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SYNTHESIS OF ARYL IODIDES FROM ARYL HALIDES AND POTASSIUM IODIDE BY MEANS OF NICKEL CATALYST[1)]

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Facile synthesis of aryl iodides from aryl halides was reported. $NiBr_2$-Zn catalyzed the halogen exchange reaction of aryl bromides with potassium iodide under mild conditions. At elevated temperatures, $NiBr_2$-PBu_3 was an effective catalyst.

For Finkelstein-type halogen exchange reaction of nonactivated aryl halides, copper(I) salts are generally used as the source of halide ions.[2)] The reaction is, however, of limited synthetic importance, because an aryl iodide, which is relatively expensive and versatile, is not accessible by the reaction. In the course of our

$$\mathrm{ArI\ (or\ Br) + CuBr\ (or\ Cl)} \xrightleftharpoons{\;/\!/\;} \mathrm{ArBr\ (or\ Cl) + CuI\ (or\ Br)}$$

study of a nucleophilic displacement catalyzed by transition metal, we have found that nickel-phosphine complexes are effective for that kind of exchange reaction.[3,4)]

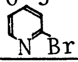
$$\mathrm{ArBr\ (or\ Cl) + KI} \xrightarrow{\text{Ni catalyst}} \mathrm{ArI + KBr\ (or\ Cl)}$$

In this paper, we will communicate facile synthesis of aryl iodides from aryl halides and potassium iodide by means of nickel catalysts.

As shown in Table 1, the catalyst composed of nickel bromide and zinc powder as a reducing agent is very effective for the exchange of aryl bromides with an iodide ion in HMPA (Run 1-4). $Ni(PPh_3)_3$[5)] or $Ni(CO)_2(PPh_3)_2$ has little activity under the similar condition. The reaction is reversible but goes nearly to the completion by the use of a relatively small excess of potassium iodide (2.5 equiv.). By-products such as biaryls (coupling product) and, in lesser amount, reduced materials (dehaloprotonation product) are also formed. The addition of PBu_3 suppresses the side reaction at the expense of the rate of reaction (Run 5). Other ligands such as PEt_3, PPh_3, and $P(O\underset{Ph}{-\bigcirc})_3$ are less effective than PBu_3.

At elevated temperatures, no reducing agents are necessary for the catalytic reaction.[6)] The presence of a donar ligand such as PBu_3, PEt_3, or NBu_3 contributes to a better yield but not essential for the reaction (Run 6, 7). As the added ligand is easily separated from the reaction mixture by the extraction with conc. HCl, this is a facile and useful method for preparation of thermally stable aryl iodides. For example, a mixture of p-bromoacetophenone (995 mg, 5 mmol), KI (4.15 g, 25 mmol), $NiBr_2$ (26 mg, 0.12 mmol), PBu_3 (0.12 ml, 0.25 mmol), and DMF (5 ml) was heated to reflux for 2 hrs with stirring under nitrogen. The reaction mixture was then shaken with pentane-benzene-water. The organic layer was washed successively with water, conc. HCl, aqueous solution of $Na_2S_2O_7$, and water, and dried over

Table 1. Synthesis of Aryl iodides

Run	R-X	Temp. (°C)	Time (h)	RX/Ni (mole ratio)	Additive	Conversion (%)[a]	Yield R-I (%)[a]	Yield R-R (%)[a]
1	C_6H_5-Br	50	1.5	50	Zn	96	77	15
2	p-$CH_3OC_6H_4$-Br	50	1.5	25	Zn	96	78	16
3	p-$CH_3COC_6H_4$-Br	50	1.5	50	Zn	99	76	22
4	p-ClC_6H_4-Br	50	1.5	50	Zn	92	81[b]	9[b]
5	C_6H_5-Br	50	3	50	PBu_3+Zn	80	74	5
6	C_6H_5-Br	140	12	40	PBu_3	93	89	0
7	C_6H_5-Br	150	24	40	-	38	34	0
8	C_6H_5-Cl	150	12	40	PBu_3	-[c]	13	0
9		153	12	25	PBu_3	69	42	0

Reaction conditions: for runs 1-5, aryl bromide, 0.5 mmol; KI, 1.25 mmol; $NiBr_2$, 0.01-0.02 mmol (0.059-0.118 ml of 0.17 M-DMF solution); Zn, 0.085 mmol; PBu_3, 0.02 mmol (when used); HMPA, 0.44 ml; under N_2. For runs 6-9, aryl halides, 1 mmol; KI, 3 mmol; $NiBr_2$, 0.025-0.04 mmol; PBu_3, 0.05-0.08 mmol; DMF, 1 ml; under N_2.

a) Yield based on aryl halide used. Values determined by GLC analysis.

b) R= 4-ClC_6H_4. p-Diiodobenzene was present ($<1\%$). c) Not determined.

Na_2SO_4. Evaporation of solvent gave 1.16 g of crude p-iodoacetophenone (95%). Recrystallization from EtOH gave 0.80 g of pure iodide (66%). Mp 83.5-84°C (lit,[7] 84°C). Aryl chloride and heteroaromatic bromide are also subject to the exchange, but the reaction is incomplete at the present conditions (Run 8, 9).

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