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Metallic Nickel-Catalyzed Reduction of Aryl Halides with Zinc Powder and Ethanol[1)]

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Synopsis. Aryl halides were exclusively reduced in ethanol to give the corresponding arenes in the presence of zinc powder and a catalytic amount of metallic nickel under nitrogen. The reduction was accelerated by adding excess zinc powder to the catalyst system. A probable reaction pathway is presented.

The hydrogenolysis of organic halides is an important reaction in organic synthesis.[2)] Recently, the reduction of aryl halides has been achieved by using new reducing agents and methods, e.g., alkali metals,[3)] $NaBH_4$–Cu,[4)] naphthalene radical anion,[5)] Pd/C–H_2,[6)] and Ni–ultrasonic irradiation.[7)] On the other hand, low-valent nickel complexes were capable of adding aryl halides to produce reductive coupling products.[8,9)]

In previous papers we reported that the hydrogen transfer reaction[10)] and hydrogenation[11)] were catalyzed by metallic nickel, which was easily prepared by the reaction of nickel bromide with zinc powder. In order to reduce aryl halides, a simple catalyst system using a catalytic amount of the metallic nickel, a large amount of zinc powder, and ethanol is reported in this paper. Compared with other methods, the advantages of this method are easy access to the reagents, simple operation, and no need for a hydrogen gas-cylinder. We present some observations that shed light on the reduction mechanism.

Experimental

Materials. The solvents were distilled by ordinary methods. The other reagents were commercially available and were used without purification.

General Procedure for the Reduction of Aryl Halides. To a 100 cm^3 flask fitted with a condenser, a septum inlet, and a magnetic stirring bar were added anhydrous nickel bromide (0.4 mmol), zinc powder (40 mmol), and ethanol (15 cm^3). After the atmosphere was replaced with nitrogen the catalyst was allowed to stand overnight at room temperature. To the mixture were added bromobenzene (12 mmol) and distilled water (120 mmol) in ethanol (5 cm^3). The mixture was stirred with a magnetic stirrer at 800 rpm, and then kept in a thermostated bath. The reaction was stopped by shaking with toluene and saturated aqueous NaCl; the toluene extract was then subjected to GLC analysis.

Analysis. The gas chromatographic analyses were made by using a Shimadzu GC-8A apparatus with a TC detector and helium carrier gas using a 3 m column of PEG 20M, Silicone DC200, Silicone DC710, and Molecular Sieve 13X.

Results and Discussion

In the presence of metallic nickel and zinc powder iodobenzene was quantitatively reduced to give benzene in *N,N*-dimethylformamide (DMF) under an atmospheric pressure of hydrogen. The reduction of iodobenzene was carried out in ethanol under nitrogen, as well as in DMF under hydrogen. Table 1 shows that ethanol (the conversion of iodobenzene, 92% after 24 h) was the best solvent among such protic solvents as methanol (50%), 1-propanol (38%), 2-propanol (55%), and water (25%) for the reduction; ethanol behaved like a hydrogen source. Metallic nickel could not be prepared in tetrahydrofuran and toluene. It was reported that precipitated nickel (Urushibara nickel) could be prepared in the reaction of nickel halide with zinc powder in water, and Urushibara nickel-N was made by refluxing that precipitated nickel in alcohol.[12)] They are precipitates, and the metallic nickel in this report is a colloidal particle. As shown in Table 2, no reduction took place in the absence of metallic nickel; the reduction was accelerated by adding excess zinc powder to the catalyst system. Zinc powder acted as both a reductant and a base. Instead of using excess zinc powder, the addition of triethylamine, quinoline, triphenylphosphine, or potassium iodide to the catalyst system was ineffective for the reduction. A modification of the

Table 1. Effect of Solvents on the Reduction of Iodobenzene[a)]

Solvent	Conv./%	Yield of benzene/%
DMF[b)]	98	90
EtOH	92	90
i-PrOH	55	49
MeOH	50	46
n-PrOH	38	35
H_2O	25	14

a) Iodobenzene 12 mmol, $NiBr_2$ 0.4 mmol, Zn 40 mmol, solvent 20 cm^3, temp 60 °C, time 24 h, under N_2. b) Under H_2.

Table 2. Acceleration of the Reduction of Iodobenzene with Zinc Powder[a)]

Zn/mmol	Time/h	Conv./%
0	24	0
1.2	6	16
4	6	24
12	6	40
24	6	58
40	6	82
40[b)]	24	0
60	6	85
80	6	86

a) Iodobenzene 4 mmol, $NiBr_2$ 0.4 mmol, EtOH 20 cm^3, temp 60 °C, under N_2. b) In the absence of $NiBr_2$.

Table 3. Effect of H_2O on the Reduction of Bromobenzene[a)]

Added H_2O/mmol	Yield of benzene/%
0	47
60	62
120	72
360	62
600	38

a) Bromobenzene 12 mmol, $NiBr_2$, 0.4 mmol, Zn 40 mmol, EtOH 20 cm^3, temp 60 °C, time 36 h, under N_2.

Table 4. Reduction of Various Aryl Halides Catalyzed by Metallic Nickel in Ethanol[a)]

Aryl halide	Additive[b)]	Time/h	Yield of arene/%
PhI	None	24	90
PhBr	None	36	47
PhBr	H_2O	36	72
PhCl	None	36	35
PhCl	H_2O	36	47
p-$CH_3C_6H_4Br$	H_2O	48	93
p-$CH_3OC_6H_4Br$	H_2O	48	93
p-HOC_6H_4Br	H_2O	48	79
1-$C_{10}H_7Br$	H_2O	48	89
p-BrC_6H_4Cl	H_2O	48	11+53[c)]
p-$CH_3COC_6H_4Cl$	H_2O	48	57
$PhCH_2Cl$	None	0.5	56[d)]+32[e)]

a) Aryl halide 12 mmol, $NiBr_2$ 0.4 mmol, Zn 40 mmol, EtOH 20 cm^3, temp 60 °C, under N_2. b) H_2O (120 mmol) was added. c) Chlorobenzene. d) Toluene. e) Bibenzyl.

procedure was made for reducing less reactive halides. Bromobenzenes were reduced in order to provide the corresponding benzenes in good yields by the addition of an optimum amount of water. An optimized amount of added water was necessarily for the reduction, and a large amount of water deactivated the catalyst (Table 3). The temperature near 60 °C was suitable for the reduction. The reduction of aryl halides is listed in Table 4. No coupling products were detected in the reduction of aryl halides, except for benzyl halides.

One possible pathway for the catalytic reduction of aryl halides is presented in the following equations, 1—6:

$$NiBr_2 + Zn \longrightarrow Ni^0 + ZnBr_2 \tag{1}$$

$$Ni^0 + EtOH \longrightarrow HNi(OEt) \tag{2}$$

$$2HNi(OEt) + Zn \longrightarrow H_2 + 2Ni^0 + Zn(OEt)_2 \tag{3}$$

$$ArX + H_2 \xrightarrow{Ni^0} ArH + HX \tag{4}$$

$$2HX + Zn(OEt)_2 \longrightarrow ZnX_2 + 2EtOH \tag{5}$$

$$2HX + Zn \longrightarrow ZnX_2 + H_2 \tag{6}$$

An active species for the catalytic hydrogenolysis of aryl halides is metallic nickel (Ni^0) prepared by reducing nickel(II) bromide with zinc powder (Eq. 1). A gas buret was connected to the reaction system; the generation of hydrogen was confirmed by gas chromatography, suggesting that ethanol is not only a solvent, but also a hydrogen-donor,[13—15)] as is shown in Eqs. 2 and 3. It was reported that metallic nickel catalyzed the conversion of 2-propanol to acetone and H_2.[16)] In our experiments other paths for hydrogen generation were negligible. This is because there were only small detectable amounts of acetaldehyde (gas) and hydrazone derived from the reaction of 2,4-dinitrophenylhydrazine with the reduction reaction mixture. Aryl halide is catalytically hydrogenated to give arene on the reacion sites of Ni^0 via an oxidative adduct (ArNiX). The generated hydrogen halide was caught by a zinc compound and zinc powder (Eqs. 5 and 6).

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