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Synthesis and Study of Electrochemical Properties of the Sterically Hindered Phenol Derivatives and the Corresponding Radicals

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Abstract—1-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-2-arylbenzimidazoles were synthesized by the condensation of 2,6-di-*tert*-butyl-*p*-benzoquinone imine with aromatic aldehydes. 2-(3,5-Di-*tert*-butyl-4-hydroxybenzylidene)benzimidazoles were synthesized by the reaction of 2-aminobenzimidazole with 2,6-di-*tert*-butyl-4-hydroxybenzaldehyde. The substances were characterized by elemental analysis, IR and NMR spectra. The electrochemical reduction and oxidation of these compounds and phenoxy radicals derived from them was studied by cyclic voltammetry. The stability of the studied phenoxy radicals was confirmed by the electron spin resonance method.

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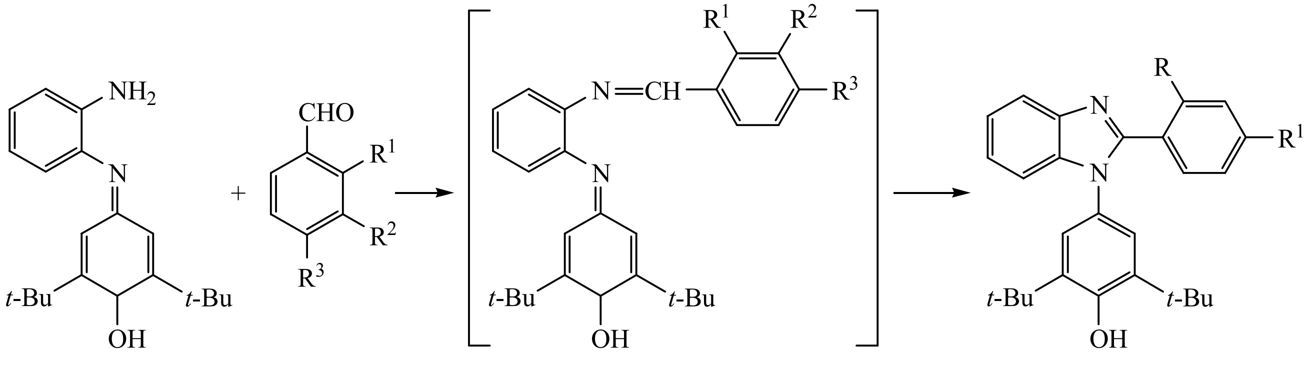
The chemistry of sterically hindered phenols is updated continuously with a new information, because of both the practical significance of phenols (radioprotectors, antioxidants, etc.) and due to the studies of the cell biochemistry, as the most important biochemical processes are associated with reversible hydroxylation reactions of oxidized and reduced forms of phenols (α-tocopherol, ubiquinone, nicotinamide, and flavin adenine dinucleotides NADH, FADH2) [1, 2].

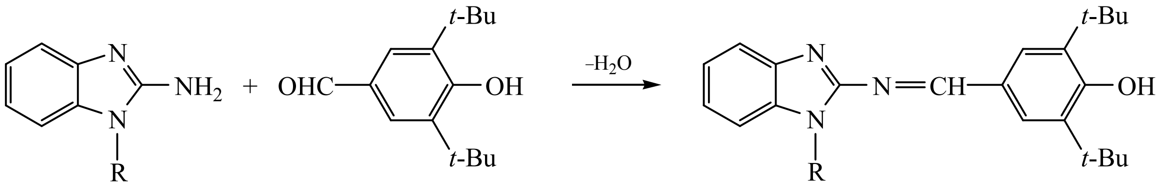
Continuing systematic investigations in this area we now report on the synthesis and properties of 1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-arylbenzimidazoles **I**–**X** and 2-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)benzimidazoles **XI–XIII**, the starting compounds in the synthesis of new bisphenols and other biologically active substances. Compounds **I–X** were synthesized by condensation of 2,6-di-*tert*-butyl-*p*-benzoquinone imine with aromatic aldehydes (method *A*).



I–**X**

I, R = R^1 = H; **II**, R = H, R^1 = OCH_3; **III**, R = OCH_3, R^1 = H; **IV**, R = R^1 = OCH_3; **V–VIII**, X, R = H; **IX, IX**, R = Cl; R^1 = $N(CH_3)_2$ (**V**), OH (**VI**), NO_2 (**VII**), Br (**VIII**), H (**IX**), CH_3 (**X**).

Synthesis of 2-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)benzimidazoles **XI–XIII** was carried out by condensation of 2-aminobenzimidazole with 2,6-di-*tert*-butyl-4-hydroxybenzaldehyde (method *B*).



XI–XIII

XI, R = H; **XII**, R = CH_3; **XIII**, R = $C_6H_5CH_2$.

The composition and structure of the obtained compounds **I–XIII** are confirmed by IR and NMR spectroscopy and elemental analysis (Tables 1).

The IR spectra of the whole series of 1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-arylbenzimidazoles **I–X** are identical. They include characteristic bands of stretching vibrations of non-associated (ν = 3560 cm^{-1}) and associated (ν = 3450 cm^{-1}) OH groups, bands of the stretching vibrations of C–H bonds of the aromatic ring (ν = 3050–3000 cm^{-1}), bands of the stretching sym-metric and asymmetric vibrations of C–H bonds of *tert*-butyl groups (ν = 2950–2850 cm^{-1}), and absorption bands of aromatic bonds of the rings (ν = 1600–1550 cm^{-1}). In addition, the spectra include the absorption band of bending vibrations of *tert*-butyl groups (δ = 1395–1385 cm^{-1}), and CH of aromatic rings (δ = 900–750 cm^{-1}). In the IR spectra of 2-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)benzimidazoles, in addition to these bands, there are the bands of C=N stretching vibrations (ν = 1660 cm^{-1}).

The ^1H NMR spectra of the synthesized compounds contain a singlet of protons of *tert*-butyl groups (δ = 1.38 ppm), a singlet of the proton of the hydroxy group (δ 5.80), disappearing at adding D_2O, and the signals of aromatic protons (δ = 7.2–7.9 ppm).

The electrochemical properties of 1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-arylbenzimidazoles, 2-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)benzimidazoles, and respective phenoxy radicals were studied by cyclic voltammetry on a stationary platinum disk electrode in acetonitrile. The reference electrode was the saturated calomel electrode, the auxiliary electrode was a platinum spiral; as a background electrolyte tetraethylammonium perchlorate was used. The depolarizer concentration in the cyclic voltammetry was 5×10^{-3} mol l^{-1}, the background electrolyte concentration 0.1 mol l^{-1}.

Table 1. Yields, melting points, and elemental analysis data of the derivatives of sterically hindered phenols **I-XIII**

Comp. no.	Synthesis method	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
				C	H	N		C	H	N
I	*a*	80	232–233	79.44	10.15	7.01	$C_{27}H_{41}N_2O$	79.21	10.02	6.84
II	*a*	78	258–259	76.82	9.63	6.52	$C_{28}H_{42}N_2O_2$	76.71	9.59	6.39
III	*a*	82	229–230	77.03	9.28	6.49	$C_{28}H_{42}N_2O_2$	76.71	9.59	6.39
IV	*a*	76	234–235	74.75	9.34	6.22	$C_{29}H_{43}N_2O_3$	74.52	9.21	5.99
V	*a*	86	239–240	77.48	9.57	9.45	$C_{29}H_{45}N_3O$	77.16	9.53	9.31
VI	*a*	80	219–220	76.73	9.58	6.84	$C_{27}H_{40}N_2O_2$	76.41	9.43	6.60
VII	*a*	80	215–216	71.74	8.68	9.50	$C_{27}H_{39}N_3O_3$	71.52	8.61	9.27
VIII	*a*	84	209–210	66.85	8.05	6.11	$C_{27}H_{39}N_2OBr$	66.53	8.01	5.75
IX	*a*	80	215–216	73.44	9.6	6.56	$C_{27}H_{39}N_2OCl$	73.22	8.81	6.33
X	*a*	76	202–203	78.01	10.20	6.76	$C_{28}H_{42}N_2O$	77.78	9.95	6.64
XI	*b*	78	191–192	74.26	9.84	12.02	$C_{22}H_{35}N_3O$	73.94	9.80	11.76
XII	*b*	80	194–195	74.91	9.63	11.67	$C_{23}H_{35}N_3O$	74.79	9.48	11.38
XIII	*b*	74	200–201	78.23	9.04	9.61	$C_{29}H_{39}N_3O$	78.20	8.76	9.44

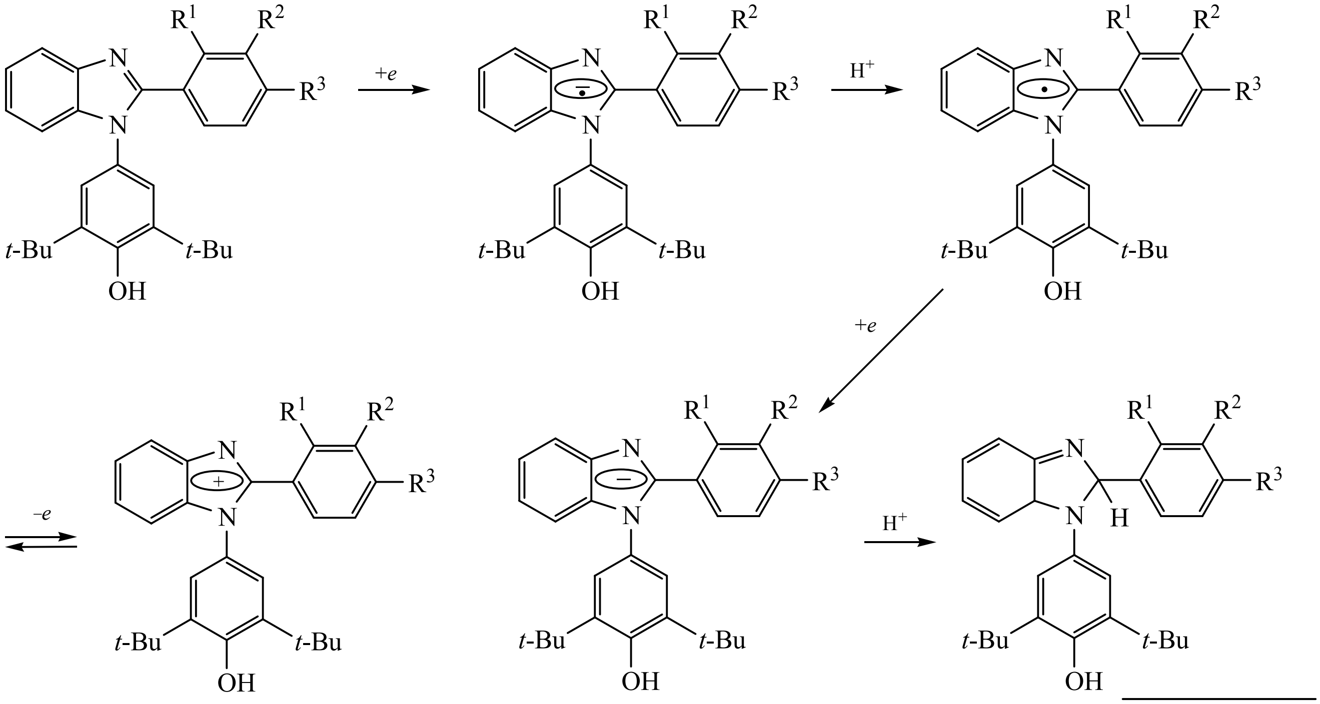
Table 2. Electrochemical characteristics of reduction of compounds **I–XIII** measured by cyclic voltammetry

Comp. no.	Reduction				Oxidation						ΔE_{pac}, V	Secondary peaks			
	$-E^1_{pc}$, V	$-E^2_{pc}$, V	I^1_{pc}, μA	I^2_{pc}, μA	$-E^1_{pa}$, V	$-E^2_{pa}$, V	$-E^3_{pa}$, V	I^1_{pa}, μA	I^2_{pa}, μA	I^3_{pa}, μA		$-E'_{pc}$, V	$-E''_{pc}$, V	I'_{pc}, μA	I''_{pc}, μA
I	1.81		26.0		0.20			24.0			60	0.14	1.77	15.5	25.0
II	1.92		26.0		0.10			25.5			80	0.18	1.87	14.0	25.5
III	1.94		25.5		0.18			25.0			60	0.12	1.89	13.5	24.5
IV	2.03		28.0		0.20			25.0			80	0.12	1.98	15.5	26.5
V	1.86		25.0		0.20			25.0			60	0.14	1.80	15.0	23.5
VI	1.82		25.0		0.20			25.0			80	0.12	1.78	14.5	23.5
VII	1.12		24.5	30.0	1.06	1.58	0.35	24.0	25.0	14.00	60	0.29		18.0	
VIII	1.74	1.64	25.0		0.18			25.0			60	0.12	1.68	13.5	24.0
IX	1.76		25.0		0.18			250			80	0.10	1.69	13.5	24.5
X	2.04		30.0		0.10			29.5			60	0.14	1.96	15.0	26.0
XI	1.78	2.00	23.0	24.0	0.29			23.0			100	1.73		21.5	
XII	1.76	2.10	24.0	25.0	0.30			23.5			103	1.70		21.5	
XIII	1.79	2.12	23.5	25.0	0.28			24.5			105	1.74		22.0	
Tetraethylammonium perchlorate	0.38		25.0		0.32			25.0			60				

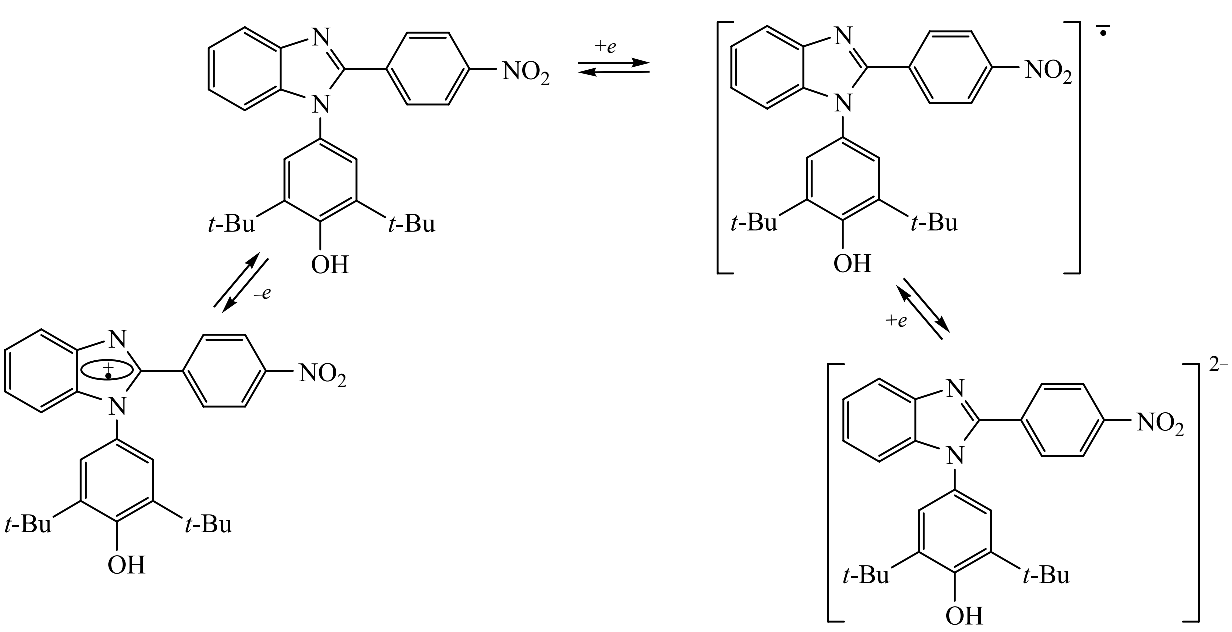
Cyclic voltammograms were taken in an argon atmosphere. The device was tested using an ohmic equivalent (EQ-2) and standard ferrocene solution. The number of electrons in the elementary step was determined by comparing the values of limiting currents of the studied compounds with the current of triphenylpyrilium perchlorate at the same concentration (5×10^{-3} mol l^{-1}), which is reduced reversibly by a single-electron process in the first stage, and which is taken as a reference.

Table 2 shows the data on the electrochemical reduction of 1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-arylbenzimidazoles and 2-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)benzimidazoles. As can be seen, the electrochemical reduction of 1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-arylbenzimidazoles **I–VI**, **VIII–X** proceeds in one step as a one-electron irreversible process resulting in the formation of a radical anion. In the cyclic voltammograms the first cathode wave corresponds to the formation of the radical anion. The radical anions diffuse partially from the electrical double layer and are protonated or dimerized [3]. The anode branch of the curve includes the wave of oxidation of the radical formed at the protonation of the radical anion. In the secondary cycle of the cyclic voltammograms a wave of reconstruction of the cation is clearly seen. The currents of the radical oxidation are about equal to the currents of reduction of the formed cations. For example, for the compound **I** E_{pa} = –0.20 V, ΔE_{pc} = 60 mV, indicating the reversibility of the redox transition of the radical to the cation. The anion formed at the reduction is protonated affording a dihydro derivative [4, 5]: this process represents the next chemical stage after the electrochemical one. The proton donor for the anion-radical and anion may be the phenol fragment of the molecule of the parent compound. In the second cycle of the anodic branch of cyclic voltammetry curve a reversible wave is detected of dihydrobenzimidazole oxidation to the radical cation. The shift of the wave potential of the dihydrobenzimidazole oxidation by more than 60 mV (as in electrochemically reversible processes) indicates that the formed cation radicals are unstable and decompose in the subsequent chemical stage, releasing proton and forming a radical. The data obtained are in good agreement with the published data on the electrochemical oxidation of derivatives of sterically hindered phenols [6, 7]. The mechanism of electrochemical reduction of compounds **I–VI, VIII–X** is as bellow.

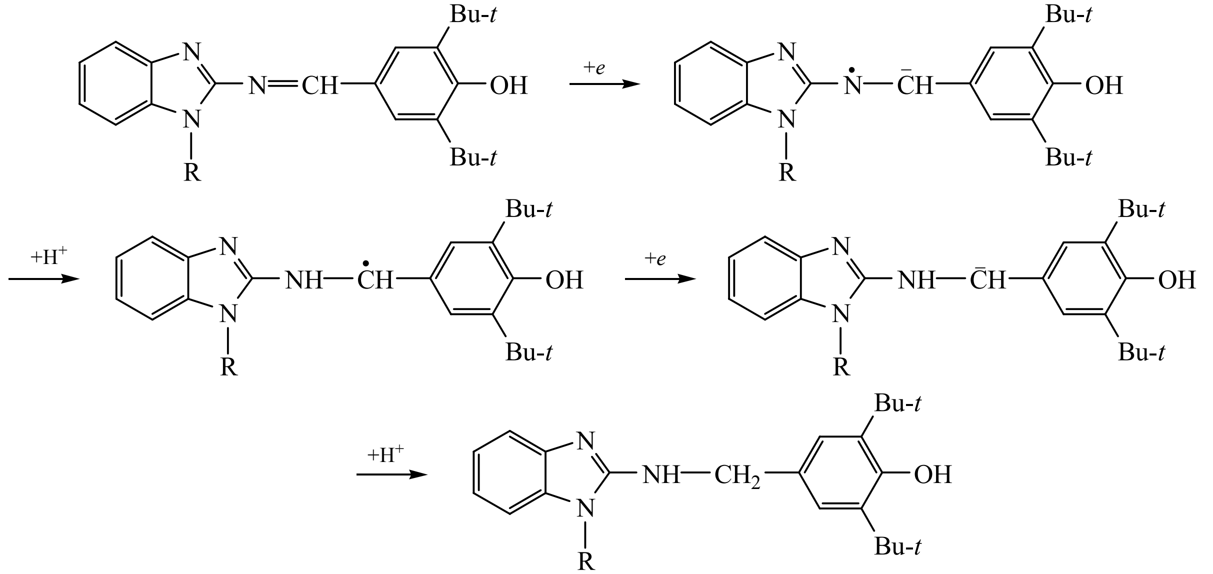
The electrochemical reduction of 1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(4'-nitrophenyl)-benzimidazole **VII** proceeds through two one-electron waves. The reduction of aromatic nitro compounds in aprotic solvents has been studied fairly extensively by classical polarography [8, 9]. For instance, the polyarogram of nitrobenzene in acetonitrile contains two waves, first is reversible and corresponds to the



transfer of one electron (E_{pc} = –1.00 V), and the second is three-electron irreversible wave (E_{pc} = –1.50 V), which is not always clearly expressed due to the presence of a maximum. The first cathode wave in the cyclic voltammogram curve is associated with the reversible one-electron reduction of nitro group at the potential E_{pc} = –1.12 V to form a radical anion. The ratio of the currents of cathode and reversible anode waves indicate the relative stability of the generated anion radicals. The second reversible cathode wave (E_{pc} = –1.64 V) is associated with the further reduction of the anion radical to the dianion. The anode branch of the curve includes a one-electron oxidation wave of substrate **VI** at E_{pa} = –0.35 V. In the second cycle a reversible reduction wave of the radical cation at E_{pc} = –0.29 V is fixed. Taking this into account, the mechanism of electroreduction of compound **VI** can be interpreted as follows:



The electrochemical reduction of 2-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)benzimidazoles **XI–XIII** proceeds through two one-electron irreversible waves and fits into the overall scheme of the C=N bond reduction [10]. The mechanism of electrochemical reduction of compounds **XI** and **XIII** is similar:



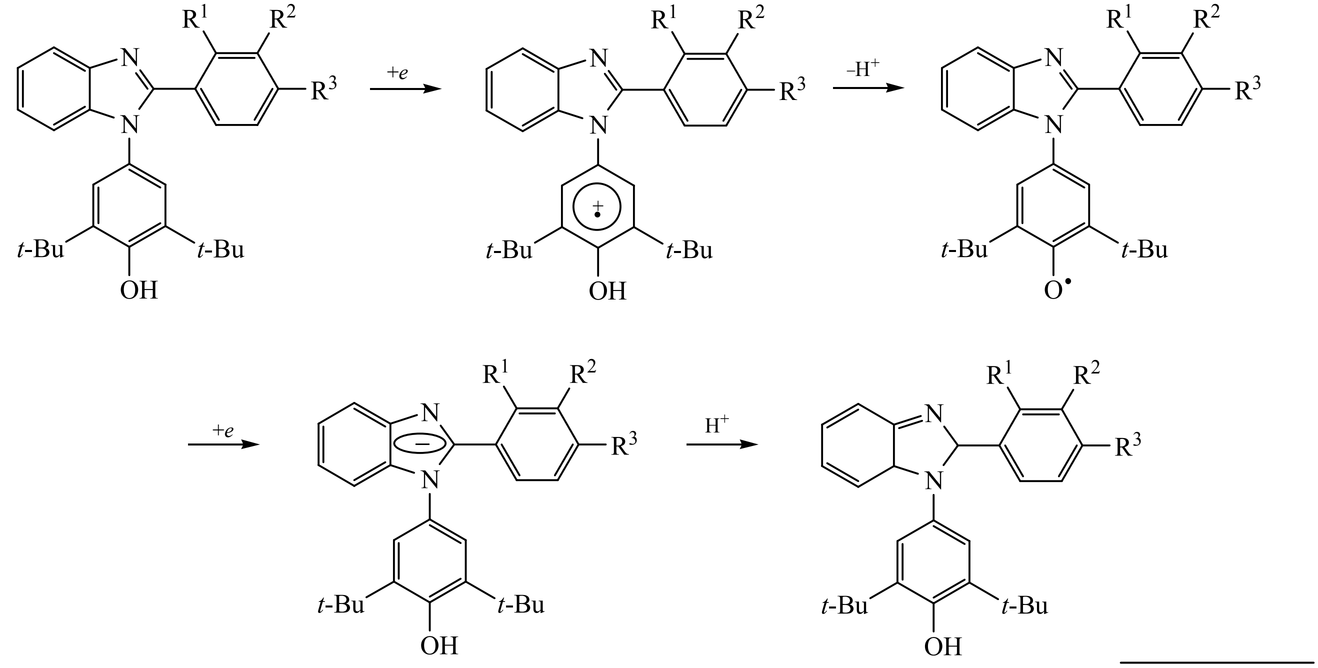
The electrochemical oxidation of the synthesized compounds **I–XIII** was studied by cyclic voltammetry under the same conditions as the reduction (Table 3). To compare the results, Table 3 presents the cyclic voltammogram data of 2,4,6-tri-*tert*-butylphenol and ferrocene as the standard substance for the determining the number of electrons and electrochemical reversebility of redox stages of oxidation.

Cyclic voltammograms of oxidation of compounds **I, VI–X** in acetonitrile on the stationary electrode show that the anodic oxidation is a one-electron

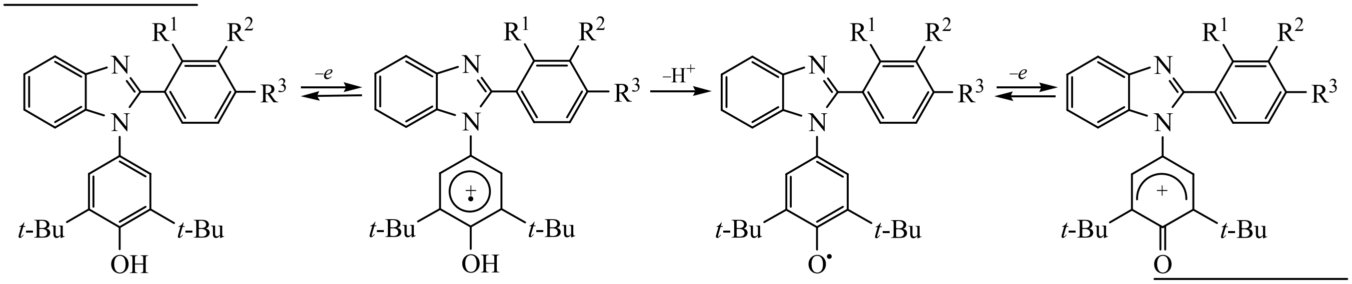
Table 3. Electrochemical oxidation characteristics of compounds **I–XIII** measured by cyclic voltammetry.

Comp. no.	Anode curve				Cathode curve		ΔE_{pac}, V	Secondary peaks					
	E^1_{pa}, V	E^2_{pa}, V	I^1_{pa}, μA	I^2_{pa}, μA	E^1_{pc}, V	I^1_{pc}, μA		E'_{pa}, V	E''_{pa}, V	E'_{pc}, V	I'_{pa}, μA	I''_{pa}, μA	I'_{pc}, μA
I	1.25		24.5		0.26	24.0							
II	0.96	1.42	23.0	26.0	0.88	21.5	80			1.34			
III	0.94	1.44	24.0	25.5	0.86	23.0	80			1.38			
IV	0.94	1.35	25.0	26.0	0.88	26.0	60			1.27			
V	0.90	1.46	25.0	23.0	0.82	23.5	80			1.38			
VI	0.88		24.5		0.34	24.0							
VII	1.50		24.0		1.00	23.5							
VIII	1.30		24.0		0.60	23.5							
IX	1.27		24.5		0.65	24.0							
X	1.04		22.0		0.50	21.0							
XI	1.40		24.5		0.20	24.0		0.14	0.90	0.82	23.5	24.5	24.0
XII	1.45		25.0		0.23	26.5		0.15	0.92	0.84	26.0	25.0	24.0
XIII	1.52		25.0		0.25	25.5	60	0.17	0.92	0.84	25.0	25.0	24.5
Tetraethylammonium perchlorate	1.38		25.0		1.32	25.5	60						
Ferrocene	0.42		25.0		0.36	25.0							

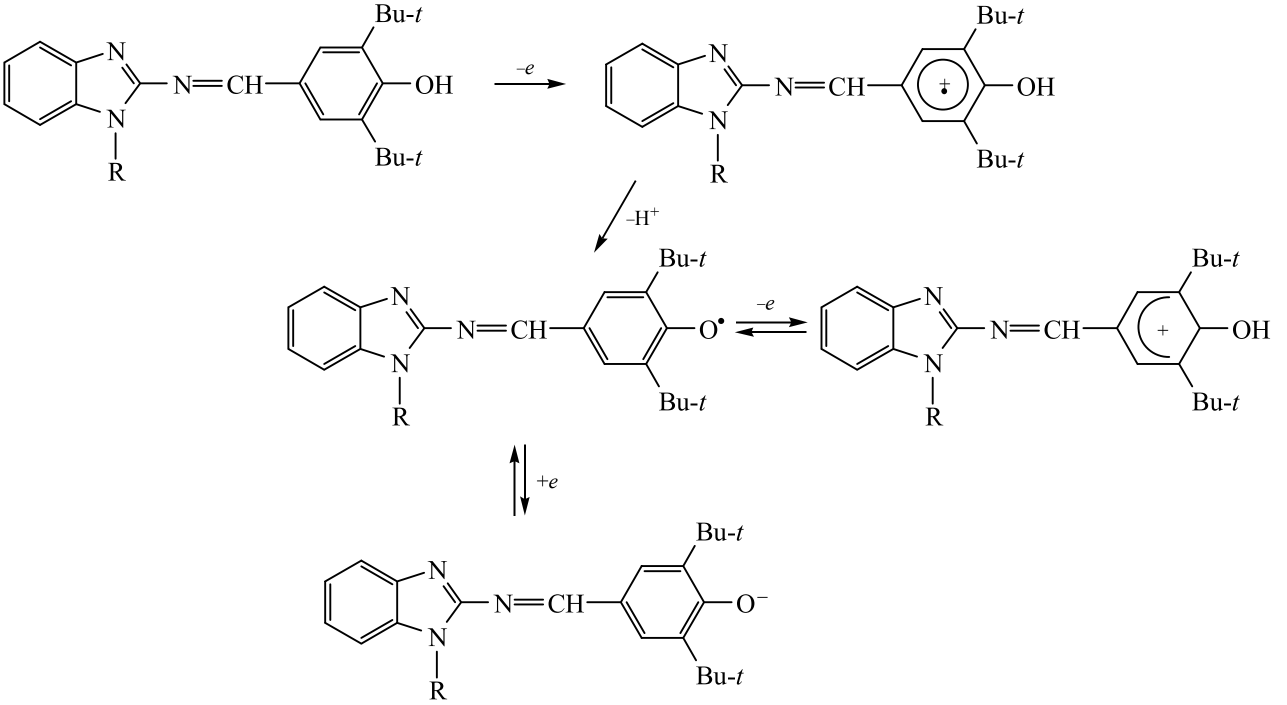
process leading in the first stage to the formation of the radical cation. The number of electrons (1.02–1.08) is somewhat overestimated with respect to ferrocene due to the presence of traces of water in acetonitrile, which is quite difficult to remove. Water in aprotic solvent behaves as an alkali (due to the preferred solvation of H^+). Adding water to the electrochemical cell (50%) leads to 1.5-fold increase of the oxidation peak, that is, OH reacts with the radical cation as with an acid. Analysis of primary and secondary cycles of the cyclic voltammograms of the compounds oxidation shows that the electrochemical process is irreversible, that is, the stability of the cation radicals formed is rather low. In the cathode region of the cyclic voltammograms the peak is clearly seen of the phenoxy radical reduction to the anion. This indicates that the cation radicals of the substrate are fragmented through the cleavage of a proton (the proton is identified by adding phenol) to form a phenoxy radical. The mechanism of electrochemical oxidation of compounds **I, VI–X** is shown below.



The electrochemical oxidation of 1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-arylbenzimidazoles **II–V** proceeds through two one-electron waves, the first wave is reversible. The anode branch of the curve at a potential E_{pa} = 0.96 includes a single-electron wave of the formation of radical cation, the ratio of the anode and cathode currents of the reversible waves of the cyclic voltammograms indicates the relative stability of the resulting radical cations. Further, at E_{pa} = 1.42 V the radical cation is oxidized to the cation, the latter is fragmented by splitting off the proton. The mechanism of electrooxidation of compounds **II–V** is interpreted as follows:



The electrochemical oxidation of 2-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)benzimidazoles **XI–XIII** in the first cycle of the cyclic voltammogram shows irreversibility of the electrochemical process, that is, the cation radicals formed are unstable. In the cathode region of the cyclic voltammogram a peak of reduction of phenoxy radical to the anion is clearly seen, the latter is fragmented by the cleavage of a proton to form a phenoxy radical. In the repeated cycle a reversible wave of the oxidation of the anion to the radical is seen, the latter also is oxidized reversibly. The mechanism of electrochemical oxidation of compounds **XI–XIII** is as follows:



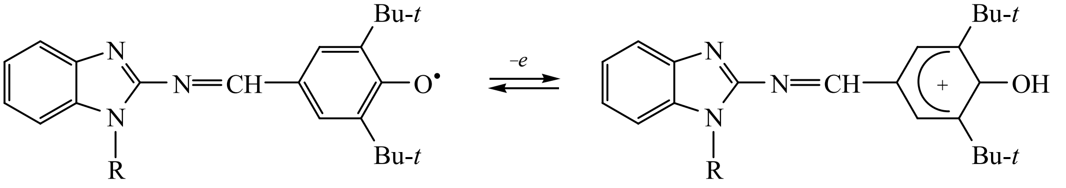
For the electrochemical study, the phenoxy radicals from 2-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)(alkyl) arylbenzimidazoles **XI-XIII** were obtained independently by chemical routes. The starting compounds were oxidized in acetonitrile with lead dioxide PbO_2 under argon. The solutions changed their color from green to greenish-brown.

At the oxidation of compounds **XI–XIII** in acetonitrile with lead dioxide in an ESR spectrometer probe at 298 K, the formation of a radical was registered even in the first moment of the process. The spectrum is a triplet with the intensity ratio 1:2:3 due to the splitting of the energy levels of the unpaired electron on the protons of 3,5-di-*tert*-butyl-phenoxy fragment:

Compound	**XI**	**XII**	**XIII**
$a_i^{3.5}$, mT	0.20	0.21	0.24
g-Factor	2.0032	2.0035	2.0039

The hyperfine coupling constant on the protons of phenoxy fragment varies from 0.20 to 0.24 mT depending on the influence of different substituents in the ring. The *g*-factors are close to that of the free electron (2.0023) and are consistent with those of phenoxy radicals [11, 12]. The absence of splitting of the signal of unpaired electron on the amine fragment protons suggests that the associated chain is not conductive.

Continuing the studies, we investigated electrochemical properties of the phenoxy radicals formed from compounds **XI–XIII**. The cyclic voltammetry oxidation curve of a solution of a compound **XI–XIII** in acetonitrile with PbO_2 virtually repeats the second cycle curve of the corresponding parent compound. For various compounds, the ratio of the peak heights of oxidation of the radical obtained in a solution and of the unused parent compound on the anode branch is different for different compounds. The compounds **XI–XIII** are oxidized with more difficulty than the respective phenoxy radicals. The oxidation currents of compounds **XI–XIII** are approximately equal to the reduction currents of the formed cations indicating the reversibility of the radical to cation redox transition. The mechanism of oxidation of phenoxy radicals of compounds **XI–XIII** is as follows:

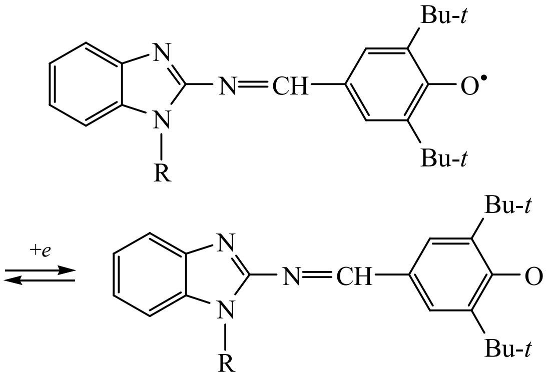


The electrochemical oxidation–reduction data for the phenoxy radicals produced in solution by the reaction of the parent compound with PbO_2 are as follows:

Radical from the compound	**XI**	**XII**	**XIII**
Anode curve, V	0.90	0.92	0.92
Cathode curve, V	0.84	0.84	0.84
Difference, mV	60	80	80

The radicals are reduced in one irreversible one-electron wave. The peak currents of oxidation and reduction (Tables 2, 3) are omitted, since the concentration of the generated radicals in the solution is unknown. In the first stage it is difficult to reduce the radicals at the potentials –1.40 to –1.52 V, that is, they act as weak oxidants. By the example of compound **XII** the first reversible reduction wave of the radical at E_{pc} = –0.40 V is the same as that on the cathodic branch of the cyclic voltammogram of the oxidation of the parent compound.

The mechanism of reduction of the radicals obtained from compounds **XI–XIII** is interpreted as follows:



EXPERIMENTAL

The IR spectra of the synthesized compounds were recorded on a double-beam spectrophotometer Specord IR-75 from the tablets with anhydrous KBr, the ^{1}H NMR spectra were taken on a UNITY-300 spectrometer (300 MHz), solvent $CDCl_3$, internal reference TMS. The ESR spectra were recorded on a Radiopan SE/X-2543 radiospectrometer in evacuated ampules (5×10^{-3} mm Hg). Cyclic voltammograms were recorded on a potentiostat P-5827 with a source of triangular pulses [13], and a LKD-4 recorder.

Acetonitrile was dried by conventional methods and distilled in a vacuum. Tetraethylammonium perchlorate was prepared from 10% ammonium hydroxide solution and recrystallized from hot isopropyl alcohol and water.

1-(3,5-di-*tert*-Butyl-4-hydroxyphenyl)-2-phenylbenzimidazole (I). A mixture of 3.10 g (0.01 mol) of 2,6-di-*tert*-butyl-*p*-benzoquinone imine and 1.06 g (0.01 mol) of benzaldehyde was heated gradually to 200°C and stirred at this temperature for 2 h. The mixture was cooled to 120°C, 20 ml of anhydrous toluene was added, the heating with stirring was continued until complete dissolution of the melt. Then the mixture was cooled to 20°C, the precipitate was separated, washed with hexane (15 ml), and dried. Yield 3.20 g (80%), white powder, mp 232–233°C (from toluene). Found, %: C 79.44, H 0.15, N 7.01. $C_{27}H_{41}N_2O$. Calculated, %: C 79.21, H 10.02, N 6.84.

Compounds **II–X** were prepared similarly.

2-(3,5-di-*tert*-Butyl-4-hydroxybenzylidene)benzimidazole (XI). To a solution of 1.33 g (0.01 mol) of 2-aminobenzimidazole in 25 ml of anhydrous toluene was added 2.34 g (0.01 mol) of 2,6-di-*tert*-butyl-4-hydroxybenzaldehyde. The mixture was heated with a Dean–Stark trap for 1.5 h, then cooled, filtered, and the solvent was removed in vacuo. Yield 7.27 g (78%), pale-yellow powder, mp 191–192°C (from hexane). Found, %: C 74.26, H 9.84, N 12.02. $C_{22}H_{35}N_3O$. Calculated, %: C 73.94, H 9.80, N 11.7.

Similarly were prepared compounds **XII** and **XIII**.

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