Experimental Section

Materials.—Acetonitrile and nitromethane (Eastman Organic Chemicals Spectrograde) were pretreated by procedures described previously.[4] A sample of tetramethylene sulfone (sulfolane) furnished through the courtesy of the Shell Development Co., Emeryville, Calif., was distilled at reduced pressure over a boiling range of 144–147° (20 mm). It was established by vapor phase chromatography that the colorless distillate, mp 27–28°, was virtually water free. Eastman Organic Chemicals Spectrograde toluene and Spectrograde carbon tetrachloride and J. T. Baker Chemical Co. resublimed iodine and Matheson Co. chlorine were used without further purification.

The Kinetic Studies.—The rates of reaction of chlorine with toluene in the various solvent mixtures which were employed were investigated by spectrophotometric methods which were patterned closely after those used in a previous investigation.

Equilibrium Constants for Iodine Complex Formation of Acetonitrile, Nitromethane, and Tetramethylene Sulfone.—To investigate the acetonitrile–iodine complex a series of carbon tetrachloride solutions were prepared in which the acetonitrile concentrations ranged from 0.125 to 3.00 M and in which the iodine concentrations were all the same ($0.600 \times 10^{-3}\ M$). The optical densities of these solutions were determined at a number of wavelengths in the region of major visible absorption of iodine (440–580 mμ) using halogen-free solutions of corresponding acetonitrile concentrations as blanks. Other details of the general methods of measurement and of the calculation of the equilibrium constant by the procedure of Ketelaar are described elsewhere.[5] Similar procedures were used in evaluating equilibrium constants for the tetramethylene sulfone–iodine and nitromethane–iodine complexes in carbon tetrachloride. The extent of interaction of nitromethane and iodine is small, and it was found that a minimum nitromethane concentration of about 1 M was required to produce significant changes in the halogen spectrum in carbon tetrachloride. The equilibrium constants for the acetonitrile[6,7] and sulfolane[7] complexes have been reported previously but have been remeasured to develop a set of figures for comparison which are the outgrowth of experimentation in a single laboratory.

Registry No.—Toluene, 108-88-3; tetramethylene sulfone, 126-33-0; acetonitrile, 75-05-8; nitromethane, 75-52-5.

Acknowledgment.—The authors are indebted to the National Science Foundation and to the Petroleum Research Fund of the American Chemical Society for grants in support of this research.

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Sulfonation–Debutylation of 2,6-Di-*t*-butyl-*p*-cresol

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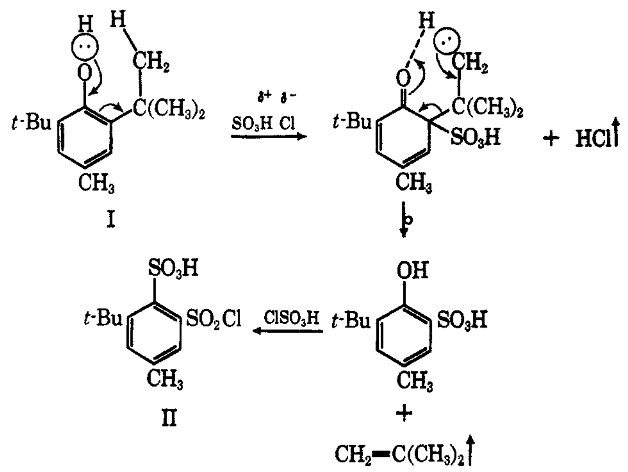
An attempt to chlorosulfonate 2,6-di-*t*-butyl-*p*-cresol (I) in the *meta* position by treating it with chlorosulfonic acid in chloroform solution at 0–25° led instead to formation of 6-chlorosulfonyl-2-*t*-butyl-*p*-cresol (II). It is suggested that the debutylation which occurred under these mild conditions may be accounted for by initial formation of a sulfo-substituted cyclohexadienone intermediate followed by a cyclic rearrangement (Scheme I). The tendency of 2,4,6-trialkylphenols containing at least two *t*-butyl substituents to form 4-halo-substituted, alkylated, 2,5-cyclohexadienones by attack of the electrophilic halonium ion has already been established.[1,2] It appears that attack on the *ortho* position of such a compound by a hydroxysulfonyl cation promotes debutylation.

Scheme I



The structure of compound II was confirmed by its conversion, *via* hydriodic acid reduction, to the disulfide, 2,2′-dithiobis(6-*t*-butyl-*p*-cresol) (III). The latter compound was prepared independently by treatment of 2-*t*-butyl-*p*-cresol with sulfur monochloride. This disulfide was, in turn, reduced with lithium aluminum hydride to a crude form of the related mercaptan, from which a crystalline O,S-bis(2,4-dinitrophenyl) derivative was prepared.

The facts that disulfide III could not be acetylated with acetic anhydride–pyridine mixture, and would not form a colored salt, suggests that if it is phenolic, that the phenol groups are highly hindered. Infrared analysis of this compound indicates presence of a hindered phenol rather than a quinoid structure. The actual objective of our synthetic program was the preparation of dithiobisphenols having a degree of steric hindrance about both the phenol and disulfide functions. No difficulty was experienced in preparing a compound of this type, namely, 4,4′-dithiobis(2,6-diisopropyl-3,5-xylenol) (IV), by treatment of 2,6-diisopropyl-3,5-xylenol (V) with sulfur monochloride in a manner similar to the treatment of 2-*t*-butyl-*p*-cresol.

Experimental Section[3]

2-*t*-Butyl-6-chlorosulfonyl-*p*-cresol (II).—A solution of 54.0 g (0.300 mole) of 2,6-di-*t*-butyl-*p*-cresol (Catalin Corp.) in 200 ml of chloroform was cooled to 0° in an ice-salt bath. To it was added, dropwise, 76.9 g (0.66 mole) of chlorosulfonic acid, over a 1-hr period, with mechanical stirring. The solution, after standing for 72 hr at 25°, was poured onto ice, and the layers were separated. The chloroform layer and chloroform extract of the aqueous layer were combined, washed with water, dried over anhydrous calcium chloride, and evaporated *in vacuo*. The resultant 40.4 g (51%) of brown oil, when triturated with *n*-hexane, crystallized to a solid with mp 45–53°. By repeated recrystallizations of the product from 9:1 pentane–chloroform at −78°, 8.9 g of violet crystals, mp 58–60°, were obtained.

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[1] G. M. Coppinger and T. W. Campbell, *J. Am. Chem. Soc.*, **75**, 734 (1953).

[2] L. E. Forman and W. C. Sears, *ibid.*, **76**, 4977 (1954).

[3] Melting points were determined with a Fisher–Johns apparatus and are uncorrected. Infrared spectra were obtained from KBr pellet and Nujol/Fluorolube split mull sample preparations with a Perkin-Elmer Model 21 instrument.

Anal. Calcd for $C_{11}H_{15}ClO_3S$: S, 12.20; Cl, 13.50. Found: S, 12.22; Cl, 12.16.

Reduction of II with Hydriodic Acid.—To a solution of 8.90 g of II in 25 ml of benzene, 70 ml of glacial acetic acid, and 35.8 g of 50% aqueous hydriodic acid were added. The mixture was stirred, and the resultant solution permitted to stand for 16 hr at 25°. About 80% of a solution of 22.1 g of sodium thiosulfate in 100 ml of water was required to decolorize the iodine which had precipitated. The benzene layer was washed with water, dried over anhydrous sodium sulfate, and evaporated. From the resultant 6.7 g of amber oil, 3.0 g of fine, pale yellow crystals, mp 112.5–114.0°, were obtained by triturating with 8 ml of *n*-pentane, and cooling to −78°. The melting point of this compound was not depressed when mixed with III which was prepared independently as indicated below.

Anal. Calcd for $(C_{11}H_{15}OS)_2$: C, 67.64; H, 7.74; S, 16.4. Found: C, 67.27; H, 7.82; S, 16.3.

2,2′-Dithiobis(6-*t*-butyl-*p*-cresol) (III).[4]—To a mechanically stirred mixture of 110 g (0.500 mole) of 2-*t*-butyl-*p*-cresol (mp 47–48°, Koppers Co.), 0.5 g of sulfur, and 150 ml of toluene was added, dropwise, a solution of 37.2 g of sulfur monochloride (0.283 mole) in 100 ml of toluene, at 30°, over a 2-hr period under nitrogen atmosphere. The reaction mixture was heated to 80° for an additional 40 min, and then stripped of toluene and excess sulfur monochloride *in vacuo*. By dissolving the resultant 126 g of brown syrup in 185 ml of hot absolute ethanol, and cooling slowly to 0°, a yellow crystalline product was formed. The 39.4 g of product (40%, mp 103–108°) collected, when recrystallized from hot methanol, yielded 25.6 g of disulfide, mp 111–113°. Another 10 g of disulfide of the same melting point was obtained by reworking the combined alcoholic filtrates.

Elemental analysis of this compound corresponded with results obtained from the compound obtained by HI reduction of II. Compound III did not react with alcoholic silver nitrate.

The infrared absorption spectrum of this compound shows a sharp band at 3500 cm^{-1} suggesting a hindered phenol stretching band, a strong absorption at 1170 cm^{-1} for the C–O stretching band, and a fairly strong band at 862 cm^{-1} for the out-of-plane C–H aromatic bonding absorption. There are bands corresponding to all of these in the infrared spectrum of 2,2′-thiobis(6-*t*-butyl-*p*-cresol) (Sadtler Spectrum 18746). There is no quinoid carbonyl band in the 1610–1670 cm^{-1} region.

Reduction of III with $LiAlH_4$.—A solution of 5.00 g of III in 50 ml of anhydrous ether was added, dropwise, to a mechanically stirred slurry of 1.0 g of $LiAlH_4$ in 200 ml of anhydrous ether at 0°, and the mixture was allowed to react further at 34°. By working up the product in the usual manner, 4.3 g of oily product was obtained. Amperometric titration of this oil with alcoholic silver nitrate indicated that 86% of mercaptan calculated as 2-*t*-butyl 6-mercapto-*p*-cresol (VI) was present.

O,S-Bis(2,4-dinitrophenyl) Derivative of VI.—A solution of 1.84 g (0.00938 mole) of crude VI in 10 ml of aqueous alkali containing 0.74 g of NaOH was combined with a solution of 4.0 g of 2,4-dinitrochlorobenzene in 60 ml of absolute ethanol, and the mixture refluxed for 30 min. By adding 60 ml of water to the mixture, and cooling, a yellow solid was formed. The 5.12 g of product was recrystallized from 160 ml of 1:1 chloroform–ethanol to yield 1.67 g of lemon yellow crystals, mp 212–214°.

Anal. Calcd for $C_{23}H_{20}N_4O_9S$: S, 6.07; N, 10.60; mol wt, 528.5. Found: S, 6.12; N, 9.99; mol wt (mass spectrometry), 528.

The infrared spectrum of this compound showed no evidence of either an OH stretching band or a quinoid carbonyl band.

4,4′-Dithiobis(2,6-diisopropyl-3,5-xylenol) (IV).—By treating 40.0 g of 2,6-diisopropyl-3,5-xylenol (V), mp 94–96°, with 13.3 g of sulfur monochloride in the same manner used for preparation of III from 2-*t*-butyl-*p*-cresol, 48.5 g of a yellow crystalline mass was obtained. By repeated fractional crystallization of this product from 9:1 ethanol–toluene, 5.3 g of yellow crystals, mp 150.5–152.5, were obtained. A sample, recrystallized to mp 152.3–154.0, was analyzed.

The diisopropylxylenol used for this synthesis was obtained by isopropylating 3,5-xylene in presence of oleum, according to the method of Cowie.[5] A benzoate (VII) of this phenol of mp 177.0–177.5° was prepared. The infrared absorption spectrum of this phenol was very similar to that of 2,3,5,6-tetramethylphenol. Both spectra contained sharp single bands at 3600 cm^{-1} associated with sterically hindered OH groups, thus suggesting 2,6 substitution.

Anal. Calcd for $(C_{14}H_{21}OS)_2$ (IV): C, 70.81; H, 8.92; S, 13.54. Found: C, 71.35; H, 9.11; S, 13.74. Calcd for $C_{14}H_{22}O$ (V): C, 81.48; H, 10.75. Found: C, 81.76; H, 10.80. Calcd for $C_{21}H_{26}O_2$ (VII): C, 81.25; H, 8.44. Found: C; 81.12; H, 8.59.

Registry No.—I, 128-37-0; II, 13811-20-6; III, 1620-66-2; IV, 13862-51-6; O,S-bis(2,4-dinitrophenyl) derivative of VI, 13811-22-8; VII, 13811-23-9.

Acknowledgment.—We are indebted to Mr. J. K. Clark for infrared spectroscopic analysis of the compounds described.

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[4] The sulfuration conditions used follow, in general, the method used by E. B. Hotelling, R. J. Windgassen, E. P. Previc, and M. B. Neuworth, *J. Org. Chem.*, **24**, 1598 (1959), to prepare a crude form of disulfide III. These workers catalytically reduced the crude product to 2-*t*-butyl-6-mercapto-*p*-cresol, mp 40–42°.

[5] C. T. Cowie, British Patent 688,740 (1951).

Metal Sulfide Catalysts for Hydrogenation of Halonitrobenzenes to Haloanilines

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The selective hydrogenation of aromatic halonitro compounds to haloamines is difficult because reductive dehalogenation is enhanced by amino substitution in the ring.[1] Dehalogenation has been shown to occur with platinum,[1–3] palladium,[1–3] rhodium,[4] nickel,[5] and copper chromite[6] catalysts. It takes place more readily with bromine than with chlorine-substituted compounds.[1,5]

The selectivity of a platinum catalyst can be greatly increased by the addition of critical amounts of specific inorganic[7] or organic[8] bases. The bases probably function by selectively poisoning the catalyst for the reductive dehalogenation. It is well known that alkali in larger quantities promotes dehalogenation.

Rhenium sulfide had been shown to have excellent selectivity for reducing nitro groups without dehalogenation.[9]

The utility of the sulfides of the platinum metals,[10] platinum, palladium, rhodium, and ruthenium, and of cobalt sulfide for this reaction is now described.

The results for the hydrogenation of chloro- and of bromo-substituted nitrobenzenes are given in Table I. There was no detectable dechlorination with the sulfides of platinum, palladium, rhodium, ruthenium, and

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[10] (a) F. S. Dovell and H. Greenfield, *ibid.*, **87**, 2767 (1965). (b) H. Greenfield and F. S. Dovell, paper presented at 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, B121.