Electrochemical reduction of 5-halo-5-nitro-1,3-dioxanes and 2-halo-2-nitro-1,3-propanediols

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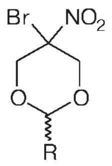
The character of the first stage of reduction of 5-X-5-nitro-1,3-dioxanes **1—10** and 2-X-2-nitro-1,3-propanediols **11** and **12** is independent of the nature of halogen (X = Br, Cl) and substituents in position 2 of the dioxane cycle. The transfer of two electrons to a molecule of compound **1—12** is accompanied by the anionoid elimination of halogen and formation of the anion of nitronic acid. The high mobility of halogen is mainly due to the acceptor nitro group capable of further transformations in the α-position to halogen. The direction of further reduction involving the electron transfer to electrochemically active groups in the aromatic fragment of the molecule is determined by the nature of these groups. Chloro-, bromo-, and iodophenyl-substituted derivatives **4**, **5**, and **8—10** are reduced as typical halobenzenes. In the case of nitrophenyl-substituted compounds **3** and **7**, the dioxane cycle opens to form dianions of *p*- and *m*-nitrobenzaldehydes along with the reduction of the nitroso group through the stages of formation of the radical anion and radical anion of the nitroso group. The radical anions of the nitro and nitroso derivatives were identified by ESR.

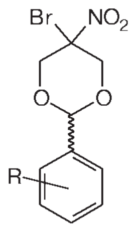
Key words: 5-halo-5-nitro-1,3-dioxanes, 5-halo-5-nitro-1,3-propanediols, electrochemical reduction, elimination of halogen, radical anion, ESR spectroscopy.

5-Bromo-5-nitro-1,3-dioxane (**1**) (Bronidox) and 2-bromo-2-nitro-1,3-propanediol (**11**) (Bronopol, Vantol, Bronitol) are some of the most required antimicrobial additives (preservatives, stabilizers) for water-containing medicinal and cosmetic compositions due to their relative chemical stability, hypoallergenic effect, a wide spectrum of antimicrobial activity, and a series of other properties.[1] The biological effect of these compounds is associated with the oxidation of thiol groups of the dehydrogenase enzymes of the cellular wall to give disulfide groups. Non-specificity of such a mechanism provides a universal character of the effect of these antiseptics and the absence of adaptation to them,[1] and search for analogs with the close activity spectrum concerns, to a great extent, the class of 5-halo-5-nitro-1,3-dioxanes.

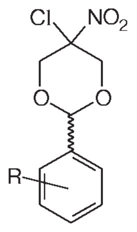
Oxidative activity of geminal nitrobromides is explained by the electron-deficient character of the bromine atom, and their electrochemical characteristics could quantitatively describe this important property. We studied the electrochemical reduction (ER) of 5-halo-5-nitro-1,3-dioxanes **1—10** and 2-halo-2-nitro-1,3-propanediols **11** and **12** to reveal the factors (the nature of halogen, substituents, dioxane cycle) determining the mobility of halogen in processes of electron transfer.



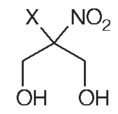
1, 2



3—6



7—10



11, 12

X = Br (**11**); Cl (**12**)

Results and Discussion

Despite diverse studies of the physicochemical and biological properties of cyclic acetals, information on their electrochemical behavior is very restricted. It is only known that dioxanes are in the group of most difficultly reducible compounds,[2] and 5-nitro-5-alkyl- and 2-(nitrophenyl)-5,5-dialkyl-1,3-dioxanes in a water-alcoholic medium (pH 12.7) are reduced as typical nitro compounds with the transfer of four electrons per molecule.[3]

The potentials of the first stages of polarographic ER of compounds **1—12** in DMF against Et_4NClO_4 (0.1 mol L^{-1}) lie in the near-cathodic region of potentials (Table 1). Several subsequent waves are observed at more

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negative potentials in the polarograms of compounds **3—5**, **7—10** containing electrochemically active groups in the aromatic fragment of the molecule. The ER process at the first stage is impeded by the adsorption of the components of the redox system. This is indicated by the morphology of the polarograms and the fact that the potentials of the first waves depend on the material of the electrode. For example, for compounds **3** and **7** (Fig. 1), the pronounced current drop is observed after the first wave, and the adsorption maximum is detected for compound **5**. The ER of all compounds on a mercury dropping (MD) electrode occurs much more easily than that on a glass-carbon (GC) electrode (see Table 1). It is most likely that the adsorption of dioxanes **1—10** and propanediols **11** and **12** on mercury facilitates this process.

Table 1. Characteristics of waves (MDE) and peaks (GCE) of reduction of 5-halo-5-nitro-1,3-dioxanes **1—10** and 2-halo-2-nitro-1,3-propanediols **11** and **12** in DMF against 0.1 *M* Et_4NClO_4 as supporting electrolyte

Compound	$-E_{1/2}{}^a$/V (MDE)	$2.3RT/\alpha nF$ ^{b} /mV	n^c	$i_{an}/i_{cat}{}^d$	$-E_p{}^a$/V (GCE)
1	0.66	115	2.0	0.66	1.10
2	0.66	100	2.0	0.74	1.14
3	0.63	105	2.0	0.80	1.02
	1.48	63	1.0	0.60	1.48
	1.84	84	0.6	0.10	
	2.13	115	1.5	0.14	
	2.44	115	1.2	0	
4	0.65	105	2.1	0.68	1.03
	2.63	94	2.1	0	
	2.89	84	1.8	0	
5	0.78	32	2.1	0.60	1.03
	2.04	94	1.9	0	
6	0.71	62	2.0	0.80	1.20
7	0.88	94	2.0	0.28	1.21
	1.41	63	1.0	0.75	1.43
	1.89	105	1.6	0.42	
	2.74	200	2.7	0	
8	1.02	94	2.0	0.46	1.34
	2.62	105	2.2	0	
	2.87	100	2.2	0	
9	1.01	115	1.9	0	1.34
	2.91	136	2.6	0	
10	1.02	115	2.0	0.48	1.33
	2.65	170	2.0	0	
11	0.66	115	2.0	0.75	1.14
12	1.04	115	2.0	0	1.34
p-Nitrobenzaldehyde	1.12	63	1.0	0.60	
	1.67	65	1.2	0.46	
p-Nitrobenzaldehyde—**7** (1 : 1)	0.88	94	2.0	0.28	
	1.13	63	1.0	0.60	
	1.42	63	1.2	0.60	
	1.67	65	1.5	0.40	
	1.89	105	1.9	0.42	
	2.74	200	2.7	0	
m-Nitrobenzaldehyde	1.27	63	1.0	0.60	
	2.11	80	2.6	0	
	2.42	90	2.6	0	

Note. Concentration of compounds $C = 1 \cdot 10^{-3}$ mol L^{-1}, $T = 298$ K.

[a] Obtained *vs*. $Ag/AgNO_3$ in MeCN (0.01 mol L^{-1}).

[b] Calculated by the formula $2.3RT/\alpha nF = (E_{3/4} - E_{1/4})/0.954$.

[c] Number of electrons determined by the method of comparison with the one-electron reduction wave of *p*-nitrobenzaldehyde.

[d] The ratio of the limiting anodic commutated current (i_{an}) to the limiting cathodic current (i_{cat}) for the reversible process under chosen conditions ($f = 10$ Hz, $t_1 = 0.5$ s) is equal to 0.60.

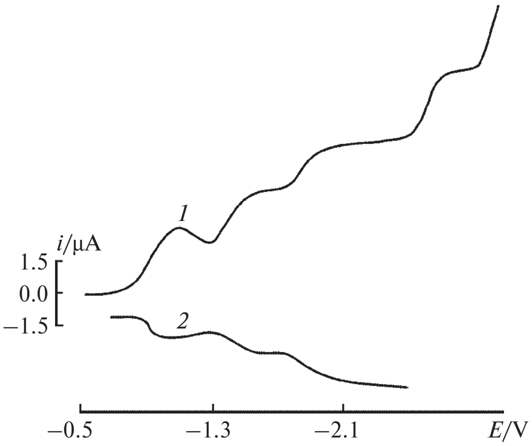


Fig. 1. Classical (*1*) and commutated (*2*) polarograms of compound **7** recorded in DMF against Et_4NClO_4 (0.1 mol L^{-1}) as supporting electrolyte.

According to the data of cyclic voltammetry (CVA), the first cathodic peak is irreversible for compounds **1—12** on a glass-carbon electrode (Fig. 2), and its height corresponds to the transfer of two electrons. The oxidation currents of the ER products are detected in the region of potentials of the first wave in the commutated curves of

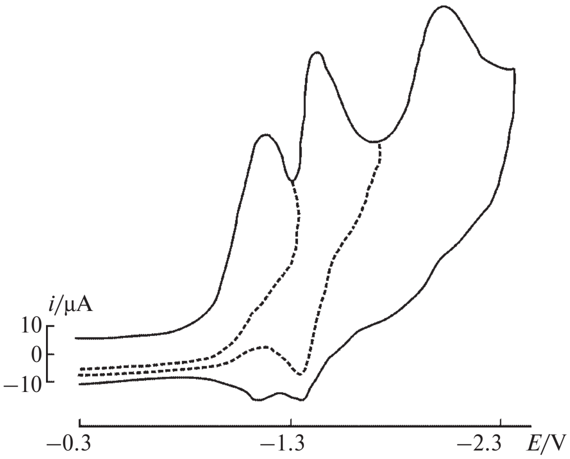


Fig. 2. Cyclic voltammogram of a solution of dioxane **7** ($3 \cdot 10^{-3}$ mol L^{-1}) in the DMF—Et_4NClO_4 (0.1 mol L^{-1}) system on a glass-carbon electrode at a potential sweep of 100 mV s^{-1}. Dotted lines designate the reverse branches of CVA for the potential reverse after the first and second reduction peaks.

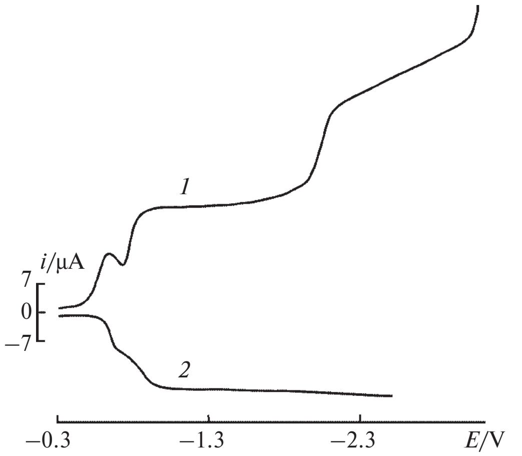


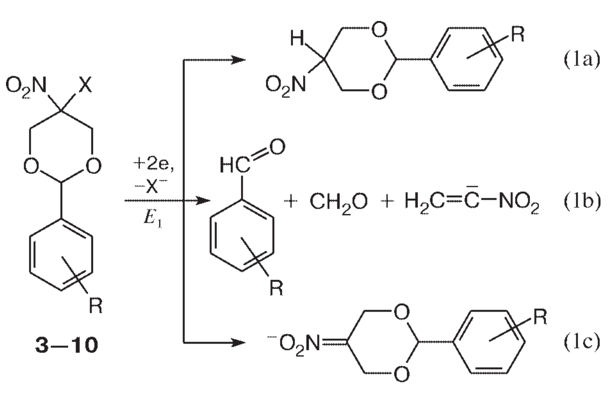
Fig. 3. Classical (*1*) and commutated (*2*) polarograms of compound **5** recorded in DMF against Et_4NClO_4 (0.1 mol L^{-1}) as supporting electrolyte.

all bromo-derivatives and some chloro-derivatives (see Table 1). The reduction potentials of 5-bromo-5-nitro-1,3-dioxanes **1—6** and 2-bromo-2-nitro-1,3-propanediol (**11**) almost coincide. The same is characteristic of chloro derivatives **8—10** and **12**, and the latter are reduced more worse than the corresponding 5-bromo-substituted derivatives. Substituents in the aryl fragment of the molecule weakly affect the potentials of the first stage of ER in the series of both 5-bromo derivatives **3—6** and 5-chloro derivatives **7—10**: electron-withdrawing groups and atoms (NO_2, Cl, Br) somewhat facilitate and electron-releasing groups (NEt_2) impede electron transfer. A noticeable influence of the R substituent is observed in compound **5** (Fig. 3), which is probably related to its strong adsorption on the electrode surface. The addition of a tenfold (with respect to the depolarizer) amount of a proton donor, *viz.*, phenol, does not change the characteristics of the first wave and, hence, protons are not involved in the potential- and current-determining stages. This behavior of the bromo and chloro derivatives is characteristic of the two-electron cleavage of the C—X bond.[2] In the considered case, the transfer of two electrons at the first stage results, evidently, in the elimination of the halide ion from position 5. Halide ions are oxidized on mercury (or mercury is oxidized in the presence of halide ions) at potentials near –0.8 V, whereas on glass-carbon this process occurs at much more positive potentials.[2] This is precisely the oxidation of the halide ions formed by the reduction of compounds **1—12** which results in the appearance of the anodic current in the commutated curves of these compounds on a mercury dropping electrode. 5-Chloro-5-nitro-1,3-dioxanes **7—10** and 2-chloro-2-nitro-1,3-propanediol (**12**) are reduced at potentials of –0.88—–1.02 V. The chloride ions formed in this process are oxidized on mercury at more positive potentials, and the anodic commutated current depends strongly on the choice of the oxidation potential. Therefore, for some compounds (**7**, **8**, **10**) the anodic current is detected, and for others (**9**, **12**) it is not.

The obtained results imply that the reaction site at the first stage of ER of compounds **1—12** is always the C—X bond, and all other structural fragments of the molecule do not undergo transformations at this stage. It is noteworthy that the electrochemical cleavage of the C—X bond is very easy in electron transfer processes, *i.e.*, halogen in the *gem*-position to the nitro group is very mobile. A comparison of the ER potentials for 2-bromoethanol ($E_{1/2}$ = –2.45 V)[4] and studied compounds **1—6** and **11** shows that the electron transfer with the C—Br bond cleavage on a mercury electrode is energetically more favorable, in the latter case, by 168—175 kJ mol^{-1}. The transition from 2-halo-2-nitro-1,3-propanediols **11** and **12** to dioxanes **1—10** and the presence of substituents in position 2 of the dioxane cycle have almost no effect on the electron-withdrawing properties of the C—X bond. In other words, the dioxane cycle itself insignificantly affects the properties of the C—X bond and serves a weak conductor of electronic effects of groups from position 2 to position 5 of the heterocycle.

The main factor determining the energy gain for electron transfer and electrochemical mobility of halogen in position 5 is the presence in the α-position of the electron-withdrawing nitro group capable, in turn, of further electrochemical transformations. According to the known schemes of ER of organohalogen compounds,[2,4] three directions are possible for stabilization of the carbanion formed by the two-electron reduction of dioxanes **3—10** (Scheme 1): formation of the dehalogenated product (Eq. (1a)), opening of the heterocycle to form benzaldehyde derivatives *via* the mechanism of coupled elimination (Eq. (1b)), and formation of the corresponding anion of nitronic acid (Eq. (1c)).

Scheme 1



3—10

3a—10a

The first and third directions are possible for dioxanes **1**, **2** and propanediols **11**, **12**. It is known[3] that 2,5-dimethyl-5-nitro-1,3-dioxane is reduced at the potential $E_{1/2} = -1.66$ V. Nitroaliphatic compounds are reduced at close potentials (for example, for 2-methyl-2-nitro-1-propanol $E_{1/2} = -1.82$ V).[5] For all compounds, except for **3** and **7**, reduction waves are absent in this potential region, which concludes that dehalogenated products are not formed in noticeable amounts by Eq. (1a). The reaction products do not contain substituted benzaldehydes, which, in the case of compounds **4—6** and **8—10**, should be reduced in the potential region about −2.4 V.[2] The formation of *p*- and *m*-nitrobenzaldehydes can be assumed from compounds **3** and **7**, respectively, by opening of the dioxane cycle. Under identical conditions, we recorded the polarograms of *p*- and *m*-nitrobenzaldehydes, whose characteristics are presented in Table 1. For *p*-nitrobenzaldehyde, two reversible reduction waves are detected, which correspond to the formation of the radical anions ($E_{1/2}{}^1 = -1.12$ V) and dianions ($E_{1/2}{}^1 = -1.67$ V).

The absence of waves at these potentials in the polarograms of compound **7** (see Table 1) indicates that at the first stage of ER of dioxane **7** the heterocycle is not opened to form *p*-nitrobenzaldehyde. Similar conclusion follows from a comparison of the ER potentials of compound **3** and *m*-nitrobenzaldehyde.

It is most likely that for all compounds **1—12** reduction at the first stage is completed with the formation of anions of the corresponding nitronic acids **1a—12a** (Eq. (1c)). The presence of the nitro group in the α-position to the leaving halogen substantially facilitates the stage of electron transfer and also stabilizes the product of two-electron transfer due to the formation of the anion of nitronic acid, which is electrochemically inactive in an aprotic medium.

The second wave for dioxanes **3** and **7** containing the nitro group in the benzene fragment is one-electron and reversible (see Fig. 1, Table 1). Paramagnetic species, whose spectra are characteristic of radical anions of nitroaromatic compounds, are detected by ESR at potentials of this wave under electrolysis conditions (Fig. 4). Therefore, the second wave of these compounds correspond to the ER of the nitrophenyl fragment of nitronates **3a**, **7a** to radical dianions **3b** and **7b** (**3b:** $a_{N} = 1.070$, $a_{H(6')} = 0.389$, $a_{H(2'),H(4')} = 0.333$, $a_{H(5')} = 0.111$, $a_{H(2)} = 0.056$ mT; **7b:** $a_{N} = 0.944$, $a_{H(3'),H(5')} = 0.333$, $a_{H(2'),H(6')} = 0.100$, $a_{H(2)} = 0.178$ mT) (Schemes 2 and 3).

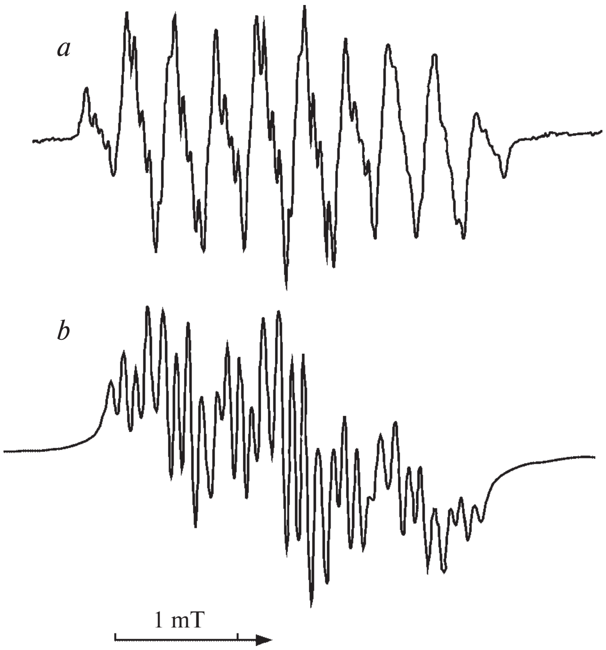
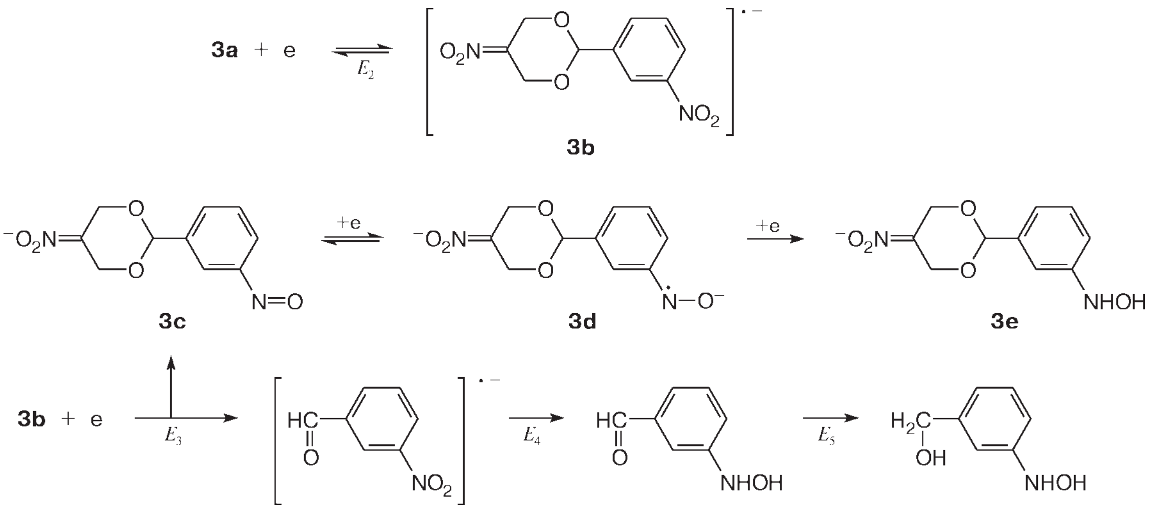
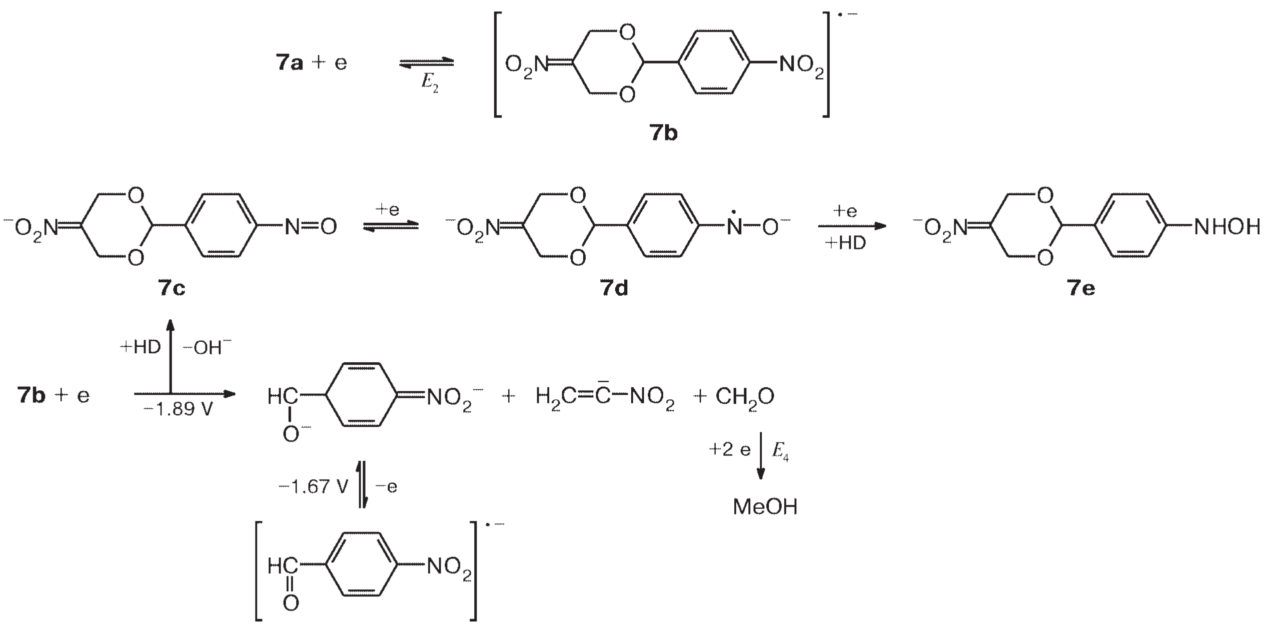


Fig. 4. ESR spectra of radical dianions **3b** (*a*) and **7b** (*b*) generated in the DMF—Et_4NClO_4 (0.1 mol L^{-1}) system by the electrochemical reduction of solutions of dioxanes **3** and **7** (10^{-3} mol L^{-1}) at potentials of the second peaks on a platinum helical electrode directly in the resonator of an ESR spectrometer.

Scheme 2



Scheme 3



Similar radical anions were detected previously[3,6] for the chemical reduction of 2-nitrophenyl-1,3-dioxanes in tetrahydrofuran; however, the authors gave only the constants of spin-spin interaction with the nitrogen atom nucleus. Our values for these constants for radical dianions **3b** and **7b** agree reasonably with published data.[3,6] These radicals are stable in the time scale of voltampere measurements (seconds) but, according to the ESR measurements, their lifetime is much shorter than that of radical anions of simple nitrobenzenes. One of the reasons for this is the consumption of the radical dianions in the homogeneous reaction involving more readily reducible initial compounds **3** and **7**.

The subsequent ER of compounds **3** and **7** proceeds through different ways (see Schemes 2 and 3). The third and fourth reduction waves (see Table 1) are detected in the polarograms of compound **7** (see Table 1). Rather stable reduction products were detected at potentials of the third wave by the commutator polarography; they are oxidized in the same potential region (i_{an}/i_{cat} = 0.42). Electrolysis results in radical anions of nitroso derivative **7d** (a_N = 0.856, $a_{H(3')}$ = 0.378, $a_{H(5')}$ = 0.283, $a_{H(2'),H(6')}$ = 0.100, $a_{H(2)}$ = 0.189 mT). In addition, when the voltammogram is recorded on a platinum electrode directly in the resonator of an ESR spectrometer with potential reverse after the third cathodic peak was passed, peaks of oxidation of the ER products appear in the inverse branch of the curve, and radical anions of *p*-nitro- and *p*-nitrosobenzaldehydes were detected by ESR. Therefore, the transfer of the fourth electron to the molecule of compound **7** along with the reduction of the nitro group to hydroxylamine results in opening of the dioxane cycle and formation of the dianion of *p*-nitrobenzaldehyde. The oxidation of this dianion at less cathodic potentials ($\Delta E_{1/2}$ = 0.22 V) was established by methods of commutator polarography and CVA. Since the relative anodic commutated current (i_{an}/i_{cat} = 0.42) for the third wave is somewhat lower than that for the second reduction wave of *p*-nitrosobenzaldehyde (i_{an}/i_{cat} = 0.46), we can assume that heterocycle opening with the formation of dianions of *p*-nitrobenzaldehyde is the main route of the four-electron ER of compound **7**. Radical anions of *p*-nitrosobenzaldehyde can be obtained by ER of both *p*-nitrosobenzaldehyde and nitroso derivative **7c**.

Direct data on the nature of other products of heterocycle opening are lacking. Note that the potential of the fourth wave is close to the ER potentials of aliphatic aldehydes, and the waves characteristic of the reduction of the nitro group are absent. This suggests the formation of the electrochemically inactive anion of nitroethylene and formaldehyde reduced at potentials of the fourth wave (see Scheme 3).

In the case of compound **3**, radical dianion **3b** formed at the second stage (see Scheme 2) is further reduced in three steps with the total transfer of three electrons to the molecule (see Table 1). The radical anion of the nitroso derivative **3d** was detected by ESR at potentials of the third wave (a_N = 0.833, a_H = 0.444, a_H = 0.389, a_H = 0.311, $a_{H(5')}$ = 0.111, $a_{H(2)}$ = 0.056 mT). The $E_{1/2}$ values of the fourth and fifth polarographic waves for compound **3** exactly coincide with the potentials of the second and third waves of *m*-nitrobenzaldehyde (see Table 1). The fast potential reverse after passing the fourth cathodic peak under CVA conditions on a platinum electrode made it possible to detect by ESR the appearance in a solution of new paramagnetic species, whose spectra coincide completely with those of the radical anions of *m*-nitro- and *m*-nitrosobenzaldehydes. Evidently, as in the case of compound **7**, the process of reduction of the nitro group to hydroxylamino group and opening of the dioxane cycle with the formation of the dianion of *m*-nitrobenzaldehyde compete during the transfer of the fourth electron to the molecule of compound **3**. As shown in a special experiment with *m*-nitrobenzaldehyde (see Table 1), this species (unlike the dianion of *p*-benzaldehyde, which is rather stable due to the formation of the quinoid structure) is protonated under experimental conditions, which results in the reduction of the nitro group to hydroxylamino group and of the aldehyde group to CH_2OH group (see Scheme 2).

The reduction of compounds **4**, **5**, and **8—10** can be interpreted on the basis of concepts about the mechanism of ER of compounds **3** and **7**. At the first stage, the two-electron transfer occurs with elimination of the halide ion in the dioxane cycle and formation of the anion of the corresponding nitronic acid. Electrochemically active groups of the aromatic fragment of the molecule are reduced at the next stages. Chloro-, bromo-, and iodophenyl derivatives **4**, **5**, and **8—10** are irreversibly reduced as typical halobenzenes with transfer of two electrons (see Table 1), cleavage of the C—X bond, and protonation of the carbanion that formed. This assumption agrees with the values of ER potentials, which coincide with the potentials of chloro-, bromo-, and iodobenzenes, respectively.[2] The C—Cl bonds of dichloro derivatives **4** and **8** are reduced stepwise; therefore, three waves are observed for these compounds, and the potential of the latter virtually coincides with the potential of the second reduction wave of monochloro derivative **9**. However, it is yet unclear which of these two bonds is cleaved first. In cannot be ruled out that both C—Cl bonds are reduced competitively.

Thus, the direction of ER of 2-aryl-5-halo-5-nitro-1,3-dioxanes at the first stage is independent of the nature of halogen in position 5 and the nature of substituents in the benzene cycle. The transfer of two protons is accompanied by the anionoid elimination of halogen at very low potentials. The oxidation of thiol groups of enzymes of the cellular wall needs the transfer of two electrons and two protons. Therefore, we can assume that compounds **1—12** play the role of acceptors of these species when they are used as antiseptics. This process is similar to the electrochemical two-electron reduction of an acceptor followed by the protonation of the nitronate anion and formation of the corresponding nitro compounds. Since the mechanisms of the first stages of ER of all studied compounds are similar, the reduction potentials ($E_{1/2}$ or E_p) are the quantitative measure of their oxidative activity. The compounds under study are adsorbed on a mercury electrode, and the experimentally measured potentials (see Table 1), reflecting mainly the electron-withdrawing properties of the molecule, also include some unknown value of the adsorption energy. On a glass-carbon electrode adsorption is manifested to a lower extent and, therefore, reduction potentials on this electrode material can be considered as the primary quantitative estimation of the antiseptic properties of compounds **1—12**. Nevertheless, it is worth mentioning that at the qualitative level the change in the ER potentials in the series of studied compounds (except for compound **5**) on a mercury electrode almost coincides with the data for a glass-carbon electrode.

Experimental

5-Halo-5-nitro-1,3-dioxanes were synthesized by heating of 2-halo-2-nitro-1,3-propanediol **11** or **12** with corresponding aldehyde in benzene in the presence of *p*-toluenesulfonic acid under conditions of azeotropic distilling off the water evolved. The diastereomeric composition of thus obtained products was not studied. All compounds had adequate spectroscopic and analytical characteristics. The physicochemical constants of dioxanes **1**, **2**, and **7** coincided with those in Ref. 7. The elemental composition and melting points of the newly obtained dioxanes are presented in Table 2.

The electrochemical reduction of dioxanes **1—10** and propanediols **11** and **12** was studied by methods of classical and commutator polarography, CVA, and electrolysis at controlled potential in combination with ESR in DMF against 0.1 *M* Et_4NClO_4 as supporting electrolyte. Polarograms were detected on PU-1 and LP-7e polarographs. The characteristics of the capillary: $m = 0.71$ mg s^{-1}, $t_1 = 0.5$ s. The switching velocity was 10 Hz. Cyclic voltammograms were recorded on a PI-50-1 potentiostat using a glass-carbon disk electrode with the diameter $d = 2$ mm, which was embedded into Teflon. The potential

Table 2. Elemental composition and melting points of synthesized dioxanes **3—6** and **8—10**

Compound	M.p. /°C	Found / Calculated (%)			Molecular formula
		C	H	N	
3	120—122	36.26 36.04	2.82 2.70	8.86 8.41	$C_{10}H_9BrN_2O_6$
4	146—147	33.21 33.61	1.96 2.24	4.36 3.92	$C_{10}H_8BrCl_2NO_4$
5	147—151	28.72 28.99	2.04 2.17	3.51 3.88	$C_{10}H_9BrINO_4$
6	98—100	46.44 46.80	5.05 5.29	7.45 7.80	$C_{14}H_{19}BrN_2O_4$
8	123—126	38.05 38.40	2.37 2.56	4.75 4.48	$C_{10}H_8Cl_3NO_4$
9	65—67	42.66 43.17	2.94 3.24	4.76 5.09	$C_{10}H_9Cl_2NO_4$
10	121—123	37.46 37.21	2.55 2.79	4.05 4.34	$C_{10}H_9BrClNO_4$

sweep was 100 mV s^{-1}. A silver electrode Ag/$AgNO_3$ in MeCN (0.01 mol L^{-1}) ($E_0^{Fc/Fc+}$ = +0.16 V) was used as the reference electrode. A Pt wire served as the auxiliary electrode. The solution was deaerated with argon. The concentration of the substrate in polarographic measurements was $1 \cdot 10^{-3}$ mol L^{-1}, and that for recording cyclic voltammograms was $3 \cdot 10^{-3}$ mol L^{-1}. The temperature of measurements was 298 K. Procedures for purification of solvents and supporting salts and polarographic measurements were described previously.[8]

ESR studies in combination with electrolysis were carried out at 298 K on an installation, which combines an SE/X-2544 ESR spectrometer, a PI-50-1 potentiostat, and an electrochemical cell developed at the Institute of Organic and Physical Chemistry.[9] The setup makes it possible to conduct an electrochemical process directly in the resonator of the ESR spectrometer. The working electrode was a platinum coil, the auxiliary electrode was a platinum wire, and the reference electrode was a silver wire. Solutions were deaerated by the triple repetition of the freezing—evacuation—thawing out cycle.

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