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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis and Antioxidative Effect of Aromatic Disulfides

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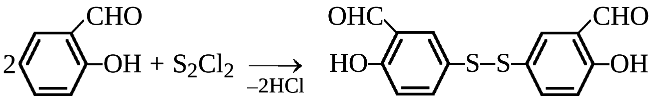
Abstract—Bis(4-hydroxy-3-formylphenyl) and bis[3-alkyl(aryl)iminomethyl-4-hydroxyphenyl] disulfides were prepared. Their reaction with cumylperoxy radicals was studied, and the inhibiting effect on the cumene oxidation was examined.

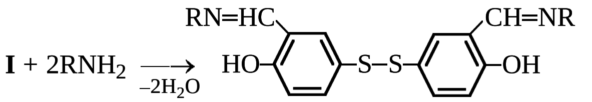
We has show previously [1] that bis[3-alkyl(aryl)-aminomethyl-4-hydroxyphenyl] sulfides effectively inhibit cumene oxidation. Proceeding with studies aimed at preparing various classes of organosulfur compounds and elucidating the mechanism of their inhibiting effect [2–4], we prepared in this work aromatic disulfides with azomethine fragments and evaluated their antioxidative performance in oxidation of cumene.

The starting compound, bis(4-hydroxy-3-formylphenyl) disulfide, was prepared by the reaction of salicylaldehyde with S_2Cl_2 in the presence of zinc as catalyst:



I

Subsequent condensation of **I** with primary aliphatic and aromatic amines gave the corresponding bis[3-alkyl(aryl)iminomethyl-4-hydroxyphenyl] disulfides **II**–**V** in high yields:



II–IV

where R = CH_3 (**II**), *tert*-C_4H_9 (**III**), C_6H_5 (**IV**), $C_6H_5CH_2$ (**V**).

The purity of **II**–**V** was checked by thin-layer chromatography, and the composition and structure were confirmed by elemental analysis and by IR and ^1H NMR spectroscopies.

The IR spectrum of **I** contains characteristic absorption bands of the hydroxy group at 3320 cm^{-1}. The IR spectra of **II**–**V** contain azomethine bands at 1639–1640 cm^{-1}, and the hydroxyl band is shifted to 3165 cm^{-1}.

In the ^1H NMR spectra of **II**–**V**, we have not revealed, in contrast to the spectrum of **I**, the broadened signal of the formyl proton (10.37 ppm). The spectra contain proton signals of radicals R at the N atom; the signals of nonequivalent protons of two symmetrically arranged benzene rings give a doublet at 7.0 and 7.4 ppm. The signals of the hydroxyl protons are shifted downfield by 0.4 ppm relative to **I**, giving a doublet at 10.9–11.6 ppm. This may be due to weaker intramolecular hydrogen bonding between the hydroxy group and azomethine nitrogen atom, compared to the carbonyl oxygen atom in **I**.

To evaluate the antioxidative performance of **I**–**V** in elementary steps of inhibition of cumene oxidation, we studied the reactions of these compounds with cumylperoxy radicals (CPR) and cumyl hydroperoxide (CHP).

The capability of disulfides **II**–**V** to terminate oxidation chains in reactions with peroxy radicals was evaluated for the example of cumene oxidation at 60°C, initiated by azobis(isobutyronitrile) (AIBN), in the presence of **II** (Fig. 1).

From the induction period, we calculated the stoichiometric coefficient of inhibition, *f*, equal to the number of oxidation chains terminating in molecule of the inhibitor and its transformation products:

$$f = \tau v_i/[\mathrm{In}]_0,$$

where v_1 is the initiation rate (under the examined conditions, $v_1 = 2 \times 10^{-7}$ $l\,mol^{-1}\,s^{-1}$, and $[\mathrm{In}]_0$ is the initial inhibitor concentration.

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From the kinetics of oxygen uptake, we calculated the rate constants of the reactions of the inhibitors with CPR, k_7 [5, 6]. For this purpose, the kinetic curves of oxygen uptake were transformed from the coordinates $[O_2]$–τ to the coordinates $[O_2]^{-1}$–τ^{-1}:

$$k_7 = \tan\alpha k_2[\mathrm{RH}]v_i/f[\mathrm{In}]_0,$$

where $\tan\alpha$ is the slope of the straight line in the coordinates $[O_2]^{-1}$–τ^{-1}; $k_2 = 1.51$ l mol^{-1} s^{-1}, rate constant of chain initiation [1, 2]; [RH] = 6.9 M, concentration of the substance subject to oxidation; and v_i, initiation rate (under our conditions, $v_i = 2 \times 10^{-7}$ l mol^{-1} s^{-1}).

The high antioxidative performance of **II**–**V** was also confirmed by experiments on cumene autooxidation at 110°C (Fig. 2), and the kinetic parameters of the reaction were determined (Fig. 2). As seen from Table 1, the parameters f for **II**–**V** vary in the range from 1.8 to 2.4, and the rate constant k_7 of the reaction of inhibitors with peroxy radicals, from 1.92×10^4 to 2.72×10^4 l mol^{-1} s^{-1}. The products of transformations of **II**–**V** in reaction with CPR also show a certain inhibiting effect: The oxidation rate after the induction period is somewhat lower than the rate of uninhibited oxidation (Fig. 1).

We found that all the compounds **I**–**V** actively decompose CHP.

The kinetic curve of CHP decomposition in the presence of **I**–**V** is typical of autocatalytic reactions (Fig. 3). The autocatalytic character of the kinetic curves shows that decomposition of CHP is effected not by compounds **I**–**V** themselves, but by products of their transformation in the first, slow, step of the reaction with CHP.

To determine the reaction order, we studied how the initial rate of catalytic decomposition of CHP depends on the reactant concentrations. We found that the reaction is first-order with respect to both inhibitor and CHP.

To determine the reaction stoichiometry, CHP was taken in excess. The stoichiometric coefficient ν was calculated by the formula

$$\nu = \frac{[\mathrm{ROOH}]_0 - [\mathrm{ROOH}]_\infty}{[\mathrm{In}]_0},$$

where $[\mathrm{ROOH}]_0$ and $[\mathrm{ROOH}]_\infty$ are, respectively, the initial and final CHP concentrations, and $[\mathrm{In}]_0$ is the initial inhibitor concentration.

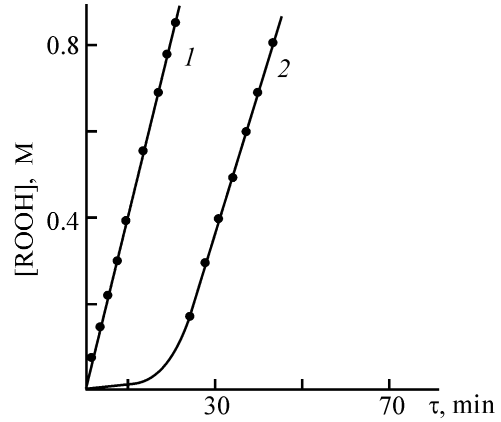

Fig. 1. Variation of CHP concentration [ROOH] with time τ in initiated oxidation of cumene (*1*) in the absence and (*2*) in the presence of **II**. [AIBN] = 2×10^{-2}, [In] = 3×10^{-4} M; 60°C.

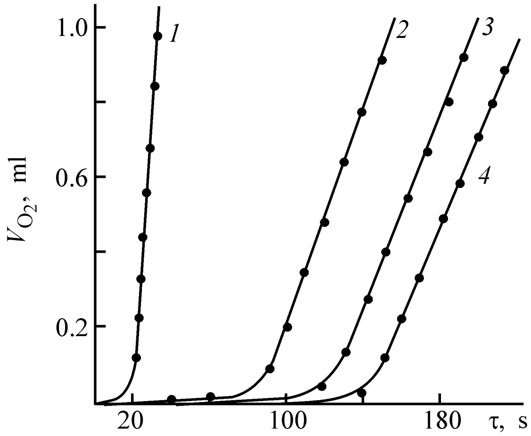

Fig. 2. Volume V_{O_2} of oxygen taken up in autooxidation of cumene at 110°C vs. time τ. Inhibitor added ([In] = 5×10^{-6} M): (*1*) none, (*2*) **II**, (*3*) **III**, and (*4*) **V**.

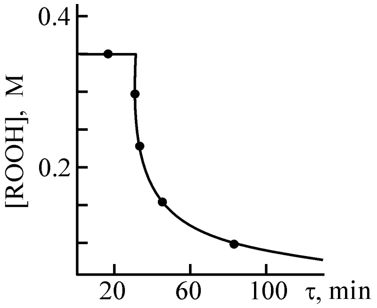

Fig. 3. Variation with time τ of the CHP concentration [ROOH] in the course of decomposition in the presence of inhibitor **I** ([In] = 5×10^{-5} M, 110°C).

As seen from Table 1, one inhibitor molecule (with its transformation products) decomposes more than 10^4 CHP molecules.

Table 1 shows that the coefficient f increases from 1.6 to 1.8–2.4 in going from disulfide **I** to **II**–**V**.

Table 1. Parameters of reactions of **I**–**V** with CPR and those of catalytic decomposition of CHP

Compound	f	$k_7 \times 10^{-4}$, l mol^{-1} s^{-1}	ν	Compound	f	$k_7 \times 10^{-4}$, l mol^{-1} s^{-1}	ν
I	1.6	1.92	18000	**IV**	2.2	2.5	26000
II	2.4	2.72	24000	**V**	2.1	2.4	20000
III	1.8	2.12	38000				

Table 2. Characteristics of compounds **II**–**V**

Compound	Yield, %	mp, °C	Found, %/Calculated, %				Formula
			C	H	S	N	
II	55	144–145	$\frac{57.42}{57.81}$	$\frac{5.19}{4.85}$	$\frac{19.80}{19.29}$	$\frac{8.91}{8.43}$	$C_{16}H_{16}N_2O_2S_2$
III	60	127–128	$\frac{63.72}{63.44}$	$\frac{6.46}{6.77}$	$\frac{15.79}{15.39}$	$\frac{7.25}{6.73}$	$C_{22}H_{28}N_2O_2S_2$
IV	75	119–120	$\frac{68.10}{68.41}$	$\frac{4.67}{4.41}$	$\frac{13.60}{14.05}$	$\frac{6.39}{6.14}$	$C_{26}H_{20}N_2O_2S_2$
V	80	131–132	$\frac{62.65}{69.40}$	$\frac{5.15}{4.99}$	$\frac{13.61}{13.23}$	$\frac{5.33}{5.78}$	$C_{28}H_{24}N_2O_2S_2$

This may be due to the presence of the N=C bond, which also terminates oxidation chains. A similar trend is observed with the parameter ν. The highest ν, 38000, is exhibited by *tert*-butyl-substituted disulfide **III**.

Table 1 shows that f and k strongly depend on the radical R in **II**–**V**. As compared to the related sulfides (ν = 5680–9000), disulfides **II**–**V** have higher ν, i.e., their inhibiting power is considerably higher; the k_7 and f values are, by contrast, somewhat higher for sulfides [$f = 1.36–6.00$, $k_7 = (1.99–7.96) \times 10^{-4}$ l mol^{-1} s^{-1}] [1].

EXPERIMENTAL

The IR spectra were recorded on a Specord 75-IR spectrophotometer, and the ^{1}H NMR spectra, on a Bruker spectrometer (300 MHz); the chemical shifts (ppm) are given in the δ scale relative to internal TMS.

Cumyl hydroperoxide was purified as described in [7], with the subsequent distillation; chlorobenzene and cumene were purified by a common procedure based on sulfonation of impurities with concentrated sulfuric acid [8, 9]. The CHP concentration was determined by iodometric titration [7] of intermittently taken samples. Experiments on CHP decomposition were performed in chlorobenzene at 110°C in a glass bubbler in an inert gas atmosphere; the CHP concentration was varied within 0.16–0.64 M, and the concentrations of **I**–**V**, within 10^{-5}–5×10^{-3} M.

Experiments on initiated oxidation of cumene were performed on a manometric unit [9]; as initiator served AIBN (initiation rate constant at 60°C 10^{-5} l mol^{-1} s^{-1} [10]). The initiator concentration was 2×10^{-2} M in all the experiments, and the concentration of **I**–**V**, $(1–5) \times 10^{-4}$ M.

Bis(4-hydroxy-3-formylphenyl) disulfide I. A solution of 6.7 g (0.05 mol) of S_2Cl_2 in 20 ml of CCl_4 was added with stirring to a solution of 12.2 g (0.1 mol) of salicylaldehyde in 30 ml of absolute CCl_4. The mixture was allowed to stand for 24 h, after which the solvent was distilled off and the residue was triturated with benzene. Yield of disulfide **II** 6.5 g (72%), mp 105°C.

Found, %: C 54.49, H 3.68, S 20.56.
$C_{14}H_{10}O_2S_2$.
Calculated, %: C 54.90, H 3.29, S 20.93.

Bis[3-alkyl(aryl)iminomethyl-4-hydroxyphenyl] disulfides II–**V**. A three-necked 100-ml flask equipped with a stirrer, reflux condenser, and dropping funnel was charged with a solution of 0.05 mol of disulfide **I** in 30 ml of anhydrous CCl_4, and 0.1 mol of appropriate amine was added dropwise over a period of 5 h with stirring and cooling with ice. Then the mixture was stirred for 5 h at 30 – 40°C. The reaction product was washed with water and dried over Na_2SO_4; the solvent was distilled off, and the residue was recrystallized. The yields, melting points, and elemental analyses of **II**–**V** are listed in Table 2.

CONCLUSION

Bis(4-hydroxy-3-formylphenyl) disulfide was prepared; its reactions with primary amines gave the corresponding bis[3-alkyl(aryl)iminomethyl-4-hydroxyphenyl] disulfides. These disulfides inhibit cumene oxidation and catalytically decompose cumyl hydroperoxide.

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