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Synthesis of Sterically Hindered Phenolic Compounds from Indole and Its Derivatives

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Abstract—Reactions of 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate with indole and its derivatives gave a series of sterically hindered phenolic compounds having various functional groups. The products are potentially capable of inhibiting radical chain oxidation processes according to different mechanisms.

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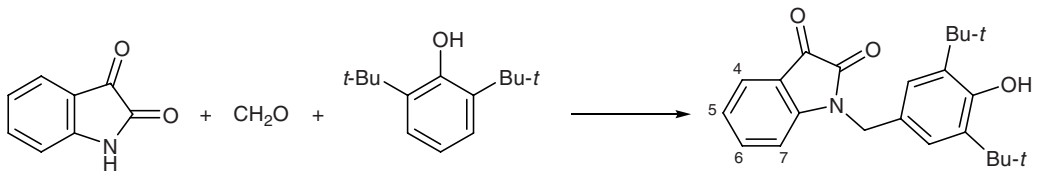
Design of effective polyfunctional stabilizers characterized by internal synergism [1] is a promising line in the field of stabilization of organic media and polymeric materials. Interest in sterically hindered phenolic compounds based on indole and its derivatives is related to the possibility of obtaining such polyfunctional stabilizers. Indole derivatives themselves are known as light and heat stabilizers for poly(vinyl chloride) and other chlorine-containing polymers [2]; introduction of sterically hindered phenolic fragments could give rise to additional antioxidant properties. Some indole derivatives such as substituted isatins (in particular, *N*-methylisatin 3-thiosemicarbazone) are known as medical agents [3]. Sterically hindered phenols also constitute structural fragments of a number of drugs [4]. Therefore, compounds derived from indole and sterically hindered phenols may be promising from the viewpoint of biological activity.

In the present work we synthesized sterically hindered phenol derivatives on the basis of indole, tryptophane, and isatin. Our attempts to effect condensation of indole (**I**) or isatin (**II**) with 2,6-di-*tert*-butylphenol (**III**) and formaldehyde were unsuccessful. The reaction with indole in the presence of an acid catalyst resulted in the formation of unidentified compounds, presumably as a result of indole condensation. When a solution of isatin (**II**), phenol **III**, and formaldehyde in alcohol was heated for 15 h under reflux, only 7% of 1-(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,3-dihydro-1*H*-indole-2,3-dione (**IV**) was formed (according to the ^{1}H NMR data; Scheme 1).

3,5-Di-*tert*-butyl-4-hydroxybenzyl acetate (**V**) is an effective benzylating agent which ensures introduction of 3,5-di-*tert*-butyl-4-hydroxybenzyl fragments into molecules of various compounds. We previously [5] summarized methods for activation of benzyl acetate **V** toward weak nucleophiles, which are based on generation of reactive intermediates, 2,6-di-*tert*-butyl-4-methylidenecyclohexa-2,5-dien-1-one (**VI**) and substituted benzyl cation **A** (Scheme 2).

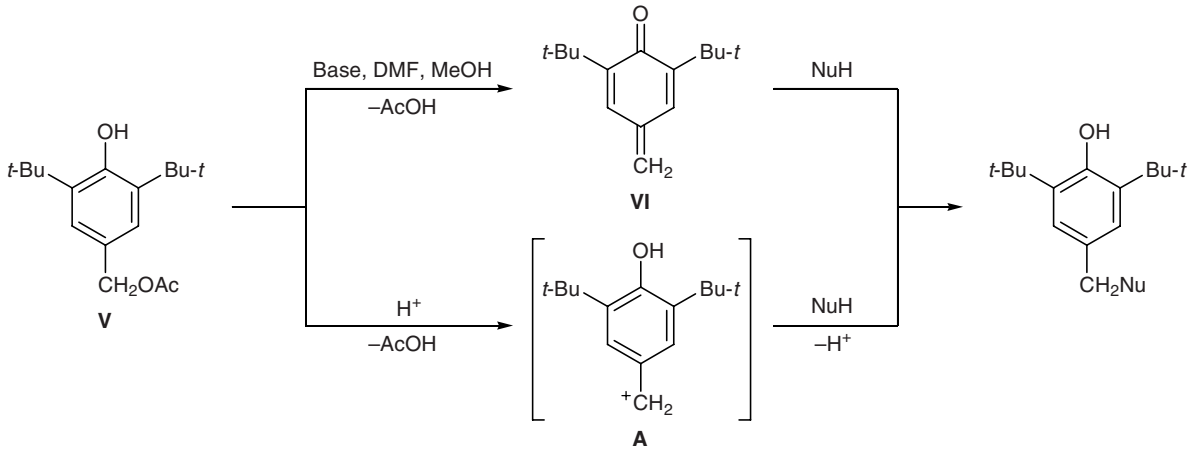
We have found that the ability of indole (**I**) to undergo polymerization in acid medium [6] hampers

Scheme 1.

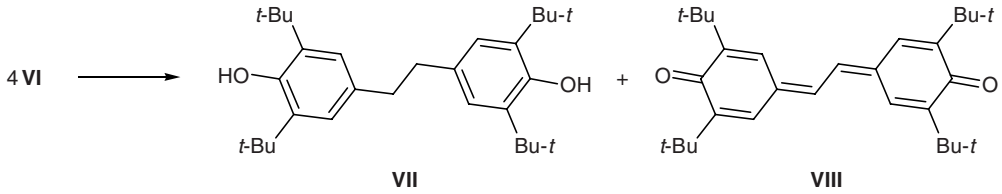


II **III** **IV**

Scheme 2.



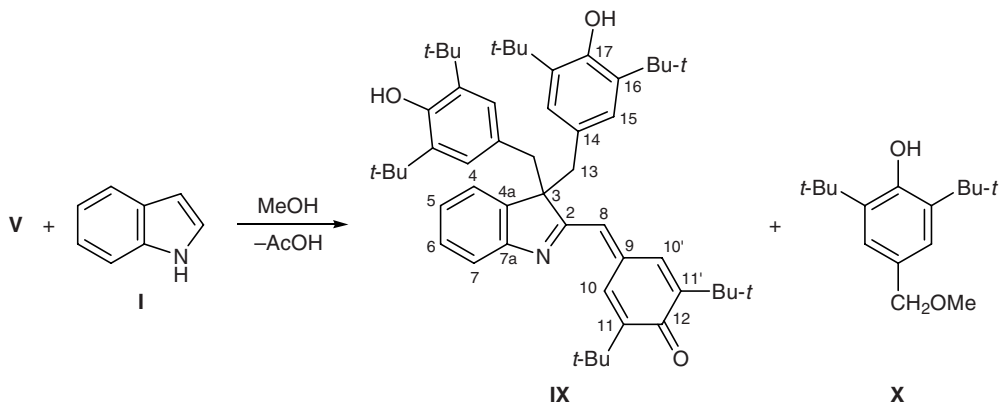
Scheme 3.



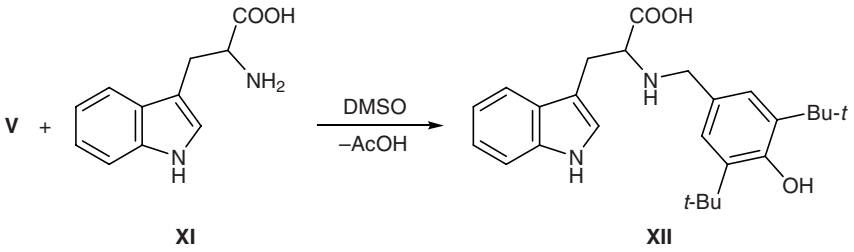
its reaction with benzyl acetate **V** through carbocation **A**. We also failed to obtain condensation product of indole (**I**) with benzyl acetate **V** in the presence of bases or in dipolar aprotic solvents. Presumably, the basicity of indole (pK_a –2.4 [7]) and hence its nucleophilicity are insufficient for the reaction with methylenequinone **VI** to occur. Under the above conditions for generation of methylenequinone **VI** from benzyl acetate **V**, the main components of the reaction mixture were products resulting from side transformations of **VI**, i.e., compounds **VII** and **VIII** (Scheme 3).

As we showed previously [8], benzyl acetate **V** in alcoholic solution exists in equilibrium with methylene quinone **VI**. The fraction of the latter may be controlled by varying the concentration and temperature. Raising the overall concentration decreases the equilibrium concentration of methylene quinone **VI**; therefore, the contribution of its dimerization and disproportionation can be reduced. In fact, when a 0.025 M solution of benzyl acetate **V** and indole (**I**) (molar ratio 3:1) in methanol was stirred for 24 h at 50°C, we isolated from the reaction mixture by fractional crystallization 4-[3,3-bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3*H*-indol-2-ylmethylidene]-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (**IX**) in 15% yield (calculated on the initial indole) and ether **X** (20%, calculated on ben-

Scheme 4.



Scheme 5.



XI **XII**

zyl acetate **V**) (Scheme 4). According to the ^{1}H NMR data, the tarry residue contained 10% of 2,6-di-*tert*-butyl-4-methoxymethylphenol (**X**), traces of **I** and **IX**, and unidentified products.

The structure of compound **IX** was proved by one- and two-dimensional ^{1}H and ^{13}C NMR and IR spectroscopy. Signals in the ^{1}H and ^{13}C NMR spectra were assigned on the basis of the 2D HMBC and HSQC spectra recorded from solutions in $CDCl_3$, $(CD_3)_2CO$, and C_6D_6. The position of the methylene quinone fragment on C^2 rather than on C^3 followed from equivalence of two $ArCH_2$ groups in the ^{1}H NMR (only one *AB* pattern was observed; Fig. 1) and ^{13}C NMR spectra (δ_C 43.2 ppm, s) and from the absence of cross peaks between CH= proton and C^8, CH_2 protons and C^{10}, and 10(10′)-H and C^3 in the 2D HMBC spectra, while a cross peaks between 7-H and C^3 was observed. Thus the reaction of benzyl acetate **V** with indole (**I**) in methanol results in exhaustive benzylation of the latter and is accompanied by oxidation of the sterically hindered phenol fragment in position *2* of the indole ring.

Tryptophane (**XI**) is a stronger nucleophile {pK_a(NH_2) 9.39 [9]} than indole, and it reacted with benzyl acetate **V** in DMSO under mild conditions (Scheme 5). The structure of compound **XII** thus formed was proved using two-dimensional ^{1}H and ^{13}C NMR techniques. Methylene protons of the $ArCH_2$ groups gave cross peaks with the CH= carbon atoms, and coupling between the CH= proton and $ArCH_2$ methylene carbon atom was observed in the 2D HMBC spectrum, which unambiguously indicated the position of the sterically hindered phenol fragment in molecule **XII**.

Isatin **II** readily reacted with benzyl acetate **V** to give compound **IV**. In this case, activation of benzyl acetate **V** is achieved by carrying out the reaction in dipolar aprotic solvents (such as DMSO) or in the presence of acid catalysts. Taking into account that the nucleophilicity of the NH group in molecule **II** is even lower than in indole (**I**), we presumed that the reaction of isatin (**II**) with methylene quinone **VI** in DMSO begins with protonation of the carbonyl group in **VI** by the acidic NH proton. It is known that benzyl acetate **V** in dipolar aprotic solvents readily reacts with weak acids, e.g., with hydrogen sulfide [5]. Substituted isatin **IV** can be converted into the corresponding hydrazone **XIVa** and thiosemicarbazone **XIVb** which attract interest as potential polyfunctional stabilizers and biologically active substances (Scheme 6). Compounds **XIVa** and **XIVb** were synthesized by heating the reactants in boiling alcohol according to standard procedure. When isatin (**II**) was treated first with phenylhydrazine or thiosemicarbazide and then with benzyl acetate **V**, mixtures of products with different numbers

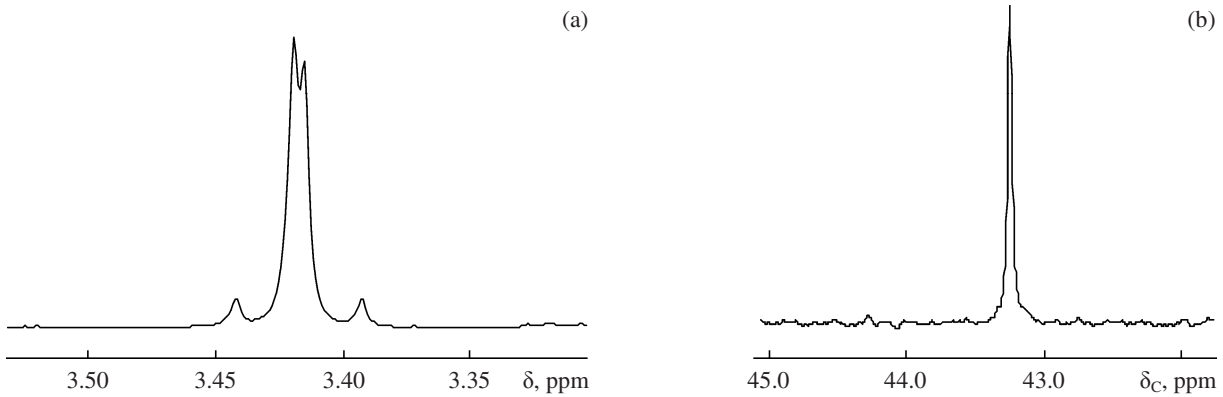
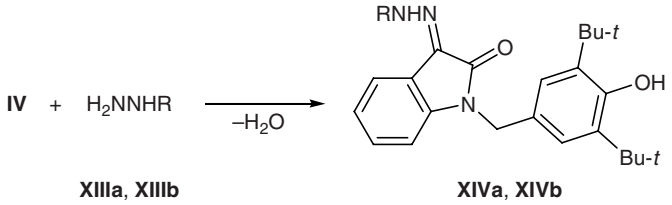


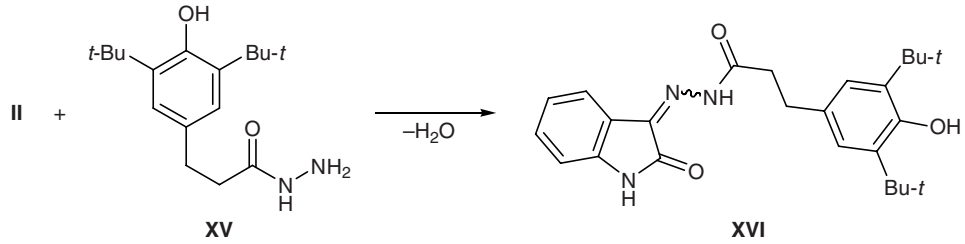
Fig. 1. Fragments of the (a) ^{1}H and (b) ^{13}C NMR spectra of compound **IX** in acetone-d_6.

Scheme 6.



R = Ph (**a**), $NH_2C(S)$ (**b**).

Scheme 7.



of 3,5-di-*tert*-butyl-4-hydroxybenzyl groups were obtained, regardless on the mode of activation of benzyl acetate **V**.

The reaction of isatin (**II**) with acylhydrazine **XV** possessing a sterically hindered phenol fragment gave acylhydrazone **XVI** (Scheme 7). Like compounds **XIVa** and **XIVb**, product **XVI** is capable of trapping peroxy radicals and forming complexes with metals.

Acylhydrazone **XVI** crystallized in two forms **XVIa** and **XVIb** having the same elemental composition but different solubilities, melting points, and R_f values. Acylhydrazones give rise to stereoisomers due to restricted rotation about the C–N and N–N bonds, as well as due to *Z*/*E* isomerism with respect to the double C=N bond [10]. Presumably, the isolated crystalline forms of **XVI** are *Z* and *E* isomers, and each isomer in solution exists as a mixture of stereoisomers due to restricted rotation about the C–N and N–N bonds. This follows from the dependence of the NH signal position in the ^{1}H NMR spectra upon the concentration and solvent polarity:

Solvent	$CDCl_3$ (dilute)	$CDCl_3$ (concd.)	DMSO-d_6
δ(=NNH), ppm	7.810	7.880	10.738
δ(NH), ppm	12.400	9.400	11.008

Protons of the methylene group neighboring to the carbonyl group resonated as two triplets corresponding to *cis* (δ 3.155 ppm) and *trans* (δ 2.738 ppm) [11] arrangement of the 2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)ethyl substituent with respect to the C–N bond (Fig. 2).

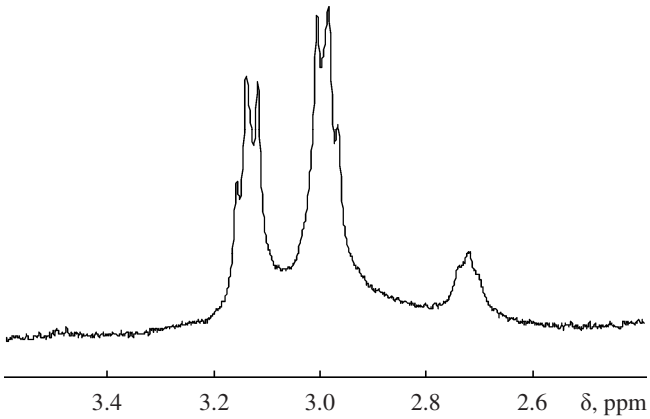


Fig. 2. A fragment of the ^{1}H NMR spectrum of *N*′-(2-oxo-2,3-dihydro-1*H*-indol-3-ylidene)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionohydrazide (**XVIb**) in $CDCl_3$.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-400 spectrometer at 400 and 100 MHz, respectively; the chemical shifts were measured relative to the corresponding solvent signals. The IR spectra were obtained on a Bruker Vector-22 spectrometer with Fourier transform at a resolution of 1 cm^{-1}.

1-(3,5-Di-*tert*-butyl-4-hydroxybenzyl)-2,3-dihydro-1*H*-indole-2,3-dione (IV). *a*. A solution of 1.47 g (0.01 mol) of isatin (**II**), 2.06 g (0.01 mol) of 2,6-di-*tert*-butylphenol (**III**), and 1.5 ml of a 33% formaldehyde solution in 15 ml of ethanol was heated for 20 h

under reflux with stirring. The mixture was cooled to room temperature, poured into 150 ml of water, and extracted with methylene chloride. The extract was dried over $MgSO_4$, and the solvent was distilled off under reduced pressure to obtain 2.9 g (83%) of a dark red tarry material containing 7% of compound **IV** (according to the ^{1}H NMR data).

b. A solution of 1.47 g (0.01 mol) of isatin (**II**) and 2.78 g (0.01 mol) of 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate (**V**) in 25 ml of DMF was stirred for 3 h at 70°C. The mixture was cooled to room temperature, and the precipitate was filtered off, washed with water, and dried in air until constant weight. Yield 1.32 g (36%). From the filtrate we isolated an additional portion of compound **IV**, 1.91 g (52%), orange crystals, mp 245–246°C (from acetone). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.40 s (18H, CMe_3), 4.81 s (2H, CH_2), 5.23 s (1H, OH), 6.91 d (1H, 7-H, ^3J = 7.5 Hz), 7.09 t (1H, 5-H, ^3J = 7.2 Hz), 7.16 s (2H, H_{arom}), 7.55 t (1H, 6-H, ^3J = 7.5 Hz), 7.59 d (1H, 4-H, ^3J = 7.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.45 (C**Me**$_3$); 34.54 (**C**Me$_3$); 44.61 (CH_2); 111.18, 118.02, 123.83, 124.90, 125.51, 125.61, 136.86, 138.33, 151.45, 153.89 (C_{arom}); 158.50 (NC=O); 183.74 (C=O). Found, %: C 75.99; H 7.57; N 3.54. $C_{23}H_{27}NO_3$. Calculated, %: C 75.62; H 7.40; N 3.82.

c. A solution of 1.47 g (0.01 mol) of isatin (**II**) and 2.78 g (0.01 mol) of 3,5-di-*tert*-butyl-4-hydroxybenzyl acetate (**V**) in a mixture of 15 ml of formic acid and 15 ml of acetone was stirred for 20 h at 70°C. The mixture was cooled to room temperature, and the precipitate was filtered off, washed with water, and dried in air until constant weight. Yield 1.47 g (40%), orange crystals. From the filtrate we isolated an additional portion, 1.6 g (44%), of a red tarry substance which contained 20% of compound **IV** (according to the ^{1}H NMR data).

4-[3,3-Bis(3,5-di-*tert*-butyl-4-hydroxybenzyl)-3*H*-indol-2-ylmethylidene]-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (IX). A solution of 1.17 g (0.01 mol) of indole (**I**) and 8.34 g (0.03 mol) of compound **V** in 300 ml of methanol was stirred for 24 h at 50°C. The mixture was cooled to room temperature, and the precipitate was filtered off, washed with a small amount of methanol, and dried in air until constant weight. Yield 1.15 g (15%), yellow–orange crystals, mp 195–197°C. IR spectrum, ν, cm^{-1}: 3623 (OH), 1613 (C=O). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 1.17 s (36H, CMe_3), 1.23 s (9H, CMe_3), 1.37 s (9H, CMe_3), 3.42 d.d (4H, CH_2, ^2J = 14.0 Hz), 5.68 s (2H, OH), 6.57 s (4H, 15-H), 7.28 d (1H, 7-H, ^3J = 7.7 Hz), 7.31 t.d (1H, 6-H, ^3J = 7.7, ^4J = 1.0 Hz), 7.40 d (1H, 10-H, ^4J = 2.0 Hz), 7.42 t.d (1H, 5-H, ^3J = 7.7, ^4J = 1.0 Hz), 7.50 s (1H, 8-H), 7.69 d (1H, 4-H, ^3J = 7.7 Hz), 8.66 d (1H, 10′-H, ^4J = 2.0 Hz). ^{13}C NMR spectrum (acetone-d_6), δ_C, ppm: 30.03 (C**Me**$_3$), 30.19 (C**Me**$_3$), 30.74 (C**Me**$_3$), 34.99 s (**C**Me$_3$), 36.00 s (**C**Me$_3$), 36.33 s (**C**Me$_3$), 43.25 t (CH_2, ^1J = 129.0 Hz), 67.13 s (C^3), 122.26 d.d (C^7, ^1J = 161.0, ^3J = 8.4 Hz), 124.63 d.d (C^4, ^1J = 159.0, ^3J = 7.5 Hz), 126.90 d (C^6, ^1J = 155.0 Hz), 126.90 d (C^{15}, ^1J = 155.0 Hz), 128.01 t (C^{14}, ^2J = 5.0 Hz), 128.78 d.d (C^5, ^1J = 161.0, ^3J = 7.8 Hz), 131.48 d ($C^{10'}$, ^1J = 164.0 Hz), 131.73 d (C^8, ^1J = 153.0 Hz), 136.34 d (C^{10}, ^1J = 159.0 Hz), 137.12 s (C^{16}), 137.71 s (C^9), 143.11 s (C^{3a}), 149.51 s (C^{11}), 150.67 s ($C^{11'}$), 153.37 t (C^{17}, ^3J = 8.7 Hz), 158.12 s (C^{7a}), 180.44 s (C^2), 187.78 t (C^{12}, ^3J = 9.0 Hz). Found, %: C 83.1; H 9.47; N 1.83. $C_{53}H_{71}NO_3$. Calculated, %: C 82.71; H 9.23; N 1.82.

The filtrate was evaporated by half and poured into 300 ml of water. The precipitate was filtered off, washed with water, dried in air until constant weight, and washed with hexane to isolate 1.53 g (20%) of 2,6-di-*tert*-butyl-4-methoxymethylphenol (**X**) as a light brown powder with mp 100–101°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.44 s (18H, CMe_3), 3.39 s (3H, OCH_3), 4.34 s (2H, CH_2), 5.17 s (1H, OH), 7.13 s (2H, H_{arom}). The hexane filtrate was evaporated under reduced pressure. The residue was a dark orange tarry material containing (according to the ^{1}H NMR data) 10% of ether **X**, traces of compounds **I** and **IX**, and unidentified products.

2-(3,5-Di-*tert*-butyl-4-hydroxybenzylamino)-3-(1*H*-indol-3-yl)propionic acid (XII). A solution of 2.04 g (0.01 mol) of tryptophane (**XI**) and 2.78 g (0.01 mol) of compound **V** in 60 ml of DMSO was stirred for 3 h at 70°C. The mixture was treated with 200 ml of a 10% aqueous solution of sodium chloride, and the precipitate was filtered off, washed with water, and dried in air until constant weight. Yield 4.09 g (97%), colorless powder. ^{1}H NMR spectrum (CD_3OD), δ, ppm: 1.36 s (18H, CMe_3), 3.20–3.25 d.d (1H, 3-CH_2, ^2J = 15.3, ^3J = 8.8 Hz), 3.45–3.52 d.d (1H, 3-CH_2, ^2J = 15.3, ^3J = 4.6 Hz), 3.77–3.82 d.d (1H, CHCO, ^3J = 8.8, ^3J = 4.6 Hz), 3.93 s (2H, NCH_2), 7.02 t (1H, 5-H, ^3J = 8.2 Hz), 7.03 s (2H, *o*-H), 7.12 t (1H, 6-H, ^3J = 8.2 Hz), 7.18 s (1H, 2-H), 7.37 d (1H, 7-H, ^3J = 8.2 Hz), 7.60 d (1H, 4-H, ^3J = 8.2 Hz). ^{13}C NMR spectrum (CD_3OD), δ_C, ppm: 28.00 (CH_2);

30.59 (C**Me**$_3$); 35.51 (**C**Me$_3$); 51.87 (CH_2N); 62.50 (CHN); 109.33 (C^3); 125.14 (C^2); 112.53, 119.33, 120.33, 122.87, 123.27, 127.38, 128.39, 138.34, 139.79, 156.27 (C_{arom}); 173.67 (C=O). Found, %: C 74.15; H 8.21; N 6.52. $C_{26}H_{34}N_2O_3$. Calculated, %: C 73.93; H 8.06; N 6.64.

1-(3,5-Di-*tert*-butyl-4-hydroxybenzyl)-2,3-dihydro-1*H*-indole-2,3-dione 3-(phenylhydrazone) (XIVa). A solution of 3.65 g (0.01 mol) of compound **IV**, 1.55 g (0.012 mol) of phenylhydrazine (**XIIIa**) hydrochloride, and 1.68 ml (0.012 mol) of triethylamine in 50 ml of ethanol was heated for 4 h under reflux with stirring. The mixture was cooled to room temperature, and the precipitate was filtered off, washed with ethanol, and dried in air until constant weight. Yield 3.89 g (85%), yellow crystals, mp 203–205°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 s (18H, CMe_3), 4.90 s (2H, CH_2), 5.19 s (1H, OH), 6.92 d (1H, 7-H, ^3J = 8.0 Hz), 7.00–7.50 m (7H, H_{arom}), 7.17 s (2H, H_{arom}), 7.67 d (1H, 4-H, ^3J = 8.0 Hz), 12.85 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.49 (C**Me**$_3$); 34.55 (**C**Me$_3$); 43.75 (CH_2); 109.62, 114.61, 119.12, 121.69, 123.38, 124.68, 126.82, 127.29, 128.12, 129.66, 136.55, 140.87, 142.98 (C_{arom}); 153.58 (C=N); 162.47 (C=O). Found, %: C 76.87; H 7.50; N 8.89. $C_{29}H_{33}N_3O_2$. Calculated, %: C 76.48; H 7.25; N 9.23.

1-(3,5-Di-*tert*-butyl-4-hydroxybenzyl)-2,3-dihydro-1*H*-indole-2,3-dione 3-(thiosemicarbazone) (XIVb). A solution of 3.65 g (0.01 mol) of compound **IV**, 1.53 g (0.012 mol) of thiosemicarbazide (**XIIIb**) hydrochloride, and 1.68 ml (0.012 mol) of triethylamine in 50 ml of ethanol was stirred for 4 h on heating under reflux. The mixture was cooled to room temperature, and the precipitate was filtered off, washed with ethanol, and dried in air until constant weight. Yield 2.65 g (60%), yellow crystals, mp 235°C (decomp.). ^{1}H NMR spectrum (benzene-d_6), δ, ppm: 1.40 s (18H, CMe_3), 4.96 s (2H, CH_2), 6.11 s (1H, OH), 7.13 t (1H, 5-H, ^3J = 7.3 Hz), 7.17 d (1H, 7-H, ^3J = 7.9 Hz), 7.30 s (2H, *o*-H), 7.40 t (1H, 6-H, ^3J = 7.9 Hz), 7.71 d (1H, 4-H, ^3J = 7.3 Hz), 8.17 s (1H, NH_2), 8.44 s (1H, NH_2), 11.62 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.45 (C**Me**$_3$); 34.54 (**C**Me$_3$); 44.19 (CH_2); 110.38, 119.71, 121.09, 123.37, 124.99, 125.92, 128.57, 131.69, 136.71, 143.85 (C_{arom}); 153.84 (C=N); 161.27 (C=O); 180.36 (C=S). Found, %: C 66.01; H 6.99; N 12.48. $C_{24}H_{30}N_4O_2S$. Calculated, %: C 65.75; H 6.85; N 12.78.

***N′*-(2-Oxo-2,3-dihydro-1*H*-indol-3-ylidene)-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionohydrazide (XVIa, XVIb).** A solution of 1.47 g (0.01 mol) of isatin (**II**) and 2.92 g (0.01 mol) of 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionohydrazide (**XV**) in 50 ml of ethanol was heated for 4 h under reflux. The mixture was cooled to room temperature, and the precipitate was filtered off, washed with ethanol, and dried in air until constant weight. Yield of **XVIa** 2.56 g (61%), yellow crystals, mp 214–216°C (from acetonitrile). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.45 s (18H, CMe_3), 2.30 t (2H, C**H**$_2$Ar, ^3J = 7.8 Hz), 3.21 br.t (2H, CH_2CO), 5.07 s (1H, OH), 6.97 d (1H, 7-H, ^3J = 7.7 Hz), 7.08 s (2H, *o*-H), 7.14 t (1H, 5-H, ^3J = 7.6 Hz), 7.41 t (1H, 6-H, ^3J = 7.7 Hz), 7.64 br.s (1H, 4-H), 7.88 s (1H, NH), 9.40 s (1H, =NNH). Found, %: C 71.58; H 7.60; N 9.64. $C_{25}H_{31}N_3O_3$. Calculated, %: C 71.26; H 7.36; N 9.98.

From the filtrate we isolated 0.7 g (17%) of yellow compound **XVIb**, mp 223–224°C (from acetonitrile). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.47 s (18H, CMe_3); 2.74 br.t (0.5H, CH_2CO); 3.01 t (2H, C**H**$_2$Ar, ^3J = 7.8 Hz); 3.16 t (1.5H, CH_2CO, ^3J = 7.8 Hz); 5.09 s (1H, OH); 6.94 d (1H, 7-H, ^3J = 7.8 Hz); 7.03–7.16 m (3H, *o*-H, 5-H); 7.35 t (1H, 6-H, ^3J = 7.8 Hz); 7.60 d (1H, 4-H, ^3J = 7.3 Hz); 7.80 s, 7.90 s, and 8.13 s (1H, NH); 12.40 s and 12.95 s (1H, =NNH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 30.35 (C**Me**$_3$); 30.50 (**C**H$_2$Ar); 34.32 (**C**Me$_3$); 34.52 (**C**H$_2$CO); 111.00, 120.59, 120.82, 123.20, 124.89, 131.13, 131.52, 132.91, 136.12, 140.93 (C_{arom}); 152.19 (C=N); 162.62 (C^2=O); 175.79 (C=O). Found, %: C 71.44; H 7.58; N 9.68. $C_{25}H_{31}N_3O_3$. Calculated, %: C 71.26; H 7.36; N 9.98.

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