The Sulfurization of Sterically Hindered Phenols with Sulfur. A Convenient Synthesis of 4,4'-Thio-bis-[2,6-dialkylphenols] and 2,6-Dialkyl-4-mercaptophenols

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The anion of 2,6-disubstituted sterically hindered phenols is an ambident anion exhibiting the properties of a phenoxide anion and a carbanion. Due to the steric hindrance by the 2- and 6-substituents, the carbanion reacts more easily with electrophilic agents than the phenoxide ion. It is also known that the thiophilicity of a carbanion is higher than that of a phenoxide ion. On the basis of these facts, it can be expected that hindered phenols react with sulfur in the presence of a base. We report here a convenient method for the preparation of 4,4'-thio-bis-[2,6-dialkylphenols] and 2,6-dialkyl-4-mercaptophenols from sterically hindered phenols and sulfur.

When a mixture of 2,6-di-t-butylphenol, sulfur, and potassium hydroxide in ethanol was stirred at room temperature for 1 hr followed by neutralization with hydrochloric acid, 63% of the phenol was converted to a mixture of mono- and polysulfides. The yields of the sulfides determined by $^1$H-N.M.R. were as follows: monosulfide 34%, disulfide 9%, trisulfide 7%, and tetrasulfide 10%.

The ratio phenol:sulfur:potassium hydroxide seriously affected the course of the reaction. Both conversion of phenol and yield of monosulfide were maximum at a ratio phenol:sulfur (atom)=1:3, whereas the use of a large excess of sulfur increased the yield of polysulfides. The
optimum ratio phenol:potassium hydroxide for the production of the monosulfide was found to be 2:3. In refluxing ethanol, the reaction was complete within 30 min. Longer reaction time apparently gave rise to a retro reaction of the sulfides to give the original phenol. The use of different alcohols as solvents gave the following yields of monosulfide: methanol, 42%; ethanol, 65%; propanol, 68%. These results indicate that the solubility of sulfur in the solvent plays an important role in the reaction.

The influence of the 2,6-substituents is shown in the Table. Steric factors decisively control the reaction. Thus, only phenols having substituents in both α-positions react with sulfur to give the corresponding thio-bis-phenols under the above described conditions; less hindered phenols such as 2-methylphenol and unsubstituted phenol do not react under the same conditions. It has been reported that the reaction of phenol with sulfur in the presence of sodium hydroxide at 140–180°C leads to the formation of isomeric thio-bis-phenols.

The reaction of sterically hindered phenols (1) with sulfur is considered to proceed as follows. The ambident anion 2a−2b, formed from 1 and a base, reacts with sulfur to give the intermediate 3, which in turn reactive with a second carbanion 2b to give mono- and polysulfides (4) and the corresponding dianions (5). The mono- and polysulfides 4 presumably are in a thermodynamical equilibrium in the reaction solution.

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\text{Conversion and Yields in the Reaction of 2,6-Dialkylphenols (1) with Sulfur}^a
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\begin{align*}
\text{R}^1 & \quad \text{R}^2 & \quad \text{Conversion} & \quad \text{Yield} & \quad \text{for } x = \\
\text{1-C}_6\text{H}_4 & \quad \text{1-C}_6\text{H}_4 & 100 & 65 & 14 & 6 & 15 \\
\text{1-C}_6\text{H}_4 & \quad \text{CH}_3 & 62 & 25 & 16 & 9 & 9 \\
\text{1-C}_6\text{H}_4 & \quad \text{H} & 40 & 16 & 13 & 9 & 9 \\
\text{CH}_3 & \quad \text{CH}_3 & 65 & 27 & 23 & 7 & 8 \\
\end{align*}
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\(a\) Reaction conditions: Ratio phenol: sulfur: potassium hydroxide = 1:3:1.5; refluxing ethanol, 30 min; neutralization with 3N hydrochloric acid.

\(b\) Conversion of phenol and yields of product were determined by \(^1\)H-N.M.R. spectrometry. The spectral data for all compounds prepared were identical with those of authentic samples prepared by simple modifications of known methods.

\(c\) Yield of isolated product.

\[\text{Reaction of 2,6-Di-1-p-tolylphenol with Sulfur:}\]

A solution of 2,6-di-1-p-tolylphenol (4.1 g), sulfur (19 g), and potassium hydroxide (1.7 g) in ethanol (15 ml) was refluxed for 30 min. Then benzene (100 ml), 3N hydrochloric acid (80 ml), and zinc dust (5.0 g) were added to the solution. The reaction mixture was stirred at room temperature for 1 hr, filtered, and the benzene layer isolated. The two products were separated by extraction of the benzene layer with aqueous sodium hydroxide. Evaporation of the benzene solution and recrystallization of the residue from hexane gave 4,4'-thio-bis-[2,6-di-1-tolylphenol] (6). The aqueous phase was neutralized with 3N hydrochloric acid and extracted with benzene. The benzene extract was evaporated and the residue recrystallized from hexane to give 2,6-di-t-butyl-4-mercaptophenol (7).

The yields of products in the reaction mixture were determined by \(^1\)H-N.M.R. spectrometry: 4,4'-thio-bis-[2,6-di-1-tolylphenol], 65%; 2,6-di-t-butyl-4-mercaptophenol, 35%.

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