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Mechanism of Low-Molecular Alkenes Interaction with Sulfur-Containing Spatially Hindered Phenols under Conditions of Thermal Modification of Polymer Materials

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Abstract—Transformations in the course of high-temperature modification of polyolefins under action of sulfur-containing modifiers have been studied using hexene-1 and hexane as model compounds. Composition of products of thermolysis of bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl] disulfide and bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl] sulfide at 200–270°C has been elucidated by means of thermogravimetry and gas chromatography–mass spectrometry. Mechanism of olefins modification with sulfides and disulfides involving the formation of biradical intermediates is discussed.

Keywords: spatially hindered phenol, sulfur-containing polymer modifier, biradical, sulfur-containing olefin, thermolysis, TOF chromatography–mass spectrometry

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Using functional modifiers is a simple cost-effective approach to improve the properties of polymer materials, in particular, their resistance to organic solvents, oil, and water as well as durability under severe operation conditions [1]. Chemical modification of polymers can take place either during the synthesis (at the chain growth stage via copolymerization with an antioxidant bearing double C=C bond or at the chain termination stage via interaction of the macroradical with thiol-containing additives [2]) or during molding of the final product (grafting of spatially hindered phenols [1, 3]).

Studies of thermolysis kinetics of a series of phenolic antioxidants have revealed that some disulfides are capable of chemical modification of polymers under conditions of their thermal processing [4]. Importantly, such modification can be performed using standard processing equipment.

Spatially hindered phenols can act as reducing agents [5]. For instance, bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl] disulfide **I** and bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl] sulfide **II** possess strong antioxidant properties and are applied in manufacturing stabilized polymer compositions [6]. When used in combination, compound **I** has enhanced 2–4 times the antioxidant action of vitamin E, Mexidol, and other drugs [7].

Disulfides can undergo thermal decomposition to yield radical species [8]. The energy of heat-induced cleavage of the S–S bond (60 kcal/mol) to give sulfide radicals is noticeably lower than that of the ArO–H bond yielding phenoxyl radical (82 kcal/mol) [9].

The radicals formed upon thermal decomposition of disulfides are oxidizers capable of interaction with olefins and other polymer fragments. The influence of the modifiers on the modified polymer properties is of practical importance.

Earlier we have observed enhancement of basic mechanical properties of glass-filled polyamide in the

course of its thermal treatment in the presence of up to 1 wt% of disulfide **I** [10]. In particular, the impact viscosity and the strength at break have increased, leading to the increase 1.5 times in the material wear resistance. Larger concentrations of modifiers may be used. Furthermore, a composition based on epoxy resins containing 2.0–2.4 wt% of sulfur-containing phenolic modifier TAB (a mixture of 2-*tert*-butylphenol di- and polysulfides [11]) has been tested for microelectronic devices protection against external actions (including exposure to radiation) [12]. The same modifier has been used in manufacturing waterproof articles from epoxy resins [13].

The available data have revealed that modification efficacy of the less hindered methylated phenol disulfides is higher than that of their *tert*-butyl analogs [14].

In this work we aimed to elucidate the mechanism of chemical transformations in the course of polymers modification with sulfur-containing phenol antioxidants using the low-molecular models. Direct study of the corresponding polymer mixtures should have involved complicated analysis of non-volatile reaction mixtures.

Earlier studies of transformations of phenosanes (phenol antioxidants of polypropylene) revealed that phenosanes were oxidized to form methylenequinones [15]. Probably, the oxidation products were more reactive towards polypropylene than the starting phenols.

Further it was shown that the structure of the phenosane-derived methylenequinones was more complex than had been expected, and those products were prone to thermolytic decomposition [16]. Using dimeric methylenequinones, it was demonstrated that the process followed the radical mechanism [17]. Likely, the radicals formation led to unique properties of phenosanes allowing for efficient modification of polypropylene.

In this work we used hexene-1 as a low-molecular model of a polyolefin (the alkene structure corresponded to ethylene trimer formed via disproportionation chain termination), whereas disulfide **I** [18] and sulfide **II** [19] were used as model modifiers. All the reactants were volatile; hence, their interaction in the course of heating could be tracked with chromatography–mass spectrometry technique.

The decomposition of modifiers **I** and **II** at heating at 200–250°C was studied by means of thermogravimetry, differential scanning calorimetry, and pyrolytic chromatography–mass spectrometry.

Decomposition of compound **I** started at 205°C, its thermolysis at heating at a rate 10 deg/min (200–240°C) occurring via two pathways (Scheme 1). In particular, disulfide **I** mainly decomposed via the path *a* (cleavage of the S–S bond) to form a pair of identical radicals **III** that were further stabilized to yield thiol **IV** along with the dehydrogenation products: sulfur-containing dienones **V** and **VI** (88% in total).

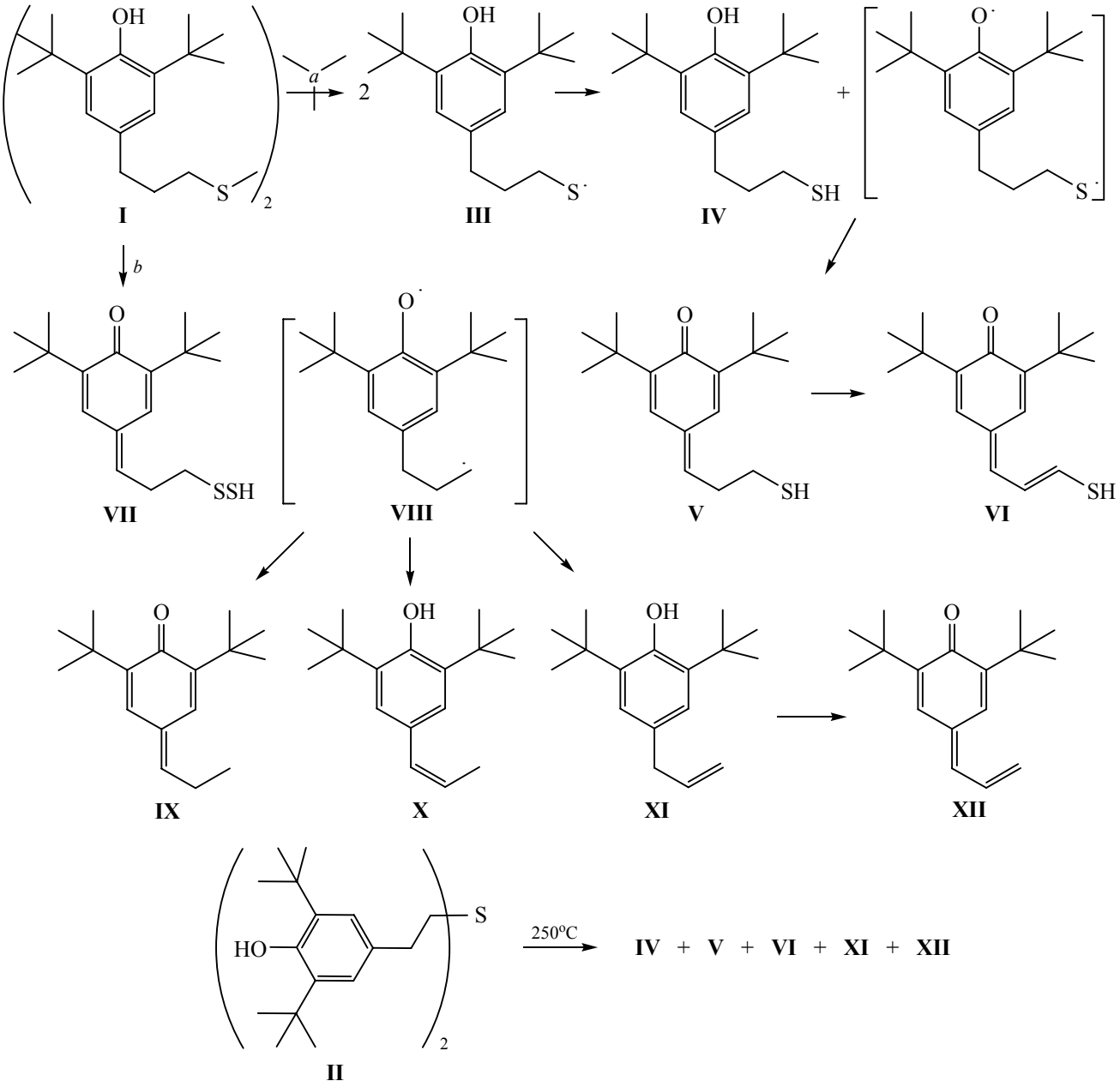
Another pathway *b* of the disulfide transformation (cleavage of the $–CH_2–S_2–$ bond) was a minor one; however, its contribution grew at heating. In the course of thermolysis at 240°C, that pathway yielded 6% of the sulfur-containing dienone **VII** and 6% of the sulfur-free compounds **IX**–**XII**.

Sulfide **II** was stable against heating up to 250°C. Its thermolysis at 250–270°C occurred with the cleavage of the $–CH_2–S–$ bond to yield a mixture containing 52% of thiol **IV**, 9% of compound **V**, 13% of allylphenol **XI**, 17% of dehydrogenation product of the latter (**XII**), and other minor products (less than 1%). The formation of thiols during alkyl sulfides thermolysis has been discussed elsewhere [20].

The revealed products of thermolysis of phenol modifiers **I** and **II** pointed at the oxidative character of the process accompanied with the transformation of phenols into methylenequinones. In the case of the pathway *a*, methylenequinones were likely formed from the O,S-biradical. Thermolysis via the pathway *b* apparently gave another biradical that was stabilized via elimination of hydrogen from one of the fragments of the aliphatic chain of the *para*-substituent to yield 4-methyl-, 4-vinyl-, 4-allyl-, and 4-allenyl-2,6-di-*tert*-butylphenols. The participation of biradicals in the transformations of methylenequinones has been earlier observed in [21]. Hence, thermolysis of sulfur-containing compounds **I** and **II** likely occurred via the biradical or the related mechanism.

We further studied under conditions of the high-temperature processing the interaction of disulfide **I** with hexane and hexene-1, low-molecular models simulating polyolefins. It has been demonstrated that both positions at the double bond of propene are substituted with $CH_3S–$ groups upon interaction with methyl disulfide in the presence of boron trifluoride etherate at 0°C [22]. The interaction of hexyl radical with disulfides leads to non-branched sulfides [23].

Scheme 1.

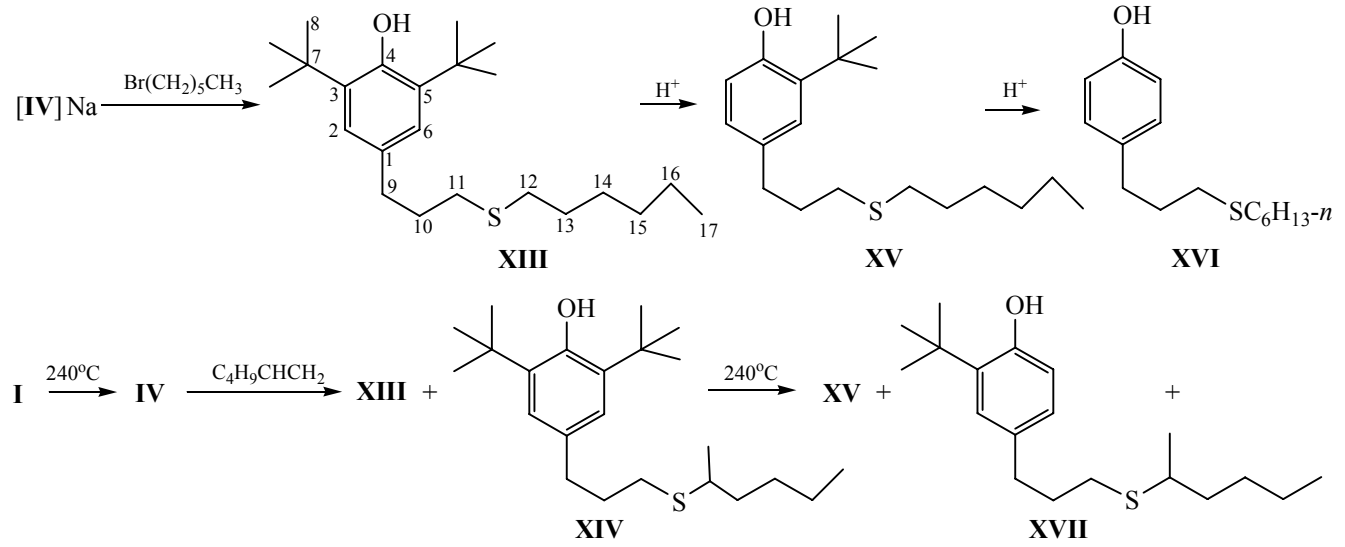


These reactions have not been studied at elevated temperature.

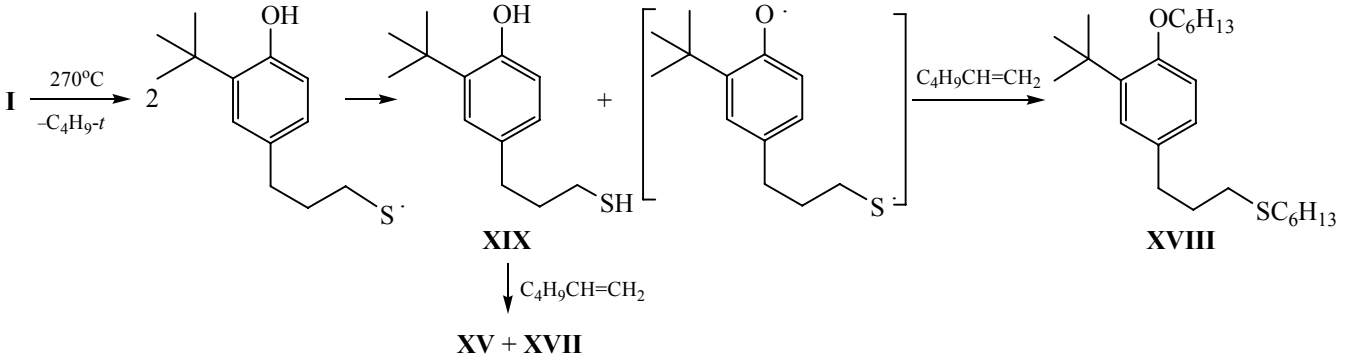
Two groups of compounds were identified in the reaction mixture obtained via interaction of hexene-1 with disulfide **I** at 240°C by means of gas chromatography–mass spectrometry. The first group consisted of olefins (mainly branched ones), whereas the second group mainly contained the products of interaction of disulfide **I** with hexene-1 (two isomeric sulfides **XIII** and **XIV** in the 1 : 3 ratio) and the products of de-*tert*-butylation (compounds **XV** and **XVI** in the same ratio), the total content of products **XIII**–**XVI** in the mixture being 75%. 4-Methyl-, 4-ethyl, 4-propyl-, and 4-allyl-2,6-di-*tert*-butylphenols (1% of each) were found in the reaction mixture as well (Schemes 2, 3).

Sulfide **XIV** was isolated from the reaction mixture, whereas sulfide **XIII** was obtained by an independent synthesis from sodium salt of thiol **IV** and 1-bromohexane. Further de-*tert*-butylation of compound **XIII** in the presence of 0.05 wt% of *p*-

Scheme 2.



Scheme 3.



toluenesulfonic acid at 180°C yielded compounds **XV** and **XVI**.

Reaction of hexene-1 with disulfide **I** at 260–280°C gave 4-propyl- and 4-allyl-2-*tert*-butylphenols as the major products (65% in total); isomers of dihexyl sulfide were present in the mixture as well. Partial de tert-butylation of 2,6-di-*tert*-butylphenol derivatives into the corresponding derivatives of 2-*tert*-butylphenol resulted in the formation of noticeable amounts of O-alkylation products. The major fraction of those products comprised six isomers of compound **XVIII** (17% in total) containing two hexyl fragments each along with isomeric sulfides **XV** and **XVII** (5% in total, in the ratio of 1 : 4 with the isomer containing a branched aliphatic chain prevailing). The observed elimination of sulfur in the course of thermolysis of the modifier determined the temperature range of its application (<260°C). A similar process of desulfurization of sulfur-containing spatially hindered phenols was described earlier [24] but was not studied under the conditions used in this work.

We additionally studied the interaction of hexane (a model of inert aliphatic chain of a polyolefin) with disulfide **I** under conditions of the radical decomposition of the latter at 240°C. Kinetics of a similar reaction of 2,4,6-tri-*tert*-butylphenoxyl radical with decane at 130°C has been studied earlier, but its products has not been identified [25].

Hexane oligomers were not found in the reaction mixture containing thiol **IV** (50%), a series of products of compound **I** thermolysis, and a number of isomeric pairs of hexyl-, heptyl-, octyl-, and nonyl-2,6-di-*tert*-butylphenols along with a pair of sulfur-containing isomers **XIII** and **XIV** in the 3 : 1 ratio. In contrast to the above-discussed reaction of compound **I** with hexene-1, the products with non-branched aliphatic

chain (**XIII** and others) prevailed in the reaction mixture. The total content of products of reaction of disulfide **I** with hexane in the mixture was 5%.

To conclude, the modification of olefins with disulfides involves the relatively inert saturated fragments in addition to the reactive double bonds. In particular, this leads to the formation of more complex compounds containing aliphatic fragments covalently linked to the phenol antioxidant. The obtained results are useful for development of processes of targeted modification of polymer materials with sulfur-containing additives.

EXPERIMENTAL

Pyrolytic experiments and studies by means of high resolution mass spectrometry were performed using an Agilent 7200 Q-TOF chromatograph equipped with an HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) and a CDS Pyroprobe 5000 pyrolysis attachment. The chromatography conditions are as follows: helium as carrier gas at 1 mL/min; column temperature program: 2 min at 50°C, heating from 50 to 280°C at a rate 10 deg/min, and 20 min at 280°C; evaporator temperature 280°C; ions source temperature 230°C. Mass spectrometry conditions: ionization at 70 eV, scanning rate 10 scans/s at 30–650 Da.

Studies by means of gas chromatography–mass spectrometry were performed using an HP 5890 series II chromatograph equipped with an HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm) and an HP 5971 mass-selective detector. The chromatography conditions: helium as carrier gas at 1 mL/min; column temperature program: 2 min at 50°C, heating from 50 to 300°C at 10 deg/min, and 30 min at 300°C; evaporator temperature 300°C; and ions source temperature 175°C. Mass spectrometry conditions: ionization at 70 eV, scanning rate 1.2 scans/s at 30–650 Da.

Thermogravimetric analysis was performed using a Netzsch STA 409 PC instrument in helium atmosphere at heating rate 10 deg/min.

^{1}H and ^{13}C NMR spectra were recorded using Bruker AM-400 and AV-600 instruments. Experiments under pressure were run in a 50 mL rotating steel pressure reactor.

Bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl] disulfide **I** and bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propyl] sulfide **II** (99% of the main component) were obtained via crystallization from ethanol. 2,6-Bis(1,1-dimethylethyl)-4-(3-thiopropyl)phenol **IV** was obtained via hydrogenation of disulfide **I** [26].

Thermolysis of compound I. The compound was stable under inert atmosphere up to 200°C. The thermolysis products were obtained via maintaining the sample in a pyrolysis chamber at 240°C during 10 s. The products composition was as follows: thiol **IV** (73%), thiopropenylphenol **V** (13%), thiodienylphenol **VI** (1.5%), methylenequinone **XII** (4.7%), and hydrosulfide **VII** (6%).

Thermolysis of compound II. The compound was stable under inert atmosphere up to 250°C. The thermolysis products were obtained via maintaining the sample in a pyrolysis chamber at 300°C during 10 s. The products composition was as follows: thiol **IV** (52%), methylenequinone **XII** (17%), allylphenol **XI** (14%), and compound **V** (9%).

2,6-Bis-(1,1-dimethylethyl)-4-(3-thiopropyl)phenol (IV). Found: *M* 280.1846. $C_{17}H_{28}OS$. Calculated: *M* 280.1855. Mass spectrum, *m*/*z* (I_{rel}, %): 57 (100), 280 (74), 265 (70), 219 (45), 41 (21), 209 (17).

2,6-Bis(1,1-dimethylethyl)-4-(3-thiopropenyl)phenol (V). Found: *M* 278.1694. $C_{17}H_{26}OS$. Calculated: *M* 278.1699. Mass spectrum, *m*/*z* (I_{rel}, %): 278 (79.3) [M^+], 263 (100.0), 221 (28.4), 217 (66.5), 207 (72.3), 204 (21.4), 193 (37.1), 189 (27.5), 179 (41.5), 147 (28.3), 128 (23.8), 115 (24.4), 77 (26.4), 57 (54.8), 41 (70.7).

2,6-Bis(1,1-dimethylethyl)-4-(3-disulfanylallyl)-phenol (VII). Found: *M* 310.1427. $C_{17}H_{26}OS_2$. Calculated: *M* 310.1420. Mass spectrum, *m*/*z* (I_{rel}, %): 310 (17) [M^+], 245 (29), 189 (60), 133(16), 128 (17), 57 (100), 41 (18).

4-(1-Propenyl)-2,6-bis(1,1-dimethylethyl)phenol (X). Found: *M* 246.1983. $C_{17}H_{26}O$. Calculated: *M* 246.1978. Mass spectrum, *m*/*z* (I_{rel}, %): 246 (53) [M^+], 231 (100), 141 (7), 129 (8), 128 (8), 115 (8), 91 (8), 57 (12), 41 (11).

4-Allyl-2,6-bis(1,1-dimethylethyl)phenol (XII). Found: *M* 246.1974. $C_{17}H_{26}O$. Calculated: *M* 246.1978. Mass spectrum, *m*/*z* (I_{rel}, %): 246 (31) [M^+], 231 (100), 203 (4), 159 (4), 128 (3), 115 (5), 57 (8), 41(5).

α-Vinyl-2,6-bis(1,1-dimethylethyl)methylenequinone (XII). Found: *M* 244.1819. $C_{17}H_{24}O$. Calculated: *M* 244.1827. Mass spectrum, *m*/*z* (I_{rel}, %): 244 (29.2) [M^+], 201 (37.7), 187 (50.4), 173 (25.0), 159 (22.3), 145 (100.0), 129 (21.0), 128 (26.1), 57 (43.0).

Interaction of disulfide I with hexane. 0.5 g of disulfide **I** and 30 mL of *n*-hexane were placed in a 50 mL steel rotating pressure reactor; the latter was purged with argon and sealed. The mixture was kept at 240°C during 10 h, and the obtained transparent solution was evaporated. According to gas chromatography–mass spectrometry results, the residue (0.44 g of oily substance) contained 48% of thiol **IV**, 2% of 2,6-di-*tert*-butylphenol, 3% of 4-methyl-2,6-di-*tert*-butylphenol, 5% of 4-ethyl-2,6-di-*tert*-butylphenol, 5.5% of 4-propyl-2,6-di-*tert*-butylphenol, 10% (in total) of compound **XI** and its two isomers, 3% of 4-thiopropyl-2-*tert*-butylphenol **XIX**, 11% of high-boiling compounds **I** and **II**; 2% (in total) of the following eight compounds (pairs of isomers with linear and branched aliphatic chains in the 3 : 1 ratio): 4-hexyl-, 4-heptyl-, 4-octyl-, and 4-nonyl-2,6-di-*tert*-butylphenols; and sulfur-containing isomers **XIII** and **XIV**. Aliphatic hydrocarbons with the extended chain were not found.

Interaction of disulfide I with hexene-1 at 240°C. 1.5 g of disulfide **I** and 15 mL of *n*-hexene-1 were placed in a 50 mL steel rotating pressure reactor; the latter was purged with argon and sealed. The mixture was kept at 240°C during 6 h and then evaporated. The residue (1.6 g) was distilled in a vacuum to obtain 0.4 g of the olefin fraction and 1.0 g of residue.

Cyclododecane, two isomers of dodecene, 2-methylundecane, and 5-methylundecane (the products of condensation of two hexene-1 molecules) along with octadecene (the trimerization product) were identified in the olefin fraction. The presence of three isomers of dihexyl sulfide (*M* 202, $C_{12}H_{26}S$) was confirmed.

The residue contained 46% of isomers **XIV** and **XIII** in the 2.5 : 1 ratio and 31% of their mono-de-*tert*-butylated isomers (**XVII** and **XV**) in the same ratio. The following sulfur-free phenols were isolated from the reaction mixture by means of thin-layer chromatography and identified: 2,6-di-*tert*-butylphenol and its 4-methyl, 4-ethyl, and 4-allyl derivatives (5.5% in total). On top of that, the fraction contained 6% of high-boiling derivatives (compounds **I** and **II** and their de-*tert*-butylation products) along with 7% of branched olefins.

2,6-Di-*tert*-butyl-4-[3-propylthio-(2-hexyl)]phenol (XVII). Isolated by TLC on silica gel with a 1 : 1 $CHCl_3$–hexane mixture as eluent. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 t (3H, $\underline{CH_3}CH_2$, $^3J_{HH}$ 10 Hz), 1.26 d (3H, $\underline{CH_3}CH$, $^3J_{HH}$ 10 Hz), 1.24–1.50 m (6H, CH_2), 1.44 s (18H, *t*-Bu), 1.82–1.93 m and 2.49–2.67 m (6H, CH_2S), 2.68 t (2H, CH_2, $^3J_{HH}$ 11 Hz), 2.75 q (2H, CH_3CH_2S, $^3J_{HH}$ 10 Hz), 5.05 s (1H, OH), 6.99 s (3H, Ar-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.92 (C^{16}), 21.28 (C^{17}), 28. 82 (C^{15}), 29.75 (C^{10}), 30.20 (C^8), 31.58 (C^{14}), 31.99 (C^{13}), 34.14 (C^7), 34.91 (C^9), 36.65 (C^{11}), 39.81 (C^{12}), 124.77 ($C^{2,6}$), 132.12 (C^1), 135.57 ($C^{3,5}$), 151.72 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 364 (47) [M^+] (calculated: 364.2794), 293 (11), 246 (67), 231 (84), 219 (28), 189 (100), 175 (10), 147 (14), 57 (46), 55 (18), 43 (40), 41 (36).

Interaction of disulfide I with hexene-1 at 260–270°C. A mixture of 0.8 g of disulfide **I** and 10 mL of hexene-1 were kept in a rotating steel pressure reactor at 260–270°C during 8 h. The formed solution was evaporated in a vacuum. According to gas chromatography–mass spectrometry results, the residue (0.9 g) contained 51% of 4-propyl-2-*tert*-butylphenol, 14% of 4-allyl-2-*tert*-butylphenol, four isomers of 2-*tert*-butyl-4-(3-hexylthiopropyl)phenyl hexyl ether (17% in total), three isomers of dihexyl sulfide (10% in total), and 8% of isomeric sulfides **XV** and **XVII** in the 1 : 2 ratio.

2-*tert*-Butyl-4-(3-hexylthiopropyl)phenyl hexyl ether. Mass spectrum, *m*/*z* (I_{rel}, %): 392(25) [M^+] (calculated: 392.3107), 274 (34), 217 (34), 190 (26), 175 (42), 147 (24), 133 (33), 57 (26), 43 (100), 41 (44). $C_{25}H_{44}OS$.

2,6-Di-*tert*-butyl-4-(3-hexylthiopropyl)phenol (XIII). 4.8 g of thiol **IV** was added to a solution of 0.4 g of sodium disolved in 5 mL of methanol, methanol was evaporated, and the mixture was kept in a vacuum while stirring at 80°C during 1 h. 0.5 mL of DMF and 3 g of 1-bromopentane were added to the residue. The suspension was stirred at 100°C during 4 h. The reaction mass was dissolved in chloroform and twice washed with water to get 4.8 g (68%) of dark oily substance containing 95% of sulfide **XIII** (GC–MS). The product was purified by silica gel chromatography of the solution in chloroform to obtain colorless oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.94 t (3H, CH_3, $^3J_{HH}$ 10 Hz), 1.28–1.50 m and 1.49 s (18H, *t*-Bu); 1.59–1.69 m, 1.88–1.98 m and 2.54–2.63 m (8H, CH_2S), 2.68 t (2H, CH_2, $^3J_{HH}$ 7.5 Hz), 5.1 s (1H, OH), 7.04 s (2H, Ar-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.91 (C^{17}), 22.42 (C^{16}), 28.82 (C^{15}), 29.94 (C^{10}), 30.31 (C^8), 31.23 (C^{11}), 31.33 (C^{12}), 31.33 (C^{14}), 31.99 (C^{13}), 34.14 (C^7), 34.77 (C^9), 124.84 ($C^{2,6}$), 132.08 (C^1), 135.64 ($C^{3,5}$), 151.77 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 364 (47) [M^+] (calculated: 364.2794), 293 (11), 246 (67), 231 (84), 219 (28), 189

(100), 175 (10), 147 (14), 57 (46), 55 (18), 43 (40), 41 (36). $C_{23}H_{40}OS$.

De-*tert*-butylation of 2,6-di-*tert*-butyl-4-(3-hexylthiopropyl)phenol sulfide (XIII). A mixture of 3 g of sulfide **XIII** and 60 mg of *p*-toluenesulfonic acid were stirred at 200°C during 0.6 h and then subjected to chromatography on silica gel eluting with a 3 : 2 chloroform–hexane mixture. The fraction with R_f 0.35 was evaporated to obtain 2.2 g of 2-*tert*-butyl-4-(3-hexylthiopropylphenol **XV**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (3H, CH_3, $^3J_{HH}$ 10 Hz), 1.25–1.45 m and 1.43 s (9H, *t*-C_4H_9), 1.55–1.65 m (2H, CH_2), 1.85–1.96 m (2H, CH_2), 2.51–2.59 m (4H, CH_2), 2.62 t (2H, $ArCH_2$, $^3J_{HH}$ 7.2 Hz), 5.25 s (1H, OH), 6.60 d (1H, Ar-H, $^3J_{HH}$ 7.8 Hz), 6.88 d.d (1H, Ar-H, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.8 Hz), 7.09 d (1H, Ar-H, $^4J_{HH}$ 1.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.86 (C^{17}), 22.35 (C^{16}), 28.42 (C^{15}), 29.42 (C^{10}), 29.44 (C^8), 31.25 (C^{12}), 31.32 and 31.34($C^{13,14}$), 31.93 (C^{11}), 34.17 (C^7), 34.29 (C^9), 116.23 (C^5), 126.33 and 126.96 ($C^{4,6}$), 133.00 (C^1), 135.74 (C^3), 152.29 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 308 (85) [M^+] (calculated: 308.21 (68), 190 (70), 175 (100), 163 (14), 147 (22), 133 (67), 57 (20), 43 (26), 41 (28). $C_{19}H_{32}OS$.

The fraction with c R_f 0.15 was evaporated to get 0.3 g of **4-(3-hexylthiopropyl)phenol (XVI).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 t (3H, CH_3, $^3J_{HH}$ 6.9 Hz), 1.2–1.4 m (6H, CH_2), 1.49–1.60 m (2H, CH_2), 1.79–1.90 m (2H, CH_2), 2.44–2.52 m (4H, CH_2S), 2.62 t (2H, $ArCH_2$, $^3J_{HH}$ 7.2 Hz), 4.90 s (1H, OH), 6.71–6.76 br.d (2H, Ar-H, $^3J_{HH}$ 9.0 Hz), 7.01–7.05 br.d (2H, Ar-H, $^3J_{HH}$ 9.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.91 (C^{17}), 22.42 (C^{16}), 28.48 (C^{15}), 29.51 (C^{14}), 29.51 (C^{13}), 29.51 (C^{10}), 31.26 (C^{12}), 31.99 (C^{11}), 33.79 (C^9), 115.06 ($C^{3,5}$), 129.41 ($C^{2,6}$), 133.54 (C^1), 153.54(C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 252 (18) [M^+] (calculated: 252.1542), 134 (100), 107 (34), 77 (13), 61 (6), 55 (7), 43 (11), 41 (13). $C_{15}H_{24}OS$.

Di-[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl] sulfide. Mass spectrum, *m*/*z* (I_{rel}, %): 189(100), 57 (91), 246 (81), 231 (57), 248 (30), 219 (27), 526 (17), 147 (14), 280 (8).

Di-[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl] disulfide. Mass spectrum, *m*/*z* (I_{rel}, %): 57 (100), 223 (62), 167 (40), 219 (28), 280 (19), 264 (18), 250 (15). 207 (11), 189 (10), 558 (8).

4-Allyl-2,6-di-*tert*-butylphenol. Mass spectrum, *m*/*z* (I_{rel}, %): 231 (100), 246 (27), 57 (19), 232 (17), 41 (7), 129 (6).

2,6-Di-*tert*-butyl-4-methylene-2,5-cyclohexadien-1-one. Mass spectrum, *m*/*z* (I_{rel}, %): 161 (100), 203 (49), 175 (40), 218 (28) [M^+] (calculated: 218.167), 91 (16), 77 (11), 115 (11), 105 (10). $C_{15}H_{22}O$.

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