ISSN 1070-3632, Russian Journal of General Chemistry, 2017, Vol. 87, No. 1, pp. 22–28. © Pleiades Publishing, Ltd., 2017.
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Reactions of Benzazole-2-thiones with 3,5-Di-*tert*-butyl-4-hydroxybenzyl Acetate

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Received May 26, 2016

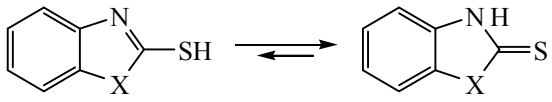
Abstract—The benzylation of benzothiazole(oxazole, imidazole)-2-thiones with 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate involves either the sulfur or nitrogen atom depending on the reaction conditions. The *S*- and *N*-benzylation products of benzazole-2-thiones are kinetically and thermodynamically controlled products, respectively. The use of 3,5-di-*tert*-butyl-4-hydroxy-benzyl acetate allows sterically hindered hydroxybenzyl derivatives of benzazole-2-thiones to be generally synthesized under milder conditions than in known methods of their synthesis.

Keywords: sterically hindered phenols, benzothiazole-2-thione, oxazole-2-thione, imidazole-2-thione, benzylation

DOI: 10.1134/S1070363217010054

Benzazole-2-thione derivatives are widely used as polymer additives (stabilizers, rubber accelerators, corrosion inhibitors) [1–4]. Furthermore, they are biologically active compounds which exhibit anti-inflammatory, analgesic, antibacterial, and fungicide properties [5–9]. This fact generates interest in the synthesis and properties on sterically hindered phenol derivatives of benzazole-2-thiones [10].

Benzothiazole(oxazole and imidazole)-2-thiones undergo thione–thiol tautomerization, which allows preparation of both the N- and S-derivatives of these compounds [11]. According to published data, benzothiazole-2-thione [12] and 1,3-dihydrobenzimidazole-2-thione [9] exist in the thione form in both solution and melt. The same is true of benzoxazole-2-thione, whose ^{13}C NMR spectrum contain a signal of the C=S group (181 ppm) and does not contain a signal of the =C–S group (167 ppm [12]).



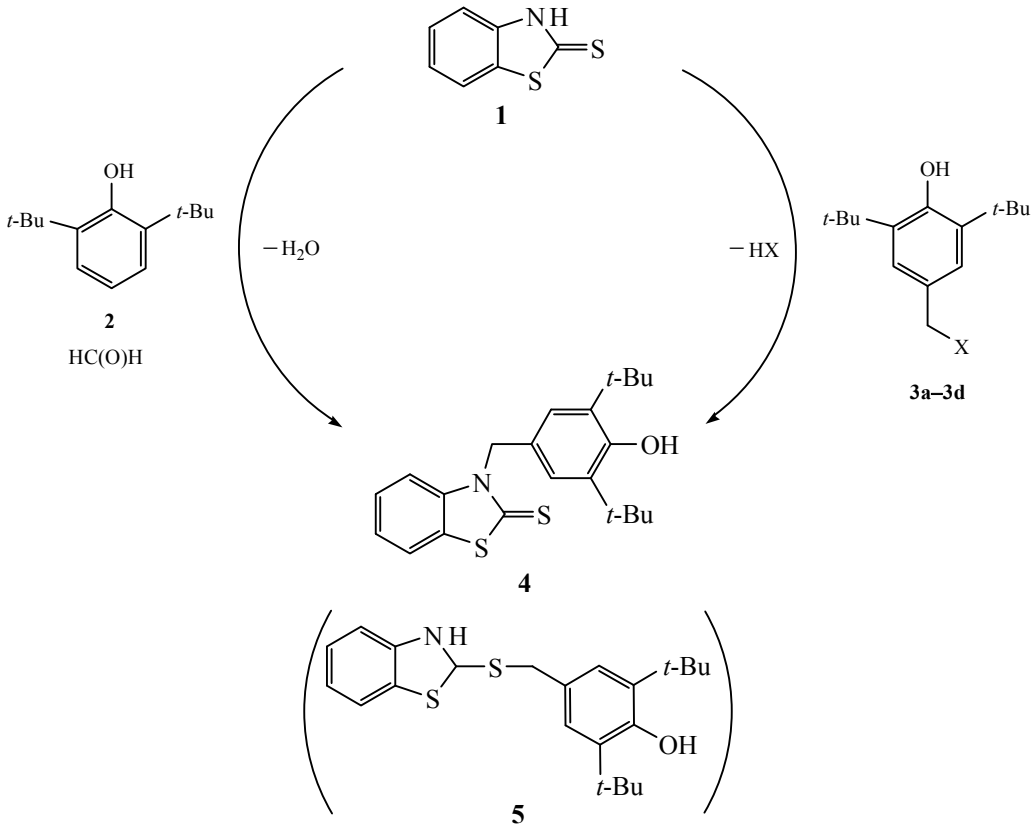
X = O, S, NH.

At the same time, it should be noted that these compounds are frequently named mercaptobenzothiazoles, mercaptobenzoxazoles, and mercaptobenzimidazoles [4, 13]. The same confusion takes place with some of their derivatives. Thus, in the patents [1, 2], the pilot commercial antioxidant stabilizer Agidol-70 was assigned the name *S*-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2-mercaptobenzothiazole. At the same time, in the patent [14], the same stabilizer is named *N*-(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzothiazole-2-thione.

There are two known synthetic approaches to sterically hindered hydroxybenzyl derivatives of benzothiazole-2-thione: the Mannich reaction of compound **1**, formaldehyde, and 2,6-di-*tert*-butylphenol **2** and the reaction of compound **1** with benzylating agents **3a–3d**.

The synthesis of compound **4** by the Mannich reaction in an isopropanol or a DMF solution in the presence of a base (dibutylamine) was reported in [12, 15]. An analogous reaction of benzothiazole-2-thione with 2-*tert*-butyl-4-methylphenol in the presence of an acid catalyst (conc. HCl) gives rise to an *S*-benzyl derivative [16]. The same effect of the acid–base catalysis on the reaction route is observed in reactions of benzothiazole-2-thione **1** with benzylating agents. The reaction of compound **1** with benzyl alcohol **3a** in the presence of H_2SO_4 forms an *S*-benzyl derivative **5** [17]. At the same time, benzyl bromide **3b** and quaternary ammonium salt **3d** reacts with benzo-thiazole-2-

Scheme 1.

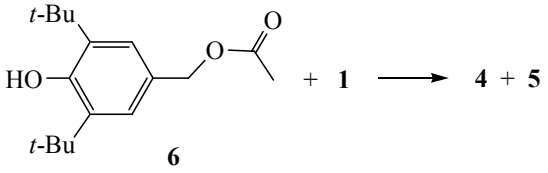


thione **1** in the presence of trimethylamine react to form an *N*-benzyl derivative **4** [18]. Controversial data are available for the reaction of benzothiazole-2-thione with 3,5-di-*tert*-butyl-4-hydroxybenzylamine **3c**. According to [12, 15, 19], this reaction in DMF and absolute ethanol yields compound **4**. At the same time, according to the patent [20], this reaction in toluene provides compound **5** (Scheme 1).

It should be noted that the synthesis of compound **5** is complicated by the isomerization of the latter to thione **4**. The isomerization occurs under heating in a solvent or without it and is accelerated in polar solvents or in the presence of base catalysts [15].

In the present work we have studied the reaction of 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate **6** with benzothiazole-2-thione **1**. As known, acid, base, and dipolar aprotic solvent activate benzyl acetate **6** in reactions with weak nucleophiles [21].

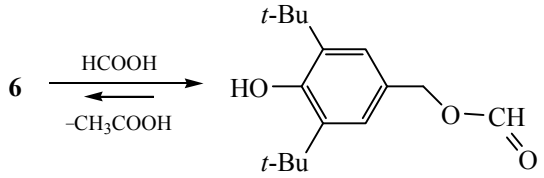
The reaction of benzyl acetate **6** with benzothiazole-2-thione was performed for 2–3 h in DMF or a mixture of acetone with formic acid (1 : 1) at 40–50°C, or in a mixture of isopropanol and acetone (3 : 2) in the presence of KOH at ambient temperature. With DMF and acetone–formic acid solvents, equimolar reagent amounts were used. In the presence of KOH, a double excess of benzothiazole-2-thione was used to prevent side reactions of benzyl acetate **6** in the alkaline medium [22]. The reaction progress was monitored by TLC. It was found that the reaction of benzyl acetate **6** with benzothiazole-2-thione always gave two isomers, specifically, the *N*- and *S*-benzylation products.



When formic acid was used, the product mixture always contained benzyl formate **7** formed from unreacted benzyl acetate **6** [23].

Compositions of the benzylation products of benzothiazole-2-thione

Reaction conditions	Fraction of the reaction product, %			
	4	**5**	**6**	7
DMF	72.5	23.5	4	–
Acetone–formic acid	42.0	49.0	–	9
In the presence of KOH	76.0	24.0	–	–



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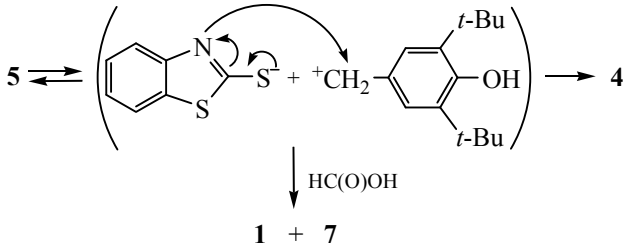
The product ratio was measured by ^{1}H NMR spectroscopy as the intensity ratio of the proton signals of the CH_2N (5.21 ppm), CH_2S (4.60 ppm), and CH_2O (5.14 ppm) groups. The compositions of the reaction mixtures are listed in the table.

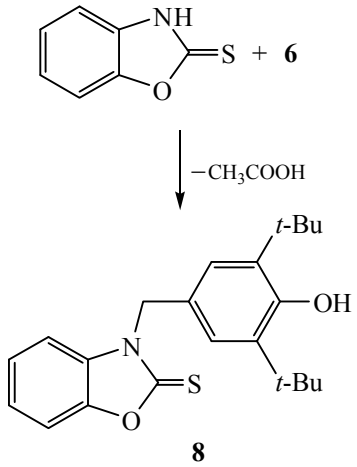
The reaction of benzothiazole-2-thione **1** with benzyl acetate **6** in DMF for 7 h at 50°C forms, according the ^{1}H NMR data, *N*-benzyl derivative **4**. The reaction in acetone–formic acid (1 : 1) at ambient temperature for 1 day gave 53% of compound **5**. According to the ^{1}H NMR data, the filtrate contained 59% of compound **5**, 20% of compound **4**, 11% of benzyl acetate **6**, and 10% of benzyl formate **7**. When heated in DMF at 50°C for 5 h, *S*-benzyl derivative **5** completely isomerizes to *N*-(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzothiazole-2-thione **4**. The isomerization of compound **5** in an acetone–formic acid medium, other conditions are the same, gives a mixture of compounds **4**, **5**, and **7** (71.5 : 20 : 8.5, respectively). The appearance of compound **7** among the isomerization products is indicative of the elimination of the 3,5-di-*tert*-butyl-4-hydroxybenzyl fragment in the course of isomerization of *S*-benzyl derivative **5** to *N*-benzyl derivative **4**.



The resulting data allow us to consider compounds **5** and **4** a kinetically and a thermodynamically controlled products, respectively. These products easier interconvert in a basic compared to an acid medium.

Thus, the reaction of 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate with 2-mercaptobenzothiazole can provide either *N*- or *S*-benzylation products, depending on conditions.

According to published data, the alkylation and acylation of benzoxazole-2-thione, too, can take the way of N- and S-substitution [4]. We found that benzoxazole-2-thione reacts with benzyl acetate **6** in DMF or a mixture of acetone with formic acid under heating, or in a mixture of acetone with formic acid in the presence of KOH at ambient temperature gives rise to *N*-benzyl derivative **8**.



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The structure of compound **8** was established by X-ray diffraction analysis. The molecules of compound **8** in crystal represent two nearly planar fragment linked together by a methylene bridge (Fig. 1), as a result of which the angle between these fragment is determined of the conformation of sp^3 carbon and equals 112.98(3)°. The bond lengths and the bond and torsion angles span ranges typical of each bond type [24]. The crystal packing of compound **8** (Fig. 2) is primarily determined by O^{14}–$H^{14}\cdots S^2$ hydrogen bonds [the O···S distance is 3.616(7) Å and the OHS angle is 141.4(6)°] which bind the molecules into infinite chains. In their turn, the latter form a 3D network due to C–H···π interactions (the H···Cg distances are 2.85–2.96 Å and the C–H···Cg angles are 121°–126°, where Cg is the centroid of the aromatic ring).

The conversion of benzyl acetate **6** after a 24 h reaction in DMF at ambient temperature was 26%.

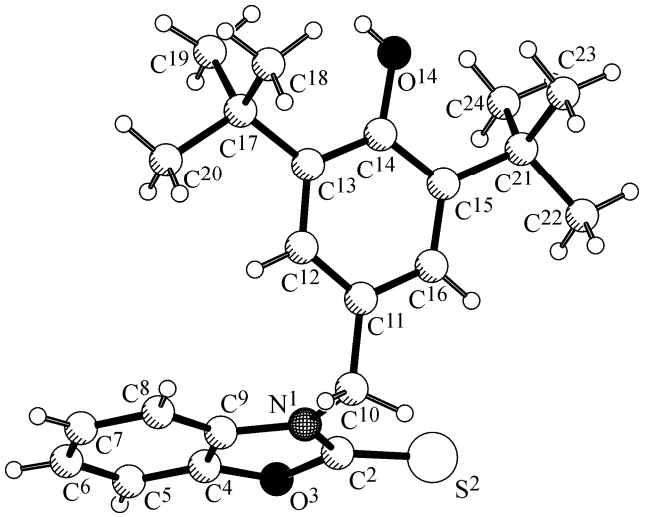


Fig. 1. Molecular structure of compound **8** in crystal.

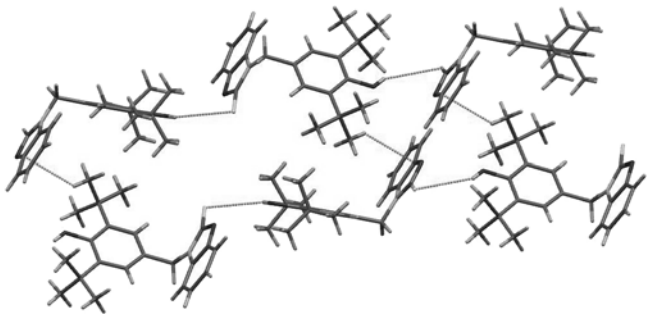
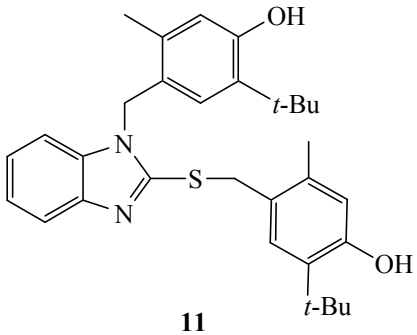


Fig. 2. Packing of and noncovalent interactions in the crystal of compound **8** (projection on the *a*0*c* plane).

Along with the starting reagents, the reaction mixture contained 21% of *S*-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2-mercaptobenzoxazole **9** (4.56 ppm, CH_2S) and 5% of *N*-(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzoxazole-2-thione **8** (5.34 ppm, CH_2N). Thus, the isomerization of the *S*-benzyl to *N*-benzyl derivative in benzoxazole-2-thione occurs faster than in benzothiazole-2-thione.

Bespalov et al. [9] found that 1,3-dihydrobenzimidazole-2-thione is alkylated by the sulfur atom and aminomethylated by the nitrogen atoms to give mono- and bisaminomethylation products. It should be noted alkylation with alkyl halides was performed in the presence of alkali. Amery et al. [25] described in their patent the synthesis of 2-thioimidazoles and imidazoline-2-thiones containing one and more sterically hindered *para*-hydroxyphenyl groups, which found application as antioxidants in mineral and vegetable oils, fats, rubber resins and vulcanized rubber, and polyurethanes and polyolefins. Thus, di-*N*-benzyl derivative **10** was prepared by hours-long heating at 120–130°C of benzimidazole-2-thione with either Mannich base **3d** or phenol **2** and paraform in the presence of dimethylamine. It should be noted that, according to the same patent, the reaction of 2-*tert*-butyl-4-(dimethylamino)methyl-5-methylphenol with 1,3-dihydrobenzimidazole-2-thionein a 1 : 2 ratio gives rise to 2-[(5-*tert*-butyl-4-hydroxy-2-methylbenzyl)sulfanyl]-3-[(5-*tert*-butyl-4-hydroxy-2-methylbenzyl)]benzimidazole **11**.



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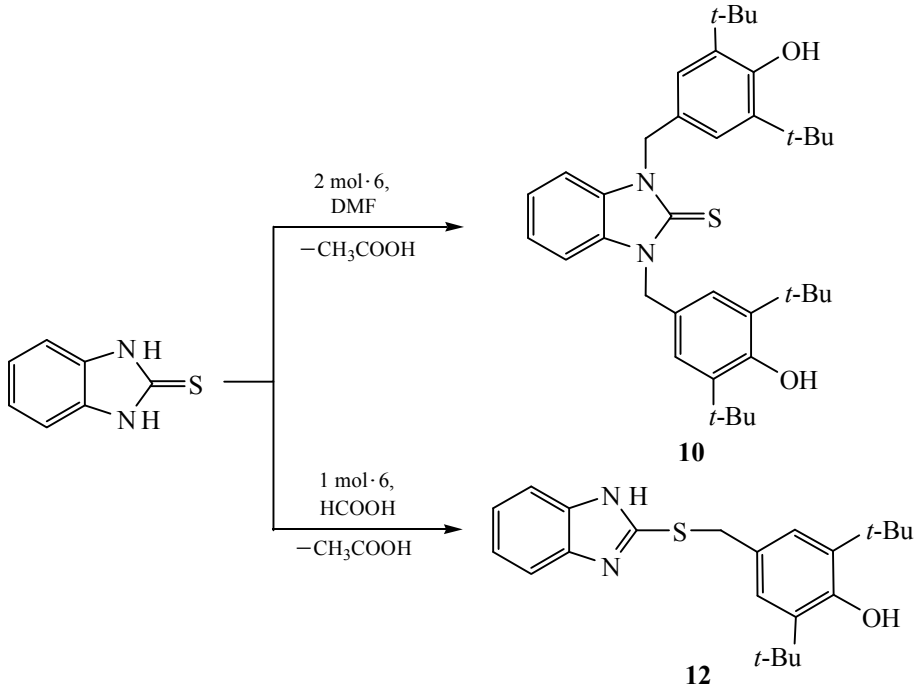
We found that the reaction of 1,3-dihydrobenzimidazole-2-thione with benzyl acetate **6** in DMF at a 1 : 2 reagent ratio yields di-*N*-benzyl derivative **10** both under heating and at ambient temperature. The same reaction in an acetone–formic acid medium provides *S*-benzyl derivative **11**.

Like *S*-benzyl derivative **5**, compound **12**, when heated in DMF for 50°C for 5 h, isomerizes to *N*-benzyl deruvatives. The ^{1}H NMR spectrum of the reaction products no longer contains the CH_2S proton signal (4.82 ppm); instead, CH_2N proton signals (5.51 and 5.45 ppm) from di-*N*-benzyl derivative **10** and, apparently, to the mono-*N*-benzyl derivative appear (Scheme 2).

Thus, in the present work we determined conditions for the synthesis of *S*- and *N*-benzylation products of benzothiazole(oxazole, imidazole)-2-thiones in the reactions of the corresponding benzazole-2-thiones with

Scheme 2.



3,5-di-*tert*-butyl-4-hydroxybenzyl acetate. The use of benzyl acetate **6** generally allows more facile synthesis of sterically hindered hydroxybenzyl derivatives of benzazole-2-thiones than known methods of their synthesis.

EXPERIMENTAL

The ^{1}H NMR spectra were measured on a Bruker AVANCE-600 instrument (600.13 MHz) relative to the residual proton signals of deuterated solvents. Elemental analysis was performed on a EuroEA-3000 analyzer (EuroVector, Italy).

The unit cell parameters of compound **8** and the intensities of 15492 reflections were measured on a Smart Apex II CCD diffractometer (296 K, MoK_α radiation, graphite monochromator, φ- and ω-scanning, θ_{max} 26.00°). Crystal of compound **8** ($C_{22}H_{27}NO_2S$, *M* 369.51), monoclinic, space group *P*21/*n*, *a* 9.929(8), *b* 9.985(8), *c* 20.904(17) Å, β 101.696(11)°, *V* 2029(3) Å^3, *Z* 4, *F*(000) 792, d_{calc} 1.209 g/cm^3, μ 0.175 mm^{-1}. The structure was decoded and refined first isotropically and then anisotropically using SHELXL-97 [26]. The hydrogen atoms were located geometrically. Final *R* factors: R_1 0.0852 for 1606 unique reflections with $I > 2\sigma(I)$ and wR_2 0.2643 for 3992 unique reflections.

All calculations were performed using WinGX [27] and APEX2 [28]. Molecular visualization was accomplished with PLATON [29] and MERCURY [30]. The crystal data were deposited at the Cambridge Crystallographic Data Center (CCDC 1472194).

***N*-(3,5-Di-*tert*-butyl-4-hydroxybenzyl)benzothiazole-2-thione (4).** A solution of 1.39 g (0.005 mol) of benzyl acetate **6** and 0.835 g (0.005 mol) of benzothiazole-2-thione **1** in 12 mL of DMF was heated for 7 h at 50°C and then cooled down to ambient temperature and poured into aqueous NaCl. The precipitate that formed was filtered off, washed with water, and dried in air. Yield 1.87 g (97%), mp 155–157°C (ethanol) (mp 152–153°C [12]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.42 s (18H, CMe_3), 5.21 s (1H, OH), 5.62 s (2H, CH_2N), 7.25–7.32 m (4H, $H^{5,6}$, ArH), 7.33–7.40 m (1H, H^4), 7.46–7.52 m (1H, H^7). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.2 ($C\underline{Me}_3$), 34.3 ($\underline{C}Me_3$), 49.7 (CH_2N), 113.2, 121.2, 124.6, 124.7, 125.2, 126.8, 127.8, 136.3, 141.8, 153.7 (Ar), 189.9 (C=S).

2-[(3,5-Di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]-benzothiazole (5). A solution of 0.8 g (0.003 mol) of benzyl acetate **6** and 0.5 g (0.003 mol) of benzothiazole-2-thione **1** in a mixture of 6 mL of acetone and 6 mL of formic acid was allowed to stand at

ambient temperature for 1 day. The precipitate was filtered off, washed with water, and dried. Yield 0.59 g (53%), mp 143–144°C (ethanol) (mp 140.5–141.8°C [17]). The filtrate was poured into aqueous NaCl. The precipitate was filtered off and recrystallized from ethanol to obtain an additional 0.24 g of compound **5**. The total yield of compound **5** was 73%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.45 s (18H, CMe_3), 4.58 s (2H, CH_2S), 5.24 s (1H, OH), 7.29 s (2H, ArH), 7.43–7.52 m (2H, $H^{5,6}$), 7.78 d (1H, H^7, ^3J = 7.9 Hz), 7.96 d (1H, H^4, ^3J = 8.2 Hz).

Reaction of benzyl acetate 6 with benzothiazole-2-thione in the presence of of KOH. To solution of benzyl acetate **6**, 0.375 g (0.0014 mol) and benzothiazole-2-thione **1,** 0.5 g (0.003 mol) in 2.5 mL of acetone was added a solution of 0.15 g (0.003 mol) of KOH in 3.5 mL of isopropanol. The reaction mixture was stirred at ambient temperature for 3 h and then poured into aqueous NaCl. The precipitate that formed was filtered off, washed with water, and dried to obtain 0.42 g (80.8%) of a mixture of the reaction products. The list of the products is shown in the table.

***N*-(3,5-Di-*tert*-butyl-4-hydroxybenzyl)benzoxazole-2-thione (8).** *a*. A solution of 0.921 g (0.003 mol) of benzyl acetate **6** and 0.5 g (0.003 mol) of benzoxazole-2-thione in 10 mL of DMF was heated at 50°C for 3.5 h. The reaction mixture was cooled down to ambient temperature and poured into aqueous NaCl. The precipitate that formed was filtered off, washed with water, and dried in air. Yield 1.12 g (89.6%), mp 147–148°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.43 s (18H, CMe_3), 5.26 s (1H, OH), 5.34 s (2H, CH_2N), 7.10–7.15 m (1H, H^4), 7.21–7.29 m (2H, $H^{5,6}$), 7.33–7.37 m (1H, H^4), 7.36 s (2H, ArH). Found, %: C 71.69; H 7.21; N 3.92. $C_{22}H_{27}NO_2S$. Calculated, %: C 71.51; H 7.36; N 3.79.

b. In a similar way, from a mixture of 0.92 g (0.003 mol) of benzyl acetate **6** and 0.51 g (0.003 mol) of benzoxazole-2-thione, 6 mL of acetone, and 6 mL of formic acid under heating at 50°C for 4.5 h we obtained 1.01 g (81%) of compound **8**.

c. A mixture of 0.92 g (0.003 mol) of benzyl acetate **6**, 0.51 g (0.003 mol) of benzoxazole-2-thione, 6.5 mL of acetone, and 6.5 mL of formic acid was allowed to stand at ambient temperature for 1 day to obtain 0.97 g (78%) of compound **8**.

d. A mixture of 0.375 g (0.0013 mol) of benzyl acetate **6**, 0.4 g (0.0026 mol) of benzoxazole-2-thione, 2.5 mL of acetone, and a solution of 0.15 g (0.0026 mol) of KOH in 3.5 mL of isopropanol was allowed to stand at ambient temperature for 3.5 h to obtain 0.33 g (66%) of compound **8**.

1,3-Bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-1,3-dihydrobenzimidazole-2-thione (10). *a.* A mixture of 0.92 g (0.0033 mol) of benzyl acetate **6** and 0.25 g (0.0016 mol) of 1,3-dihydrobenzimidazole-2-thione in 7 mL of DMF was heated at 60°C for 2.5 h, cooled down to ambient temperature, and poured into aqueous NaCl. The precipitate that formed was filtered off, washed with water, and dried in air. Yield 0.93 g (95%), mp 244–245°C (ethanol) (mp 240°C [24]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 s (36H, CMe_3), 5.18 s (2H, OH), 5.51 s (4H, CH_2N), 7.14–7.19 m (2H, $H^{5,6}$), 7.20–7.25 m (2H, $H^{4,7}$), 7.39 s (4H, ArH).

b. A mixture of benzyl acetate **6** and 1,3-dihydrobenzimidazole-2-thione in DMF was allowed to stand at ambient temperature for 1 day to obtain 96% of compound **10**.

2-[(3,5-Di-*tert*-butyl-4-hydroxybenzyl)sulfanyl]-1*H*-benzimidazole (12). *a*. A mixture of 0.46 g (0.0016 mol) of benzyl acetate **6**, 0.25 g (0.0016 mol) of 1,3-dihydrobenzimidazole-2-thione, 3 mL of acetone, and 3 mL of formic acid was heated at 40°C for 6 h. The reaction mixture was cooled down to ambient temperature and poured into aqueous NaCl. The precipitate that formed was filtered off, washed with water, and dried in air. Yield 0.56 g (92%), mp 168–170°C (benzene). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.34 s (18H, CMe_3), 4.73 s (2H, CH_2N), 5.23 s (1H, OH), 7.17 s (2H, ArH), 7.23–7.30 m (2H, $H^{5,6}$), 7.71–7.78 m (2H, $H^{4,7}$). Found, %: C 71.45; H 7.83; N 7.27. $C_{22}H_{28}N_2OS$. Calculated, %: C 71.70; H 7.66; N 7.60.

b. A solution of benzyl acetate **6** and 1,3-dihydrobenzimidazole-2-thione in a 1 : 1 mixture of acetone and formic acid at ambient temperature for 2 days to obtain 98% of compound **12**.

ACKNOWLEDGMENTS

The work was financially supported by the Ministry for Education and Science of the Russian Federation in the framework of the basic part of the State Contract for 2014–2016.

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