obtained from the reactions of the sulfenyl chlorides with 2,4,6-tri-*tert*-butylaniline were employed.

ESR Measurements. Radical **2a** was generated in benzene or hexane by the following procedures: (a) treatment of **1a** with lead dioxide and potassium carbonate; (b) UV photolysis of **1a** alone or in the presence of di-*tert*-butyl peroxide; (c) reaction of **1a** with di-*tert*-butyl diperoxyoxalate. The UV photolysis was carried out by using a JEOL JES-UV-1 apparatus. All ESR samples were carefully deoxygenated by three freeze–thaw–pump cycles. ESR spectra were recorded on a JEOL JES-ME-3X spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. Hyperfine splitting constants and *g* values were determined by comparison with those for Fremy's salt in K_2CO_3 aqueous solution (a_N, 13.09 G; *g*, 2.0057).

Crystal data for 2a: monoclinic, $a = 9.352$ (2) Å, $b = 14.315$ (5) Å, $c = 18.426$ (3) Å, $\beta = 93.23$ (2)°, $V = 2462.8$ Å, $Z = 4$, $d_{calcd} = 1.12$ g cm^{-3}. Systematic absences for $0k0$, $k = 2n + 1$ and $h0l$, $l = 2\ n + 1$ established the space group as $P2_1/c$. The cell dimensions were obtained by a least-squares refinement of 15 reflections on a Rigaku AFC5 apparatus equipped with a rotating-anode X-ray generator and using a graphite monochrometer (λ(Cu Kα) = 1.5418 Å).

Solution and Refinement of the Structure of 2a. A single crystal of approximate dimensions 0.35 × 0.15 × 0.10 mm was used for the $2\theta-\theta$ scan data collection ($2\theta \leq 128°$). Three reflections were monitored every 100 reflections, and the examination at the end of the data collection showed no sign of crystal decomposition. The data were corrected for Lorentz and polarization effects but not for absorption. Among the 4274 unique reflections collected, 1820 were considered to be observed at the $2.5\sigma(F_0)$ level.

The structure was solved with MULTAN 74[29] and was refined by block-diagonal least-squares methods. On the difference maps, 27 hydrogen atoms were found. Positions of the remaining hydrogen atoms were estimated from standard geometry. The final refinements, with anisotropic temperature factors for heavy atoms and isotropic temperature factors for hydrogen atoms, were 0.086 for R and 0.081 for R_w.[30] The final value of $[\sum w(|F_0| - |F_c|)^2(m - n)]^{1/2}$, where m is the number of observation and n is the number of variables, was 2.34. In these calculations anomalous dispersion corrections were applied to the scattering factors of S, O, and N atoms.[31]

Registry No. 1a, 70741-37-6; **2a**, 70741-30-9; **2b**, 62991-72-4; **2c**, 81536-47-2; 2,4,6-tri-*tert*-butylaniline, 961-38-6; 4-nitrobenzenesulfenyl chloride, 937-32-6; 4-chlorobenzenesulfenyl chloride, 933-01-7; 3,5-dichlorobenzenesulfenyl chloride, 74282-78-3.

Supplementary Material Available: Tables listing final values of atomic coordinations (Table II), anisotropic thermal parameters (Table III), hydrogen atom parameters (Table IV), bond distances (Table V), and bond angles (Table VI) and an ESR spectrum for **2a** (6 pages). Ordering information is given on any current masthead page. Lists of observed and calculated structure factor amplitudes for **2a** are available from the authors.

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(29) Main, P.; Liessinger, L.; Woolfson, M. M., Germain, G.; Declercq, T. P. "*MULTAN 74: A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*"; Universitys of York, England, and Louvain, Belgium, 1974.

(30) $R = \sum(|F_0| - |F_c|)/\sum|F_0|$; $R_w = [\sum w(|F_0| - |F_c|)^2/\sum w|F_0|^2]^{1/2}$.

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Reduction of Organic Halides by Water and Zinc Effected by Nickel

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A new method for the reduction of a variety of organic halides has been developed. The reaction takes place under mild conditions and employs water, zinc, and a catalytic amount of nickel chloride, triphenylphosphine, and iodide ion. The reduction of *p*-chloroanisole by this method was investigated in some detail. The reaction rate was first order in nickel and aryl halide but independent of the water concentration. A brief mechanism of this reaction is presented.

There are a number of methods for the hydrogenolysis of carbon–halogen bonds using transition-metal catalysts.[1] Recent attention has centered on the use of hydride sources in conjunction with transition metals to effect reduction of organic halides. Ashby and Lin reported that mixtures of $LiAlH_4$ with stoichiometric or catalytic amounts of $FeCl_2$, $CoCl_2$, $NiCl_2$, and $TiCl_3$ are effective in removal of halo or tosylate groups from organic compounds.[2] Bis(triphenylphosphine)nickel chloride has been demonstrated to be an efficient reduction catalyst when used in conjunction with sodium borohydride,[3] and palladium(0) with sodium methoxide,[4a] sodium formate,[4b] and triethylammonium formate[5] as hydride sources has been used in the reduction of aryl halides. All of the above methods suffer from some disadvantages. The use of powerful hydride sources such as $LiAlH_4$ and $NaBH_4$ leads to low selectivity, since these reagents are capable of reducing a number of other functional groups. Palladium is very expensive and does not react with as wide a variety of organic halides as nickel.

It is known that a mixture of nickel(II) salt, triphenylphosphine, and a reducing agent (such as zinc) in a dipolar aprotic solvent such as DMF will generate zero-valent tris(triphenylphosphine)nickel.[6,7] This highly air-sensitive reagent is able to oxidatively add a large number of organic halides[8-10] to form intermediates which

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Table I. Reduction of Various Organic Halides by Zinc, Water, and Ni°/I⁻

example	organic halide (RX)	solvent	reaction temp, °C	reaction time, h	% conversion to products	
					R-H	R-R
1[a]	*p*-chloroanisole	DMF/H_2O (25:1)	70	15	6	3
2	*p*-chloroanisole	DMF/H_2O (25:1)	70	2	96.8	2.5
3	*p*-chloroanisole	DMF/H_2O (50:1)	70	2	88.3	11.7
4	*p*-chloroanisole	DMF/D_2O (25:1)	70	1	68	24
5	*p*-chlorotoluene	DMF/H_2O (25:1)	70	2	92	8
6	chlorobenzene	DMF/H_2O (25:1)	70	2	66	36
7	chlorobenzene	methanol	60	20	99	
8	*p*-chlorobenzonitrile	DMF/H_2O (25:1)	70	1	90	10
9	*p*-chlorobenzyl alcohol	DMF/H_2O (25:1)	70	3	97	3
10	triphenylbromomethane	DMF/H_2O (50:1)	60	3	100	
11	1-bromoadamantane	DMF/H_2O (50:1)	60	3	95	5
12	cyclohexyl bromide	DMF/H_2O (25:1)	50	1	46	

[a] No iodide was added to this reaction.

are capable of undergoing a large number of useful reactions. One of these reactions (reduction) has been observed as a side reaction in reactions of aryl halides with Ni(0) in the presence of water or other protic compounds,[11,12] but until now reduction was never the major reaction or catalyzed by nickel.

We report a selective method for the reduction of a variety of organic halides (including aryl chlorides) under mild conditions which involves reaction of the organic halide with zinc, water, and a catalytic amount of nickel chloride, triphenylphosphine, and sodium iodide.

Results

As shown in Table I, example 1, when attempts were made to reduce aryl chlorides with water and zinc by using a catalytic amount of $NiCl_2$ and triphenylphosphine in DMF, only a small fraction of the starting material reacted. When a catalytic amount of sodium iodide (or bromide) was added to the reaction mixture, reduction occurred quickly and catalytically in nickel as shown in Table I for a variety of organic halides.

Although our primary interest was in the reduction of aryl chlorides, examples 10–12 demonstrate that the scope of the reaction extends beyond aryl and vinyl halides. While it may not be surprising that reduction takes place under our reaction conditions with triphenylbromomethane and 1-bromoadamantane, it is unexpected that this reaction is as efficient as it is with a typical alkyl halide such as cyclohexyl bromide. One might expect competing reactions such as β elimination and the formation of phosphonium salts to preclude the reduction process, but as example 12 illustrates, the reaction does not fail under these conditions, and cyclohexyl bromide is consumed rapidly at 50 °C to yield a mixture of 46% cyclohexane and 54% cyclohexene (the result of β-hydrogen elimination).

It should be noted that, in some cases, substantial amounts of coupled products were obtained. Even at low nickel concentrations coupling was still occurring, and as examples 2 and 3 show, the ratio of reduction to coupling was dependent upon the water concentration employed. It was possible to eliminate coupling completely by using alcohol as the solvent as shown in example 7, but the reaction was much slower. When D_2O was used in place of H_2O, mass spectral analysis of the anisole produced in example 4 revealed that it was monodeuterated, but the amount of coupling increased.

Table II. *p*-Chloroanisole Concentration as a Function of Time[a]

$100([PCA]_t/[PCA]_0)$	time, min	$100([PCA]_t/[PCA]_0)$	time, min
96.0	2	41.6	20
88.1	5	26.6	30
69.6	10	15.0	45
53.9	15	9.9	60

[a] $[PCA]_0 = 0.54$ M; $[H_2O]_0 = 1.09$ M; [Ni] = 0.033 M; [TPP] = 0.19 M $[I^-] = 0.22$ M; temperature = 60 °C. Regression analysis reveals that the data fit the expression $\hat{y} = 100.62 \times 10^{-0.041x}$; $R = 0.991$.

Table III. Effect of Various Reaction Parameters on the Reaction Rate of *p*-Chloroanisole at 60 °C[a]

[Ni]	$[H_2O]_0$	$[D_2O]_0$	$[I^-]$	$10^4 k_{obsd}$, sec^{-1}
0.033	1.09		0.22	−6.8
0.016	1.09		0.22	−3.3
0.033	2.14		0.22	−7.2
0.033		1.09	0.22	−7.3
0.033	1.09		0.11	−7.2
0.033		1.09	0.11	−7.5
0.033	0.55		0.11	−6.8
0.033	0.55		0.056	−4.9
0.033	0.55		0.029	−3.7

[a] In all experiments $[PCA]_0 = 0.54$ M.

Table IV. Ratio of Reduction to Coupling for PCA

anisole(initial)/DMB(initial)	$[H_2O]_0/[PCA]_0$	[Ni], M	k_r/k_c
2.13	2.0	0.016	1.1
1.93	2.0	0.033	0.97
1.13	1.0	0.033	1.1
5.3	4.0	0.033	1.3

As the data in Table II indicate, the reduction of *p*-chloroanisole (PCA) was found to be first order in *p*-chloroanisole concentration, but at very high ratios of PCA to Ni the reaction is pseudo zero order in aryl halide. By use of the observed first-order rate constants, the effects of various reaction parameters on the rate of reaction were evaluated (Table III).

Although water is not involved in the rate-determining step, the water concentration and whether D_2O or H_2O was used had a profound effect on the amount of coupling that was observed. In order to gain further insight into the mechanism of the reaction, we investigated the ratio of reduction to coupling as a function of various reaction parameters. The initial rate of reduction over the initial rate of coupling is adequately expressed by the ratio of

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Table V. Rate of Formation of Hydrogen Gas from Ni° and H_2O[a]

time, min	volume cm^3	rate, cm^3/min
5	3.6	0.72
15	10.5	0.70
25	17.5	0.70
35	24.7	0.71
85	59.5	0.70

[a] [Ni] = 0.067 M; [H_2O] = 2.1 M; [I^-] = 0.11 M; temperature = 60 °C.

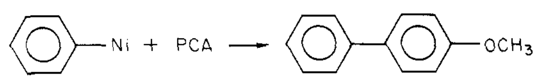
anisole to 4,4′-dimethoxybiphenyl (DMB) produced initially (less than 10% conversion). This ratio was evaluated for a number of reactions (Table IV). It was found that this ratio was independent of the nickel concentration, but it was directly proportional to the initial water to *p*-chloroanisole ratio. It should be mentioned that the amount of reduction relative to coupling increased throughout the course of the reactions.

Hydrogen gas was evolved during the reactions, but it was very minor. It appears that no hydrogen was produced before the aryl chloride was added, but gas evolution continued after all of the aryl chloride was consumed. The gas evolution was only noticeable at high nickel and water concentrations as shown in Table V. The hydrogen in that case was produced at a steady rate (1.6×10^{-5} M s^{-1}) and was not the result of reaction of zinc and water, for the same mixture without nickel did not produce hydrogen.

In most experiments small amounts of benzene were produced. This was the result of oxidative addition of triphenylphosphine[13] followed by hydrolysis of the resulting phenylnickel species. In addition, small amounts of 4-methoxybiphenyl were produced when *p*-chloroanisole was reacted. Once again, this product was the result of reaction of triphenylphosphine and arose from reaction of phenylnickel with PCA to yield the cross-coupled product.[14]

$$PPh_3 + Ni° \rightarrow PhNi\text{-}P(Ph)_2 \quad (1)$$

$$PhNi + H_2O \rightarrow C_6H_6 \quad (2)$$


(3)

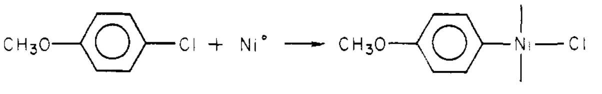
Discussion

Although the scope of this reaction has not been adequately assessed, it is evident from the examples presented that its utility is fairly extensive. Aside from competition from *β* elimination (with organic halides possessing *β*-hydrogen), coupling, and perhaps phosphonium salt formation[15] (which we have not observed), there appear to be few general limitations to the reaction. Even with alkyl halides possessing *β*-hydrogen it is evident that reduction will take place, and with some optimization (e.g., lower temperature and a protic solvent) the reduced product might be obtained in good to excellent yield. The reaction works well with aryl and vinyl[16] iodides, bromides, and chlorides, but fluorides are unreactive. With alkyl halides the chlorides react more slowly than the corresponding bromides and iodides, and once again the fluorides are unreactive. The only limitation presently known with certainty is that nitro substituents completely inhibit the reaction, and this appears to be a general limitation for all reactions involving low-valent nickel.[11,17-19]

The reduction of *p*-chloroanisole is first order in nickel and aryl halide. The overall rate of reaction is independent of the initial water concentration and is the same for D_2O and H_2O. Although iodide ion is required for the catalytic reaction to take place, at concentrations of iodide of 0.11 M or greater the reaction rate is independent of the iodide concentration. Even at concentrations lower than 0.11 there is not a linear dependence ($k = (1.85 \times 10^{-3})[I^-]^{0.457}$) as noted from the last three entries in Table III.

At iodide concentrations of 0.11 M or greater, the rate of reaction of *p*-chloroanisole is adequately expressed by the expression in eq 4. This suggets that the rate-determining step in the reaction is oxidative addition of PCA to some nickel species (presumably $Ni(PPh_3)_3$) to yield species I (eq 5), which undergoes further reaction to ultimately yield either reduced (anisole) or coupled (4,4′-dimethoxybiphenyl) product.

$$\text{rate} = k[\text{Ni}][\text{PCA}] \quad (4)$$


(5)

I

Since the ratio of the rate of anisole formation to the rate of dimethoxybiphenyl formation is independent of the nickel concentration, coupling and reduction must be of the same overall order in nickel. This ratio is dependent upon the initial water to PCA ratio; therefore, the rate of reduction over the rate of coupling is given by expression 6, where k_r is the rate constant for reduction and k_c is the rate constant for coupling. When k_r/k_c is evaluated by using this expression (Table IV), one notes that it is about 1 in all cases.

$$\frac{\text{rate of reduction}}{\text{rate of coupling}} = \frac{k_r[H_2O]}{k_c[\text{PCA}]} \quad (6)$$

Although hydrogen is probably formed by the mechanism in eq 7–9, nickel hydrides probably do not play a significant role in the formation of anisole. The reasons for this conclusion are as follows: (1) the rates of reduction and coupling are much faster than the rate of formation of hydrogen; (2) if oxidative addition of water were competing with oxidative addition of aryl halide, then before the aryl halide were added to the reaction mixture one would expect a great deal of nickel hydride to already be in solution, so that when aryl chloride were added, one would expect a great deal of reduction, which is not the case. It was observed that reduction increased steadily relative to coupling as the reaction progressed and was lowest at the beginning.

$$Ni° + H_2O \rightarrow NiH \quad (7)$$

$$2NiH \rightarrow Ni(H_2) + Ni^{II} \quad (8)$$

$$Ni(H_2) \rightarrow H_2 + Ni° \quad (9)$$

The simplest mechanism which accommodates the available data is shown in eq 10–13. The rate-determining

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[14] Nakamura, A.; Otsuka, S. *Tetrahedron Lett.* **1974**, 463.

[15] Cassar, L.; Foa, M. *J. Organomet. Chem.* **1974**, *74*, 75.

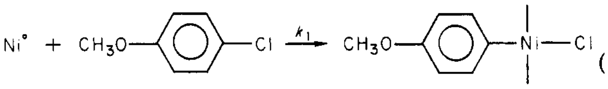
[16] Vinyl halides were reduced under our reaction conditions, but the volatility of the products prevented quantitative analysis, and the results, therefore, were not presented in Table I.

[17] Cassar, L.; Ferrar, S.; Foa, M. *Adv. Chem. Ser.* **1974**, *No. 132*, 252.

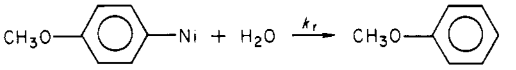
[18] Tsou, T. T.; Kochi, J. K. *J. Chem. Soc.* **1979**, *101*, 6319.

[19] Berman, R. S.; Kochi, J. K. *Inorg. Chem.* **1980**, *19*, 248.

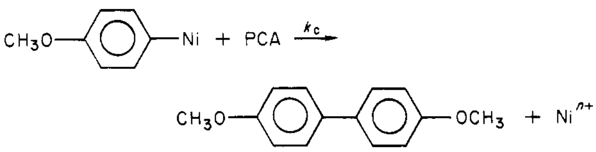
[20] Much of the recent work on coupling of aryl halides by nickel has implicated Ni(I) as a reactive intermediate; for example: Tsou, T. T.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 7547.



(10)



(11)



(1

$$Ni^{n+} + I^- + {}^n/_2Zn \rightarrow Ni^\circ + I^- + {}^n/_2Zn^{2+} \quad (13)$$

step is the oxidative additon of *p*-chloroanisole to Ni to yield an arylnickel species (eq 10). Either this nickel(II) speices or a nickel(I) species[20] then quickly reacts with either water (eq 11) or aryl chloride (eq 12) to yield anisole or dimethoxybiphenyl. From the current data it is unwarranted to speculate further on the more intimate details of the mechanism or the oxidation state of the nickel species involved in reactions 11 and 12.

The role of iodide in this reaction is presently unknown, but we believe that it plays a role in the reduction of nickel by zinc. It has been reported that iodide promotes another nickel-catalyzed reaction driven by zinc, and a similar conclusion was reached in that case.[7] In our case, iodide (or bromide) is required to make the process catalytic in nickel. In the absence of iodide, nickel hydroxide or nickel oxide is formed which is not reducible by zinc under the reaction conditions. In the presence of iodide this is either converted to nickel iodide or a nickelate salt, which is reducible by zinc, to regenerate the active catalyst (eq 13). This step is dependent upon the iodide concentration, and at relatively low iodide concentrations this step is slow enough that we begin to observe an iodide dependence for the reaction of *p*-chloroanisole.

Using a steady-state approximmation for $CH_3OC_6H_4Ni$, we can arrive at eq 14–16, which is what was arrived at

$$\frac{d[\text{anisole}]}{dt} = \frac{k_r k_1[Ni^\circ][PCA][H_2O]}{k_r[H_2O] + K_c[PCA]} \quad (14)$$

$$\frac{d[DMB]}{dt} = \frac{k_c k_1[Ni^\circ][PCA]^2}{k_r[H_2O] + k_c[PCA]} \quad (15)$$

$$\frac{\text{rate of anisole formation}}{\text{rate of DMB formation}} = \frac{k_r k_1[Ni^\circ][PCA][H_2O]}{k_c k_1[NI^\circ][PCA]^2} = \frac{k_r[H_2O]}{k_c[PCA]} \quad (16)$$

empirically from the data. The overall rate is given by eq 17 and 18, which once again give the expression derived empirically.

$$-\frac{d[PCA]}{dt} = \frac{d[DMB]}{dt} + \frac{d[\text{anisole}]}{dt} \quad (17)$$

$$-\frac{d[PCA]}{dt} = k_1[PCA][Ni^\circ] \quad (18)$$

Although this appears to be a reasonable mechanism for the reduction of *p*-chloroanisole, it is questionable whether it is a general mechanism for the reduction of organic halides by water and Ni°. As with other reactions involving Ni° and organic halides,[12] this reaction is very sensitive to substituent and solvent effects.

In conclusion, the general utility of this reaction to every bench chemist is emphasized. Although the reactions are run under an inert atmosphere, there is no need for special equipment. The reagents are all air stable, easily and safely manipulated, and relatively inexpensive. The method can be used to completely reduce polychlorinated aromatics. As an example, 1,2,4-trichlorobenzene was reduced to benzene in greater than 90% yield in four 4 h at 50 °C. The method can also be used to replace halogen with deuterium, and unlike the Grignard reaction, this can be accomplished easily with aryl chlorides such as chlorobenzene.

Experimental Section

Materials. The organic halides and the deuterium oxide were purchased from Aldrich and were used without further purification. The nickel chloride and triphenylphosphine were purchased from Alfa, and the zinc and DMF were obtained from Matheson Coleman and Bell and used as received.

General Procedure. A 50-mL two-necked flask equipped with a magnetic stirring bar was charged with 0.13 g (0.0010 mol) of $NiCl_2$, 1.5 g (0.0057 mol) of triphenylphosphine, 1.0 g (0.0067 mol) of NaI, and 2.0 g (0.030 mol) of zinc powder. The flask was sealed by placing a rubber serum cap over one neck of the flask and a stopcock adapter in the other. The vessel was connected to a double manifold vacuum line by rubber tubing and was evacuated and filled with nitrogen several times. Thirty milliliters of nitrogen-purged solvent was then introduced by syringe through the serum cap on the flask. This mixture was stirred magnetically for 15–30 min at 40–60 °C to form the red-brown catalyst. A mixture of 0.020 mol of the organic halide and 0.0047 mol of the internal standard was then added and reacted at the specified temperature for the specified time.

Mixed Solvents. The DMF–H_2O solvent mixtures listed in Table I were prepared on a volume to volume basis. The mixtures were placed in a sealed flask and purged with nitrogen for at least 0.5 h before use. When D_2O (Aldrich Gold Label) was used, then the DMF was dried over molecular sieves (3A) to give rid of residual H_2O prior to mixing with the D_2O.

Analysis. Identification of reaction products was made by gas chromatography by comparison of retention times to authentic samples. An HP5830 gas chromatograph equipped with a flame-ionization detector and a $^1/_8$ in. × 6 ft. stainless steel 3% OV-17 column was used. Toluene was used an an internal standard except for the reaction of *p*-chlorotoluene where anisole was used. In the kinetic runs, samples were periodically removed via syringe and quenched by dilution in acetone and exposure to air. The decrease in aryl halide concentration with time was used to determine the rate of reaction. Rate constants were determined by fitting the data with a computer curve-fitting program. Deuterium incorporation was determined by GC/MS.

Hydrogen Gas Measurement. A 50-mL two-necked flask charged with 0.26 g (0.0020 mol) of $NiCl_2$, 3.0 g (0.0115 mol) of triphenylphosphine, 0.50 g (0.0033 mol) of NaI, and 3.0 g (0.046 mol) of zinc was purged and connected to a 100-mL burret filled with water. Thirty milliliters of a 2.1 M water solution in DMF was added, and the catalyst formed. Thirty minutes later, 2.0 mL of *p*-chloroanisole was added and reacted at 60 °C. The hydrogen gas evolved after the aryl halide had been reduced was measured by water displacement from the buret by using a leveling bulb. There was no sign of hydrogen production in the 30 min prior to the addition of the *p*-chloroanisole. The gas produced was flammable, confirming that it was hydrogen.

Acknowledgment. I thank B. V. Watkins for her experimental assistance and Dr. D. Kemp for mass spectral analysis. I also thank Union Carbide Corp. for permission to publish this information.

Registry No. *p*-Chloroanisole, 623-12-1; chlorobenzene, 108-90-7; *p*-chlorobenzonitrile, 623-03-0; *p*-chlorobenzyl alcohol, 873-76-7; triphenylbromomethane, 596-43-0; 1-bromoadamantane, 768-90-1; cyclohexyl bromide, 108-85-0; zinc, 7440-66-6; water, 7732-18-5; nickel chloride, 7718-54-9; triphenylphosphine, 603-35-0; sodium iodide, 7681-82-5.