

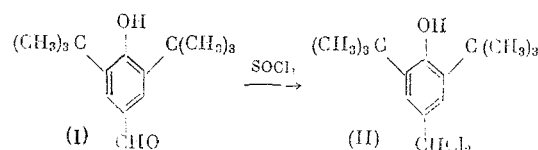
4-HYDROXY-3,5-DI-TERT-BUTYLBENZALCHLORIDE IN THE SYNTHESIS OF STERICALLY HINDERED PHENOLS

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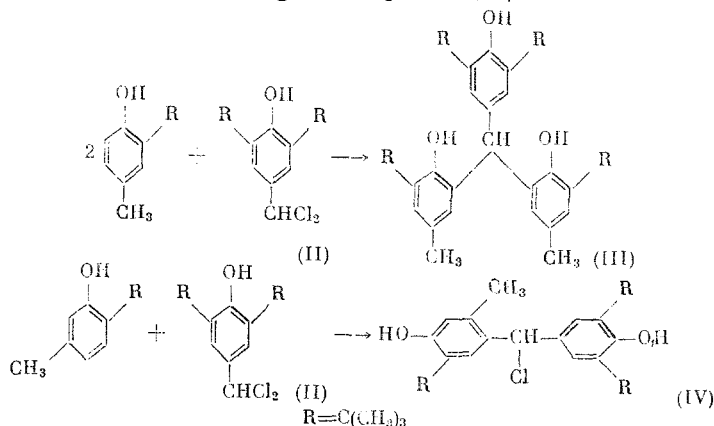
Sterically hindered phenols are the most typical inhibitors of oxidation of fats, oils, fuel, and polymer materials. These compounds have also been widely used in experimental biology [1]. It is therefore very important to develop new ways of synthesizing sterically hindered phenols. In the present work, to synthesize derivatives of such phenols we used 4-hydroxy-3,5-di-tert-butylbenzaldehyde (I), which is a relatively unreactive compound and seldom used for synthesizing phenol derivatives. The only literature references [2-4] deal with condensation of this aldehyde with compounds containing mobile hydrogen atoms. However, condensation of aldehyde (I) with amines takes place in relatively severe conditions [4] and attempts to condense it with alkyl phenols have been unsuccessful.

We have studied an unusual reaction of aldehyde (I) with thionyl chloride, leading to a high yield of 4-hydroxy-3,5-di-tert-butylbenzalchloride (II), which, unlike (I), readily reacts with many substances:



The structure of (II) was confirmed by the UV and infrared spectra and by chemical reactions. In particular, the infrared spectrum of (II) contains a band due to free hydroxyl (3640 cm^{-1}), indicating the presence of only sterically hindered hydroxyl, and bands due to combined hydroxyl and the carbonyl group are absent.

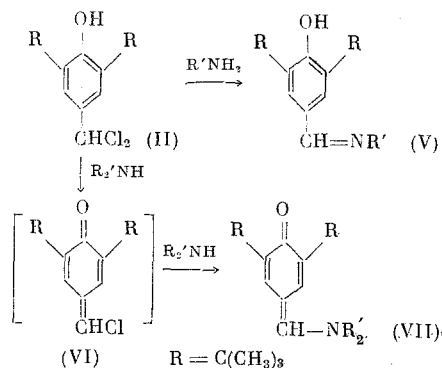
The solution of (II) in an alcohol readily converts it to the initial aldehyde (I). Considerable interest attaches to the reactions of (II) with alkyl phenols, which readily condense with it at room temperature. Thus the reaction of (II) with 4-methyl-2-tert-butyl phenol gives the corresponding trisphenol (III), and that of (II) with 3-methyl-6-tert-butyl phenol gives bisphenol (IV):



The reaction of benzal chloride (II) with primary amines takes place with removal of hydrogen chloride and leads to formation of the expected Schiff bases (V). The reaction of (II) with monoethanolamine gave the corresponding azomethine, identical to that described in [4]. Our azomethines were readily converted to aldehyde (I) when treated with HCl under mild conditions.

The reactions of (II) with secondary amines are different. In this case the first stage is evidently removal of hydrogen halide, accompanied by rearrangement of the aromatic system of phenol bonds to cyclohexadienone (VI), which then reacts with the amine to form the corresponding methylenequinone (VII):

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References [5, 6] describe the preparation of stable aminomethylene-quinones by oxidation of the corresponding aminomethyl derivatives of 2, 6-di-tert-butylphenol. Note that Filar and Winstein [7] observed the formation of methylenequinones during dehydrohalogenation of 4-hydroxybenzyl bromides. Our aminomethylenequinones (VII) are stable substances. They are identical to the analogous compounds synthesized by a different procedure [5, 6] and readily hydrolyzed by HCl to form aldehyde (I). The infrared spectra of (VII) do not contain bands characteristic of the OH group, but exhibit a band at $1610\text{--}1630\text{ cm}^{-1}$ characteristic of conjugated carbonyl in quinonemethide compounds.

EXPERIMENTAL

4-Hydroxy-3,5-di-tert-butylbenzaldehyde (II). We shook 20 g of aldehyde (I) and 50 ml of thionyl chloride for 10–15 min. Solution was complete and the reaction mass was left for 12 h. The thionyl chloride was removed, a small amount of hexane added to the residue, and the crystalline product filtered; the product was recrystallized from hexane with intense cooling. The yield of (II) was 9.7 g (79%) and the mp 98° . Found: C 62.91; 62.83; H 7.91; 7.77; Cl 25.10%. $\text{C}_{15}\text{H}_{22}\text{Cl}_2\text{O}$. Calculated: C 62.91; H 7.91; Cl 25.10%.

Solution of 0.01 M of (II) in 20 ml of ethanol or methanol led to a rise in temperature to $33\text{--}36^\circ\text{C}$ and then to precipitation of aldehyde (I); the yield was 2 g (85%) and the mp 189° . A mixed melt with the known substance showed no depression of the melting point.

Bis(2-hydroxy-3-tert-butyl-5-methylphenyl)-(4-hydroxy-3,5-di-tert-butylphenyl) methane (III). We dissolved 9.8 g of 2-tert-butylmethylphenol and 8.7 g of (II) in 90 ml of hexane. The contents were mixed at 20° for 9 h and left overnight. The crystalline precipitate was separated and recrystallized from hexane; the yield was 10.9 g (66.7%) and the mp $199\text{--}200^\circ$. Found: C 82.03; 81.91; H 9.71; 9.65%. $\text{C}_{37}\text{H}_{52}\text{O}_3$. Calculated: C 81.61; H 9.55%.

4,4'-Dihydroxy-2'-methyl-3,5,5'-tri-tert-butylphenylchloromethane (IV). We dissolved 15.6 g of 3-methyl-6-tert-butylphenol and 13.7 g of (II) in 100 ml of hexane. The mixture was stirred for 15 h at 20° . The crystalline precipitate was separated, washed with hexane and crystallized from dichloroethane; the yield was 19.7 g (94%) and the mp 238° . Found: C 74.87; 74.98; H 8.75; 8.68; Cl 8.92%. $\text{C}_{26}\text{H}_{37}\text{ClO}_2$. Calculated: C 75.01; H 8.91; Cl 8.52%.

4-Hydroxy-3,5-di-tert-butylbenzaliminoethanol (V). To a solution of 3.5 g of ethanolamine in 30 ml of dichloroethane was added 5.8 g of (II) in 20 ml of dichloroethane. After 3 h the crystalline precipitate was separated, washed with water, dried and recrystallized from CCl_4 ; the yield was 4.78 g (86%) and the mp $151\text{--}152^\circ$. According to [4], the mp is $152\text{--}154^\circ$. Solution of (V) in ethanol in the presence of HCl gave crystals of aldehyde (I); the yield was 85%.

α -(N-Diethyl)-2,6-di-tert-butylaminomethylenequinone (VIIa) was obtained in a similar way by reacting (II) with diethylamine; the yield was 86.9% and the mp $134\text{--}135^\circ$. A mixture of 1.45 g of (VII), (VIIa), and 1 ml of concentrated HCl was kept for 1 h. The crystalline precipitate of (I) was recrystallized from benzene; the yield was 85%.

α -(N-Dimethyl)-2,6-di-tert-butylaminomethylenequinone (VIIb) was obtained in the same way from (II) and dimethylamine; the yield was 84% and the mp $171\text{--}173^\circ$. According to [6], the mp is $173\text{--}175^\circ$.

α -(N-Piperidyl)-2,6-di-tert-butylmethylenequinone (VIIc) was obtained from (II) and piperidine; the yield was 77%. It was recrystallized from CCl₄; the mp was 169-170°. According to [6], the mp is 170-171°.

CONCLUSIONS

We have obtained 4-hydroxy-3,5-di-tert-butylbenzaldehyde by reacting 4-hydroxy-3,5-di-tert-butylbenzaldehyde with thionyl chloride, and have studied its reactions with alcohols, phenols, and amines.

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