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# FREE RADICALS IN ELECTROCHEMICAL REDUCTION OF 3,5-DICARBETHOXY-1,4-DIHYDROPYRIDINES WITH NITROPHENYL GROUPS IN POSITIONS 2, 4, AND 6

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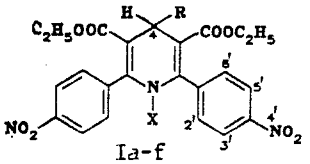
UDC 547.822.1:541.138.3:
543.422.27

*In the electrochemical reduction of 2,6-bis- and 2,4,6-tris(nitrophenyl) derivatives of 3,5-dicarbethoxy-1,4-dihydropyridine, in the first stage, one of the para-nitrophenyl groups in position 2 or 6 of the heterocycle is reduced. Free radicals have been obtained and identified, the primary species being ion radicals of the nitrophenyl type. The presence of the heterocycle in the molecule of the 1,4-dihydropyridine derivative stabilizes secondary free radicals of the nitrosophenyl type. In the process of electrochemical reduction, no evidence has been found of any intramolecular transfer of electrons or protons from the dihydropyridine part of the molecule to the nitrophenyl groups. Derivatives of 2,6-bis(p-nitrophenyl)-3,5-dicarbethoxy-1,4-dihydropyridine have been synthesized, and the oxidation and methylation of these derivatives have been studied.*

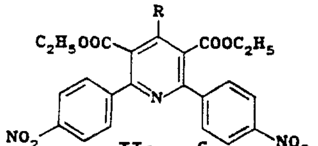
Among the derivatives of 1,4-dihydropyridine (1,4-DHP) with a nitrophenyl fragment in position 4, certain compounds have been found to have very definite cardiovascular activity, for example the preparation nifedipine (Corinfar), which is 4-(o-nitrophenyl)-3,5-dicarbethoxy-2,6-dimethyl-1,4-DHP. In the course of searching for compounds that offer promise in medical applications, derivatives of 1,4-DHP with nitrophenyl fragments in various positions of the heterocycle have been synthesized and studied.

The mechanism of electrochemical reduction of 3,5-dicarbethoxy- and 3,5-dicyano-1,4-DHP with a nitrophenyl substituent in position 4 has been examined in detail [1-3]. If p-nitrophenyl substituents are introduced into positions 2 and 6 of the 1,4-DHP, while either retaining or removing the nitrophenyl substituent in position 4, certain special features of the electroreduction mechanism are observed, related to the introduction of the second nitrophenyl fragment and to the shift of the reaction center from the 4-nitrophenyl group to the 2-nitrophenyl group. In all cases, the primary electroreduction involves, first of all, the nitrophenyl fragment, and anion radicals or dianion radicals of the nitrobenzene type are formed. Here we are reporting on a more detailed study of the formation and structure of these anion radicals.

We have investigated the course of electrochemical reduction, in DMFA, of 3,5-dicarbethoxy derivatives of 1,4-DHP containing nitrophenyl groups in positions 2 and 6 (compounds Ia-c, f) or in positions 2, 4, and 6 (compounds Id, e). Certain data are presented on the electrochemical reduction of the model compounds IIc, e, f, which are the oxidized forms of the corresponding 1,4-DHPs.



Ia-f



IIc,e,f

I a $X=CH_3$, b —f) X=H; I, IIa ,c) $R=4\text{-}ClC_6H_4$, b) $R=C_6H_5$, d) $R=4\text{-}NO_2C_6H_4$, e) $R=3\text{-}NO_2C_6H_4$, f) $R=CH_3$

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Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 481-487, April, 1991. Original article submitted May 29, 1990; revision submitted September 4, 1990.

TABLE 1. Electrochemical Characteristics ($E_{1/2}$, i) of Compounds Ia-f and IIc, e, f (c = $5 \cdot 10^{-4}$ M) in DMFA on a Background of 0.1 M $(C_4H_9)_4NClO_4$*

| Compound | $-E^{I}_{1/2}$, V | $-E^{II}_{1/2}$, V | $-E^{III}_{1/2}$, V | $-E^{IV}_{1/2}$, V | $-E^{V}_{1/2}$, V | $-E^{VI}_{1/2}$, V | $i^{I}$, μA | $i^{II}$, μA | $i^{III}$, μA | $i^{IV}$, μA | $i^{V}$, μA | $i^{VI}$, μA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ia | 1,03 | — | — | 1,57 | 2,28 | — | 1,30 | — | — | 3,36 | 2,8 | — |
| Ib | 1,01 | 1,20 | — | 1,50 | 1,94 | 2,7 | 1,20 | 0,60 | — | 0,52 | 2,8 | 4,2 |
| Ic | 1,06 | 1,14 | — | 1,54 | 2,00 | 2,7 | 1,12 | 0,84 | — | 0,48 | 2,8 | 4,1 |
| Id | 0,97 | 1,19 | 1,30 | 1,58 | 2,00 | 2,7 | 1,12 | 1,12 | 0,44 | 0,40 | 1,8 | 4,0 |
| Ie | 0,97 | 1,17 | 1,32 | 1,48 | 1,95 | 2,6 | 1,12 | 1,12 | 0,44 | 0,40 | 1,8 | 4,0 |
| If | 1,01 | 1,29 | — | 1,52 | 2,00 | 2,7 | 1,32 | 0,32 | — | 0,64 | 2,8 | 4,2 |
| IIc | 0,95** | — | — | 1,45 | 1,91 | — | 2,52 | — | — | 2,52 | 3,5 | — |
| IIe | 0,98** | — | — | 1,60 | 2,00 | 2,34 | 2,46 | — | — | 3,75 | 2,5 | 1,8 |
| IIf | 0,98** | — | — | 1,50 | 1,95 | 2,46 | 2,50 | — | — | 3,50 | 4,4 | 8,5 |

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*$E_{1/2}$ referred to SCE.

**On cyclic voltammetric curves, and with dilution of solution, two reversible one-electron stages of reduction are observed on the polarograms, with a potential difference of 100-150 mV.

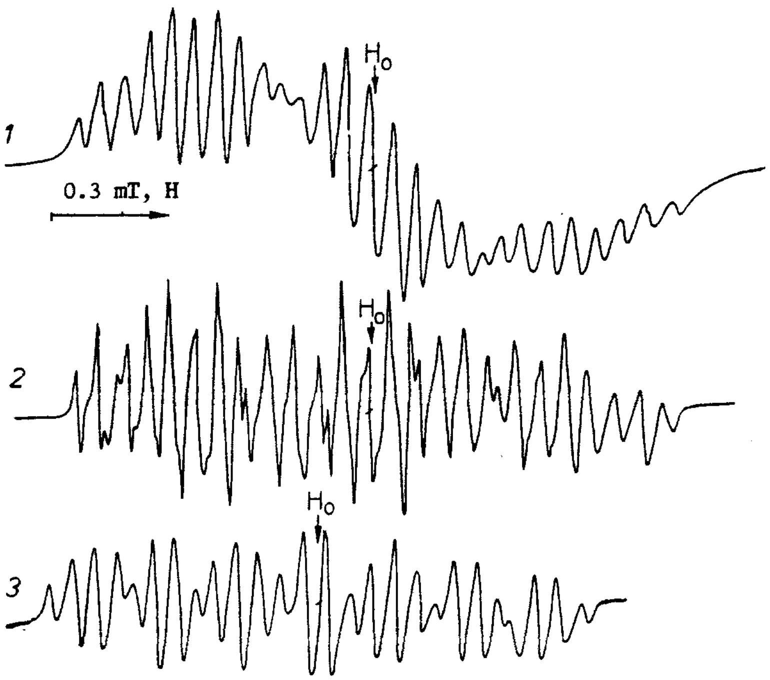

Fig. 1. ESR spectra of ion radicals of compound Ia in DMFA, recorded at different ECG potentials: 1) anion radical of original molecule (E = —1.1 V); 2) anion radical with localization of unpaired electron on one nitrophenyl fragment (E = —1.6 V); 3) anion radical of p-substituted nitrosobenzene (E = —0.6 V after generation at —1.8 V).

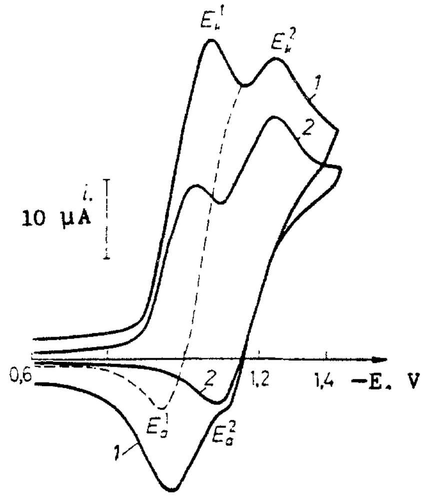

Fig. 2. Cyclic voltammetric curves taken for compound If in DMFA on background of 0.1 M tetrabutylammonium perchlorate at different potential sweep rates: 1) 100 mV/sec; 2) 10 mV/sec. Depolarizer concentration $1 \cdot 10^{-3}$ M.

In anhydrous DMFA, the electrochemical reduction of these compounds proceeds in stages, including both electrochemical and chemical reactions. By means of cyclic voltammetry, we detected the redox systems that are governed by these processes; and by means of ESR we registered free-radical species that are formed in the course of electrochemical generation (ECG) of the original molecules. We will examine in detail the first stages of electroreduction, accomplished in the potential interval from —1.0 to —1.3 V.

For the N-substituted compound Ia in this potential interval, we observe only one reduction wave, at a potential of —1.03 V. It corresponds to a one-electron reversible process of formation of relatively stable primary anion radicals

TABLE 2. ECG Potentials and HFS Constants in ESR Spectra of Ion Radicals Formed by Electroreduction of Compounds Ia-f in DMFA

| Compound | ECG potential, V | $a \cdot 10^4$, T | | | | | |
|---|---|---|---|---|---|---|---|
| | | $a_{N_1}$ | $a_{2',H}$ | $a_{3',H}$ | $a_{4',N}$ | $a_{5',H}$ | $a_{6',H}$ |
| I a | −1,1 | 1,29 | 0,88 | 3,05 | 7,63 | 3,05 | 0,88 |
| | −0,6 | 0,99 | 0,99 | 3,51 | 6,09 | 2,57 | 0,99 |
| I b | −1,1 | ... | ... | ... | ... | ... | ... |
| | −1,4 | 0,94 | 0,94 | 3,16 | 9,24 | 3,16 | 0,94 |
| | −0,6 | 0,99 | 0,99 | 3,63 | 7,14 | 2,80 | 0,99 |
| I c | −1,1 | 1,05 | 1,05 | 2,93 | 8,60 | 2,93 | 1,05 |
| | −1,4 | 1,05 | 1,05 | 3,04 | 9,01 | 3,04 | 1,05 |
| | −0,8 | 1,05 | 1,05 | 3,27 | 6,20 | 2,46 | 1,05 |
| I d | −1,1 | ... | ... | ... | ... | ... | ... |
| | −1,3 | 1,11 | 1,11 | 3,10 | 8,43 | 3,10 | 1,11 |
| | −1,5 | 3,39 ($H_4$) | 1,17 | 3,10 | 10,24 | 3,10 | 1,17 |
| I e | −1,1 | ... | ... | ... | ... | ... | ... |
| | −1,3 | 1,11 | 1,11 | 3,04 | 8,54 | 3,04 | 1,11 |
| | −1,5 | 0,94 ($H_4$) | 3,16 | 9,95 (N) | 3,16 (H) | 0,94 | 3,51 |
| I f | −1,1 | 1,05 | 1,05 | 3,28 | 8,43 | 3,28 | 1,05 |
| | −1,3 | 0,94 | 0,94 | 2,93 | 9,13 | 2,93 | 0,94 |
| | −0,7 | 0,94 | 0,94 | 3,69 | 7,14 | 2,81 | 0,94 |

(Fig. 1, spectrum 1). For the N-unsubstituted derivatives Ib-f, the height of the first polarographic wave is also close to the one-electron wave, but its reversibility is considerably poorer than for Ia. For compounds Ib, c, f we observe one more wave in this potential interval, and for Id, e two more polarographic waves. The potential of the first additional wave is shifted ~0.2 V toward more negative values in comparison with the potential of the first reduction wave, and its height differs considerably among the compounds (Table 1). On the cyclic voltage—current curves, this wave corresponds to a reversible redox system. The intensity of the new redox system and, correspondingly, the quantity of secondary species, depends on the original concentration of the compound and the rate of potential sweep. Thus, for compound If (Fig. 2), the ratio of heights of the first and second reduction peaks, with a $10^{-3}$ M concentration of the substance, is 0.95 with a potential sweep rate 100 mV/sec, but 1.40 with a sweep rate 10 mV/sec. If the solution is diluted tenfold, the second reduction peak appears only with a potential sweep rate 50 mV/sec; and at 10 mV/sec, the ratio of peak heights is 0.86. This indicates the chemical nature of generation of secondary species and the relatively slow rate of this reaction. We believe that these species are anions of the original molecules, formed as a result of interaction of an anion radical with the original molecule, as was shown in the case of 4-nitrophenyl-3,5-dicyano-2,6-dimethyl-1,4-DHP [1, 3].

The values of the half-wave potential $E_{1/2}$ of the first and second species are quite insensitive to the electronic properties of the substituent R. The change from the methyl group with electron-donor properties (If) to the electron-acceptor p-nitrophenyl substituent (Id) facilitates the reduction of the molecule by 40 mV, and the anion by 100 mV. No linear correlation is observed between the reduction potential and either the Taft $\sigma^0$ constant or the Hammett $\sigma$ constant characterizing the substituent in the phenyl ring in position 4 of the heterocycle. This means that the substituent R can influence the reduction potential only through steric effects, even though any direct steric influence of this substituent on a nitrophenyl group in position 2 (or 6) of the heterocycle is very improbable.

In the course of ECG of compounds (Ib-f), ESR spectra registered the presence of primary anion radicals and also secondary dianion radicals. However, the primary radicals were quite unstable, and we were unable to determine the HFS constants for the anion radicals of Ib, d, e.

Analysis of the HFS of the ESR spectra (Table 2) indicates that, in the anion radicals and also in the dianion radicals of compounds Ia-f, the unpaired electron is delocalized mainly on one of the nitrophenyl fragments in position 2 (or 6) and the nitrogen atom of the heterocycle. The HFS constant due to the proton on the nitrogen atom could not be determined in the ESR spectra of the anion radicals, possibly because of the extreme broadening of the individual signals (Fig. 1, spectrum 1). Such broadening was not observed for either the anion radicals or dianion radicals of the previously studied 4-nitrophenyl derivatives of 1,4-DHP [1-3]. This may be evidence of influence of the second nitrophenyl fragment, leading to "migration" of the unpaired electron from one nitrobenzene ring to the other through the unshared electron pair of the nitrogen atom of the heterocycle [4]. Support for this hypothesis may be found in the fact that, for compound Ia (Fig. 1, spectrum 2), and also for compounds Ib, c, f, the width of the individual signals decreases and the ESR spectra become better resolved if the generation potential is increased to −1.5 to −1.6 V. The next stage of reduction of the nitro group corresponds to this potential. In this case, obviously, one of the nitro groups is further reduced, and the unpaired electron is localized on the other nitrophenyl fragment.

On the cyclic voltammetric curves of Ia-c, f in the interval of potentials from 0 to —1.7 V, with reverse sweep, we detected a redox system of a nitrosophenyl derivative; and by means of ESR we detected signals of ion radicals of p-substituted nitrobenzene (Fig. 1, spectrum 3), if the radical generation potential was held at —1.7 V and was then reduced sharply to —0.8 V. The mechanism of formation of nitrosophenyl derivatives in the process of reducing 4-nitrophenyl derivatives of 1,4-DHP is similar to that examined in [1-3] and will not be discussed here.

As noted above, on the polarograms for the 2,4,6-trinitrophenyl derivatives Id, e, still another wave appears at a potential of —1.3 V, a wave that is not observed for the 2,6-dinitrophenyl derivatives of 1,4-DHP. The height of this wave does not reach the one-electron level; on the cyclic voltammetric curves, it corresponds to a reversible redox system, the intensity of which depends on the original concentration of the substance and the potential sweep rate, the same as the "dianion radical/anion" redox systems described above. In the process of ECG of compounds Id, e, when the generation potential is increased, we do not observe any narrowing of the individual lines in the ESR spectrum; but on the background of signals of the dianion radicals the signals of another radical begin to increase rapidly. The individual lines of the new ESR spectrum are considerably narrower, which is characteristic for isotropic ion radicals (under the conditions of our experiment, $\Delta H \approx 0.12$ Oe). From an analysis of the HFS it follows that these signals correspond to the ESR spectrum of ion radicals of the p- and m-nitrophenyl derivatives (Id and Ie), in which there is no HFS constant due to the nitrogen atom of the heterocycle, and a new HFS constant appears due to the proton. This indicates reduction of the nitrophenyl fragment in position 4 of the heterocycles.

A comparison of the reduction potentials and HFS constants of the anion radicals of the 4-nitrophenyl fragment for the trinitroaryl compounds Id, e with the corresponding values for substances containing methyl groups in positions 2 and 6 [2, 3] shows that, in the case of compounds Id, e, the reduction potentials are shifted 120-130 mV toward more negative values; and the HFS constants on the nitrogen atom of the nitro group are about 0.4 Oe larger than for the previously studied compounds. This means that the electron-acceptor properties of the DHP part of the molecule at the moment of reduction of the 4-nitrophenyl fragment are considerably weaker in comparison with the original compound, as a result of deprotonation at the nitrogen atom of the heterocycle and partial reduction of the nitrophenyl fragments in positions 2 and 6 of the 1,4-DHP ring.

In the ESR spectra of compounds Id, e, we were unable to detect any signals from ion radicals with a nitrosophenyl structure, either from substituents in positions 2 or 6 or from the substituent in position 4 of the DHP ring, even though on the cyclic voltammetric curves with a sweep of potential to —2.8 V we observed a small oxidation peak at —0.7 V, which can be attributed to the formation of a nitrosophenyl derivative.

The subsequent polarographic waves at —2.0 and —2.7 V may be due to further reduction of the second nitrophenyl grouping or double bonds in the 1,4-DHP ring [2].

When we compare the potentials of the first wave of electrochemical reduction of 4-(p-nitrophenyl) derivatives of 2,6-bis(p-nitrophenyl)-1,4-DHP with the potentials of the corresponding 2,6-dimethyl-1,4-DHP (2, 3), we observe not only a shift of the reduction potentials of the dinitrophenyl derivatives toward more positive values, but also a displacement of the reaction center from the nitrophenyl group in position 4 of the DHP ring to the nitrophenyl fragment in position 2 (or 6) of the heterocycle.

On the basis of the results we have presented, we could not exclude the possibility of intramolecular transfer of electrons and protons in the electrochemical process, since it is known [5] that derivatives of 1,4-DHP are readily oxidized. Therefore, we carried out the electrochemical reduction of model compounds 2,6-bis(p-nitrophenyl) derivatives of pyridine (IIc, e, f) — the oxidized form of 1,4-DHP. We found that the pyridine-derivative nitro compounds are reduced more readily, by ~100 mV, in comparison with the corresponding dihydropyridine-derivative nitro compounds. By means of ESR, we detected signals of electrochemically generated ion radicals. The total length of the ESR spectra registered for the pyridines is considerably shorter (~15-20 Oe) than the lengths of the ESR spectra of the anion radicals and dianion radicals of the corresponding 1,4-DHP derivatives (27-30 Oe); and their HFS indicates greater degeneration of the individual signals. Although we were unable to decipher completely the HFS of the ESR spectra of the anion radicals of 2,6-bis(p-nitrophenyl) derivatives of pyridine, we can state that none of the ESR spectra registered with ECG of the dinitrophenyl derivatives of 1,4-DHP is the ESR spectrum of the corresponding pyridine.

Thus, the introduction of two or three nitrophenyl substituents into the 1,4-DHP ring in positions 2 and 6 or positions 2, 4, and 6, does not lead to intramolecular charge transfer from the DHP to the nitrophenyl part of the molecule in the course of reduction of these compounds. The shift of the reaction center from the nitrophenyl group in position 4 of the heterocycle [3] to the nitrophenyl fragment in position 2 is evidently due to an increase in electrophilic properties of the latter fragment as a result of conjugation with the $\pi$-electron system of the 1,4-DHP ring, which is not realized in the case of the 4-nitrophenyl substituent with preservation of the 1,4-DHP structure of the heterocycle.

## EXPERIMENTAL

PMR spectra were taken in a Bruker WH-DS instrument (90 MHz), internal standard TMS. The results from elemental analysis of compounds Ia, c, d, f and IIc, f for C, H, and N match the calculated values.

The methylation of compound Ic was performed in accordance with [6]; compounds Ib, e were obtained in accordance with [7], and their oxidized forms IIc, f were obtained in accordance with [8].

The electrochemical studies of compounds Ia-f were performed in anhydrous DMFA [9] on a background of tetrabutylammonium perchlorate (0.1 M). Classical polarograms and cyclic voltammetric curves were obtained by means of a PAR-170 electrochemical system (USA), using a three-electrode cell. The cathode was a mercury dropping electrode with forced detachment of drops (t = 0.5 sec, m = 0.90 mg/sec); the anode was a platinum wire; the comparison electrode was an aqueous saturated calomel electrode equipped with a transfer bridge for operation in nonaqueous solvents. Cyclic voltammetric curves were registered on a stationary glassy carbon electrode; the potential sweep rate was varied from 0.1 to 0.01 V/sec.

Free radicals were obtained by the ECG method using a three-electrode scheme, on the surface of a flat platinum electrode in a cell placed in the resonator of an ER-9 ESR spectrometer (East Germany) [10].

**1-Methyl-4-(p-chlorophenyl)-2,6-bis(p-nitrophenyl)-3,5-diethoxycarbonyl-1,4-dihydropyridine(Ia,$C_{30}II_{26}ClN_3O_8$).** To a solution of 0.58 g (0.01 mole) of the dihydropyridine Ic in 10 ml of dimethoxyethane, 0.29 g (0.012 mole) of sodium hydride was added. After completion of the anion formation (10 min), 0.28 g of methyl iodide was added. After 4 h, the reaction mixture was poured into 30 ml of water. The resulting precipitate was crystallized from ethanol, mp 191-193°C. PMR spectrum ($CDCl_3$): 0.93 (6H, t, $OCH_2CH_3$); 2.44 (3H, s, N—$CH_3$); 3.91 (4H, q, $OCH_2CH_3$); 5.13 (1H, s, 4-H), 7.22-7.71 ppm (12H, m, arom.). Yield of compound Ia 0.4 g (67%).

**4-Aryl-2,6-bis(p-nitrophenyl)-3,5-diethoxycarbonyl-1,4-dihydropyridine (Ic, d).** A 0.02-mole quantity of the corresponding aldehyde, 9.48 g (0.04 mole) of the ethyl ester of p-nitrobenzoylacetic acid, and 7.7 g (0.1 mole) of ammonium acetate in 10 ml of glacial acetic acid was refluxed for 3 h. The precipitate was filtered off and recrystallized from ethanol, obtaining Ic, d.

**4-(p-Chlorophenyl)-2,6-bis(p-nitrophenyl)-3,6-diethoxycarbonyl-1,4-dihydropyridine (Ic, $C_{29}H_{24}ClN_3O_8$)**, mp 238-239°C. PMR spectrum ($CDCl_3$): 0.93 (6H, t, $OCH_2CH_3$); 3.91 (4H, q, $OCH_2CH_3$); 5.20 (1H, s, 4-H), 5.86 (1H, s, N—H); 7.26-8.31 ppm (12H, m, arom.). Yield of compound Ic 3.4 g (29%).

**2,4,6-Tris(p-nitrophenyl)-3,5-diethoxycarbonyl-1,4-dihydropyridine (Id, $C_{29}H_{24}N_4O_{10}$)**, mp 263-265°C. PMR spectrum ($CDCl_3$): 0.91 (6H, t, $OCH_2CH_3$); 3.88 (4H, q, $OCH_2CH_3$); 5.35 (1H, s, 4-H); 6.02 (1H, s, N—H); 7.40-8.31 ppm (12H, m, arom.). Yield of compound Id 5.9 g (51%).

**4-Methyl-2,6-bis(p-nitrophenyl)-3,5-diethoxycarbonyl-1,4-dihydropyridine (If, $C_{24}H_{23}N_3O_8$).** A 0.3-g quantity (5 mmoles) of aldehyde ammonia and 1.19 g (5 mmoles) of the ethyl ester of p-nitrobenzoylacetic acid in 15 ml of ethanol was refluxed for 2 h. The precipitate was separated and crystallized from ethanol; mp 131-132°C. PMR spectrum ($CDCl_3$): 1.00 (6H, t, $OCH_2CH_3$); 1.31 (3H, d, 4-$CH_3$); 3.97 (4H, q, $OCH_2CH_3$); 5.13 (1H, s, 4-H); 5.80 (1H, s, NH); 7.40-8.28 ppm (8H, m, arom.). Yield of compound If 0.55 g (46%).

**2,6-Bis(p-nitrophenyl)-3,5-diethoxycarbonylpyridine (IIc, f).** A 1-mmole quantity of the corresponding dihydropyridine Ic, f was dissolved in 20 ml of glacial acetic acid and heated to boiling, after which 0.33 g (3 mmoles) of sodium nitrite was added in portions over the course of 20 min. The reaction mixture was cooled to 0°C, and the precipitate was separated and crystallized from methanol.

**4-(p-Chlorophenyl)-2,6-bis(p-nitrophenyl)-3,5-diethoxycarbonylpyridine (IIc, $C_{29}H_{22}ClN_3O_8$)**, mp 163-164°C. PMR spectrum (DMSO-$d_6$): 0.73 (6H, t, $OCH_2CH_3$); 3.84 (4H, q, $OCH_2CH_3$); 7.17-8.44 ppm (12H, m, arom.). Yield of compound IIc 0.5 g (87%).

**4-Methyl-2,6-bis(p-nitrophenyl)-3,5-diethoxycarbonylpyridine (IIf, $C_{24}H_{21}N_3O_8$)**, mp 135-136°C. PMR spectrum (DMSO-$d_6$): 1.02 (6H, t, $OCH_2CH_3$); 3.22 (3H, s, 4-$CH_3$); 4.15 (4H, q, $OCH_2CH_3$); 7.73-8.35 ppm (8H, m, arom.). Yield of compound IIf 0.42 g (88%).

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# MOLECULAR COMPLEXES OF AROMATIC N-OXIDES WITH TETRACYANOETHYLENE

**A. V. Ryzhakov and L. L. Rodina**

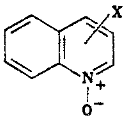
UDC 547.821.3'339.2'54-386.07:543.87

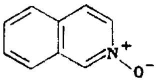
*Donor—acceptor interaction of tetracyanoethylene with aromatic N-oxides leads to the formation of two kinds of molecular complexes of the π,π-type: π-complexes and charge-transfer complexes. A correlation is observed between the reactivity of the N-oxides and the electronic properties of the substituents in the N-oxides.*

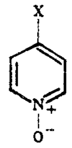
Heterocyclic N-oxides can be regarded as nitrones, the dipolar function of which enters in part into the aromatic system. As a consequence, in reactions of N-oxides with dipolarophiles it is necessary to consider both their capability of 1,3-dipolar cycloaddition and the possibility of forming donor—acceptor complexes [1].

We studied the interaction of aromatic N-oxides with tetracyanoethylene (TCE), which seems, on one hand, to be an extremely active dipolarophile, and on the other, a strong π-acceptor [2, 3].

We have investigated the interaction with TCE of aromatic N-oxides of quinolines (Ia-g), isoquinoline (II), and pyridines (IIIa-d), containing both electron—acceptor and electron—donor substituents:


Ia-q


II


IIIa-d

I a) $X=4\text{-}NO_2$, b) $X=4\text{-}Cl$, c) $X=H$, d) $X=4\text{-}CH_3$, e) $X=4\text{-}SCH_3$, f) $X=4\text{-}OCH_3$, g) $X=2\text{-}CH_3$,
III a) $X=OCH_3$, b) X=N-morpholyl, c) $X=OH$, d) $X=ONa$

## π-COMPLEXES

It was established that the interaction of the N-oxides Ib-g, II, and IIIa, b, d with TCE initially leads to the formation of colored "weak" complexes that exist only in solution in equilibrium with the original components. In the UV spectra of these π-complexes (Fig. 1), new "charge transfer" bands appear, but the positions of the absorption bands of the original components remain unchanged. By the continuous variation method [4] we found the equilibrium constants for the formation of π-complexes ($K^{eq}$), and we also showed that their composition corresponds to 1:1 stoichiometry (Table 1).

The equilibrium constants of π-complex formation for the N-oxides Ib-f show a linear correlation with the $\sigma_n^+$ constants of the substituents:

$$\lg K_i^{eq} = \lg K_0^{eq} + \rho\sigma_n^+,$$

where $K_i^{eq}$ and $K_0^{eq}$ are the equilibrium constants of π-complexation of the substituted and unsubstituted quinoline N-oxides, respectively; $\rho$ is the reaction constant; $\sigma_n^+$ is the Hammett constant for the para-substituent. The slope of the straight-line plot (Fig. 2) gives $\rho = -0.84$ (20°C, $CHCl_3$). The negative value of $\rho$ indicates that the N-oxides manifest electron—donor properties in this reaction; the relatively large value of $\rho$ indicates a large demand of the

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Leningrad State University, Leningrad. Petrozavodsk State University, Petrozavodsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 488-492, April, 1991. Original article submitted December 26, 1989.