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Ultrasounds in Synthetic Reactions. III. Reduction of Organic Halides with Nickel(II) Chloride–Zinc–Water[1]

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Synopsis. The reductive dehalogenation of aryl chlorides as well as other organic halides was facilitated with nickel(II) chloride–zinc–water in hexamethylphosphoric triamide irradiated with ultrasound.

There are a number of methods for the reduction of alkyl or aryl halides using transition metals.[2] But aryl chlorides are rather resistant to the reduction. It is known that low valent nickel complexes *in situ* generated from nickel(II) salt–zinc powder-triphenylphosphine(TPP) in *N*,*N*-dimethylformamide(DMF) are able to oxidatively add a large number of organic halides to yield coupling products.[3,4] The reduction of aryl halides also proceeds with a similar reagent: zinc–water–a catalytic amount of nickel(II) chloride–TPP–sodium iodide in DMF.[5] But the work-up procedure is frequently troublesome due to the presence of TPP. Recently Takagi and Hayama[6] reported that the Ullmann type coupling reaction could be effectively achieved by means of *in situ*-generated nickel(0) species in hexamethylphosphoric triamide(HMPA) without TPP.

We wish to report a convenient method for the reduction of aryl halides, especially aryl chlorides, under mild conditions; aryl halides, zinc, water, nickel(II) chloride, and sodium iodide are sonicated in HMPA to yield the dehalogenated products. Ultrasound-irradiation is known to accelerate a variety of organic reactions, particularly those involving metals.[1,7]

Experimental

Materials and Analysis. HMPA was dried over Molecular Sieves 5A, distilled under nitrogen *in vacuo*, and stored over Molecular Sieves 5A. All other reagents were used as obtained commercially. Reaction products were identified by the comparison of retention times in GLC and mass spectra (JEOL D 300 mass spectrometer) with those of the authentic samples. The yields of products were determined by GLC (Shimadzu GC 3AH using a Silicone GE SE-52 20 wt% on Chromosorb W AW, or FFAP 10 wt% on Chromosorb W AW DMCS column).

General Procedures for Reduction Reactions. To a 50 cm^3 3-necked flask, which contained 0.98 g(15 mmol) of zinc powder, 1.30 g(10 mmol) of nickel chloride, and 0.90 g(6 mmol) of chlorobenzene, 0.3 cm^3(16.7 mmol) of water, 0.200 g of toluene(an internal standard for GLC analysis) and 15 cm^3 of HMPA were added under nitrogen atmosphere and the mixture was irradiated with ultrasound(53 W, 41 kHz) at 60 °C. The yields of products were determined by GLC.

Results and Discussion

The reactions of aryl halides with zinc, nickel chloride, water and sodium iodide were carried out in HMPA at 60 °C under ultrasound-irradiation.

$$\text{R-X} \xrightarrow[\text{H}_2\text{O, NaI, HMPA, 60 °C}]{\text{NiCl}_2\text{, Zn, Ultrasound}} \text{R-H}$$

Several reaction parameters were examined and the results are shown in Table 1. The ease of reduction of halobenzenes decreased in the order: iodobenzene>bromobenzene>chlorobenzene(runs 1,2, and 4), which is consistent with the proposed oxidative addition mechanism.[4,5,6,8] Iodobenzene and bromobenzene gave a small amount of the coupling product, biphenyl, whereas chlorobenzene and other aryl chlorides afforded only a trace amount of the coupling byproducts. Iodobenzene could be reduced without the coupling byproduct when cobalt(II) acetate or iron(II) sulfate was used instead of nickel(II) chloride(runs 12 and 13). The higher selectivity in the reduction compared with that using TPP[5] is favorable as a synthetic method. The increasing amount of sodium iodide and nickel chloride increased the yield(runs 3—7). The role of sodium iodide is not clear, but it may promote the reduction of nickel chloride by zinc[4,5] and/or the reduction of an arylnickel intermediate.[6] The yield decreased when the reduction was carried out in DMF. The reduction was not observed in tetrahydro-

Table 1. Effect of various reaction parameters on the reaction of halobenzenes[a]

Run	Ph-X	NiCl_2 / mmol	NaI / mmol	Reaction time/h	Yield of PhH/%
1	Ph-I	10	6	0.5	87[g]
2	Ph-Br	10	6	1	91[h]
3	Ph-Cl	10	0	2	64
4	Ph-Cl	10	6	2	81
5	Ph-Cl	10	12	2	93
6	Ph-Cl	5	6	2	54
7	Ph-Cl	7.5	6	2	69
8	Ph-Br	5	6	4	81
9	Ph-Br[b]	5	6	4	64
10	Ph-Br[c]	5	6	4	56
11	Ph-Br[d]	5	6	4	0
12	Ph-I[e]		8	4	93
13	Ph-I[f]		6	4	92

a) Reaction conditions: Ph-X, 5 mmol; Zn, 15 mmol; H_2O, 0.3 cm^3; HMPA 15 cm^3; 60 °C under sonication. b) Solvent: DMF 15 cm^3. c) Solvent: THF 13 cm^3 and HMPA 2 cm^3. d) Solvent: THF 15 cm^3. e) $\text{Co(OOCCH}_3)_2$(7.5 mmol) instead of NiCl_2. f) $\text{Fe}_2\text{(SO}_4)_3$(2.5 mmol) instead of NiCl_2. g) Biphenyl yield, 13%. h) Biphenyl yield, 7%.

TABLE 2. REDUCTION OF VARIOUS ORGANIC HALIDES[a]

Run	Organic halide	$\mathrm{NiCl_2}$ mmol	NaI mmol	Reaction time/h	Yield %
14	$\mathrm{C_6H_5Cl}$	10	6	4	95
15	p-$\mathrm{MeC_6H_4Cl}$	15	6	3	100
16	p-$\mathrm{MeOC_6H_4Cl}$	15	6	3	86
17	p-$\mathrm{HOCH_2C_6H_4Cl}$	10	6	1	15
18	p-$\mathrm{NCC_6H_4Cl}$	10	6	1	22
19	1-$\mathrm{C_{10}H_7Cl}$[b]	10	6	8	100
20	$\mathrm{C_6H_5CH_2Cl}$	10	6	1	47[c]
21	n-$\mathrm{C_7H_{15}Cl}$	10	6	1	85
22	$\mathrm{C_6H_{11}Br}$[d]	10	6	1	82

a) See Table 1 for reaction conditions. b) 1-Chloronaphthalene. c) The yield of bibenzyl was 50%. d) Bromocyclohexane.

furan(THF), but proceeded by the addition of a small amount of HMPA to THF(runs 10 and 11). Although the reaction proceeded with ordinary stirring, the ultrasonic irradiation could increase the rate of reaction by 20—50%.

The reduction of various aryl chlorides as well as alkyl halides proceeded smoothly in rather short reaction time to give the reduction products in very high yields with the exception of p-chlorobenzyl alcohol and p-chlorobenzonitrile, where the reaction stopped within an hour and the starting materials were recovered. These results are shown in Table 2.

In conclusion, the present method is a very convenient procedure for the reduction of organic halides, especially aryl chlorides.

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