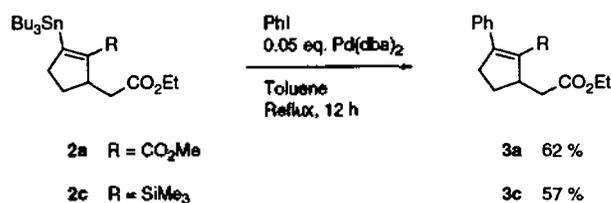


Scheme 1.



Scheme 2.

to the π -system) is inductively influenced by both α -carbonyl and β -stannyl substituents and reactive towards both electron-poor and electron-rich double bonds. This behavior is not surprising in view of the results on (π -*exo*) type cyclizations of α -carbonyl- β -stannylvinyl radicals generated from propiolates and acetylenic ketones.⁵

The substrate **1c** was converted into the product **2c** in good yield, but the substrate **1d** was recovered in high yield under identical reaction conditions. From the results, we can surmise that α -silyl- β -stannylvinyl radicals [B] are nucleophilic in nature (with high SOMO energy) and react only with electron-deficient double bonds.

The above reactions afford cyclopentene derivatives with multiple substituents, useful for further manipulations. For example, palladium-catalyzed arylation of **2a** and **2c** afforded products **3a** and **3c** in reasonable yields (Scheme 2).

The reactivity profile of substituted vinyl radicals delineated here for (π -*endo*) type cyclizations will be used as a guide in cyclopentenoid synthesis.

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Facile Reduction of Aryl Halides with Borohydride Exchange Resin-Nickel Acetate

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The combination of sodium borohydride with transition metal salts exhibits enhanced reducing abilities when compared with sodium borohydride itself.¹ Thus NaBH₄-Pd/C² or NaBH₄-PdCl₂^{3,4} and more recently NaBH₄-CuCl₂⁵ have been reported to be useful for the dehalogenation of aryl halides in alcoholic solvents. NaBH₄-[Ni(O)(Ph₃P)₃] in DMF⁶ was also reported to be effective in the hydrogenolysis of aryl bromides.

Sometime ago, borohydride exchange resin (BER) was introduced by Gibson and Baily⁷ and we reported BER is an interesting chemoselective reducing agent for carbonyl compounds in alcoholic solvents^{8,9} and several other significant applications were also presented.¹⁰ Recently we have found that BER is much more stable than NaBH₄ in methanol in the presence of nickel boride, and BER-Ni(OAc)₂ in methanol proved to be an excellent reduction system for nitro compounds.¹¹ We also found that both 4-bromonitrobenzene and 4-chloronitrobenzene were quantitatively reduced to aniline in methanol in 1 h at room temperature. This prompted us to explore the generality of the dehalogenation with BER-Ni(OAc)₂. In this paper, we wish to report that BER-Ni(OAc)₂ system is capable of reducing aryl halides in excellent yield with good selectivity.

The procedure is very simple. Aryl halide was added to the mixture of BER (5 mol equiv) and Ni(OAc)₂ (0.5 mol equiv) in methanol. The reaction mixture was then stirred at room temperature or under reflux for 1-3 h. After the reaction was completed, the resin was filtered and methanol was evaporated under reduced pressure to give the nearly pure product. The product was purified by silica gel column

Table 1. Reduction of Aryl Halides with BER-Ni(OAc)₂ in Methanol at Room Temperature

Entry	Aryl halide	Product	Time (h)	Yield(%) ^a
1			3	0
2			1	98
3			1	100
4			1	97
5			3	40, 85 ^b
6			3	74, 82 ^{d,e}
7			1	94
8			1	94(87) ^f
9			3	95
10			3	78(92) ^f
11			1	96 ^f
12			3	33, 89 ^g
13			1	95
14			1	(81)
15			1	98(93)
16			1	93(85) ^f
17			1	(92)
18			3	64, 99 ^f
19			3	83 ^h , 97 ⁱ
20			3	80 ^j , 91(84) ^k

^aGC yields for small scale reduction (1 mmol). Isolated yields in parenthesis for preparative scale reduction (10 mmol). ^bReduction was carried out under reflux for 1 h using 10 mmol equiv of BER. ^{c,d}Tetrahydronaphthalene (15%^c and 18%^d) was also produced. ^eReduction was carried out under reflux for 1 h. ^fToluene (3-6%) was also produced. ^gBenzyl amine (4%) was also produced. ^h2-Methoxypyridine (15%) was also produced. ⁱReduction was carried out at 15°C using 10 mol equiv of BER. ^jTetrahydroquinoline (19%) was also produced. ^kReduction was carried out under reflux for 1 h using 0.1 mol equiv of Ni(OAc)₂ and tetrahydroquinoline (9%) was also produced.

chromatography if necessary. In the case of 2-chlorobenzoic acid, sodium 2-chlorobenzoate was reduced to sodium benzoate,¹¹ and the benzoic acid was obtained on acidification. The results are summarized in Table 1.

As shown in Table 1, BER-Ni(OAc)₂ system did not reduce fluorobenzene (entry 1) as expected; however, rapidly reduced chloro-, bromo- and iodobenzene (entries 2, 3, and 4) in excellent yields at room temperature. However, 2,6-dimethylchlorobenzene was reduced very slowly (40% in 3 h) apparently due to the steric effect. The yield was improved to 85% by heating under reflux (entry 5). BER-Ni(OAc)₂ system tolerated hydroxymethyl, phenol, methoxy, acetal, carboxylic acid, ester, cyano, and amino groups (entries 8, 9, 10, 12, 14, 15, 16 and 18). However, small amounts (3-6%) of toluene were produced due to hydrogenolysis of benzylic groups (entries 8, 11 and 12). On the other hand, the reduction of 1-chloronaphthalene and 3-bromoquinoline (entries 6 and 20) produced considerable amounts of the corresponding tetrahydro derivatives along with the expected products, naphthalene (82%) and quinoline (91%). In the case of 2-bromopyridine (entry 19), pyridine (83%) was obtained accompanying with 2-methoxypyridine (13%) in 3 h at standard condition; however, by carrying out the reduction at 15°C using 10 mol equiv of BER, a quantitative yield of pyridine (97%) could be obtained.

In contrast to the present system, with NaBH₄-Pd/C² or NaBH₄-PdCl₂^{3,4}, either the reaction had to be carried out under basic condition or the yields were moderate (50-80%), and NaBH₄-Cu₂Cl₂⁵ system could not reduce chlorobenzene and gave poor yields on debromination of aryl bromides. NaBH₄-[Ni(0)(Ph₃P)₃] in DMF⁶ required a prolonged reaction time at elevated temperature (70°C) and gave a poor yield with chlorobenzene. BER-Ni(OAc)₂ system has another significant advantage over other NaBH₄-transition metal salt systems. Thus simple separation of BER-Ni₂B by filtration gives the methanol solution of products essentially free from boron moiety.⁷ Just in one case (entry 13), we had a difficulty to separate the reduction product of 2-chlorobenzoic acid from the resin. This was overcome by reducing its sodium salts.

In conclusion, BER-Ni(OAc)₂ system in methanol is a reagent of choice for the reduction of aryl halides because of its excellent yield, very good selectivity and simple procedure.

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