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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis, Composition, and Properties of Products Formed in Interaction of *ortho-tert*-Butylphenol with Sulfur Monochloride

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Abstract—Interaction of *ortho-tert*-butylphenol with sulfur monochloride in dimethylformamide leads to an increase in the fraction of phenol di- and polysulfides in the product. Liquid chromato-mass-spectrometry was used to determine the composition of the main groups of compounds contained in the mixture. A number of its components was isolated and produced by counter synthesis.

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The stabilizer Tioalkofen-B (TAB) is the contracted name of the product formed in the reaction of *orthotert*-butylphenol (OTBP) with sulfur monochloride. Its properties strongly depend on whether mono- or polysulfides are predominant in its mixture and, consequently, on the method and conditions of its synthesis.

A study of the thermolysis kinetics of mono-, di-, and trisulfides of phenols and of their practical properties has shown that mono- and polysulfides of phenols belong to antioxidant groups differing in their action: monosulfides of phenols are additives that are extractable from polymers and do not noticeably change their properties. Phenols containing a chain of two or more sulfur atoms in their structure can, under certain thermal treatment conditions, behave either as antioxidants or as effective modifiers of properties of polymeric materials. TAB belongs to the second group. Introduction of TAB into a formulation containing low-pressure polyethylene and a cross-linking agent of the peroxide type improves the stability of the composite being formed against action of elevated temperatures and leads to an increase in deformation characteristics and to preservation of thermal stability upon a contact with solvents [2]. Introduction of 0.5 to 1.5% TAB into a formulation of a glass-fiber plastic based on epoxy phenol-formaldehyde resin improves its strength and water resistance under conditions of prolonged keeping of articles in water [3]. TAB has been successfully used to solve one of the most complicated problems of creating reliable coatings for protection of microelectronic devices from any external factors, including radiation [4].

The aim of our study was to examine the composition of TAB and find its synthesis conditions providing the maximum efficiency as a modifier of service properties of composite polymers. To raise the fraction of "disulfides" in the reaction of phenols with sulfur monochlorides, it has been recommended to perform the process in a flow of hydrogen sulfide [5], employ iodine and powdered iron as a catalyst [6], and use basic solvents DMFA and DMSO [7], with the last way being the most effective.

The attractiveness and accessibility of the starting reagents, phenols and sulfur monochloride, and the most favorable conditions of their interaction are known, but it is difficult to find in organic chemistry a reaction more complex, ambiguous, and poorly studied than the reaction in question [8]. The expected disulfides are contained in reaction mixtures in amounts smaller than 30%, and it is impossible to isolate these compounds by simple methods from a reaction mass with a complex composition. Previously, we have made an attempt to study the composition of products formed in the interaction of OTBP with sulfur monochloride by GLC [9]. This technique, which, as a rule, requires heating of high-boiling samples to a temperature of 300°C, failed to furnish an objective picture because of the complex composition of the mixture of products being formed, and primarily due to the poor thermal stability of polysulfides of phenols: their noticeable decomposition is observed at temperatures of 140°C and higher [10]. It has been suggested to analyze the composition of a mixture of 2,6-di-*tert*-butylphenol polysulfides by liquid chromatomass-spectrometry [11], and this technique became the basis of analytical studies.

EXPERIMENTAL

When the reaction of OTBP with S_2Cl_2 was performed without a solvent and with hexane, nitromethane, and acetonitrile, the compositions of the products formed were approximately the same. In each case, monosulfide (1) was quantitatively predominant over other components and its content was 30 to 45%. An example of synthesis of TAB in toluene was described in the patent [11]. Performing this reaction in DMFA sharply changed the composition of the reaction mass. Synthesis of TAB in DMF. To a solution of 300 g $(1.96 \text{ g mol}^{-1})$ of 98% OTBP in 250 ml of DMF, cooled to -20° C is added, under vigorous stirring in the course of 2 h, 88 ml (148 g, 1.1 g mol⁻¹) of freshly distilled sulfur monochloride in such a way that the reaction mass temperature does not exceed -5° C. The mixture is kept at room temperature for 2 h and, with agitation continued, heated to 50°C, which results in that a homogeneous mass is formed. It is dissolved in 1 l of methyl-*tert*-butyl ether, the solution is washed with a threefold amount of water, and the solvent is evaporated. This yields 340 g of a highly viscous light yellow transparent oil (TAB), which contains, according to GLC data, 1% solvent. On being heated to 50°C, the oil becomes thin.

To determine the molecular masses and the elemental composition of TAB components, we used a Finnigan MAT 8200 high-resolution mass spectrometer. Separate components in the reaction masses were identified using aTsvet gas chromatograph. The composition of TAB and its separate components was analyzed by NMR. The melting points were determined with a Kufler apparatus.



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The data presented below demonstrate that the content of monosulfide (1) decreased from 40 to 12% and p,p- di- and polysulfides (2)–(5) of 2-*tert*-butylphenol predominate: the total content of these compounds is about 70%. Compounds **6–9**, contained in an amount of 6%, are a mixture of o,p- mono- and polysulfides of 2-*tert*-butylphenol. Another group is constituted by ~10% sulfur-containing compounds **11–16**, each containing three 2-*tert*-butylphenol fragments. Also, chlorine-containing compounds were identified in TAB in minor amounts. These are represented by compound **10** (see the Scheme).

In the first stage of the study, we separated TAB into components by HPLC on a Milikhrom-1 microcolumn liquid chromatograph (2 \pm 64 mm column, stationary phase Nucleosil 100-5018, particle size 5 μ m, Macherey– Nagel, Germany) [13]. A 85 : 15 mixture of methanol and water with addition of a 1% acetic acid solution served as the mobile phase. The elution rate was 100 μ l min⁻¹.

Substances were detected with a UV detector at five wavelengths simultaneously. The chromatographic information was recorded and processed with a CHROM versatile computerized data acquisition and processing system. The purity of compounds **1–4** and **6**, isolated as described above, was not worse than 97% according to GLC.

Bis-(3-*tert***-butyl-4-hydroxyphenyl)trisulfide (3).** Oil: PMR spectrum (200 MHz, CCl₄, σ , ppm): 1.38 s (C4H9-*tert*), 4.96 s (–OH), 6.55 d (J = 7.5 Hz, H₆-arom), 7.31 d.d (J = 7.5 Hz, J'' = 1.5 Hz, H₅-arom), 7.49 d (J = 1.5 Hz, H₃-arom). Found MM (by mass spectrometry): m/z 394.10749. C₂₀H₂₆O₂S₃. Calculated: m/z 394.10749.

Bis-(3-*tert***-butyl-4-***hydroxyphenyl*)*tetrasulfide* (4). Oil: PMR spectrum (200 MHz, CCl₄, σ , ppm): 1.39 s (C₄H₉-*tert*), 5.00 s (-OH), 6.61 d (J = 9.0 Hz, H₆-arom), 7.31 dd (J' = 9.0 Hz, J'' = 2.3 Hz, H₅-arom), 7.53 d (J = 2.3 Hz, H₃-arom).

Found MM (by mass spectrometry): m/z 426.07734. C₂₀H₂₆O₂S₄. Calculated: m/z 426.07734.

Bis-1,2'-(3-*tert***-butyl-4-hydroxyphenyl)(6'**-*tert***-butyl-1'-hydroxyphenyl)sulfide (6).** Oil: PMR spectrum (200 MHz, CCl₄, σ , ppm): 1.30 s (C₄H₉-*tert*, C₆'), 1.39 s (C₄H₉-*tert*, C₂), 5.15 s (-OH, C'), 6.51 d (J = 8.5 Hz, H₆-arom), 6.79 d.d (J = 8.5 Hz, J'' = 1.5 Hz, H₅-arom), 6.84 m (H₄-arom), 6.95 d (J = 2.5 Hz, H₃-arom), 7.31 d.d (J' = 8.0 Hz, J'' = 1.5 Hz, H₅-arom), 7.39 d.d (J' = 8.0 Hz, J'' = 2.0 Hz, H₃-arom). Found MM (by mass spectrometry):

m/*z* 330.16347. C₂₀H₂₆O₂S. Calculated: *m*/*z* 330.16347.

Using this method, we also isolated from the mixture individual compounds 1 and 2, which were produced by counter synthesis. Mercaptan 17 was obtained by reduction of TAB with hydrogen, one of the most effective catalysts for reduction of du- and polysulfides to obtain mercaptans [12].

4-Mercapto-2-tert-butylphenol (17). A 0.5-1 Vishnevskii autoclave was charged with 5 g of IK-75-01 catalyst (1% mixture of freshly prepared Co, Mn, B, and K sulfides on a carbon support in the form of small globules) and 180 g of a TAB stabilizer synthesized in DMF by the method described above. The autoclave was purged with hydrogen and then a hydrogen pressure of 2 MPa was created in the device. The reaction mass was kept under vigorous agitation at 160°C for 20 h. On cooling the autoclave, the reaction mass is filtered to remove the recyclable catalyst and the filtrate is extracted with 800 ml of a 5% caustic soda solution. The aqueous alkaline extract is separated from the organic layer and acidified with hydrochloric acid, and the product is extracted with ether. After evaporating the solvent, the oil obtained is distilled in a vacuum and the fraction with bp 145–152°C/3–4 mm Hg is collected. The yield of 4-mercapto-2-tert-butylphenol (17) is 130 g at a content of the main substance equal to 92% according to GLC.

Bis-(3-*tert***-butyl-4-hydroxyphenyl)disulfide (2).** A 10-g portion of 4-mercapto-2-*tert*-butylphenol (**16**) and 1 g of KOH are dissolved in 30 ml of isopropanol, and air is bubbled through a boiling mixture for 6 h, with the composition of the reaction mass monitored by GLC. Then, the solvent is removed and the residue is washed with water to a neutral reaction to give 8 g of a light yellow oil. The oil mostly contains bis-(3-*tert*-butyl-4-hydroxyphenyl)disulfide (**2**), which is purified by column chromatography. PMR spectrum (200 MHz, CCl_4 , σ , ppm): 1.37 s (C_4H_9 -*tert*), 5.05 s (-OH), 6.58 d (J = 8.5 Hz, H₆-arom), 7.21 d.d (J' = 8.5 Hz, J'' = 2.5 Hz, H₅-arom), 7.40 d (J = 2.5 Hz, H₃-arom). Found MM (%): C 66.48, H 7.40, S 17.91. $C_{20}H_{26}O_2S_2$. Calculated (%) C 66.26, H 7.23, S 17.69.

Bis-(3-*tert***-butyl-4-hydroxyphenyl)sulfide (1).** A 50ml portion of toluene is placed in 0.5-l flask and cooled to -15° C. Simultaneously, 102 ml (0.67 g mol⁻¹) of 2-*tert*-butylphenol in 100 ml of toluene and 21 ml (0.33 g mol⁻¹) of sulfur dichloride in 50 ml of toluene are added from two dropping funnels at a rate at which the reaction mass temperature does not exceed 0°C. After the dropping

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addition is complete (in ~1 h), the reaction mass is kept at room temperature for 2 h and then is again cooled to -15°C, with the resulting precipitate filtered-off and washed with petroleum ether cooled to 0°C. This yields 52 g (47%) of bis-(3-*tert*-butyl-4-hydroxyphenyl)sulfide in the form of a white powder, mp 105–110°C. PMR spectrum (200 MHz, CCl₄, σ , ppm): 1.35 s (C₄H₉-*tert*), 4.84 s (-OH), 6.64 d (J = 8.5 Hz, H6-arom), 7.05 d.d (J' = 8.5 Hz, J'' = 2.5 Hz, H₅-arom), 7.27 d (J = 2.5 Hz, H₃-arom). The isolation of individual components from TAB in the first part of the study made us confident in the structure of *p*,*p*-linked products and served as the necessary stage in a full analysis of products contained in TAB.

The structures of all the components of TAB were found by using a new HPLC-MS system. The system included an Agilent 1200 liquid chromatograph with a diode-array detector and a Bruker micrOTOF-Q hybrid quadrupole time-of-flight mass spectrometer; Zorbax XDB-C8 column, 2.1×150 mm, 3.5μ m, eluent 2% HCOOH–MeOH (15 : 85 v/v), flow rate 0.2 ml min⁻¹, UV detection at three wavelengths. Every second of the UV spectra accessible to the system (150 spectra per minute) in the range 230–450 nm was recorded. The working parameters of mass detection were as follows: ionization by electrostatic spraying under atmospheric pressure (API-ES), scanning of negative ions in the range m/z = 120-1000, flow rate of the drying gas (nitrogen) $8 \, \mathrm{l\,min^{-1}}$, its temperature 230°C, spraying gun pressure 1.6 Bar, accuracy of molecular mass determination 0.01 Da. Peaks of substances contained in the mixture in amounts exceeding 1% were analyzed. Compounds of this kind constituted 94% of all TAB components.

The use of a high-resolution time-of-flight mass detector in the system with the HPLC-MS instrument made it possible to precisely determine empirical formulas of all the TAB components and, in combination with UV spectroscopic and mass-spectrometric data, to obtain information about their structure. Previously, it has been impossible to obtain such a vast body of data in analyses of sulfur-containing phenols [12]. The results of our HPLC-MS analysis are listed in the table.

Four types of compounds were identified in the mixture.

The first type has a general empirical formula $C_{20}H_{26}O_2Sn$. To this type belong the already known compounds 1–4 and, judging from the mass of the phenolate anion and closeness of the UV spectrum, we can

Elution time, min	Peak area, %	Phenolate anion (M–H+), <i>m/z</i>	Fragment ions, <i>m/z</i> (corresponding intensity, %)	Peaks in UV spectra, nm	Compound
3.83	11.9	329.16	180.06 (7)	250, (278)	1
4.84	30.5	361.13	180.06 (56), 213.05 (13)	(245), 278	2
5.41	3.2	363.12, 365.12 (44%)	180.06 (30)	252, 278, (305)	10
6.56	1.4	329.16	180.06 (37), 149.10 (28)	247, 286	6
6.85	24.0	393.10	180.06 (65), 212.04 (2), 213.05 (3)	230, 272, (326)	3
7.82	1.4	361.13 (25%)	180.06 (22), 181.07 (100), 213.05 (8)	292	7
8.87	10.7	425.07	180.06 (14), 181.07 (7), 212.04 (99),	(270), (325)	4
			245.02 (6)		
11.0	1.6	509.22		248, (280), (320)	11
12.05	2.5	457.04	180.06 (32), 181.07 (11), 212.04 (75), 276.99 (50) 393.10 (14)	(275), (320)	5
12.27	2.8	541.19 (37%)	361.13 (100), 181.07 (13)	(278), (325)	14
13.92	1.0	573.16 (50%)	361.13 (100), 393.10 (96)	234, (280), 330	15
14.31	1.0	541.19	211.03 (18)	245, (280)	12
15.84	3.3	573.16 (24%)	393.10 (100), 213.05 (7)	(275), (325)	13
17.93	1.6	605.13 (28%)	361.13 (35), 393.10 (23), 425.07 (100)	232, (282), (335)	16
21.16	1.9	425.07	212.04 (18)	230, (280), (325)	8
25.65	1.1	457.04	425.07 (35)	238, (285), (335)	9

Results of an HPLC-MS analysis of the composition of products formed in the interaction of 2-tert-butylphenol with S₂Cl₂

reliably class with the same type the peak with RT = 12.05 and attribute structure 5 to this peak. A characteristic feature of this group of compounds is the form of the mass spectrum. As follows from the data in the table, the signal of the phenolate anion (M–H⁺) has the highest intensity in the spectra of this group of compounds.

We attributed the second set of peaks with the same empirical formula $C_{20}H_{26}O_2Sn$, but noticeably different peak intensities and spectra to a mixture of *o*,*p*- mono- and polysulfides of 2-*tert*-butylphenol [structures **6–9**, peaks with RT = 6.56, 7.82, 21.16, and 25.65]. A characteristic feature of this group of compounds is the shift of peaks in UV spectra to shorter wavelengths, compared with the UV spectra of the isomers from the first group. Under massdetection conditions, these compounds give fragment-ion signals of substantially higher intensity, compared with the signals of the isomers from the first group. Presumably, this points to a higher lability of the phenolate (M–H⁺) of *ortho*-di- and polysulfides of phenols, compared with the anions of their *para*-isomers.

To the third set of peaks (RT = 1.0, 12.27, 13.92, 14.31, 15.84, and 17.93) corresponds the empirical formula C₃₀H₃₈O₃Sn. The form of the UV and mass spectra corresponding to these peaks is in better agreement with structures **11–16**.

Judging from the anion mass and isotropic distribution, to the peak with RT = 5.41 (fourth type) can correspond the only empirical formula $C_{20}H_{25}O_2SCI$. The specific features of the spectra corresponding to this peak attribute to it structure **10**.

CONCLUSIONS

(1) The mixture of compounds produced by interaction of *ortho-tert*-butylphenol with monochloride sulfur contains four groups of products; two of these are *p*,*p*and *o*,*p*-mono- and polysulfides of *ortho-tert*-butylphenol, the third group is constituted by compounds containing three *ortho-tert*-butylphenol fragments connected by two mono- or polysulfide bridges, and the fourth, by chlorinecontaining products.

(2) Use of dimethylformamide as a solvent in this reaction leads to an increase in the fraction of polysulfides of phenols in Tioalkofen-B.

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