by vacuum distillation, and the residue was washed thoroughly with water, dried, and recrystallized from aqueous alcohol.

Data on the 3-acylindole oximes were presented in Table 1.

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INVESTIGATION OF THE THREE-DIMENSIONAL STRUCTURES OF A NUMBER OF N-SUBSTITUTED DERIVATIVES OF 4-DECAHYDROQUINOLONE BY MEANS OF ^{13}C NMR SPECTROSCOPY

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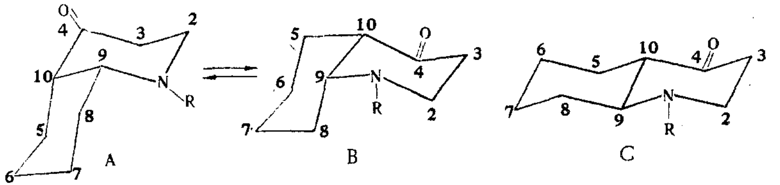
The three-dimensional structures and conformational compositions of a number of N-substituted 4-decahydroquinolones, particularly the 1-(S)-α-phenylethyl-4-decahydroquinolone isomer that is primarily formed in the asymmetric hydride reduction of 1-(S)-α-phenylethyl-$\Delta^{9,10}$-octahydro-4-quinolone and was previously assigned to the trans series on the basis of chiral-optical properties, were investigated by ^{13}C NMR spectroscopy. It is shown by means of NMR data that this compound belongs to the cis series. The lines in the ^{13}C-{^{1}H} NMR spectra of a number of 4-decahydroquinolones were assigned by means of an additive scheme for the ^{13}C chemical shifts, and criteria of the type of fusion of the two rings in the investigated class of heterocyclic compounds were established.

It has been previously shown [1] that in the asymmetric reduction of 1-(S)-α-phenylethyl-$\Delta^{9,10}$-octahydro-4-quinolone with lithium aluminum hydride, of the four possible diastereomers, only trans-1-(S)-α-phenylethyl-(9S,10S)-decahydro-4-quinolone, the assignment of which to the trans series and the determination of the absolute configuration of which were accomplished on the basis of a comparison of the circular dichroism data with the data for trans-1-decalone with a known configuration, is primarily formed. Since the trans isomer is converted to a mixture of cis and trans isomers I and II (the old numbering on the basis of chiral-optical data [1]) during isolation on the sorbents as a result of enolization, the individual isomers were obtained through the picrates in a ratio of 1:3.



II

I, III, IV

I-II $R=CH(CH_3)C_6H_5$; III $R=H$; IV $R=CH_3$

In the present research to obtain an independent verification of the previously made assignment [1] we used ^{13}C NMR spectroscopy, which is an effective method for the establish-

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ment of the structures of organic compounds and, in particular, a method for the determination of the type of fusion of two-ring systems (for example, see review [2]).

The assignment of the signals was of decisive significance for the establishment of the type of isomerism of I and II when the $^{13}C-\{^1H\}$ spectra were used, and we will therefore dwell on this problem in detail.

The assignment of the lines in the $^{13}C-\{^1H\}$ NMR spectra was made by means of a complex of well-known methods [3], including the use of the off-resonance spectra, the ^{13}C NMR spectra with selective proton decoupling, and the $^{13}C-\{^1H\}$ NMR spectra of the deuterated analogs of I and II [4]. In addition, we used various literature sources (see the papers by Eliel and Vierhapper [5, 6] on cis- and trans-decahydroquinolines).

A preliminary analysis of the $^{13}C-\{^1H\}$ NMR spectra of I and II made it possible to isolate groups of signals related to carbonyl carbon atoms (at 210 ppm), aromatic carbon atoms (at 129-150 ppm), and saturated carbon atoms (at 0-70 ppm). The signals of the nodal $C_{(9)}$ and $C_{(10)}$ atoms and the methylidyne carbon atom of the phenylethyl group, the methylene $C_{(2)}$, $C_{(3)}$, and $C_{(5)}-C_{(8)}$ atoms, and, finally, the carbon atom of the methyl group (at 8.5 ppm for isomer I and at 19.7 ppm for isomer II) were isolated by means of the off-resonance spectra. On the basis of the data from the ^{13}C NMR spectra with selective decoupling of the methylidyne proton in the phenylethyl group we were able to establish the position of the signals of the corresponding methylidyne carbon atoms (at 52.9 ppm for I and at 58.7 ppm for II).

In addition, on the basis of the literature data [5-7] we were able to assign the weakest-field signals (in the group of signals belonging to the methylene carbon atoms) to the signals of the $C_{(2)}$ and $C_{(3)}$ atoms (at 45.1 and 42.0 ppm in the spectrum of I and at 44.6 and 40.4 ppm in the spectrum of II, respectively).

The greatest difficulties were encountered in the assignment of the signals of the $C_{(5)}-C_{(8)}$ atoms, which are found at 24-31 ppm in the spectra of both isomers. To solve this problem we used the $^{13}C-\{^1H\}$ NMR spectra of deuterated (in the 8 position) analogs of I and II. Since the 8-d_2-substituted compounds were the principal isotopomers in the deuterated analogs, a comparison of the spectra of the deuterated and nondeuterated compounds made it possible to unambiguously establish the position of the signals of the $C_{(8)}$ atoms (at 31.2 ppm in the spectrum of I and at 25.2 ppm in the spectrum of isomer II) (from the isotopic shift of ∿0.8 ppm and from the character of the splittings from the constant of the $^{13}C-^2H$ spin–spin coupling) and the $C_{(7)}$ atoms (from the magnitude of the isotope shift, which is 0.2 ppm) (at 23.9 ppm in the spectrum of isomer I and at 22.8 ppm in the spectrum of isomer II). The signals at 24.9 ppm in the spectrum of isomer I and at 24.3 and 24.7 ppm in the spectrum of II, which correspond to pairs of carbon atoms, should consequently be assigned to the $C_{(5)}$ and $C_{(6)}$ pairs.

Thus the spectra can be interpreted almost completely; however, the structures of the isomers are not established in the process. The solution of this problem requires the use of model compounds that have a predesignated configuration.

It should be stated that recourse to the literature data on trans- and cis-fused decahydroquinolines [5-7] does not make it possible to solve the problem directly, since these models do not include a phenylethyl substituent, and, in addition, allowance for the effect of the carbonyl group is required.

In order to partially overcome these difficulties we investigated simpler models, viz., 4-decahydroquinolone (III) and N-methyl-4-decahydroquinolone (IV), which, according to the literature data, exist only in the form of trans isomers [8, 9].

Eliel and Vierhapper [5, 6] have investigated the ^{13}C spectra of cis- and trans-decahydroquinolines and the corresponding N-methyl-substituted derivatives, and thus the problem of the establishment of the type of isomerism of III and IV reduces to allowance for the effect of the carbonyl group.

The increments of the C=O group can be calculated on the basis of data on the ^{13}C chemical shifts in the spectra of trans- and cis-decalins and the corresponding trans- and cis-1-decalones. These increments have been obtained for the trans isomers [10] on the basis of data on the ^{13}C chemical shifts in the spectra of trans-decalin [11] and trans-1-decalone. As regards the cis isomers, unfortunately, we were unable to find data for cis-1-decalone. To calculate the increments of the C=O groups in the cis structures we therefore used the

TABLE 1. Increment of the C=O Group in trans- and cis-1-Decalones[a]

Carbon atom	Increments for the structure, ppm		
	cis-A	cis-B	trans-C
1	−2,2	−2,7	−1,6
2	−1,7	−1,7	(−1,7)
3	14,9	14,0	14,5
5	−1,5	−8,2	−8,1
6	−2,6	−0,5	(−1,3)
7	−1,2	−1,2	(−2,0)
8	−3,5	2,2	−0,3
9	3,2	5,7	1,0
10	17,4	12,3	11,0

[a] According to the data in [10-12]; in the opinion of Grover and Stothers [10], the assignments presented in parentheses are ambiguous.

TABLE 2. ^{13}C Chemical Shifts of III and Calculated ^{13}C Chemical Shifts for the IIIA, IIIB, and IIIC Forms[a]

Carbon atom	^{13}C chemical shifts, ppm			
	III,[b,c] exptl.	IIIA, calc.	IIIB, calc.	IIIC, calc.
2	46,9	46,0	38,0	45,6
3	43,4	36,1	—[d]	41,8
5	25,2	23,7	23,5	24,5
6	25,5	23,5	—[d]	25,0
7	24,1	19,1	—[d]	23,6
8	34,4	29,2	—[d]	33,7
9	63,1	58,0	59,6	63,1
10	57,2	52,2	47,9	54,3

[a] See the text for the calculation of the ^{13}C chemical shifts. [b] Data from the off-resonance spectra and data from calculations of the ^{13}C chemical shifts via an additive scheme were used in the assignment. [c] In solution in C_6D_6. [d] Signals were not observed (see [6]).

data of Blunt and co-workers [12] for cis-9-methyl-4-decalone as compared with the data of Dalling and Grant [11] for cis-9-methyldecalin.

Let us also note that whereas the trans structures are conformationally homogeneous (see structure C below), two conformers [structures A and B, which differ with respect to the orientation of, for example, the $C_{(10)}$—$C_{(5)}$ bonds relative to the piperidone (or cyclohexane) ring can exist, in principle, in the case of cis isomers.*

Thus data from the low-temperature ^{13}C NMR spectra, which ensure recording of the spectra of the individual conformers, must be used to calculate the increments of the C=O group. Precisely these low-temperature spectra were used in the calculation of the increments presented in Table 1.

An examination of the data in Table 1 shows that the character of the effect of the C=O groups on the chemical shifts of the $C_{(5)}$ atom depends substantially on the type of conformation. The shielding in cis-conformer B and trans-isomer C reaches 8 ppm, and this effect can be used in stereochemical investigations. Let us also note that the carbonyl group has a rather strong effect on the position of the signals of the $C_{(3)}$, $C_{(8)}$, $C_{(9)}$, and $C_{(10)}$ atoms.

To calculate the ^{13}C chemical shifts in the possible structures of III (cis-IIIA, cis-IIIB, and trans-IIIC) we used an additive approach; the increments of the C=O group presented in Table 1 were added to the ^{13}C chemical shifts of the conformers of cis-decahydroquinoline [6] and trans-decahydroquinoline [5]. The ^{13}C chemical shifts obtained are presented in Table 2, in which the experimental values of the ^{13}C chemical shifts are also given. Let us note that the assignment of the signals of the experimental spectrum can be made on the basis of the calculated data.

Unfortunately, Eliel and Vierhapper [6] were unable to identify a number of signals (see Table 2). A comparison can therefore be made only for some of the signals of conformers IIIB; however, even from the remaining signals it can be seen that III cannot be conformer IIIB. cis Conformer IIIA also does not satisfy the experimental data, since pronounced deviations (up to 7 ppm) for some of the atoms [for example, for $C_{(3)}$, $C_{(8)}$, $C_{(9)}$, and $C_{(10)}$] are observed in this case. Let us also note that III cannot be a mixture of conformers IIIA and IIIB, since the experimental values (Table 2) are beyond the range of the calculated values [for example, for the $C_{(9)}$ and $C_{(10)}$ atoms].

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*Disregarding the possible invertomers about the nitrogen atoms for the N-heterocyclic compounds.

TABLE 3. ^{13}C Chemical Shifts of N-Methyl-4-decahydroquinolone (IV) and Calculated Data for Structures IVA, IVB, and IVC[a]

Carbon atom	Chemical shifts, ppm			
	IV,[b,c] exptl.	IVA, calc.	IVB, calc.	IVC, calc.
2	56,8	56,7	45,8	56,6
3	40,7	35,7	39,4	40,6
5	25,0	24,9	23,5	25,3
6	25,0	23,5	20.4	25,2
7	24,3	18,5	—d	24,3
8	31,9	25,9	17,8	30,5
9	68,4	66,6	66,4	70,5
10	53,6	53,9	48,4	53,1

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[a] See the text for the calculation of the chemical shifts. [b] The assignment was made by means of the off-resonance spectra and the data from the current calculations. [c] In solution in C_6D_6. [d] A signal was not observed (see [6]).

TABLE 4. Increments of the N-Methyl Group in trans-N-Methyl-4-decahydroquinolone (IV) and trans-N-Methyldecahydroquinoline

Carbon atom	Increments, ppm		
	trans-N-methyldecahydroquinoline		IV N—CH$_{obs}$
	N—CH$_3$ (ax)[a]	N—CH$_3$ (eq)[a]	
2	8,6	10,8	9,9
3	−7,5	−1,5	−2,7
5	0,9	0,3	−0,2
6	—b	−0,3	−0,5
7	—b	0,1	0,2
8	−3,3	−1,6	−2,5
9	−3,0	7,4	5,3
10	−10,8	−1,4	−3,6

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[a] From [5]. [b] No data available.

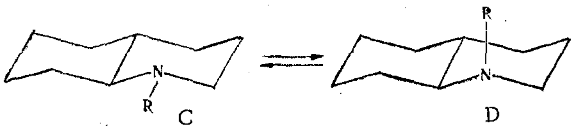
At the same time, the hypothesis of the trans structure of III should be considered to be satisfactory. Let us note, however, the existence of deviations for the $C_{(3)}$ and $C_{(10)}$ atoms, which are probably due to N invertomers of the decahydroquinolines that have axially oriented N—H bonds.

Thus it can be taken for granted that III is the trans isomer.

A similar study was made for N-methyl-4-decahydroquinolone (IV), in which the ^{13}C chemical shifts in the spectra of the conformers of cis-N-methyldecahydroquinoline [6] and trans-N-methyldecahydroquinoline [5] were used as the starting values in the additive calculations. The results of an analysis of the ^{13}C NMR spectrum and data from the calculations are presented in Table 3.

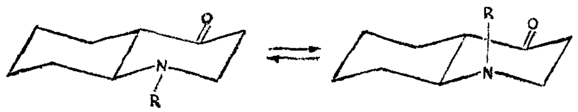
The cis structure of IV is not confirmed by the experiments [the deviations reach 6 ppm for the $C_{(7)}$ and $C_{(8)}$ atoms in isomer IVA and more than 10 ppm for $C_{(2)}$ and $C_{(8)}$ in isomer IVB]. The hypothesis of the trans structure of IV is satisfied to a better extent. The only significant deviation is observed for the $C_{(9)}$ atom.

Let us note that the analysis presented above proceeded from the assumption of homogeneity of the conformational composition in the process of inversion of the nitrogen atom. In other words, it was assumed that on passing from the reversible C ⇄ D process



C D

to the E ⇄ F process



E F

a significant shift of the equilibrium constant does not occur. In order to verify the correctness of this assumption we compared the increments of the methyl group obtained by simple subtraction of the ^{13}C chemical shifts of III and IV with the increments of the N—CH$_3$ (ax) and N—CH$_3$ (eq) groups, which were calculated by Eliel and Vierhapper [5] (see Table 4).

First of all, it should be stated that it follows from the data in [5] that only certain pairs of carbon atoms can be used as indicators of the conformational state at the ni-

TABLE 5. ^{13}C Chemical Shifts of I and II

Carbon atom	^{13}C chemical shifts, ppm	
	I^{a,b}	II^{a,b}
2	45,1	44,6
3	42,0	40,4
5	24,9	24,7
6	24,9	24,3
7	23,9	22,8
8	31,2	25,2
9	63,7	58,8
10	55,5	50,4

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[a] The assignment of the signals was made by means of off resonance, the ^{13}C isotope shift method, and the results of the calculations in this paper. [b] In solution in $CDCl_3$.

TABLE 6. Increments for the N-Phenylethyl Group,[a] ^{13}C Chemical Shifts of II, and Calculated ^{13}C Chemical Shifts of Conformations IIA and IIB (ppm)

Carbon atom	Increments, Δi	II, exptl.	IIA,[b] calc.	IIB,[b] calc.
2	−11,7	44,6	45,0	34,1
3	1,3	40,4	37,0	40,7
5	−0,1	24,7	24,8	23,4
6	−0,1	24,3	23,4	20.3
7	0,6	22,8	19,1	—[c]
8	−0,7	25,2	25,2	17,1
9	−4,7	58,8	61,9	61,7
10	1,9	50,4	55,8	50,3

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[a] Obtained from the data on the trans derivatives: $\Delta i = \delta_{IV} - \delta_{I}$. [b] Calculated by means of data for cis-N-methyldecahydroquinoline with allowance for the increments of the carbonyl group (Table 1) and the N-phenylethyl group. [c] No signal was observed (see [6]).

trogen atom [this pertains to the $C_{(3)}$, $C_{(9)}$, and $C_{(10)}$ atoms]. Using the increments for the chemical shifts for these atoms as the basis increments one can estimate the fraction of the axial conformation of the methyl group in N-methyl-4-decahydroquinolone (IV). It follows from the data in Table 4 that the fraction of axial conformation F (see above) may amount to 0.2-0.4. Thus, in fact, the certain infringement of the operation of the additive scheme in the examined compounds may be due to axially oriented substituents attached to the nitrogen atom. After establishing the structures of III and IV we again turned to an analysis of the ^{13}C NMR spectra of I and II; the type of isomer was identified by comparison of the ^{13}C chemical shifts in the spectra of I and II with the calculated ^{13}C chemical shifts for the IIIA, IIIB, and IIIC forms (Table 2). This comparison, of course, did not take into account the effect of the phenylethyl group. The ^{13}C chemical shifts of I and II are given in Table 5.

From a comparison of the data in Table 5 and Table 2 it can be seen that the ^{13}C chemial shifts in the spectrum of I correspond quite closely to the chemical shifts of isomer IIIC. Thus it can be regarded as an established fact that I is a trans isomer. In a comparison of the experimental data for model structures IIIA, IIIB, and IIIC it was observed that good agreement is not observed for any of the forms and that particularly marked deviations are observed for trans form IIIC. The insufficiently good agreement between the experimental and calculated data compelled us to resort to PMR spectroscopy, since we counted on using the vicinal $^3J_{9,10}$ constant within the framework of conformational analysis. This constant is stereospecific [13] and can be used to prove the type of fusion. However, interpretation of the PMR spectra, particularly isolation of the signals of the 9-H and 10-H protons, which is not always possible, is required for this. Using 8-d_2-substituted I and II we were able to isolate the signals of the 9-H protons in the corresponding isomers by means of the $^1H-\{^2H\}$ double resonance PMR spectra.

Suppression of some of the vicinal $^3J_{HD}$ constants for the 9-H proton made it possible to measure the $^3J_{9,10}$ constants, which were found to be 10.0 and 5.5 Hz for I and II, respectively. Since the vicinal constant has the maximum value for the diaxial configuration of the C–H bonds, it hence follows that I and II are trans and cis isomers, respectively.

The assignment of I and II to trans and cis isomers is also confirmed by means of a simple criterion based on a comparison of the sum of the ^{13}C chemical shifts of the carbon atoms of the cyclic system [14]. Thus the sum over all of the carbon atoms of the two-ring system (including the carbon atom of the C=O group) is 516.3 ppm for isomer I and 492.5 ppm for isomer II. According to [14], the smaller sum of the ^{13}C chemical shifts should correspond to the compound with the larger number of gauche (or syn-anti) interactions; thus a cis structure can be assigned to II, and a trans structure can be assigned to I. Let us note that this method is applicable only when the spectra of two isomers can be compared with one another. Thus the method cannot be used for III and IV.

Finally, we made an attempt to calculate the ^{13}C chemical shifts of cis isomer II. Since a number of signals were not identified for cis-decahydroquinoline IIIB, we used the ^{13}C spectra of two conformers of cis-N-methyldecahydroquinoline as the starting compounds and introduced corrections due to replacement of the N-methyl group by an N-phenylethyl group. The increments (Δi) of the N-phenylethyl group are obtained by comparing the ^{13}C chemical shifts of trans-N-methyl- and trans-N-α-phenylethyl-4-decahydroquinolones. The values presented in Table 1 were used as the increments of the carbonyl group. The calculated ^{13}C chemical shifts are presented in Table 6.

Let us note that of two sets of calculated data for cis conformers IIA and IIB, better agreement with the experimental values for II evidently occurs for the IIA form, although even here there are rather significant deviations [up to 5 ppm in the case of the $C_{(10)}$ atom]. However, the indicated deviations can probably be ascribed to the imperfection of the additive scheme in the case of cis conformations (in particular, reliable values of the increments of the phenylethyl group in cis compounds are not available). On the basis of the entire set of experimental data, however, we can quite confidently assign a cis structure to II.

The conformational homogeneity of II was estimated experimentally in the course of recording the low-temperature ^{13}C NMR spectra of II (see the experimental section); we did not observe the appearance of any new groups of signals belonging to the second conformer, and only a small shift of the spectral lines occurred.

The data on the three-dimensional structures of I and II obtained in this research make it possible to reexamine the previously proposed stereochemistry of the asymmetric reduction of (1S)-α-phenylethyl-$\Delta^{9,10}$-octahydro-4-quinolone with $LiAlH_4$ and to show that the four possible diastereomers, the unusually stable cis-(1S)-α-phenylethyl-(9S,10R)-decahydro-4-quinolone is primarily formed.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$, C_6D_6, and CCl_4 were recorded with a Varian XL-100 spectrometer(100 MHz) under steady-state conditions. A quartet of the methylidyne proton in the phenylethyl group with chemical shifts of 4.25 and 3.59 ppm for I and II, respectively, was observed distinctly in the spectra of I and II. These data were used to conduct experiments involving the ^{13}C NMR spectra with selective proton decoupling. The spectra of the deuterated analogs of I and II were measured under $^1H-\{^2H\}$ NMR conditions (steady-state conditions with a Gyrocode synthesizer).

The ^{13}C NMR spectra (with complete proton decoupling, off-resonance spectra) of solutions of I-IV in C_6D_6 and $CDCl_3$ were measured with a Varian CFT-20 spectrometer (20 MHz). The ^{13}C NMR spectra with selective proton decoupling and the low-temperature $^{13}C-\{^1H\}$ NMR spectra were measured with a Varian XL-100 spectrometer (25 MHz). Solutions of I and II in CS_2 were used to measure the low-temperature spectra; the signal of deuteroacetone was used as the reference signal. The measurements were made up to −110°C.

The synthesis and isolation of the cis and trans isomers of 1-α-phenylethyl-4-decahydroquinolone (I, II) and trans-4-decahydroquinolone (III) were accomplished by the methods in [1]. trans-1-Methyl-4-decahydroquinolone was obtained in 60% yield by methylation of III with formalin and formic acid [9]; the picrate had mp 178-179°C (from ethanol). Found: C 48.8; H 5.1; N 13.6%. $C_{16}H_{20}N_4O_8$. Calculated: C 48.5; H 5.1; N 14.1%. The synthesis of a mixture of selectively deuterated (in the 3 and 8 positions of the quinoline system) 1-α-phenylethyl-$\Delta^{9,10}$-octahydro-4-quinolones was carried out by the method in [4], and the subsequent reduction with $LiAlH_4$ and isolation of the 8,8-dideutero derivatives of I and II was carried out by the method in [1].

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INTERMEDIATES IN THE ELECTROLYTIC REDUCTION OF 2-PYRIDYL-1,3-INDANDIONES IN APROTIC MEDIA

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L. Kh. Baumane, and R. A. Gavar

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547.828'665

The character of the products of one-electron reduction of 2-pyridinia-1,3-indandiones (of the phthalone and ylid types) in aprotic media was studied by means of EPR spectroscopy. Free radicals with semidione structures are formed; their hfs constants are presented. Radicals with pyridinium structures are formed only under the condition of the presence of a strong electron acceptor (a cyano group) in the pyridinium ring of the molecule. The formation of unstable intermediates with dimeric structures is postulated as a result of studies by means of cyclical voltammetry.

The one-electron electrochemical reduction of 2-pyridyl-substituted 1,3-indandiones of both the phthalone and ylid types of dimethylformamide (DMF) leads to primary free radicals, for which EPR spectra can be recorded [1-3]. In the present research we attempted to establish the structures of the radicals obtained in the electrochemical reduction of isomeric N-methylpyrophthalones (I), α-N-methylquinophthalone (II), 2-pyridinia-substituted 1,3-indandione onium betaines (ylids III), and 2-methyl-2-pyridyl-1,3-indandione methiodides (IV) to compare the radicals obtained with the products of one-electron reduction of 2-phenyl-1,3-indandiones (V, VI), and to evaluate the stabilities of these radicals and the possibility of their subsequent destruction by dimerization.

The free anion radicals obtained in the electrolytic reduction of 2-pyridyl-1,3-indandiones were found to be extremely similar to the radicals obtained in the electrolytic reduction of 2-phenyl-1,3-indandiones and, at the same time, markedly different from the radicals formed in the electrolytic reduction of pyridinium salts. However, the presence of a pyridinium ring is manifested both in the destruction of the radicals — dimerization takes place in the pyridinium ring — and (for individual representatives of the investigated compounds) in the possibility of delocalization of the unpaired electron on the pyridinium substituent. These peculiarities of the intermediates in the electrolytic reduction of 2-pyridyl-substituted 1,3-indandiones are discussed in the present paper.

Primary Radical Particles

Primary free radicals, viz., products of one-electron reduction of the starting compounds in concentrations sufficient for recording by EPR spectroscopy, were obtained in the electrochemical-generation cell in anhydrous DMF. The primary radicals were obtained at potentials corresponding to the $E_{1/2}$ values of the first polarographic wave of Ia, IIIc, and IVa, b [2,

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