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.

(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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(6) B. O. Pray and F. C. Trager (to Columbia-Southern Chemical Corp.), U. S. Patent 2,791,613 (May 1957).

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(9) H. S. Broadbent, L. H. Slaugh, and N. L. Jarvis, *J. Am. Chem. Soc.*, **76**, 1519 (1954).

(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.

TABLE I
REDUCTION OF HALONITROBENZENES TO HALOANILINES

X		$XC_6H_4NO_2$ Registry no.	Wt, g	Moles	Sulfide catalyst Type	Wt, g	Temp, °C	Pressure, psig	Time, min	Yield, mole % Haloaniline	Aniline
p-Cl	*a*	100-00-5	157.6	1.0	Pt[d]	1.6	130–175	500–800	45	98.5	0
	a		157.6	1.0	Co[e]	*e*	110	500–800	400	97	0
	b		17.0	0.108	Pt[d]	0.325	145	500–800	195	100	0
	b		17.0	0.108	Pd[f]	0.325	145	500–800	150	100	0
o-Cl	*a*	88-73-3	157.6	1.0	Pt[d]	1.6	150–175	500–800	40	94.5	0
	c		78.3	0.50	Pt[d]	1.5	145	500–800	70	92.5	0
	c		78.3	0.50	Rh[d]	1.5	100–145	500–800	15	95	0
	c		78.3	0.50	Ru[d]	1.5	140–150	500–800	45	93.5	0
p-Br	*c*	586-78-7	101	0.50	Pt[d]	1.5	100–130	500–800	60	99.5	0
							130		390		
	c		101	0.50	Rh[d]	1.5	105	500–800	135	100	Trace
	c		101	0.50	Co[e]	*e*	115	500–800	90	99	Trace
	b		21.8	0.108	Pd[f]	0.325	140–150	500–800	45	36	64

[a] Experiment run in 600-ml Magne-Dash autoclave with 180 ml of methanol as solvent. [b] Experiment run in 170-ml Magne-Dash autoclave with 52 ml of methanol as solvent. [c] Experiment run in 600-ml Magne-Dash autoclave with 240 ml of methanol as solvent. [d] 5 wt % metal on carbon (Engelhard Industries). [e] Prepared *in situ* from 6.0 g of 50% Co on kieselguhr obtained from Chemetron Corp. (Girdler G-67RS) and H_2S in excess (50 psig at room temperature). [f] Bulk palladium sulfide prepared by passing H_2S into a solution of palladium chloride in aqueous hydrochloric acid. [g] Yields determined by quantitative glpc analyses. No nitro compound detected in any experiment. Failure of haloaniline and aniline yields to add up to 100% in some cases is probably due to mechanical losses.

cobalt; no detectable debromination occurred with platinum sulfide; trace debromination occurred with rhodium sulfide and cobalt sulfide; and appreciable debromination occurred with palladium sulfide.

Nickel[5] and palladium sulfide appear to be satisfactory for the reduction of chloronitro but not of bromonitro aromatic compounds. Platinum sulfide probably is the catalyst of choice in most cases because of its excellent selectivity and convenient commercial availability.

The selective hydrogenation of haloaryl nitro compounds also is applicable to polyhalo-substituted aromatics. For example, 2,5-dichloronitrobenzene was quantitatively hydrogenated with a platinum sulfide catalyst to 2,5-dichloroaniline.

The metal sulfide catalysts also are useful for the reductive alkylation[10–12] of haloaryl amines formed *in situ* by the reduction of halonitro compounds. For example, *p*-nitrochlorobenzene was quantitatively transformed to N-isopropyl-*p*-chloroaniline by reaction with hydrogen and acetone in the presence of a rhodium sulfide catalyst.

Experimental Section

A detailed description of two experiments is given to illustrate the procedure.

2,5-Dichloroaniline.—To a 600-ml stainless steel Magne-Dash autoclave were added 103.5 g (0.54 mole) of 2,5-dichloronitrobenzene (Eastman Kodak 187), 230 ml of methanol, and 3.0 g of 5% platinum sulfide on carbon (Engelhard Industries). The autoclave was sealed and purged first with nitrogen and then with hydrogen. Hydrogen was added to a pressure of 600 psig, and the reaction mixture then was heated for 1.3 hr at 85° (500–800 psig) at which point gas absorption stopped at approximately the theoretical usage of hydrogen. The autoclave was cooled and vented, and its contents were filtered to remove the catalyst. The filtrate was made strongly alkaline with dilute sodium hydroxide and the methanol solution was concentrated by distillation. Benzene was added and the remaining methanol was removed by distillation. The benzene solution was then cooled and washed with water. The combined aqueous solutions gave a negative silver nitrate test for chloride anion; thus there had been negligible dehalogenation. The benzene solution was distilled up to a pot temperature of 207° at atmospheric pressure. The residue consisted of 87 g (99.5% yield) of 2,5-dichloroaniline that melted at 48–49°; there was no depression on a mixture melting point with an authentic sample.

N-Isopropyl-*p*-chloroaniline.—To a 600-ml stainless steel Magne-Dash autoclave were added 31.5 g (0.20 mole) of *p*-nitrochlorobenzene (Eastman Kodak P-185), 158 g (2.73 moles) of acetone, and 2.5 g of 5% rhodium on carbon (Engelhard Industries). The autoclave was sealed and purged with nitrogen and then with hydrogen. Hydrogen sulfide was added to a pressure of 50 psig, followed by the addition of hydrogen to a pressure of 1300 psig. The reaction mixture then was heated with agitation for 4.4 hr at 180° (1200–1400 psig). The autoclave was cooled, vented, and the reaction product removed. The catalyst was removed by filtration and the filtrate topped to a pot temperature of 180° at atmospheric pressure. The residue was dissolved in benzene, and the benzene solution was washed twice with 5% aqueous sodium hydroxide, then twice with water. After removal of the benzene by distillation under reduced pressure, there was obtained a residue product that was shown by gas–liquid partition chromatographic analysis to contain 34 g (100% yield) of N-isopropyl-*p*-chloroaniline. Distillation of this residue gave a yellow oil (bp 100° (5 mm), mp 8–9°, $n^{32}D$ 1.5470) that was soluble in hexane, benzene, methanol, and carbon tetrachloride, insoluble in cold water, and very slightly soluble in hot water. A portion was redistilled for analysis.

Anal. Calcd for $C_9H_{12}NCl$: C, 63.71; H, 7.13; N, 8.26; Cl, 20.90. Found: C, 64.20; H, 7.19; N, 8.15; Cl, 20.21.

The hydrochloride was prepared by saturation of an ether solution with gaseous hydrogen chloride and melted at 159.5–160.5° after two recrystallizations from benzene.

Anal. Calcd for $C_9H_{13}NCl_2$: C, 52.44; H, 6.36; N, 6.79; Cl, 34.40. Found: C, 52.99; H, 6.49; N, 6.79; Cl, 33.98.

Registry No.—2,5-Dichloronitrobenzene, 89-61-2; N-isopropyl-*p*-chloroaniline, 770-40-1; N-isopropyl-*p*-chloroaniline hydrochloride, 826-22-2.

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Hydrogen Bonding in Fluoroaromatic Amines and Phenols

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Anomalous reactions of fluoroaromatic acids, amines, and phenols have been observed by us in solvents which act as hydrogen bond acceptors. The reasons