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RHODIUM CATALYZED REDUCTION OF ARYL IODIDES WITH A MODEL OF NAD(P)H[1)]

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Aryl iodides are reduced to the corresponding arenes with a model of NAD(P)H, 1-benzyl-1,4-dihidronicotinamide (BNAH), in the presence of a catalytic amount of rhodium complex. Nitro, carbonyl, and ester functions are inert under the condition.

Utility of a model of NAD(P)H as a reducing agent has been scarecely developed mainly because of its poor reducing ability. Recently, however, it was reported that the rhodium-catalyzed reduction of allylic acetates to the corresponding alkenes with a model of NAD(P)H proceeded quantitatively,[2)] which indicates that a model of NAD(P)H is able to be a synthetically useful reducing agent with the aid of an appropriate catalyst such as a transition metal. We found that aryl iodides (ArI) are reduced to the corresponding arenes (ArH) with 1-benzyl-1,4-dihydronicotinamide (BNAH) in high yields in the presence of 0.1 equivalent of $RhCl(Ph_3P)_3$ in acetonitrile in the dark at 343 K, whereas nitro, carbonyl, and ester functions are inert under the condition. Although several methods have been reported[3-10)] for the reduction of aryl halides, some of them require drastic conditions[3)] and others are accompanied by undesirable reactions of other functional groups, *i. e.*, either reductions of nitro and carbonyl functions[6)] or hydrolysis of ester function.[4,7)] Our method avoids these disadvantages.

The results and conditions of the reactions are listed in Table 1. The features of the reactions are summarized as below: First, the conversions of substrates and the yields of products are excellent in aryl iodides with an electron-withdrawing substituent (runs 1, 3, 4, and 5). The aryl iodides with an electron-releasing substituent give reduction products in lower but satisfactory yields (runs 6 and 7). Second, nitro, carbonyl, and ester functions show practically complete inertness against the reduction (runs 1, 3, and 4). Interestingly, the use of palladium complex in place of rhodium complex afforded a coupling product, biaryl, in comparable yield to that of the reduction product (run 2). A similar result has been reported in the palladium-catalyzed reduction with sodium methoxide.[7)] Finally, the present method is also applicable to the reduction of a vinyl halide (run 9).

We believe that this type of the reactions possesses synthetic utility, since BNAH is easily synthesized and stable against light and air. Application to other halides, especially to vinyl halides, and mechanistic aspect of the reaction will be presented elsewhere.

Table 1. Reduction of Aryl Halides with BNAH[a]

Run	Aryl Halide	Time/h	Conversion/%	Yield of ArH/%[b]
1	*p*-Iodonitrobenzene	3	100	100
2	*p*-Iodonitrobenzene[c]	3	100	48[d]
3	*p*-Iodoacetophenone	3	100	91
4	Methyl *p*-iodobenzoate	6	95	95[e]
5	*p*-Bromoiodobenzene	20	91	100[f]
6	*p*-Iodoaniline	23	72	80
7	*p*-Iodotoluene	23	60	80
8	3-Bromoquinoline	23	28	100[g]
9	β-Bromostyrene	1.5	100	90[h]

[a] A 343 K in the dark under an N_2 atmosphere. Aryl halide; 5.0×10^{-2} mmol, $RhCl(Ph_3P)_3$; 5.0×10^{-3} mmol, and BNAH; 1.0×10^{-1} mmol in 1 ml of CH_3CN. [b] Based on the amounts of aryl halides consumed. Determined on VPC using an internal standard. [c] 1.0×10^{-2} mmol of $Pd(OAc)_2$ was used in place of $RhCl(Ph_3P)_3$. [d] *p*,*p*'-Dinitrobiphenyl was detected (41%). [e] Traces of benzoic acid and *p*-iodobenzoic acid were detected on VPC. [f] The yield of bromobenzene. Iodobenzene was not detected on VPC. [g] The yield of quinoline. [h] The yield of styrene.

References

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