

# Synthesis and Chemical Transformations of $\beta$ -(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propionic Hydrazide

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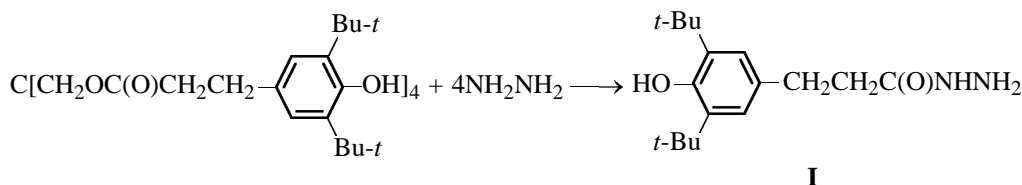
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**Abstract**—A method for synthesis of  $\beta$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic hydrazide. Certain chemical properties of the product were studied. It was found that  $\beta$ -(3,5-di-*ter*-butyl-4-hydroxyphenyl)-propionic  $\beta$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)hydrazide is highly susceptible to oxidation.

$\beta$ -(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propionic hydrazide (**I**) is an efficient antioxidant for polymeric materials [1, 2]. The polyfunctional chemical nature of this compound explains researcher's interest in its synthesis and chemical properties [3–8].

We found that hydrazide **I** can be prepared by hydrazinolysis of the full ester of pentaerythrol and  $\beta$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid which is a known commercial stabilizer Irganox 1010 [9].



The reaction was performed under the action of excess anhydrous hydrazide in a sealed ampule at 130–140°C.

We performed certain chemical transformations of hydrazide **I** and revealed a high nucleophilic activity of its hydrazine moiety.

Oxidation of hydrazide **I** with iodine in boiling alcohol gave 1,2-bis[ $\beta$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionyl]hydrazine (**II**) in a good yield even with about half the stoichiometric amount of iodine. With all iodine, compound **II** was difficult to isolate.

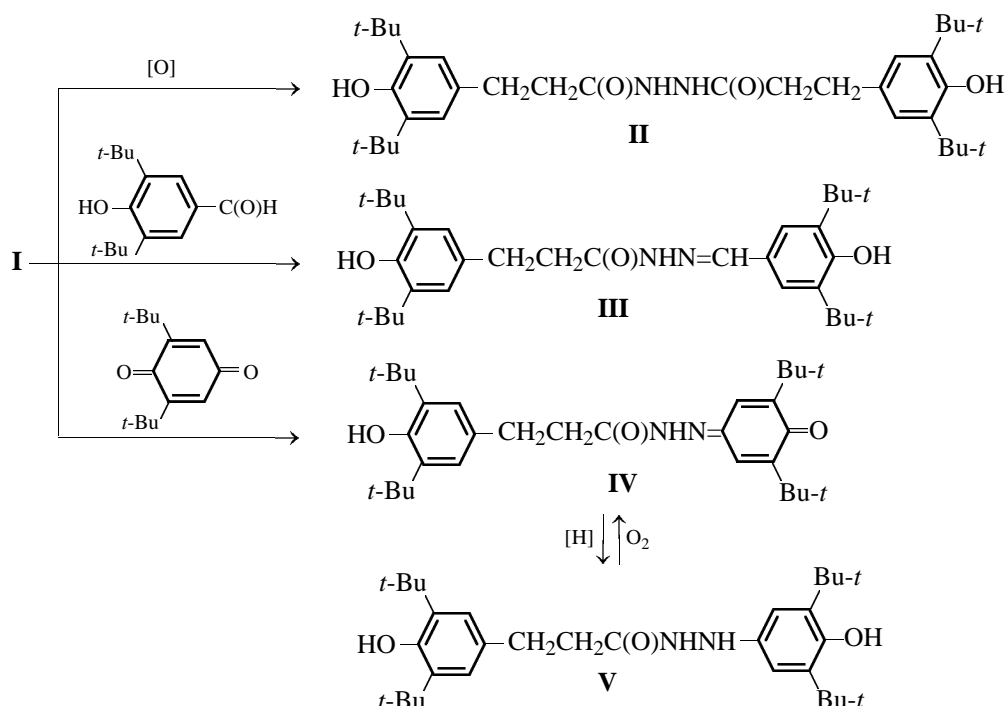
3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde and 2,6-di-*tert*-butylbenzoquinone  $\beta$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionylhydrazones (**III**, **IV**) were obtained by boiling alcoholic solutions of the reactants with catalytic amounts of hydrochloric acid. Compound **IV** was reduced with zinc in acetic acid to obtain a colorless unstable product **V**. On attempted recrystallization from ethanol and on handling in air

the latter converted to the starting compound **IV**, as evidenced by the yellow color, IR spectrum, and melting point of the product. The low stability of compound **V** is consistent with the characteristic behavior of 4-aminophenols, and the presence of two *tert*-butyl radicals *ortho* to the carbonyl group additionally favors the quinoid structure [10].

## EXPERIMENTAL

The IR spectra were recorded on a Specord M-80 spectrometer for suspensions in mineral oil.

As the full ester of pentaerythrol and  $\beta$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid we used commercial stabilizer Irganox 1010 (as received) as a colorless powder, mp 115–125°C {published data [9]: mp 118–125°C [9]}. 3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde and 2,6-di-*tert*-butylbenzoquinone were synthesized by the procedures described in [11, 12], respectively.



**$\beta$ -(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propionic hydrazide (I).** A mixture of 5.88 g of the full ester of pentaerythrol and  $\beta$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionic acid and 3 ml of anhydrous hydrazine were heated for 2 h at 130–140°C. On cooling, a crystalline product precipitated and was filtered off and washed on the filter with a cold aqueous-alcoholic mixture to obtain 4.96 g (85%) of compound **I**, mp 153–155°C (alcohol–water, 5:1) {published data [2]: mp 157–8°C}. Found, %: N 9.51, 9.45.  $\text{C}_{17}\text{H}_{28}\text{N}_2\text{O}_2$ . Calculated, %: N 9.59.

**1,2-Bis[ $\beta$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)-propionylhydrazine (II).** A solution of 1.27 g of iodine in 6 ml of ethanol was added dropwise to a solution of 1.46 g of hydrazide **I** in 10 ml of ethanol until the reaction mixture no longer decolorized and nitrogen no longer evolved. Therewith, about half the calculated volume of iodine had been consumed. The mixture was allowed to stand at room temperature for 24 h. The alcohol was removed in a vacuum, and the residue was recrystallized to obtain 0.68 g (49%) of compound **II**, mp 223–5°C (alcohol–water, 10:1) {published data [3]: mp 225–227°C}. Found, %: N 5.35, 5.70.  $\text{C}_{34}\text{H}_{52}\text{N}_2\text{O}_4$ . Calculated, %: N 5.08.

**3,5-Di-*tert*-butyl-4-hydroxybenzaldehyde  $\beta$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionylhydrazone (III).** A mixture of solutions of 0.73 g of hydrazide **I** in 6 ml of ethanol and of 0.58 g of 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde in 18 ml ethanol, and 3 drops

of hydrochloric acid were refluxed for 2 h. The solvent was removed in a vacuum to obtain 1.02 g (81%) of an almost colorless compound **III**, mp 242–243°C (ethanol–water, 5:1). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3620 (OH), 3340 (NH), 1690 (C=O), 1614 (C=N). Found, %: N 5.12, 5.22.  $\text{C}_{32}\text{H}_{48}\text{N}_2\text{O}_3$ . Calculated, %: N 5.52.

**2,6-Di-*tert*-butylbenzoquinone  $\beta$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionylhydrazone (IV).** Hydrochloric acid, 3 drops, was added to a boiling solution of 1.46 g of hydrazide **I** and 1.10 g of 2,6-di-*tert*-butylbenzoquinone in 30 ml of ethanol. Abundant yellow crystals formed. The mixture was refluxed for 30 min to obtain 2.29 g (93%) of compound **IV**, mp 262–5°C (dioxane). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3640 br (OH), 3150, 3080 (NH), 1670 (C=O), 1610 (C=N). Found, %: N 5.83, 6.10.  $\text{C}_{31}\text{H}_{46}\text{N}_2\text{O}_3$ . Calculated, %: N 5.67.

**$\beta$ -(3,5-Di-*tert*-butyl-4-hydroxyphenyl)propionic (3,6-di-*tert*-butyl-4-hydroxyphenyl)hydrazide (V).** Zinc powder, 1.95 g, was added with stirring at 70–80°C over the course of 1 h to a solution of 1.48 g of compound **IV** in 25 ml of acetic acid. The reaction mixture quickly decolorized. After that it was refluxed for 30 min and left to stand at room temperature for 16 h. Volatiles were distilled off in a vacuum, and the residue was mixed with 50 ml of cold water. Colorless crystals formed and were washed with water and dried in a vacuum over  $\text{P}_2\text{O}_5$  to obtain 1.33 g (89%) of compound **V**, mp 78–85°C. IR spectrum,  $\nu$ ,

$\text{cm}^{-1}$ : 3645 br (OH), 3270 (NH), 1680 (C=O). Found, %: N 5.17, 5.40.  $\text{C}_{31}\text{H}_{48}\text{N}_2\text{O}_3$ . Calculated, %: N 5.65.

Recrystallization from ethanol was accompanied by coloration of the solution and formation of light yellow crystals, mp 261–263°C. The melting point and IR spectrum were the same as those of compound IV.

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