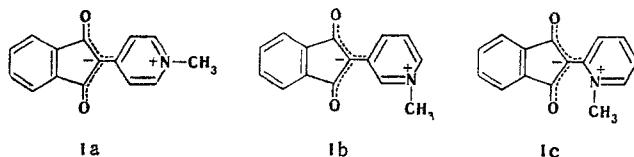
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The trend of the electrical reduction of isomeric 2-(4-pyridyl)indane-1,3-diones in dimethylformamide (DMF) was studied by classical and ac polarography, millicoulometry, ESR spectroscopy, and cyclical voltamperometry with a steady-state mercury electrode. The first reversible one-electron step leads to the formation of relatively stable anion radicals, which can be recorded by means of ESR spectroscopy. The corresponding dimers are detected in the course of prolonged electrolysis at a constant potential (at the level of the limiting current of the first wave). The second nonreversible step in the electrical reduction involves the indane-1,3-dionyl grouping and the pyridinium ring. Owing to their dipolar structure, the investigated compounds are reduced with considerably greater difficulty (by 400–550 mV) than the unsubstituted N-methylpyridinium salt.

The set of chemical transformations in the reduction of 2-(4-pyridyl)indane-1,3-diones (which are usually called pyrophthalones) has not yet been ascertained [1], despite the fact that the reduction products could have diversified biological activity.

Pyrophthalones are also of interest in the respect that their molecules contain two potentially electrically active fragments – the pyridinium ring and the indane-1,3-dionyl grouping,* which can undergo reduction either separately or as a unified conjugated system. In view of the above, within the framework of our systematic research on the reduction of substituted pyridinium salts [3, 4], we also studied the mechanism of the electrical reduction of pyrophthalone derivatives in order to find their quantitative characteristics – the reduction potentials for the primary electrical reduction steps.

In the present research we obtained the electrochemical characteristics of Ia-d in nonaqueous media (Table 1) by means of classical and ac polarography, millicoulometry, ESR spectroscopy, and cyclical voltamperometry with a steady-state mercury electrode. The quaternized compounds were selected to avoid the formation of catalytic hydrogen waves and the effects of intra- or intermolecular protonation during electrical reduction.



* This grouping is more accurately called an indane-1,3-dionide grouping, since it may be assumed that pyrophthalones exist in the form of betaine structures [2].