for 6 h at 600°C. Directly before the experiment 50 ml of benzene was passed over at 550°C. At the end of the addition of the starting compound, nitrogen was passed for another 30 min, and the catalyzate was withdrawn and collected in a receiver with water cooling. 5-Vinylindole was isolated from the catalyzates on a column 20 mm in diameter and 500 mm long, filled with silica gel L 100/250, suspended in an ethyl acetate—petroleum ether (1:5) mixture, which is used as eluent. After evaporation of the solvent and recrystallization from petroleum ether, white needlelike crystals were obtained, mp 42-43°C, which agrees with our previously obtained data [1]. 5-Ethylindole (0.4 g, 14%) was also obtained from the catalyzate. The yield of vinylindole was 0.7 g (26%).

Dehydrodecarboxylation of ethyl 5-ethylindole-2-carboxylate was carried out in analogy with the above-described procedure. From 4.12 g of ethyl 5-ethylindole-2-carboxylate, 0.56 g of 5-vinylindole (21%) was obtained.

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ACETALS OF LACTAMS AND ACID AMIDES.

67.* POLAROGRAPHIC BEHAVIOR OF ENAMINES OF THE INDOLES SERIES IN ANHYDROUS DMF

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The polarographic behavior of derivatives of 2-aminomethyleneindoxyl and 3-aminomethyleneoxindole in anhydrous DMF has been studied and the results compared with data on the polarographic reduction of substituted aminomethyleneacetophenones and of related enaminoketones and eneaminoamides. It is established that the ease of reduction is determined by the nature of the substituent on the enamine and indole nitrogen atoms and also by the presence or absence of an α -methyl group in the α -position of the eneamines (for noncyclic enaminoketones).

It is known [2] that enaminoketones, I, of the pyrrolidine, piperidine, and hexahydroazepine series, in which the enamine nitrogen atom included in a saturated ring system, are reduced at a mercury drop electrode in anhydrous DMF in two steps, the first of which is reversible and corresponds to a one-electron transfer.

In this paper, we present the results of a polarographic study of enaminoketones of the indoxyl, IIa-d, and 1-acetylindoxyl, IIIa-c, series and also the enaminoamides of the oxindole, IVa-c, series (Table 1).



*For Communication 66, see [1].

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Com~ pound	R ¹	R ²	R3	$-\frac{E_{1/2}}{V^{*}}^{1}$	×=11im/C	$-\frac{E_{1/2}}{V^*}$	$-E_{1/2}^{111}, V^{2}*$	$-E_{1/2}^{-1V},$ v *
IIa IIb IIc IId IIIa IIIb IIC IVa IVb IVc Vb Vb Vc	Me H H Me H Me Me H	Me (CH ₂) ₅ Ph <i>o</i> -NO ₂ C ₆ H ₄ Me (CH ₂) ₅ Ph Me Ph Me Me (CH ₂) ₅ Ph	H H Me	$\begin{array}{c} 2,00\\ 1,96\\ 1,72\\ 1.08\\ 1,85\\ 1,85\\ 1,86\\ 1,56\\ 2,31\\ 2,13\\ 2,38\\ 2,20\\ 2,22\\ 1,86\end{array}$	$\begin{array}{c} 1,12\\ 1,12\\ 0,79\\ 1,05\\ 1,21\\ 1,17\\ 0,99\\ 1,33\\ 1,30\\ 1,19\\ 1,32\\ 1,20\\ 1,27\end{array}$	2,662,652,551,402,522,552,43	 2,23 	2,72

TABLE 1. Polarographic Characteristics of Eneaminoketones II-V

*Saturated calomel electrode.

A comparison of the data on the polarographic reduction of heterocyclic enamines II-IV, the previously studied series of compounds I, the series of acyclic enaminoketones Va-c, and enaminoamines VIa-d of analogous structure, allows the effect of the separate structural fragments on the ease and route of the electroreduction of these systems in an aprotic medium to be evaluated. The compounds studied were synthesized by the reaction of 1-acetylindoxyl, oxindole, acetophenone, and cyanoacetamide with the diethylacetal of DMF. followed the transamination of the enaminoketones thus obtained [3-6]. The general synthetic scheme can be represented as shown on the preceding page.



The polarographic behavior of enaminoketones Va-c is closely analogous to that of their cyclic analogs I. Just as with I, they are reduced in two steps, and the potentials $E_{1/2}$ of compounds Va-c are appreciably shifted to more negative values with respect to the $E_{1/2}$ of α,β -unsaturated compounds (because of the electron-donating effect of the substituted amine group).* An important feature of aminoketones I and V is the high stability of their anion-radicals; the electrooxidation signal of the anion-radicals of compounds Va-c can be observed on cyclic voltammograms even at potential scan rates of 5 mV/sec.

In anhydrous DMF, compounds II and III (except for nitro derivative IId) are also reduced in two steps (Table 1), but in the case of enaminoamides IV, as for acyclic enamines [8], only one reduction wave is observed. It can be concluded from the values of the proportionality constant in the Ilkovic equation for the first electroreduction waves of compounds II-V and the first waves of p-nitroaniline as well as nitro derivative IId, and from data from controlled potential coulometry and cyclic voltammetry, that the first waves of all of the aminoketones studied are reversible and correspond to one-electron transfers.

As could be expected, electron transfer is hindered on going from enaminoketones I and V to enaminoamides IV. This is caused by the substantially lower electron-accepting effect of the carbamide group compared to the ketone carbonyl and to the related decrease in stability of the anion-radical A being formed compared to anion-radical B (because of the destabilizing, electron-donating effect of the amide amino group).



Nevertheless, on comparing the reduction of enaminoamides IV and acyclic enaminoamides VI, one observes a marked easing of the electroreduction of compounds IV (comparing $E_{1/2}$ for IVa with VIa and for IVc with VIc) even despite the presence in compounds VI of the additional, electron-accepting, cyano group.

Analogously, compounds II and III are reduced considerably more easily than enaminoketones V (Table 1). Since the half-wave potential of a reversible process reflects the difference in energy of the initial and final (anion-radical)

^{*}For example, the difference in the values of $E_{1/2}$ for compound Va and chalcone exceeds 0.5 V [7].



Com- pound	R'	R²	R ³	E _{1/2} , V	Com- pound	Ri	R ²	R ³	E _{1/2} , V
VIa	Me	Me	H	-2,48	VIc	Me	Me	Me	$-2,41 \\ -2,26$
VIb	H	Ph	H	-2,13	VId	H	Ph	Me	

states, such facilitation of electron transfer is obviously related to the possibility of stabilizing the corresponding anion-radical through the formation of an aromatic, indole structure:



We now consider the effect of other structural features of enaminoketones II and III on the electron-transfer process. The presence of the electron-accepting acetyl group at the "nonenamino" nitrogen atom facilitates electron transfer, although the effect is relatively small ($\approx 150 \text{ mV}$; cf. enaminoketones II and III in Table 1).

The nature of the substituent at the enamine nitrogen atom has a considerably greater influence. Thus, the conjugation of the enamine nitrogen pair of electrons with a benzene ring (enaminoketones Ic, IIc, IIIc and enaminoamide IVc) leads to a shift of the $E_{1/2}$ potentials of these compounds to more positive values ($E_{1/2} \approx 300$ mV; see Table 1) compared to the $E_{1/2}$ of the corresponding dimethylaminoenaminoketones. A similar value for a similar effect is also found in the case of acyclic enamines, but only in the absence of a substituent in the α -position. Thus, on going from enamine VIb to VIa, $\Delta E_{1/2}$ amounts to 350 mV, whereas on going from enamine VId toVIc, it is only 150 mV. Such a specific effect of a methyl group in the α -position of an enamine is probably due to the disturbance of the conjugation of the pair of electrons of the nitrogen atom by the π -electrons of the double bond or the N-aryl substituent. For enamines VIa and VIc, the introduction of a methyl group, despite its electron-donating nature, leads to some increase in the ease of reduction ($\Delta E_{1/2} = 70$ mV), which may be due to some withdrawal from conjugation of the enamine dimethylamino group. An exactly contradictory effect can be observed for enamines VIb and VId, and is probably the result of a rotation of the benzene ring of the N-phenyl substituent, leading to some strengthening of the conjugation of the enamine nitrogen with the double bond and, correspondingly, to the hindering of electron transfer ($\Delta E_{1/2} = 130 \text{ mV}$). The spatial factor related to the introduction of the α -methyl group plays a very important role. The relatively small effect of an N-phenyl group when $E_{1/2}$ of enamines VIc and VId are compared ($\Delta E_{1/2} = 150 \text{ mV}$) is obviously due to the spatial factor. Finally, we note that in the case of enaminoamides of oxindole series IV, the methyl group in the α -position of the enamine has practically no effect on the ease of electron transfer (Table 1).

The anion-radicals of compounds II, III, and V differ substantially in stability, while all of the anion-radicals of the indoxyl derivatives studied have a low stability. If it is assumed that the basic direction of the further transformations of the anion-radicals is dimerization, then for the enaminoketones that do not have an aromatic substituent at the enamine nitrogen, an increase in the volume of the substituents leads, as would be expected, to an increase in the stability of the anion-radicals. Thus, when a dimethylamino group (IIa) is replaced by a piperidine group (IIb), the electrooxidation peak of the radical anions can be observed at an applied potential scan rate of 200 mV/sec, but only at an applied potential scan rate of over 1000 mV/sec in the case of enaminoketone IIa. Introduction of an acetyl group stabilizes the anion-radical still more, and the electrooxidation peak of the anion-radical of IIIb is observed even at an applied potential scan rate of 20 mV/sec.

The enaminoketones that have a phenyl substituent at the enamino nitrogen occupy a special position. Unexpectedly, the ability of the anion-radicals of these enaminoketones (IIc, IIIc, and Vc) is significantly low. Thus while the cathodic peak for enaminoketone Va is equal to the anodic on cyclic voltammograms even at an applied potential scan rate of 5 mV/sec, the anodic peak for enaminoketone Vc only appears at an applied potential scan rate of 200 mV/sec, and its height is significantly less than that of the cathodic peak. An analogous phenomenon is observed on going from enaminoketones IIa and IIb to compound IIc. This is the basis for assuming that for these enaminoketones, disproportionation makes a definite contribution along with dimerization.

We turn now to a more detailed consideration of the electroreduction of nitroenaminoketone IId. As can be seen from the data presented, the first two waves for this compound are one-electron waves. This kind of electroreduction of aromatic nitro compounds in aprotic media was shown earlier in the case of nitro derivatives of phenylfurans [9] and furans [10] to be determined by the nature of the substituent and to occur in those cases where a powerful, electron-accepting group is conjugated to the nitro group. Even though a pair of electrons on the enamino nitrogen is conjugated to a double bond and a carbonyl group, it is doubtful whether nitroenaminoketone IId can be assigned to such compounds, since this pair of electrons would also have to be conjugated to the phenyl group. On the other hand, it is known that the stability of anion-radicals of aromatic nitro compounds depends on the presence in the molecule of substituents prone to elimination [11-13]. Thus, for example, after transfer of the first electron, an iodide ion is eliminated rather rapidly from the anion-radical of p-iodonitrobenzene, and the reaction of the resulting radical species with the solvent leads to the formation of nitrobenzene [12, 13], the rate of this process depending on the temperature. As a result, though the oxidation-reduction of the p-iodonitrobenzene/corresponding anion-radical couple is recorded on cyclic voltammograms at a low temperature, at room temperature the anodic peak pertains exclusively to the oxidation of the nitrobenzene anion-radical. In the latter case, however, the anion-radical proves to have considerable stability.

The splitting of the C—O and S—N bonds in anion-radicals of aromatic nitro compounds takes place analogously [14]:

 $\begin{array}{c|c} \mathrm{Ph} & \mathrm{CH}_{\mathbb{P}} & \mathrm{CH}_{\mathbb{P}} & \mathrm{CH}_{\mathbb{P}} & \mathrm{COH} & & \\ & & & & \\ & \mathrm{NH} & \mathrm{Se} & \mathrm{C}_{0}\mathrm{H}_{4}\mathrm{error}\mathrm{NO}_{1} & p & & \\ & & & \mathrm{NH}_{2} \end{array} \end{array} = \begin{array}{c|c} \mathrm{H}_{1,3} & \mathrm{V} & \\ & & \mathrm{CH}_{1} & \mathrm{CH}_{2} & \mathrm{COH} & \\ & & & \mathrm{NH}_{2} \end{array}$

and has been used for the preparative removal of protective groups in amino acids.

Another route for the stabilization of anion-radicals of aromatic nitro compounds while preserving the nitro function is dimerization. For example, the electroreduction of 9-nitroanthracene in an aprotic medium leads primarily to the formation of a dimer at position 10 [15]. It is of interest to note, however, that electroreduction of this dimer occurs with the elimination of a nitrate ion and rupture of a C-C bond, and the products of electrolysis are anthracene and 9-nitroanthracene [15].

It can be assumed that the basic direction of the further transformations of the anion-radical obtained as a result of the transfer of the first electron in nitroenaminoketone IId is its disproportionation with rupture of the C-N bond, leading to the formation of p-nitroaniline:



The following facts are evidence in favor of such an assumption: the polarograms of this compound show two primary one-electron waves and, judging from the $E_{1/2}$ values both have to correspond to the electroreduction of a nitro compound. The second wave coincides with the first wave for the reduction of p-nitroaniline, which is -1.45 V under these conditions. If cyclic voltammograms of enaminoketone IId in solution are taken up to the potentials of the limiting current of the first wave (Fig. 1), then the anodic peak is absent even at high applied potential scan rates. Here, the anodic peak corresponding to the second wave of the electroreduction of enaminoketone IId (if the cyclic voltammograms are taken up to the potentials of the limiting current of the applied potential, and the height of the second, cathodic peak and of the anodic peak are increased on the addition of p-nitroaniline. The fact that on repeated application of the potential to the same hanging drop of mercury, the first cathodic peak disappears and the surface of the drop turns black, is also evidence of the depth of the transformation of the anion-radical obtained in the transfer of the first electron to a molecule of nitroenamino-ketone IId. Finally, we note that after carrying out the electrolysis at the potential corresponding to the plateau of



Fig. 1. Cyclic volt/ampere curves of nitroenaminoketone IId (1, 2; c = 1 mmole/liter) and p-nitroaniline (3; c = 1 mmole/liter) in anhydrous DMF with 0.05 mole/liter tetrabutylammonium perchlorate supporting electrolyte at a potential scan rate of 200 mV/sec with an applied potential up to the limiting current plateau: 1, 3) first waves; 2) second waves.

the limiting current of the first wave of compound IId, p-nitroaniline is found, by means of TLC, among the electrolysis products. This process is not quantitative, however, and if it is assumed that the concentration of p-nitroaniline is proportional to the height of the second wave of nitroenaminoketone IId, then the result of the exhaustive electrolysis of this compound at the potential of the limiting current of the first wave is a 45% yield of p-nitroaniline.

Of course, the data presented do not allow any judgement concerning the further transformations of the indole fragment. We note only that the third wave of nitroenaminoketone IId lies in the same region of potentials as that of the electroreduction of acetophenone in this medium, and the fourth wave coincides with the second wave of p-nitroaniline.

EXPERIMENTAL

The IR spectra were taken in mineral oil on a Perkin–Elmer 457 instrument. Mass spectra were obtained on a Varian MAT 112 spectrometer with direct introduction of the sample into the ion source. Temperature of the ionization chamber was 180°C. Energy of the ionizing electrons was 70 eV. Melting points were obtained on a Boetius-type heated column.

Polarographic measurements were carried out in a thermostated $(25 \pm 0.1^{\circ}\text{C})$ cell. The working electrode was a dropping mercury with m = 0.93 mg/sec, t = 0.24 sec. The reference electrode was a silver electrode immersed in the solution being studied. The supporting electrolyte was 0.05 M tetrabutylammonium iodide in DMF. The E_{1/2} potentials of the compounds studied were recalculated relative to the S.C.E. according to a "standard" (potassium) scale [16]. The polarograms were recorded on a Radiometer PO-4 polarograph. The cyclic voltammograms were taken on hanging mercury drop with an Electrochemical System PAR-170 instrument in 0.05 M tetrabutylammonium perchlorate supporting electrolyte.

The DMF was dried with fused KOH and redistilled in vacuum.

Coulometric measurements were carried out with the use of an Electrochemical System PAR-170 by the method in [8].

The presence of p-nitroaniline among the reaction products of the electrolysis of nitroenaminoketone IId was detected by means of TLC on Silufol. Development in UV light.

Enaminoketones IIa-c and IIIa-c were prepared by the method in [3], and enaminoketone Va by the method in [5].

The elementary analyses for C, H, and N corresponded to the calculated values.

2-(p-Nitrophenyl)aminomethyleneindolonone-3 (IId, $C_{15}H_{11}N_3O_3$). A mixture of 1.14 g (5 mmoles) of enaminoketone IIb and 0.7 g (5 mmoles) of p-nitroaniline in 10 ml of glacial acetic acid is stirred for 3 h at 20°C and allowed to stand overnight. The precipitate forming is filtered off and washed with acetic acid and ether. After 24 h a precipitate forms in the mother liquor and is also filtered off. Total yield 0.85 g (61%). $T_{mp} > 300^{\circ}C$ (from DMF). IR spectrum: 3320-3150 (NH), 1685 (C=O), 1610, 1600 cm⁻¹ (C=C). M⁺ 281.

Phenylaminomethyleneacetophenone (Vc, $C_{15}H_{13}NO$). A mixture of 1.75 g (10 mmoles) of enaminoketone Va, 1 g (10 mmoles) of aniline, and 0.6 ml of acetic acid in 10 ml of isopropyl alcohol is boiled for 1 h. After cooling, the

deposit precipitating is filtered off and washed with isopropyl alcohol and ether. Yield 0.7 g (31%). T_{mp} 140-141°C (from isopropyl alcohol). IR spectrum: 1630 (C=O), 1590 cm⁻¹ (C=C). M⁺ 223.

Enamine IVa is prepared by the method in [4].

3-Phenylaminomethyleneoxindole (IVb, $C_{15}H_{12}N_2O$). A mixture of 0.55 g (2.9 mmoles) of enamine IVa, 0.38 ml (3.9 mmoles) of aniline, and 15 ml of alcohol is boiled for 1.5 h, 0.17 ml of aniline and 15 ml of alcohol are added, and the boiling is continued for another 2 h. The reaction mixture is cooled, and 0.5 g (72%) of compound IVb is filtered off. T_{mp} 266-268°C (from methanol). IR spectrum: 3140 (NH), 1680 cm⁻¹ (C=O). M⁺ 236.

3-(β -Methyl-N,N-dimethyl)aminomethyleneoxindole (IVc, C₁₂H₁₄N₂O). A mixture of 4.75 g (35.7 mmoles) of oxindole, 6.88 g of the diethylacetal of N,N-dimethylacetamide, and 105 ml of alcohol are stirred at room temperature for 1 h, 1.4 ml of the acetal is added, and stirring continued for another 1 h. The reaction mass is cooled and filtered off. The mother liquor is evaporated, the residue dissolved with petroleum ether and then with ether and compound IVc is filtered off. T_{mp} 204.5-208°C (from ethyl acetate). IR spectrum: 3100-3140 (NH), 1680 cm⁻¹ (C=O). M⁺ 202. Yield 1.57 g (23%).

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