FREE RADICALS IN THE ELECTROCHEMICAL REDUCTION OF CERTAIN MONONITRO AND DINITRO DERIVATIVES OF PYRIDINE

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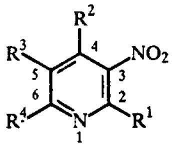
In the primary process of electrochemical reduction of substituted 3-nitropyridines in dimethylformamide, their anion radicals are formed. This also takes place in the reduction of 3,5-dinitropyridines and 3-nitropyridines with a nitrophenyl substituent at position 2 or 4. For these dinitro derivatives, however, secondary free radicals are formed as well; in a basic medium, these are the products of reduction of the corresponding Meisenheimer complexes. Serving as the reaction center for electroreduction is the nitro group on the pyridine ring, not the group on the phenyl ring. For the mononitropyridines and dinitropyridines that were studied, free radicals of the nitropyridine type are formed as the primary species. The structure of the primary and secondary free radicals was established by analysis of the hyperfine structure of their ESR spectra.

The free radicals formed by electrochemical reduction of nitro derivatives of heterocycles, particularly dinitropyridine derivatives, have been investigated only to a very limited extent [1]. The published work contains mainly information on primary anion radicals. At the same time, it has been shown that during the course of electrochemical reduction of nitro-substituted furans [2, 3] and dihydropyridines [4-6], the formation of the primary anion radicals may be accompanied by the formation of free radicals with a different structure — radicals that can be detected by ESR under conditions of their electrochemical generation.

Continuing our studies of the free radicals formed in the electrochemical reduction of nitro-substituted heterocycles, using polarography and cyclic voltammetry, we have determined the electrochemical characteristics of mononitropyridines (Ia-j) and dinitropyridines (IIa,b), and we have also accomplished the electrochemical generation of their free radicals.



Ia-j; IIa,b

Ia-d $R^1 = H$; $R^3 = COOCH_3$; $R^4 = CH_3$; Ia $R^2 = C_6H_4OCH_3$-*o*; Ib $R^2 = C_6H_5$; Ic $R^2 = C_6H_4Br$-*p*; Id $R^2 = C_6H_4NO_2$-*m*; I e-h $R^2 = H$; $R^3 = COOCH_3$; $R^4 = CH_3$; Ie $R^1 = C_6H_4OCH_3$-*o*; If $R^1 = C_6H_5$; Ig $R^1 = C_6H_4Br$-*p*; Ih $R^1 = C_6H_4NO_2$-*m*; Ii, j $R^2 = C_6H_5$; $R^3 = COOC_2H_5$; $R^4 = CH_3$; Ii $R^1 = CH_3$; Ij $R^1 = H$. IIa,b $R^2 = R^4 = H$; $R^5 = NO_2$; IIa $R^1 = C_6H_5$; IIb $R^1 = C_6H_4Br$-*p*.

All of the compounds, in solution in dimethylformamide, are reduced in several stages (Table 1).

Electronic effects of the substituents R^3 and R^4 and the phenyl ring have little influence on the change of potential of the first reduction wave, evidently because of mutual compensation of electron-donor and electron-acceptor properties of the substituents present in the molecule. For compounds Ia-j, the potentials lie in the interval from -0.9 to -1.2 V, for the most

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Latvian Institute of Organic Synthesis, Riga LV-1006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1079-1087, August, 1993. Original article submitted June 7, 1993.

0009-3122/93/2908-0918$12.50

TABLE 1. Values of Polarographic Wave Potential ($E_{1/2}$, V, relative to aqueous saturated calomel electrode), Mean Number of Electrons Involved in Electroreduction of One Molecule (n), and Reversibility (+/−) of Individual Stages of Electrochemical Reduction, with Potential Sweep Rate 20 mV/sec, for Compounds Ia-j and IIa,b in DMF on a Background of 0.1 M Tetrabutylammonium Perchlorate

Compound	Wave 1			Wave 2'			Wave 2"			Wave 3			Wave 4		
	$-E_{1/2}$	n	+	$-E_{1/2}$	n	+	$-E_{1/2}$	n	+	$-E_{1/2}$	n	+	$-E_{1/2}$	n	+
Ia	1,05	1,0	+	—	—	—	2,08	1,5	—	2,26	1,5	—	2,70	2,9	—
Ib	0,99	1,0	+	—	—	—	1,88	1,0	—	2,20	2,1	—	2,64	4,1	—
Ic	0,96	1,0	+	—	—	—	1,82	1,0	—	2,34	1,9	—	>2,6	>5	—
Id	0,89	1,0	+	1,21	0,9	+	—	—	—	2,04	2,0	—	2,36	1,6	—
Ie	1,06	1,0	+	—	—	—	1,96	1,2	—	2,18	1,2	—	2,44	1,7	—
If	0,98	1,0	+	—	—	—	1,74	1,3	—	2,03	1,7	—	2,30	1,8	—
Ig	0,92	1,0	+	—	—	—	1,67	1,6	—	2,02	1,4	—	2,36	2,3	—
Ih	0,87	1,0	+	1,27	0,9	+	—	—	—	2,04	1,8	—	2,52	2,1	—
Ii	1,21	1,0	+	—	—	—	2,10	2,0	—	2,46	1,0	—	—	—	—
Ij	1,02	1,0	+	—	—	—	1,94	2,3	—	2,25	2,1	—	—	—	—
IIa	0,68	1,0	+	1,24	0,9	+	—	—	—	2,06	2,9	—	—	—	—
IIb	0,67	1,0	+	1,21	0,8	+	—	—	—	1,92	4,0	—	—	—	—

part varying in accordance with the change of electron-acceptor properties of the substituent on the phenyl ring. Compounds Ia-d are essentially no different from compounds Ie-h, even though the potential of the first wave for the latter group of compounds is more sensitive to changes in electron-acceptor properties of the substituent than is the case for compounds Ia-d. Replacement of the methyl group by ethyl in the ester substituent R^3 (compare compounds Ib and Ij) hinders the reduction by only 30 mV; however, the introduction of a methyl group in place of a proton in the R^1 substituent - in the ortho position relative to the reaction center (see compound Ii) - hinders the reduction by 200 mV in comparison with compound Ij.

According to information reported in the literature, unsubstituted 3-nitropyridine is reduced more easily (by 80 mV) than unsubstituted nitrobenzene under the same conditions [7]. In our case, substituents introduced into the pyridine ring give hardly any change in this relationship; hence we can assume that the nitro group in the pyridine ring is subject to primary reduction in the case of compounds Id,h as well, which contain a second nitro group on the phenyl ring. In contrast, the introduction of a second nitro group into the pyridine ring (compounds IIa,b) results in a very considerable decrease (by 300 mV) of the potential of the first stage in electrochemical reduction of these compounds. It should be noted, however, that in the case of m-dinitrobenzene, the shift of potential of the first stage of reduction in comparison with nitrobenzene is considerably greater (570 mV) [7]; and we can assume that the nitropyridine ring is less sensitive to changes in electron-acceptor properties of the substituent in the meta position than is the case for nitrobenzene.

In all instances, the first wave is one-electron and reversible, possibly indicating the formation of anion radicals of the original compounds in the first stage of electroreduction.

The further stagewise reduction of compounds Ia-j and IIa,b proceeds in the potential interval from −1.2 to −2.7 V, with the formation of two or three polarographic waves (see Table 1). The heights of these waves and correspondingly the number of electrons participating in each stage exhibit differences, depending on the molecular structure.

Thus, compounds Ia-c and Ie-g, in which R^3 = $COOCH_3$, are reduced in the interval of potentials from −1.7 to −2.7 V with the formation of three polarographic waves; in all cases, the electrochemical reactions are irreversible. The potentials of these waves are shifted toward more positive values with increasing electron-acceptor properties of the substituent R^1 or R^2. However, when the methoxycarbonyl group is replaced by ethoxycarbonyl (compounds Ii,j), reduction of the anion radicals proceeds in two stages. It is extremely difficult to assign these waves to specific electrochemical processes, since the possible reactions in this interval of potentials include further reduction of the nitro group, reduction of the ester grouping in the substituent R^3, and even reduction of the double bond of the pyridine ring if sufficiently strong electron-acceptor substituents are present.

If the molecule has a second nitro group in the meta position of the phenyl substituent (compounds Id,k), the further reduction of these compounds also proceeds with the formation of three polarographic waves. However, the potential of the second wave (wave 2', Table 1) is shifted ~0.6 V into the more positive region in comparison with compounds Ib,f, which

TABLE 2. Electrochemical Generation Potentials (E, V relative to Pt electrode) and Hyperfine Interaction Constants (G) in ESR Spectra of Primary (P) and Secondary (S) Free Radicals of Compounds Ia-j and IIa,b in DMF, and of Compounds IIa,b in DMF with Added Bu_4NOH (IIa*, IIb*)

Compound	-E	Radical	Hyperfine interaction constants						
			$N_{(1)}$	$H_{(2)}$	$N_{(3)}$	$H_{(4)}$	$H,N_{(5)}$	$H_{(6)}$	N,H
Ia	1,3	P	1,31	3,11	7,71	—	—	4,43	~0,2
Ib	1,3	P	1,31	3,12	7,67	—	—	4,43	<0,2
Ic	1,3	P	1,23	2,95	7,71	—	—	4,43	0,45(2H); 0,25(2H)
Id	1,0	P	1,48	2,87	7,54	—	—	4,35	~0,2
	1,0	S	9,75(N); 3,69(H); 3,28(2H); 1,07(H)						
Ie	1,1	P	1,39	—	7,87	3,07	—	4,47	~0,2
If	0,9	P	1,23		7,54	3,03	—	4,43	0,57(2H); 0,25(2H); 0,57(H)
Ig	1,2	P	1,56	—	7,87	2,38	—	4,51	0,70(2H); 0,25(2H)
Ih	1,0	P	1,64		7,38	1,64	—	4,75	0,98(N)
	1,0	S	9,94(N); 3,30(H); 3,20(2H); 0,94(H); 0,25(N)						
Ii	1,3	P	0,66	1,35	12,79	—	—	2,54	
Ij	1,4	P	1,31	2,99	8,20	—	—	4,51	
IIa	0,9	—	No values established for constants						
IIa*	0,5	S	0,33	—	7,38	—	3,12	7,38	0,33(2H)
IIb	0,9	P	—	—	6,23	1,31	1,31	3,55	0,98(2H); 0,45(2H)
IIb*	0,5	S	0,41	—	7,83	—	3,20	4,83	0,41(2H)

do not contain a nitro group on the phenyl radical. The height of this wave does not reach the one-electron level; however, if the mercury dropping period is extended, the height of the wave does increase, reaching the one-electron level when the period is doubled but remaining unchanged as the period is further extended. On the cyclic voltammetric curves, partial reversibility of the second stage of reduction has been established.

The results from polarographic studies of compounds Id and Ik in a basic medium (with the addition of tetrabutylammonium hydroxide to the dimethylformamide) indicate that as the amount of added base is increased, the height of the first reduction wave decreases, disappearing altogether at a base concentration of $2 \cdot 10^{-2}$ M. The height of the second reduction wave reaches the one-electron level at an additive concentration of $5 \cdot 10^{-4}$ M and does not change with increasing amounts of added tetrabutylammonium hydroxide. The potentials of both the first and second reduction waves in straight DMF are not changed by the addition of the base. The reversibility of the first two stages of reduction of compounds Id,k in DMF is not changed by the addition of the base.

A similar picture of electroreduction is observed for compounds IIa,b, in which the second nitro group is in position 5 of the pyridine ring: The height of the second reduction wave reaches the one-electron level only when the mercury dropping period in DMF solution is extended, or when tetrabutylammonium hydroxide is added. The same as for compounds Id,k, the height of the first reduction wave gradually decreases with increasing amounts of added base.

A comparison of the picture of electrochemical reduction of 3,5-dinitropyridine with that of m-dinitrobenzene indicates that, for the latter compound, the potential of the second reduction wave is also shifted 0.6 V into the positive region; the electrochemical process itself is a one-electron reversible addition of a single electron to the anion radical, leading to the formation of the dianion of the original molecule. The polarographic and cyclic voltammetric studies indicated that in straight dimethylformamide, the second stage of electrochemical reduction of compounds Id,k and IIa,b also corresponds to the formation of a dianion. However, as will be shown below, this is accompanied by a slow parallel chemical reaction of conversion of the anion radicals.

As should be expected from the reversible one-electron character of the primary reduction of these compounds, their primary anion radicals are registered by ESR in the course of electrochemical generation at the potential of the first polarographic wave. As a result of deciphering the hyperfine structure of the ESR spectra, we have established values for the constants of hyperfine interaction of the unpaired electron with the nitrogen-atom nuclei and the protons of these radicals. In Table 2 we have also listed values of the potential (relative to a Pt electrode) of electrochemical generation of the corresponding radicals. These potential values are useful in terms of orientation; it should be kept in view that their values in DMF are about 0.1 V more negative, but in the basic medium (DMF with added tetrabutylammonium hydroxide) about 0.7 V more negative, in comparison with the corresponding potentials relative to an aqueous saturated calomel electrode, as this was taken as the starting point in registering the polarograms.

In contrast to the previously investigated anion radicals of 3-nitropyridines [1], the primary anion radicals of the derivatives of 3-nitropyridine included in the present study (with the exception of compound Ii) have comparatively low values of the constant of hyperfine interaction with the nucleus of the nitrogen atom in the nitro group. It can be assumed that such a lowering of the unpaired electron density is determined by the electrophilic character of the phenyl substituent in the ortho position relative to the nitro group in the pyridine ring. Actually, the ESR spectra of these radicals exhibit hyperfine structure from interaction of the unpaired electron with protons of the phenyl ring. From the values obtained for the constant of hyperfine interaction with these protons, it was found that the delocalization of the unpaired electron onto the phenyl ring amounts to about 0.1 electron. The influence of a substituent in the ortho position relative to the nitro group is also manifested upon replacement of the substituent in position 2 of the pyridine ring. Thus, replacement of a proton by the electron-donor methyl group increases the value of the constant a(N) of the nitro group by more than 4.5 G (compounds Ii,j). Less understandable is how substituents in the meta position relative to the nitro group can influence the redistribution of the unpaired electron. As a rule, in the anion radicals of nitrobenzenes or nitropyridines, changes of these substituents have relatively little effect on the unpaired electron redistribution in the anion radicals [1]. In our case, replacement of a methoxycarbonyl group by ethoxycarbonyl (compare Ib and Ij) results in a substantial increase of the constant a(N) of the nitro group. Such influence of the ethoxycarbonyl group can be explained by its steric action on the adjacent phenyl substituent: With decreasing coplanarity of the phenyl and pyridine rings, there is a redistribution of the unpaired electron from the phenyl substituent to the nitro group of the pyridine ring. This view is supported by the fact that along with the increase of unpaired electron density on the nitro group of the pyridine, in the ESR spectra of the anion radicals of compounds Ii,j we do not detect any significant interaction of this electron with the protons of the phenyl ring.

In the case of the nitropyridines Id,k, which contain a nitrophenyl substituent, free radicals of the nitropyridine type are also formed as the primary anion radicals; i.e., it is not the nitro group of the phenyl ring, but rather that of the pyridine ring, that serves as a reaction center for the primary reduction. This is consistent with the values of the electronic effects of the 3-pyridyl substituent (σ_r = 0.25) and the phenyl substituent (σ_r = −0.01) [8], and it is also consistent with the fact that the hyperfine structure constant of interaction with the nitrogen atom of the nitro group is larger for the anion radical of nitrobenzene than for the anion radical of 3-nitropyridine (see additional discussion in [1]).

Primary anion radicals were also obtained for the dinitropyridines IIa,b. Their ESR spectra have a more complex hyperfine structure in comparison with the anion radicals of compounds Ia-j; this is explained by additional interaction of the unpaired electron with the nucleus of the nitrogen atom in the second nitro group. For this reason, we were not able to decipher the hyperfine structure of the ESR spectrum for the anion radical of compound IIa. From the hyperfine structure of the ESR spectrum that was obtained for the primary anion radical of IIb, it follows that this radical is similar to the anion radicals of the mononitropyridines Ia-j with a second nitro group in the pyridine ring as a substituent. In this radical, the unpaired electron is mainly localized on the nitro group of the pyridine, with partial delocalization through the π-electron systems of both the nitropyridine and the phenyl substituent.

In contrast to the mononitro compounds, for which ESR registers only their primary anion radicals in the course of electrochemical reduction, the dinitro compounds that we have investigated may form both primary anion radicals and secondary free radicals. Thus, upon electrochemical generation of free radicals of compounds Id,k, in which the second nitro group is located in a nitrophenyl substituent, primary anion radicals of the original compounds are formed originally, with delocalization of the unpaired electron for the most part through the pyridine ring. However, these radicals disappear rapidly; and, at the same generation potentials, they are replaced by free radicals of meta-substituted nitrobenzene. In the ESR spectra of the secondary radicals, the hyperfine structure is due to delocalization of the unpaired electron through the nitrobenzene fragment only, so that the structure of the meta substituent of this nitrophenyl radical can be established only tentatively.

If it is considered that the secondary nitro-substituted radicals are formed as a result of further chemical reduction of one of the nitro groups of the dinitro compounds with the participation of protons, this sort of course of secondary radical formation might be retarded by a decrease of protogenic properties of the medium. In fact, during the course of electrochemical generation of free radicals in dimethylformamide with small amounts of added base (tetrabutylammonium hydroxide), the steady-state concentration of primary anion radicals of the dinitro compounds may increase slightly. With a further increase of the concentration of added base, however, the effect is the opposite: The steady-state concentration of

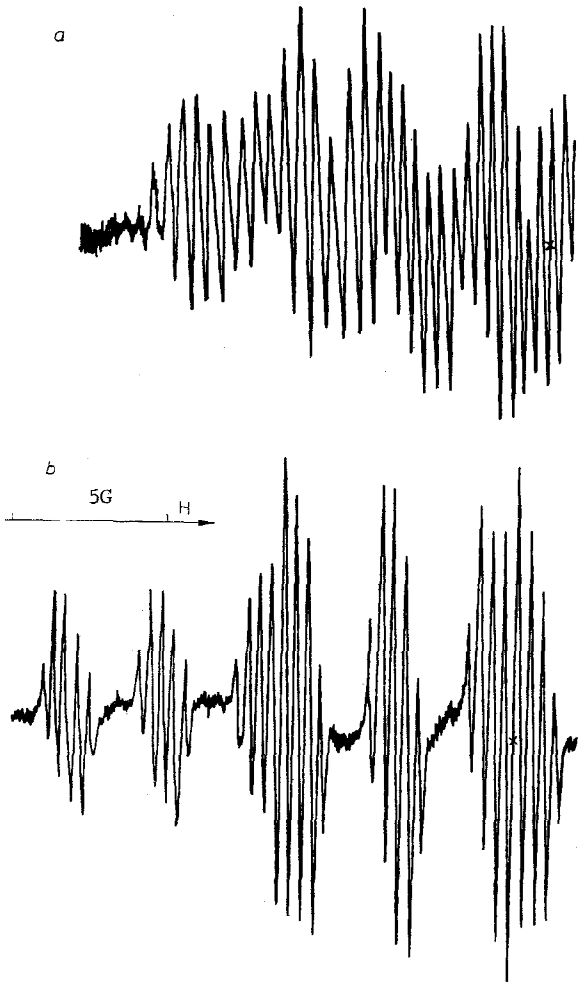


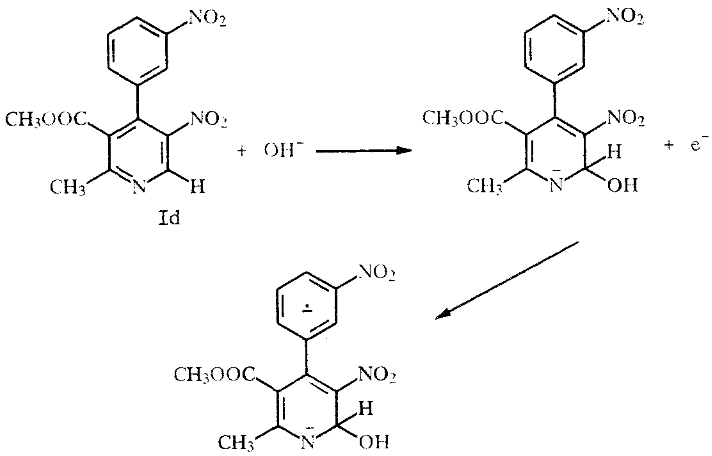
Fig. 1. Low-field half of ESR spectra of electrochemically generated free radicals of compound IIa: *a*) primary anion radicals of original compound in DMF; *b*) secondary dianion radicals of original compounds (or anion radicals of corresponding Meisenheimer complex) in DMF with the addition of $1 \cdot 10^{-3}$ M tetrabutylammonium hydroxide.

primary anion radicals decreases, and the concentration of secondary radicals of substituted m-nitrobenzene increases, indicating a decrease in the concentration of the primary anion radicals not only in the course of their protonation and subsequent reduction, but also as a result of their reaction with the nucleophilic agent.

It has been reported that the presence of nitro groups in six-membered nitrogen heterocycles brings about the formation of Meisenheimer complexes as a result of reaction of the corresponding compounds with bases [9]. The anions that are formed have the 1,2-dihydropyridine structure for the most part. Anions of the 1,4-dihydropyridine type are formed either with a high concentration of the base or in cases in which the 1,2-dihydropyridine structure is impossible [10]. In order to test the hypothesis of Meisenheimer complex formation by our compounds, we recorded absorption spectra, in dimethylformamide with added tetrabutylammonium hydroxide, of dinitro derivatives of pyridine and also the corresponding dinitro-1,2-dihydropyridines and dinitro-1,4-dihydropyridines. In all cases, an absorption band was observed in the visible part of the spectrum, indicating the formation of an anionic structure that is characteristic for Meisenheimer complexes. Thus, for the anions of m-nitrophenyl derivatives of 3-nitro-1,2-dihydropyridine and 3-nitro-1,4-dihydropyridine, the absorption maximum is observed at 500 and 506 nm, respectively. For the 3,5-dinitro derivatives, the characteristic absorption maxima are registered at 490 nm

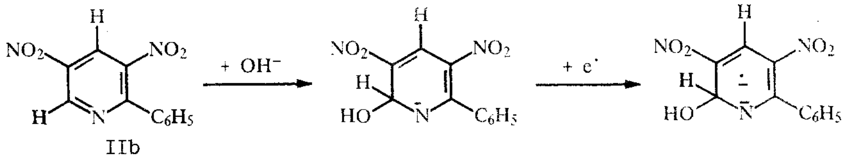
(1,2-dihydropyridine) and 560 nm (1,4-dihydropyridine). Absorption maxima are observed at 460 and 490 nm for the hypothetical Meisenheimer complexes formed in a basic medium from the corresponding m-nitrophenyl-3-nitropyridines and 3,5-dinitropyridines, respectively.

In the electrochemical reduction of the Meisenheimer complex (sodium 1,1-dimethoxy-2,4,6-trinitrocyclohexadienate), ESR spectra of the product of its one-electron reduction were registered – a dianion radical – with values of the hyperfine interaction constant that differ from the corresponding constants for the anion radical of 2,4,6-trinitroanisole [11]. In our case, the Meisenheimer complexes that are formed in the one-electron process are reduced to their anion radicals, which, when registered by ESR, appear as secondary radicals of the original compounds. For example, in the case of compound Id, the formation of the secondary free radical of the nitrophenyl type in a basic medium can be represented as follows:


Id

The formation of secondary free radicals in dimethylformamide without any added tetrabutylammonium hydroxide can be explained by assuming that the primary anion radical serves as the nucleophilic agent. Here, the hyperfine structure of the ESR spectrum of this secondary radical is hardly any different from that of the secondary radical that is formed according to the scheme shown above.

In the reduction of the dinitropyridines IIa,b, along with their primary anion radicals, secondary free radicals are also formed (Fig. 1). In straight dimethylformamide, however, these secondary radicals can be obtained in ESR-detectable concentrations only at extremely high potentials (> -2.5 V) of electrochemical generation. Such a difference of the dinitropyridines IIa,b from the nitrophenyl-substituted mononitropyridines Id,k can be explained by the lower nucleophilicity of the anion radicals of the dinitropyridines and hence the lower probability of forming secondary radicals. By using the nucleophilic agent tetrabutylammonium hydroxide in the dimethylformamide during the course of electrochemical generation, we were able to obtain secondary radicals at lower potentials, in concentrations adequate for investigation of the hyperfine structure of their ESR spectra. In contrast to the secondary radicals of compounds Id,k, which have the structure of anion radicals of meta-substituted nitrophenyl, the secondary free radicals of compounds IIa,b have the structure of a free radical of a dinitro-substituted nitrogen-containing heterocycle. The conversions of compounds IIa,b in dimethylformamide with the base and in straight dimethylformamide can be represented by analogy with what was done in the above material for compound Id:


IIb

Evidence in favor of this structure of the secondary free radicals of compounds IIa,b may be found in the hyperfine structure of their ESR spectra, indicating that one of the protons of the pyridine ring does not interact with the unpaired electron, and thus there is no complete conjugation in the pyridine ring. As a result of shortening the π-electron system of the heterocycle, the unpaired electron density on the nitro groups is increased, as is observed in comparing values of the constants of hyperfine interaction of the unpaired electron with the nitrogen atom nuclei of the nitro groups in the secondary and primary radicals of compound IIb (Table 2).

EXPERIMENTAL

The electrochemical reduction of compounds Ia-j and IIa,b ($C = 5 \cdot 10^{-4}$ M) was performed in anhydrous dimethylformamide [12] on a background of tetrabutylammonium perchlorate ($c = 10^{-1}$ M).

The polarograms and the cyclic voltammetric curves were obtained by means of a PAR-170 electrochemical system (USA), with a three-electrode cell. The cathode was a dropping-mercury electrode with forced detachment of the drop ($t = 0.5$ sec, $m = 0.90$ mg/sec) or a stationary vitreous carbon electrode; the anode was a platinum wire; the comparison electrode was a saturated aqueous calomel electrode equipped with a connecting bridge for operation in nonaqueous solvents.

The free radicals were generated under steady-state conditions on the surface of a flat platinum electrode mounted in a rectangular resonator (H_{102} type) of an ER-9 ESR spectrometer (Carl Zeiss, Jena), following a procedure given in [13]. The electrochemical generation potentials were measured in a three-electrode scheme, relative to the Pt electrode.

The ESR spectra were registered with a magnetic field sweep rate of 0.04 G, with a depth of high-frequency (100 kHz) modulation of the magnetic field 0.05-0.9 G, and with a registration time constant 0.45 sec. The magnetic field sweep was calibrated on the basis of the ESR spectrum of the anion radical of nitrobenzene [14]. For the electrochemical generation of the free radicals, we used 10^{-4} to $5 \cdot 10^{-3}$ M solutions of compounds (I, II) in dimethylformamide.

The IR spectra were obtained in a UR-20 instrument (in Nujol), the UV spectra in a Specord UV-Vis spectrometer (in ethanol), and the PMR spectra in a Bruker WH-90 spectrometer (in DMSO-d_6). The ^{13}C NMR spectra were taken in a Bruker WM 360 spectrometer (90.5 MHz) in DMSO-d_6; internal standard cyclohexane. The individuality of the substances that were synthesized was checked by means of TLC on Silufol UV-254 plates in the solvent systems chloroform–hexane–acetone–ethanol (9:7:2:1) and benzene–ethyl acetate (20:1).

The results of elemental analyses for C, H, and N were in agreement with the calculated values.

The 3-nitropyridines Ia-k and 3,5-dinitropyridines IIa,b were obtained as described in [15]. The 3-nitropyridines Ii,j were obtained by oxidizing the corresponding 3-nitro-1,4-dihydropyridines.

2,6-Dimethyl-3-nitro-4-phenyl-5-ethoxycarbonyl-1,4-dihydropyridine was obtained as described in [16].

3-Nitro-4-phenyl-5-ethoxycarbonyl-6-methyl-1,4-dihydropyridine ($C_{15}H_{16}N_2O_4$). A solution of 1.12 g (10 mmoles) of 1-amino-2-nitroethylene [17] and 2.19 g (10 mmoles) of benzylideneacetoacetic ester in 40 ml of ethanol containing 10 ml of glacial acetic acid was refluxed for 20 h. After cooling, the reaction mixture was poured into water and extracted with ethyl acetate (3 × 60 ml), washed with water, and dried with anhydrous sodium sulfate. The solvent was removed under vacuum, and the dark-colored oil was dissolved in a chloroform–hexane–acetone–ethanol solvent system (9:7:2:1) and filtered through a layer of silica gel. The solvent was removed under vacuum, and the residue was crystallized from a methanol–acetic acid mixture (4:1). Obtained a yellow substance, 1.3 g (45.5%), mp 161°C. UV spectrum, λ_{max} (ethanol): 205, 218, 268, 418 nm. IR spectrum, ν, cm^{-1} (in Nujol): 1620, 1660, 1705, 3210, 3300 cm^{-1}. PMR spectra, δ, ppm (DMSO-d_6): 1.11 (t, 3H, CH_3); 2.24 (s, 3H, 6-CH_3); 3.96 (q, 2H, OCH_2); 5.18 (s, 1H, 4-CH); 7.18 (s, 5H, arom. prot.), 7.98 (d, 1H, 2-CH); 9.87 (d, 1H, NH). ^{13}C NMR spectrum, ppm (DMSO-d_6): 13.76 (CH_3); 17.68 (6-CH_3); 39.46 ($C_{(4)}$); 59.52 (OCH_2); 106.76 ($C_{(5)}$); 126.75 (*p*-C); 127.83 (*m*-C); 128.08 (*o*-C); 128.85 ($C_{(1)}$); 134.47 ($C_{(2)}$); 143.27 ($C_{(6)}$); 144.79 ($C_{(3)}$); 166.14 (C=C).

2,6-Dimethyl-3-nitro-4-phenyl-5-ethoxycarbonylpyridine (Ii, $C_6H_{16}N_2O_4$). A mixture of 1.51 g (5 mmoles) of 2,6-dimethyl-3-nitro-4-phenyl-3-ethoxycarbonyl-1,4-dihydropyridine and 50 ml of 6 N nitric acid was stirred for 20 min at 80°C. After cooling, the mixture was diluted with water to 79 ml and then extracted three times with ethyl acetate (3 × 30 ml). The organic layer was washed with water (3 × 20 ml) and dried with anhydrous sodium sulfate; the solvent was removed under vacuum. The colorless oil was crystallized from dilute methanol. Obtained 1.27 g (85%) of colorless crystals, mp 56-60°C. PMR spectrum, δ, ppm ($CDCl_3$): 0.89 (t, $3H_3$); 2.58 (s, 3H, 6-CH_3); 2.62 (s, 3H, 2-CH_3); 4.00 (q, 2H, OCH_2); 7.31 (s, 5H, arom. protons).

3-Nitro-4-phenyl-2-ethoxycarbonyl-6-methylpyridine (Ij, $C_{15}H_{14}N_2O_4$). From 1.44 g (5 mmoles) of 3-nitro-4-phenyl-5-ethoxycarbonyl-6-methyl-1,4-dihydropyridine, as described above for Ii, obtained 1.18 g (82.5%) of Ij, mp 96-98°C. PMR spectrum, δ, ppm ($CDCl_3$): 0.84 (t, 3H, CH_3); 2.58 (s, 3H, 6-CH_3); 3.91 (q, 2H, OCH_2); 7.27 (s, 5H, arom. protons); 8.89 (s, 1H, 2-CH).

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