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Dedicated to Full Member of the Russian Academy of Sciences
I.P. Beletskaya on her jubilee

Antiradical Activity of Dioxolane Derivatives

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Abstract—1,3-Benzodioxoles synthesized by condensation of 3,6-di-*tert*-butylbenzene-1,2-diol with carbonyl compounds showed antiradical activity due to their ability to undergo one-electron oxidation with formation of stable radical cations. On this basis, the antiknock effect of their structural analogs, 1,3-dioxolanes derived from vicinal diols, was interpreted in terms of oxidation of these compounds with active radicals generated from fuel hydrocarbons to produce more stable radical or radical ion species, depending on the fuel composition. The formation of radical species was detected in model oxidation reactions of 2,2-dimethyl-1,3-dioxolane and 2,2-dimethyl-1,3-dioxolan-4-ylmethanol with radicals generated by photolysis of iron(III) chloride and benzoyl peroxide.

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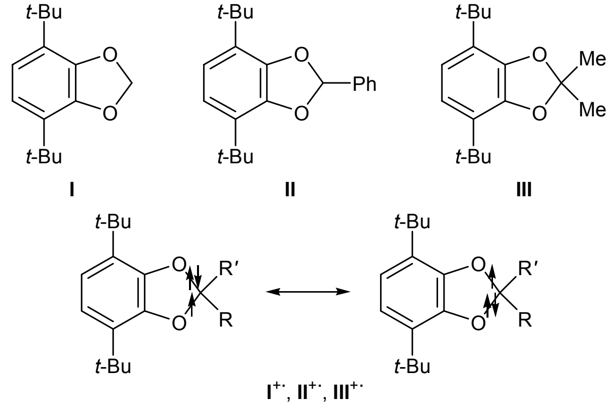
We previously showed that benzodioxoles obtained by condensation of 3,6-di-*tert*-butylbenzene-1,2-diol with aldehydes and ketones exhibit antiradical activity despite the lack of free hydroxy groups in their molecules [1, 2]. Naturally, the antiradical activity of benzodioxoles is determined by the ability of the dioxole ring to undergo one-electron oxidation to produce radical cations which were detected by ESR spectroscopy while studying the oxidation of 1,3-benzodioxoles **I**–**III** with thallium trifluoroacetate or lead(IV) oxide in trifluoroacetic acid or its mixture with methylene chloride (Scheme 1).

Scheme 1.



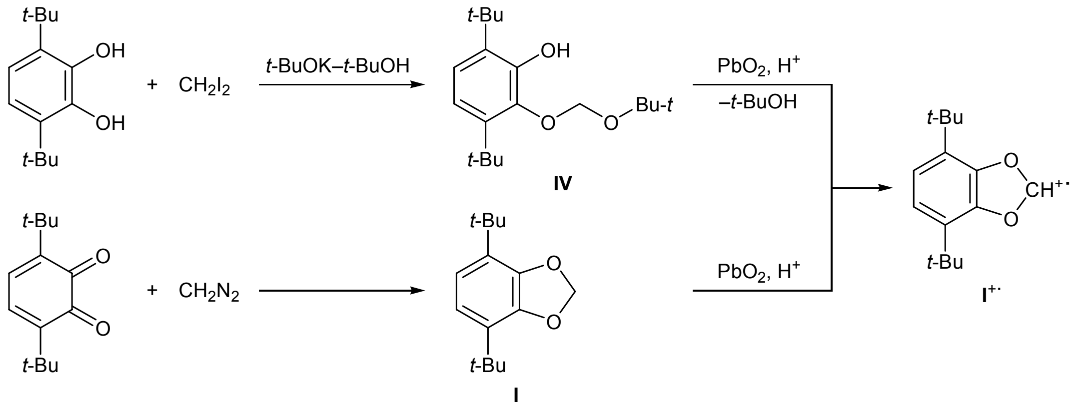
$I^{+\cdot}$, R = R′ = H; $II^{+\cdot}$, R = H, R′ = Ph; $III^{+\cdot}$, R = R′ = Me.

The ESR spectra of radical cations derived from compounds **I**–**III** indicated coupling of the unpaired electron with two equivalent aromatic protons, as well as with protons on C^2 or in groups attached thereto [CH_2, CHPh, $C(CH_3)_2$]. The ESR spectra of radical cations $\mathbf{I}^{+\cdot}$ and $\mathbf{II}^{+\cdot}$ and hyperfine coupling constants (HCC) a^H are given in Fig. 1 (see table).

The triplet signal from the ring protons with an HCC of 4.2–4.8 G may be regarded as spectral marker indicating formation of radical cations in the oxidation of acyclic precursors, 3,6-di-*tert*-butylbenzene-1,2-diol monoethers. As shown by the ESR data, the oxidation of 3,6-di-*tert*-butylbenzene-2-(*tert*-butoxymethoxy)phenol (**IV**) with PbO_2 in CF_3CO_2H–CH_2Cl_2 gave a product which was spectrally identical to the radical cation generated by oxidation of benzodioxole **I** under analogous conditions. Obviously, ether **IV** undergoes oxidative cyclization with elimination of the *tert*-butoxy group (Scheme 2). Ether **IV** was isolated instead of expected 1,3-benzodioxole (**I**) in the condensation of 3,6-di-*tert*-butylbenzene-1,2-diol with methylene iodide in the presence of potassium *tert*-butoxide in *t*-BuOH [3]. Compound **I** was synthesized in a different way, by reaction of 3,6-di-*tert*-butyl-1,2-benzoquinone with diazomethane [4].

[†] Deceased.

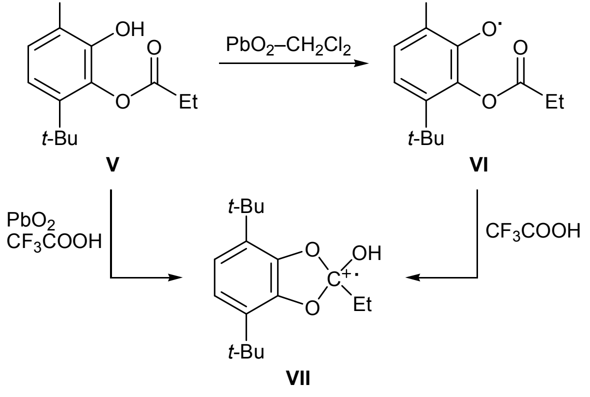
Scheme 2.



Radical cations were also formed in the oxidation of 3,6-di-*tert*-butylbenzene-1,2-diol monopropionate **V** with lead(IV) oxide (Scheme 3). The reaction direction depended on the solvent. In aprotic medium (CH_2Cl_2), *o*-carboxyphenoxyl radical **VI** was obtained, and it was converted into radical cation **VII** upon addition of an acid (CF_3COOH). Correspondingly, the spectral pattern changed (Fig. 2). In the ESR spectrum of **VI** we observed a doublet of doublets due to coupling with two nonequivalent protons in the aromatic ring. Addition of acid gave rise to paramagnetic species whose spectra were typical of radical cations with equivalent aromatic protons (triplets with $a^{\mathrm{H}}_{\mathrm{arom}}$ = 4.7, 4.8 G). Identical spectra of radical cations **VII** were obtained when monoester **V** was oxidized with PbO_2 directly in trifluoroacetic acid. Presumably, the formation of dioxolane ring is a structural factor stabilizing the radical species in protic medium.

It seemed reasonable to use the above results as model for interpretation of the antiknock activity of structural analogs of benzodioxoles, 1,3-dioxolanes that are cyclic ketals formed by condensation of vicinal diols and polyols (such as ethylene glycol, glycerol, etc.) with carbonyl compounds. Addition of dioxolanes to fuel compositions is known to considerably improve their octane number [5].

Scheme 3.



The effect of antiknock agents originates from their ability to inhibit development of radical processes leading to explosive combustion; they react with active

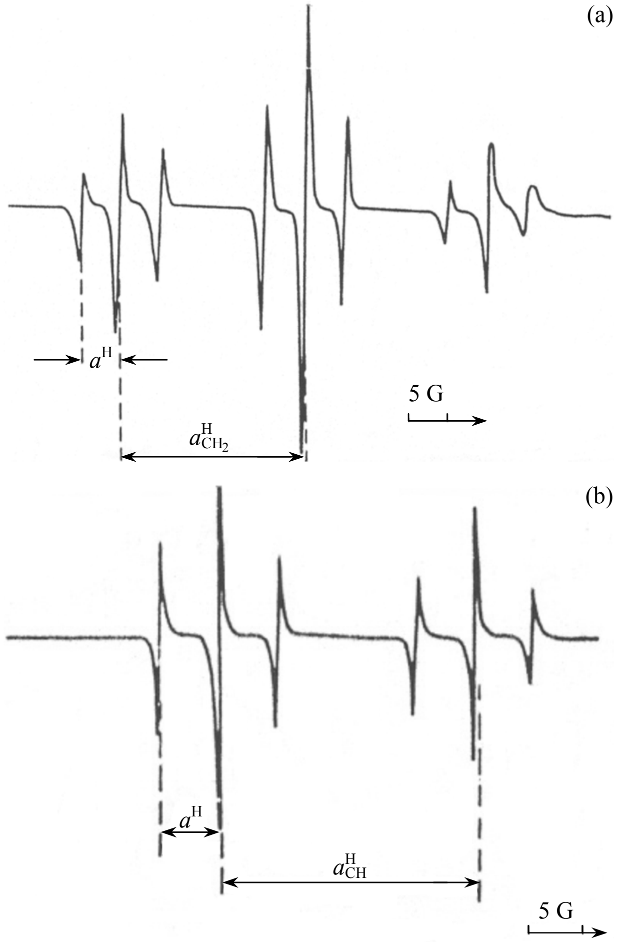


Fig. 1. ESR spectra of radical cations (a) $\mathbf{I}^{+\cdot}$ and (b) $\mathbf{II}^{+\cdot}$; 20°C, CF_3COOH.

Hyperfine coupling constants a^{H} in the ESR spectra of radical cations generated from compounds **I**–**III**

Radical cation	$a^{\mathrm{H}}_{\mathrm{arom}}$	a^{H}
$\mathbf{I}^{+\cdot}$	4.25	20.8 (CH_2)
$\mathbf{II}^{+\cdot}$	4.5	21.0 (CH)
$\mathbf{III}^{+\cdot}$	4.5	0.45 (CH)

radicals generated by oxidation of hydrocarbons and responsible for chain propagation to produce less active radicals. Radicals generated by photolysis of peroxides, as well as halogen atoms expulsed from high-valence inorganic halides, may be regarded as models of such active hydrocarbon radicals. We used both these models, $FeCl_3$ and benzoyl peroxide, to assess the possibility for radical oxidation of dioxolanes and examine the ESR parameters of the resulting radical species. The formation of radicals from ketals **VIII** and **IX** implies initial generation of active chlorine atoms from $FeCl_3$ or phenyl radicals from benzoyl peroxide [7] and their subsequent reactions (Scheme 4).

Figure 3 shows the ESR spectra of radicals **X** and **XI** generated by abstraction of hydrogen atom from 2,2-dimethyl-1,3-dioxolane (**VIII**) and 2,2-dimethyl-1,3-dioxolan-4-ylmethanol (**IX**), respectively. The shape of the spectral curves and spectral parameters did not depend on the way of radical generation. The hyperfine coupling constants for radical **X** were a^{H}_{α} = 17.2, a^{H}_{β} = 30 G, and for radical **XI**, $a^{\mathrm{H}}_{\alpha} = a^{\mathrm{H}}_{\beta 1} = 20$, $a^{\mathrm{H}}_{\beta 2}$ = 40 G, which is consistent with published data [8]. The spectrum of **X** was a doublet of doublets, and that of **XI**, a doublet of triplets. The spectral parameters did not change as the temperature rose up to disappearance of radical species on melting (>180 K [9]).

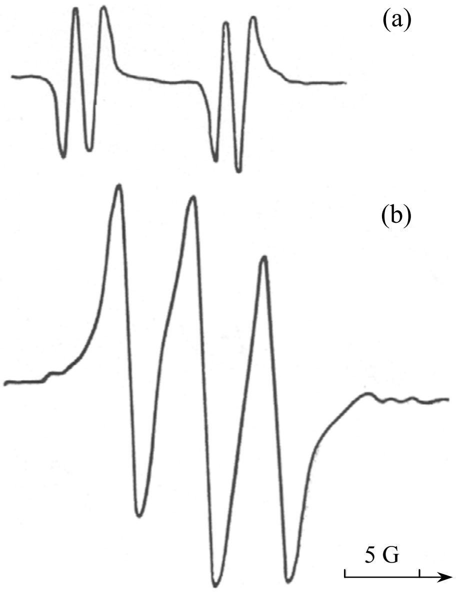
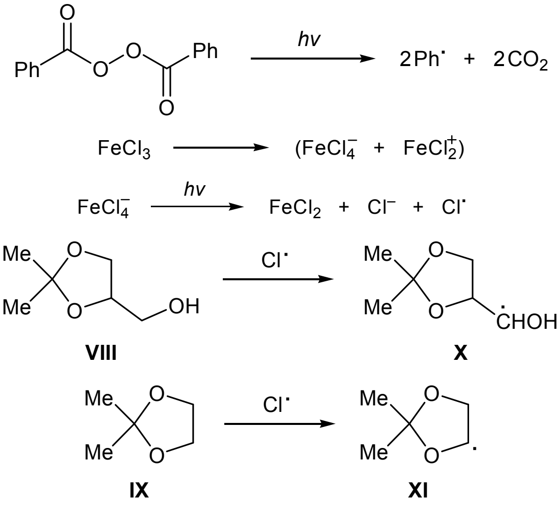


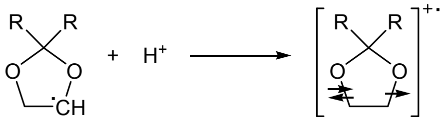
Fig. 2. ESR spectra of (a) phenoxyl radical **VI** and (b) radical cation **VII**; 20°C, CF_3COOH.

Scheme 4.



The formation of carbon-centered radicals which are sufficiently stable to be observed by ESR conforms to the antiknock effect of compounds **VIII** and **IX**. The strongest effect on the octane number was observed when these compounds were added in combination with lower alcohols, primarily with ethanol [5]. Direct ESR study of the effect of the alcohol component is experimentally difficult; however, by analogy with the above examples demonstrating structural transformations of radical species in protic medium, we may presume that alcohol as proton donor promotes transformation of carbon-centered radical into more stable cyclic radical cation (Scheme 5).

Scheme 5.



The interaction with proton donors could provide an additional contribution to the antiknock effect of ketals via formation of supramolecular structures acting as surfactants. The rate of decomposition of hydroperoxides in the shells surrounding surfactant micelles is considerably lower, so that the combustion process turns from the explosive mode to stationary [10]. Presumably, this factor is responsible for the synergistic effect of ketals upon addition to alcohol-containing gasoline [5].

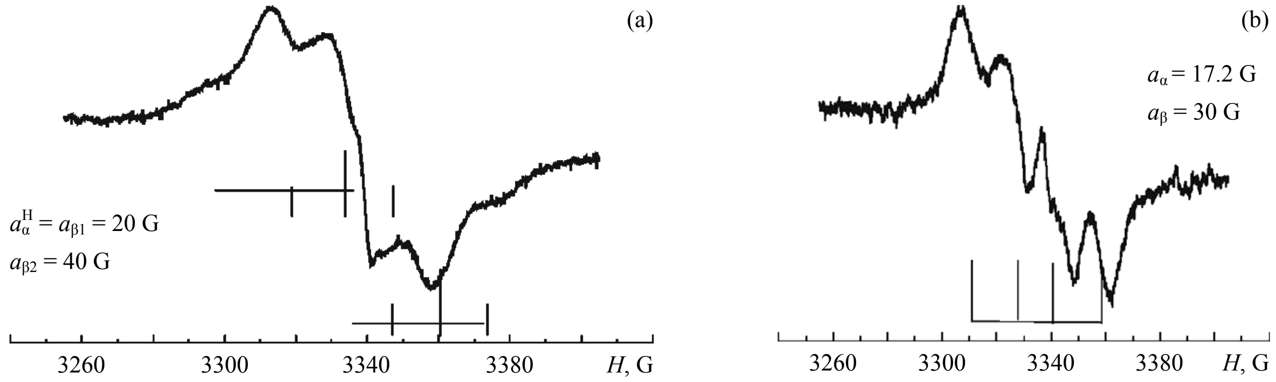


Fig. 3. ESR spectra of (a) radical **X** recorded at 136 K and (b) radical **XI** recorded at 94 K (modulation amplitude 2 G); radicals were generated by photolysis in the presence of $FeCl_3$, BS-6 filter, 40 min at 77 K.

EXPERIMENTAL

The ESR spectra were recorded on Varian E-12 and EPR-10 (SPIn Co. Ltd.) spectrometers (modulation frequency 100 kHz, temperature range 77–295 K). Radical cations were generated by oxidation of 1,3-benzodioxoles **I**–**III** and 3,6-di-*tert*-butylbenzene-1,2-diol ether **IV** and ester **V** with thallium trifluoroacetate or lead(IV) oxide in trifluoroacetic acid or its mixture with methylene chloride in evacuated ampules. The synthesis of the initial compounds was described in [11, 12].

Radicals **X** and **XI** were generated from ketals **VIII** and **IX** by adding $FeCl_3$ or benzoyl peroxide, followed by irradiation of frozen solutions (77 K) with a DRSh-1000 mercury lamp through a BS-6 filter (λ >300 nm). The temperature was maintained with an accuracy of ±3° using liquid nitrogen. The scan time was 10–15 s. A solution of ketal **VIII** or **IX**, ~0.5 ml, containing $FeCl_3$ or $(PhCOO)_2$ was placed into a quartz cylindrical ESR ampule, and the ampule was irradiated for 40 min at 77 K in a quartz Dewar flask. Three series of experiments were performed: (1) ketal **VIII** with addition of ~1 wt % of $FeCl_3$; (2) ketal **IX** with addition of 10 wt % of benzoyl peroxide; and (3) ketal **IX** with addition of $FeCl_3$. In all cases, radical species were detected, whose ESR spectra are shown in Fig. 3.

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