Synthesis of 4-(ω-Hydroxyalkyl)-2,6-di-*tert*-butylphenols and the Properties of Related Sulfides

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Abstract—Reaction of 2,6-di-*tert*-butylphenol with aliphatic linear and branched diols in an alkaline medium at a temperature of 180–220°C leads to the formation of $4-(\omega-hydroxyalkyl)-2,6-di-$ *tert*-butylphenols. The increase in the product yield and reducing the reaction temperature was reached at the catalysis of this reaction with zinc oxide. The structure of the diphenylalkane derivatives generated in side reaction was proved and the structural influence of the length of the aliphatic residue on the antioxidant effectiveness of the sulfides derived from the corresponding hydroxyalkylphenols was examined.

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A variety of spatially hindered phenols containing in the aliphatic chain of the the *para*-substituent the different functional groups can be obtained starting with 4-(ω -hydroxyalkyl)-2,6-di-*tert*-butylphenol **I**. Such compounds are required for systematic studies to reveal effective antioxidants and biologically active substances. Numerous phenol derivatives of the benzyl type have been obtained previously on the basis of industrially available 4-hydroxymethyl-2,6-di-*tert*butylphenol [1]. But to create a whole arsenal of phenols **I** efficient one-step common methods for their synthesis are required, desirably starting with the available 2,6-di-*tert*-butylphenol **II**.

Previously we have shown for the first time [2] that compound **II** reacts on heating with diols in the presence of strong bases affording compounds **I**, and in the side reaction $1,\omega$ -bis-(2,5-di-*tert*-butyl-4hydroxyphenyl)alkanes **III** are formed. The increase in the yield of compounds **I** and the decrease in the reaction temperature were achieved by adding zinc oxide to the reaction mixture. This approach is an exclusive general method for producing phenol-containing functional groups in the aliphatic chain of a *para*-substituent at any distance from the aromatic ring.

It was concluded in a later patent [3] that the key stage of alkaline alkylation of compound **II** with linear dihydric alcohols proceeding at a temperature of 235°C was the oxidative activation of the alkylating agent. This essentially radical process was initiated with an oxidant. For this purpose as the initiator *tert*-butylhydroperoxide was used, which was fed into the reactor by portions in the course of the reaction. The yield of compound **Ib** was 35%, and of compounds **Ic** and **Id**, 60%. As a by-product at the manufacturing of compound **Id** a derivative of 1,6-diphenylhexane **IIId** was identified which was characterized by melting



n = 2 (**a**), 3 (**b**), 4 (**c**), 6 (**d**), 7 (**e**), 10 (**f**).

point (mp 147–149°C; according to our data, mp 152.5–153°C, see below).

We have previously shown that the reaction of compound I with ethylene glycol occurs at a temperature above 200°C and is complicated by its typical fragmentation under the influence of bases leading to the formation of aldehydes. The latter were "trapped" by compound II to form byproducts. Yield of 4-(2-hydroxyethyl)-2,6-di-*tert*-butylphenol Ia did not exceed 25%. When ethylene glycol was replaced by di- or triethyleneglycol, then the predominant formation of 4-ethyl-2,6-di-*tert*-butylphenol [4] was observed.

In the present work we found that the reaction of

propane-1,3-diol with compound II at a temperature of 180°C in the presence of ZnO results in the formation of γ -propanol Ib. Along with this compound, methylenebisphenol IIIa and a derivative of 1,1-diphenylpropane IV were isolated, but the derivative of 1,3-diphenylpropane IIIb, whose formation could be expected according to the general scheme, was not detected in a significant amount. An authentic sample of compound IV we obtained by the reaction of compound II with allylamine in the presence of alkali [5]. In our case, compound IV is formed presumably by condensation of compounds II with propionic aldehyde, the product of dehydration of propane-1,3-diol followed by the rearrangement of the intermediately forming cyclic ether.



The reaction of 1,4-butanediol with compound II in the presence of ZnO at a temperature of 190°C resulted in the formation of 4-(4-hydroxybutyl)-2,6-di-*tert*butylphenol Ic in 76% yield and a derivative of 1,4diphenylbutane IIIc in 8% yield. This process, which takes place at the atmospheric pressure, at 50-fold scaling was successfully reproduced in a steel equipment of the pilot plant facility of the Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences. At carrying out this reaction under the same conditions but without zinc oxide the yield the compound **Ic** decreased to 25%.

The reaction of compound **II** with 1,3-butanediol in the presence of ZnO at a temperature of 200°C over 5 h led to the formation of 4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)butan-2-ol **V**, that indicates a preference for the reaction of compound **II** at the primary hydroxy group of the initial dihydric alcohol.



Compound II reacts with 2-methylpentane-2,5-diol in alkaline medium under the above conditions with the formation of a mixture of three isomeric difficultly separable 4-(ω -hydroxypentyl)-2,6-di-*tert*-butylphenols. This reaction, which has a relation to the mechanism of alkaline alkylation of phenols, will be discussed in detail in the subsequent publication.

The reaction of 2,6-di-*tert*-butylphenol with neopentylglycol in alkaline medium led to hydroxyalkylphenol **VI** in a moderate yield (15%). Along with **VI** a large quantity of methylenebisphenol **IIIa** was detected. The formation of **IIIa** indicates the ability of neopentylglycol to be split in alkaline medium with the formation of formaldehyde and isobutanol; the latter was isolated from the reaction products by distillation. The formaldehyde reacts with 2,6-di-*tert*-butylphenol to form compound **IIIa**.

A series of 4-(ω -hydroxyalkyl)-2,6-di-*tert*-butyphenols **Id–If** was obtained along the general procedure in about 50% yield; in addition the derivatives of 1, ω -diphenylalkane **IIId–IIIf** were isolated in up to 5% yield. In particular, condensation of 1,10-decanediol with 2,6-di-*tert*-butylphenol resulted in 4-(10-hyd-roxydecyl)-2,6-*tert*-butylphenol **If** in 40% yield and in compound **IIIf** in 5% yield.

Finally, we obtained from the compound II a systematic series of 4-(ω -hydroxyalkyl)-2,6-di-*tert*-butylphenols I. Further studies on the synthesis of derivatives obtained from these compounds led to the creation of non-toxic and highly effective antioxidants and the modifiers of performance properties of a wide range of polymeric materials (a review of patents, see [6]). This provided a basis for the long term prohibition of the publication [2]. Among the most accessible and interesting by the properties were sulfur-containing derivatives VII, whose properties, as we disclose below, are dependent on the length of the aliphatic fragment of the *para*-substituent in the starting compound I.

The most technologically promising among the known methods for producing sulfides **VII** was implemented on an experimental facility of the Institute of Organic Chemistry NIOCh SB RAS: a onepot reaction in the presence of DMF consisting in the consecutive action of PCl₃ on a compound **I**, and then of anhydrous Na₂S, leading to pure sulfides in 80–85% yield [7].



The results of the study of the effectiveness of sulfides **VII** as the antioxidants for polymers were obtained in Plastpolymer enterprise (St. Petersburg) [8]. They showed a high efficiency of these sulfurcontaining compounds. Therewith a remarkable

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regularity was revealed: the higher the temperature of the polymer processing, the more significant is the effectiveness of sulfides containing in their structure a longer aliphatic chain. Thus, for the stabilization of polypropylene in the process of its processing at a temperature of 240°C the most effective are compounds **VII**, n = 3,4 [9], and for the ABS (acrylonitrile– butadiene–styrene) plastics (the processing temperature 200°C) was more effective compound **VII**, n = 3) [10].

For the thermal stabilization of polyethylene at a temperature 160°C the first place by performance occupies compound **VII** with a short chain (n = 2). Even greater performance showed compound **VII**, n = 3, containing in the α -position of the aliphatic chain an additional methyl group [9]. In practice, the choice of antioxidants is limited to the sulfides with the aliphatic chain –(CH₂)_n with the distance between the aromatic ring and the sulfur atom not exceeding n = 4, but not only the antioxidant effectiveness should be taken into account, but also an important ability of the phenols di- and polysulfides to the thermal cleavage with the formation of large blocks [6].

In fats, the antioxidant activities of sulfides **VII** and their structurally relative disulfides are close, but for the latter was noted a higher reactivity in the reactions with peroxides [11]. These compounds significantly increase the antioxidant properties of the products used in medical practice (vitamin E, mexidol, and others) that determines the prospects of their use in medicine [12].

EXPERIMENTAL

Elemental composition and molecular weight of compounds were obtained at the analysis of their high resolution mass spectra taken on a Finnigan MAT 8200 mass-spectrometer at a temperature of 200°C. The ¹H NMR spectra were taken on a Varian A-56/60 instrument at operating frequency 60 MHz from 10% solutions in CDCl₃. Complete IR, UV, and ¹H NMR spectra of the synthesized compounds are listed in the atlas of spectra [14]. Their melting temperatures were determined on a Köffler heating block. The GLC analysis of reaction mixtures was performed on a gas chromatograph "Tsvet."

Reaction of 2,6-di-*tert***-butylphenol with propane-1,3-diol.** A mixture of 13.8 (0.067 mol) of 2,6-di-*tert*butylphenol, 7.5 g of NaOH, and 1.5 g of ZnO in 21 ml of propanediol-1,3 (molar ratio 1:2.8:0.26:3.8) was placed in a steel rotating autoclave of capacity 0.1 l and maintained at 180°C for 15 h. After cooling, the reaction mixture was neutralized with hydrochloric acid, extracted with ether, the organic layer was evaporated and the residue, 18.7 g, was distilled in a vacuum. 7.9 g of a fraction with the bp in the range $160-170^{\circ}$ C at 1 mm Hg was isolated, which was crystallized from *n*-heptane and gave 5.3 g (yield 30%) of compound **Ib**, mp 66.5–67.5°C. At standing in air of toluene solution of this compound the solvent slowly evaporated with the formation of transparent cubic crystals with mp 69–70°C. According to [3], mp of compound **Ib** 66.5–67.5°C.

The bottom residue, 5.0 g, was separated by column chromatography on silica gel. Eluents: a mixture of petroleum ether with benzene, benzene, a mixture of benzene with ethyl acetate. Isolated: 2.0 g of 4,4'-methylene-bis-(2,6-di-*tert*-butylphenol) **IIIa**, mp 151–153°C (by the data of [15] mp 154°C) and 0.9 g of 1,1-bis-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propane **IV**, mp 156–157°C, whose structure is established by comparison with known sample obtained by the reaction of 2,6-di-*tert*-butylenol with allylamine [5].

Reaction of 2,6-di-tert-butylphenol with 3-methylbutane-1,3-diol. A mixture of 6.6 g of 2,6-di-tert-butylphenol, 3.5 g of NaOH, and 18 g of 3-methylbutane-1,3-diol (molar ratio 1:2.7:5.3) was maintained at rotation in a steel autoclave of 0.1 l capacity for 5 h at a temperature of 200°C. The product was cooled, acidified, and extracted with ether. The extract was washed with water and evaporated to obtain 14.7 g of oil which was separated on a column with silica gel, eluent benzene-ethyl acetate 5:1 mixture. The fraction of 5.3 g of 4-hydroxyalkyl-2,6-di-tert-butylphenol was distilled in a vacuum and 4.0 g of oil with bp 160-162°C at 2–3 mm Hg was isolated. Found, m/z: 292.446. $C_{19}H_{32}O_2$ (by mass spectrometry). Calculated: M 292.240. According to ¹H NMR spectrum, it is a mixture of three isomeric 4-hydroxypentyl-2,6-di-tertbutylphenols with close content of each.

Reaction of 2,6-di-*tert***-butylphenol with butane-1,4-diol**. In a flask was placed 12 g of 2,6-di-*tert*butylphenol, 2.96 g of NaOH, 27 g of freshly distilled butane-1,4-diol, and 0.2 g of ZnO (molar ratio 1:1.3:5.5:0.03). The reaction mixture was stirred for 5 h at 190°C under an inert atmosphere with simultaneous distilling off of the formed water. After cooling, the product was neutralized with 10% hydrochloric acid and extracted with petroleum ether. Water solution was evaporated, NaCl precipitate was filtered off and butane-1,4-diol excess was separated by distillation. Organic extract was evaporated, and 16.4 g of oil was separated. According to GLC it contains 73% of 4-(4-hydroxybutyl)-2,6-di-tert-butylphenol Ib, 9% of di-tert-butylphenol, 8% of 1,4-bis-(3,5-di-tertbutyl-4-oxyphenyl)butane IIIc, and 6% of other products. The mixture was distilled in a vacuum. First fraction, 2,6-di-tert-butylphenol, 2.5 g, bp 75-100°C at 1-2 mm Hg. Second fraction, 10 g, bp 165-175°C at 1-2 mm Hg, according to the GLC consisted of 4-(4hydroxybutyl)-2,6-di-tert-butylphenol Ic. On keeping, the product solidified, mp 27-28°C (from *n*-heptane). Found, %: C 77.72; H 10.80; M 280 (by isothermal distillation). C₁₈H₃₀O₂. Calculated, %: C 77.69; H 10.78; M 278.42. ¹H NMR spectrum (100 MHz), δ , ppm (CCl₄): 1.40 s (18H, C₄H₉-tert), 1.55 m (4H, CH_2CH_2), 2.48 t (J = 7 Hz, 2H, Ar CH_2), 3.53 t (J = 8 Hz, CH₂OH), 3.80-4.40 br (2H, OH), 6.85 s (2H, ArH). Third fraction, 2.5 g, bp 175–220°C (1 mm Hg). It was applied to a column containing 50 ml of silica gel and eluted with a mixture of benzene-petpoleum ether 1:3. After evaporation of solvent was obtained 1.0 g (8%) of 1,4-bis(3,5-di-*tert*-butyl-4-oxyphenyl)butane **IIIc**, mp 126–128°C (according to [14], mp 126–128°C). Found: m/z 466.380 (mass spectrometry). C₃₂H₅₀O₂. Calculated: M 446.742. ¹H NMR spectrum (100 MHz), δ, ppm (CCl₄): 1.40 s (36H, C₄H₉-tert), 1.55 m (4H, CH₂CH₂), 2.47 t (J = 7 Hz, 4H, ArCH₂), 6.80 s (4H, ArH).

4-(3,5-Di-tert-butyl-4-hydroxyphenyl)butan-2-ol (V). In a flask was placed 12.3 g of crude 2,6-di-tertbutylphenol, 6 g of NaOH, and 27 g of butane-1,3-diol (molar ratio 1:2.7:5.3), and at a temperature of 150°C (bath temperature) under a flow of an inert gas from the reactor water was distilled off and then the reaction mixture was kept at 200°C for 5 h. After cooling, the product was diluted with water, neutralized with 10% hydrochloric acid, and extracted with ether. The solvent was evaporated and residual oil (19.3 g) was distilled in a vacuum collecting the fraction with boiling point 170°C at 2 mm Hg. 9.5 g (61%) of 4-(3,5-di-tert-butyl-4-oxyphenyl)butan-2-ol with mp 66–68°C (from hexane) was isolated. Found (mass spectrometry): m/z278.2250. C₁₈H₃₀O₂. Calculated: M 278.2246. ¹H NMR spectrum (100 MHz), δ , ppm (CCl₄): 1.17 d (J =9 Hz, CH₃CH), 1.43 s [8H, C(CH₃)₃], 1.70 m (CH₂CH), 2.58 t (J = 7 Hz, ArCH₂), 4.84 s (OH), 6.88 s (2H, ArH).

3-(3,5-Di-*tert*-butyl-4-hydroxyphenyl)-2,2-dimethylpropan-1-ol (VI). 2,6-Di-*tert*-butylphenol, 75 g, NaOH, 19 g, and neopentyl glycol, 200 g, (molar ratio 1:1.3:5.3) was placed in a steel rotating 0.5 l autoclave and maintained for 5 h at 220°C. The reaction mixture was then cooled, neutralized with 10% hydrochloric acid, and extracted with petroleum ether. 95 g of oil was obtained that contained by the GLC data 40% of 3-(3,5-di-tert-butyl-4-oxyphenyl)-2,2-dimethylpropan-1-ol, 35% of bis-(3,5-di-*tert*-butyl-4-hydroxyphenyl) methane IIIa and 4.5% of the initial 2,6-di-tertbutylphenol, as well as some other com-ponents. Compound IIIa precipitated, 19.9 g, mp 152.5-153°C (according to [15] mp 154°C). The filtrate after separation of compound **IIIa** was distilled in a vacuum. First fraction, 14.8 g of isobutanol, bp 60-95°C at 760 mm Hg. Second fraction, 11.2 g of neopentyl glycol, bp 112–113°C at 2–3 mm Hg, mp 127°C. Third fraction, 16.2 g (yield 15%), bp 160-173°C at 2-3 mm Hg, oil, solidified on keeping. After crystallization from *n*-heptane was isolated 13.2 g of 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,2-dimethylpropan-1-ol VI, mp 68-69°C. Found, %: C 79.07; H 10.67. M 292.5 (isothermal distillation). $C_{19}H_{22}O_2$. Calculated, %: C 79.02; H 11.02. M 292.44. ¹H NMR spectrum (100 MHz), δ, ppm (CCl₄): 0.85 s 6H, CH₃), 1.43 s [8H, C(CH₃)₃] 2.44 s (ArCH₂), 3.23 s (OH), 3.50 s (CH₂OH), 4.92 s (OH), 6.87 s (2H, ArH).

General procedure for joint synthesis of 4-(ωhvdroxvalkvl)-2,6-di-tert-butvlphenol (Id-If) and 1.ω-bis-(3.5-di-tert-butyl-4-hydroxyphenyl)alkanes (IIId-IIIf). In a glass reactor were placed 2,6-di-tertbutylphenol, granulated NaOH, and 1,@-alkandiol at the reagent ratio 1:1.3:4 (mol), and the mixture was stirred for 5 h in a flow of inert gas with heating at 220°C, with distilling off the reaction water. On cooling, the product was neutralized with hydrochloric acid and extracted with petroleum ether. The solvent was evaporated, and the residue containing up to 60% of alcohol I and 5% of a bis-alkane IIId-IIIf was applied to a column with silica gel and eluted successively with a mixture of petroleum ether-benzene 3:1, benzene and ethyl acetate. The evaporation of the first fraction gave 1, w-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)alkane IIId-IIIf (vield about 5%). The evaporation of the third fraction resulted in 4-(whydroxyalkyl)-2,6-di-tert-butylphenol I, which was purified by distillation in a vacuum, yield 45–60%.

4-(6-Hydroxyhexyl)-2,6-di-*tert*-butylphenol (Id), oil, bp 174–181°C at 2–3 mm Hg. Yield 46,5%. Found, %: C 78.68, H 11.27. *M* 306 (by isothermal distillation). $C_{20}H_{34}O_2$. Calculated, %: C 78.74, H 11.33. *M* 308.5. ¹H NMR spectrum (100 MHz), δ , ppm (CCl₄): 1.40 s (18H, C₄H₉-*tert*), 1.3–1.8 m [8H, (CH₂)₄], 2.45 t (*J* = 7 Hz, ArCH₂), 2.68 s (1H, OH), 3.5 t (*J* = 8 Hz, 2H, CH₂OH), 4.89 s (1H, ArOH), 6.89 s (2H, ArH).

1,6-Bis-(3,5-di-*tert***-butyl-4-hydroxyphenyl)hextane** (**IIId**), mp 152.5–153°C (from *n*-heptane), yield 7%. Found, %: C 81.93, H 10.84. *M* 492 (by isothermal distillation). Calculated, %: C 82.53, H 11.00. *M* 494.77. ¹H NMR spectrum (100 MHz), δ , ppm (CCl₄): 1.42 s (36 H, C₄H₉-*tert*), 1.1–1.9 m [8H, (CH₂)₄], 2.47 t (*J* = 7 Hz, 4H, ArCH₂), 4.80 s (2H,OH), 6.85 s (4H, Ar–H).

4-(7-Hydroxyheptyl)-2,6-di*tert*-butylphenol (If), mp 39–40°C (from *n*-heptane). Yield 40%. Found, %: C 78.83 H 11.38. *M* 320 (by isothermal distillation). C₂₁H₃₆O₂. Calculated: C 78.70 H 11.26. *M* 320.5. ¹H NMR spectrum (100 MHz), δ , ppm (CCl₄): 1.4 s (18H, C₄H₉-*tert*), 2.45 t (*J* = 7 Hz, ArCH₂), 4.89 s (ArOH), 6.85 s (2H, ArH), 1.2–1.8 m [10H, (CH₂)₅], 3.50 t (*J* = 8 Hz, CH₂OH), 2.7 s(OH).

1,6-Bis-(3,5-di-*tert***-butyl-4-hydroxyphenyl)heptane** (IIIe), mp 97–98°C (from *n*-heptane), yield 5%. Found: *m/z* 508.426 (mass spectrometry). $C_{35}H_{56}O_2$. Calculated: *M* 508.798. ¹H NMR spectrum (100 MHz), δ , ppm (CCl₄): 1.40 s (36H, C₄H₉-*tert*), 1.1–1.9 m (10H, (CH₂)₅), 2.40 t (*J* = 7 Hz, 4H, ArCH₂), 4.80 s (2H, OH), 6.80 s (4H, Ar–H).

4-(10-Hydroxydecyl)-2,6-di*tert***-butylphenol (If)**. Oil, bp176–180°C at 2–3mm Hg. Yield 39.3%. Found, %: C 79.76. H 11.88. *M* 362 (by isothermal distillation). C₂₄H₄₂O₂. Calculated, %: C 79.49, H 11.67. *M* 362.57. ¹H NMR spectrum (100 MHz), δ , ppm (CCl₄): 1.2–1.8 m (CH₂)₈, 1,4 s (18H, C₄H₉-*tert*), 2.45 t (*J* = 7 Hz, ArCH₂), 2.67 s (OH), 3.50 t (*J* = 8 Hz, 2H,CH₂OH), 4.9 s (1H, ArOH), 6.85 s (2H, ArH).

1,10-Bis-(3,5-di-*tert***-butyl-4-hydroxyphenyl)decane** (**IIIf**), mp 93–95°C (from *n*-heptane). Yield 5%. Found: m/z 550.47510 (mass spectrometry). C₃₈H6₂O₂. Calculated: *M* 550.47498. ¹H NMR spectrum (100 MHz), δ , ppm (CCl₄): 1.1–1.9 m [10H, (CH₂)₅], 1.43 s (36H, C₄H₉-*tert*), 2.47 t (*J* = 7 Hz, 4H, ArCH₂), 4.82 s (2H, OH), 6.85 s (4H, ArH).

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