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A New Coupling Reaction of Alkyl Iodides with Electron Deficient Alkenes Using Nickel Boride (cat.)−Borohydride Exchange Resin in Methanol

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The radical addition reaction of alkyl iodides with α,*β*-unsaturated esters, nitriles, and ketones proceeds in moderate to excellent yields (50−95%) using $Ni(OAc)_2$ (0.05−0.2 equiv)−BER (3−5 equiv) in methanol in 1−9 h at room temperature or at 65 °C. Nickel boride on borohydride exchange resin (BER) is a good alternative reagent to tributyltin hydride for the coupling of alkyl iodides with the electron deficient alkenes in methanol. Compared with tributyltin hydride method, this method has an advantage of simple workup, since nickel boride−BER can be removed readily by filtration.

Introduction

The carbon−carbon bond formation *via* radical addition or radical cyclization of alkyl halides with alkenes is one of important steps in the construction of organic molecules and has been successfully carried out using tributyltin hydride.[1] However, this reaction requires high temperature initiators or photolytic conditions, and although simpler methods have been devised,[2] the purification of the products from tributyltin halides is troublesome.[1c,2] Recently, we have found strong evidence suggesting that the reduction of alkyl halides with borohydride exchange resin (BER)−nickel boride proceeds *via* a radical reaction: Thus, BER−nickel boride (cat.) not only readily reduces secondary and tertiary bromides in rates comparable with the case of primary bromides, but also gives a coupled product, 2,3-diphenylbutane (30%), besides the expected reduction product ethylbenzene (70%), in the reaction with α-phenethyl bromide.[3] We also observed a 38% yield of methylcyclopentane from the reaction of 5-hexenyl iodide with nickel boride (cat.)−BER. We report here a new radical coupling reaction of alkyl iodides with α,*β*-unsaturated esters,[4] nitriles, and ketones using nickel boride (cat.)−BER in methanol.

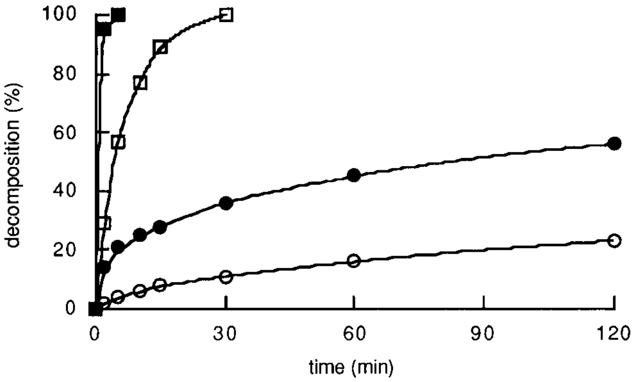
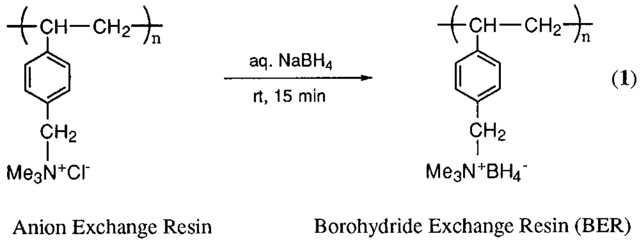


Figure 1. Rate of decomposition of BER (circle) and $NaBH_4$ (square) at methanol in the presence (black) and absence (white) of $Ni(OAc)_2$ (0.02 equiv).



(**1**)

Results and Discussion

Preparation and Stability of BER. BER can be readily prepared by treating a chloride form anion-exchange resin (Amberlite IRA 400) with aqueous $NaBH_4$ solution (**1**). The borohydride form anion exchange resin was dried *in vacuo*, and the dried resin was analyzed for borohydride content by hydrogen evolution on acidification with HCl using gas burette. The borohydride content of BER is usually 3 mmol/g of dry BER, and the BER is stable for more than 6 weeks if kept under nitrogen in a refrigerator. The stability of BER in the absence and presence of nickel boride was studied in methanol and compared with that of $NaBH_4$. As shown in Figure 1, BER decomposes much more slowly than $NaBH_4$ in methanol. Particularly in the presence of $Ni(OAc)_2$ (0.02 equiv) at room temperature, nearly 50% of BER remained active after 1 h, in contrast to the complete decomposition of $NaBH_4$ in a few minutes.

Coupling Reactions Using Nickel Boride−BER. First, we tested the coupling reactions of alkyl bromides and alkyl iodides with representative alkenes such as 1-octene, styrene, ethyl acrylate and crotononitrile and found that only the coupling of alkyl iodides with electron deficient alkenes could be carried out successfully. Then the coupling reactions of representative alkyl iodides with α,*β*-unsaturated esters, nitriles, and ketones were studied in more detail. Unlike the tin hydride method, the double bonds of these α,*β*-unsaturated compounds are readily hydrogenated with nickel boride−BER in methanol (*β*-substituted α,*β*-unsaturated compounds are much more

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[1] (a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986. (b) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 553. (c) Neumann, W. P. *Synthesis* **1987**, 665. (d) Curran, D. P. Radical Addition Reaction; Radical Cyclization and Sequential Radical Reaction. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: New York, 1991; Vol. 4, pp 715−831.

[2] (a) Weinshenker, N. M.; Crosby, G. A.; Wong, J. Y. *J. Org. Chem.* **1975**, *40*, 1966. (b) Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449. (c) Schumann, H.; Pachaly, B. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1043. (d) Curran, D. P.; Chang, C. T. *J. Org. Chem.* **1989**, *54*, 3140.

[3] Yoon, N. M.; Lee, H. J.; Ahn, J. H.; Choi, J. *J. Org. Chem.* **1994**, *59*, 4687.

[4] A part of ester couplings has been communicated: Sim, T. B.; Choi, J.; Yoon, N. M. *Tetrahedron Lett.* **1996**, *37*, 3137.

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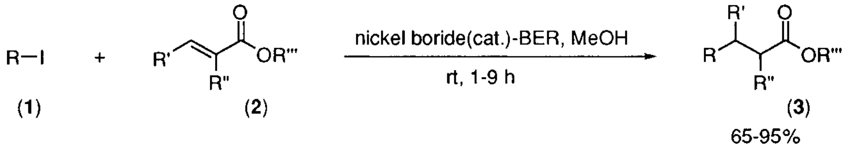
Table 1. Coupling Reaction of Alkyl Iodides with α,*β*-Unsaturated Esters Using Nickel Boride (cat.)−BER in Methanol at Room Temperature (20 °C)[a]



entry	alkyl halide (**1**)	α,*β*-unsaturated ester (**2**)	$Ni(OAc)_2$ (equiv)	time (h)	yield of **3** (%)[b]
1	cyclo-$C_6H_{11}I$	$CH_3CH{=}CHCO_2CH_3$	0.05	6	85
2	cyclo-$C_6H_{11}I$	$CH_2{=}C(CH_3)CO_2CH_3$	0.05	9	93
			0.2	1	93
3	cyclo-$C_6H_{11}I$	$CH_2{=}CHCO_2CH_2CH_3$	0.2	3	95
4	*sec*-$C_6H_{13}I$	$CH_2{=}CHCO_2CH_2CH_3$	0.2	1	92
5	*n*-$C_8H_{17}I$	$CH_3CH{=}CHCO_2CH_3$	0.05	9	68, 52[c]
			0.2	1	42
6	*n*-$C_8H_{17}I$	$CH_2{=}C(CH_3)CO_2CH_3$	0.05	9	88
			0.2	1	80
7	*n*-$C_8H_{17}I$	$CH_2{=}CHCO_2CH_2CH_3$	0.05	20	45
			0.2	3	86
8	$CH_3(CH_2)_3OCH(OCH_2CH_3)CH_2I$	$CH_2{=}CHCO_2CH_2CH_3$	0.2	3	79
9	$CH_3CH_2O_2C(CH_2)_3I$	$CH_2{=}CHCO_2CH_2CH_3$	0.2	3	76
10	$NC(CH_2)_4I$	$CH_2{=}CHCO_2CH_2CH_3$	0.2	3	78
11	*cis*-$CH_3CH_2CH{=}CH(CH_2)_2I$	$CH_2{=}C(CH_3)CO_2CH_3$	0.2	3	70[d]
12	$(CH_3)_2C{=}CH(CH_2)_2I$	$CH_2{=}CHCO_2CH_2CH_3$	0.2	3	65[d]

[a] Alkyl iodides (5 mmol) were reacted with enoates (20 equiv) using $Ni(OAc)_2$ (0.05−0.2 equiv) and BER (3 equiv) at room temperature in methanol. [b] Isolated yield. [c] Reaction was carried out with 10 equiv of methyl crotonate. [d] Reaction was carried out with 5 equiv of BER.

slowly hydrogenated than unsubstituted ones). Therefore larger amounts of unsaturated compounds (20 equiv) have to be used than in the case of the tin hydride method.

1. Coupling with α,*β*-Unsaturated Esters. Cyclohexyl iodide, 2-hexyl iodide, octyl iodide, and functionalized alkyl iodides were reacted with representative α,*β*-unsaturated esters: methyl crotonate, methyl methacrylate, and ethyl acrylate at room temperature using 20 equiv of esters. The results are summarized in Table 1. As shown in Table 1, alkyl iodides were coupled smoothly with methyl crotonate and methyl methacrylate in methanol in 6−9 h using 0.05 equiv of $Ni(OAc)_2$ and 3 equiv of BER (entries 1, 2, 5, and 6). In the couplings with ethyl acrylate, however, better yields (86−95%) were observed by increasing the amount of $Ni(OAc)_2$ from 0.05 equiv to 0.2 equiv (entries 3, 4, and 7). Presumably, since the double bond of ethyl acrylate is rapidly hydrogenated even at 0 °C by this system,[5] octyl iodide cannot compete successfully with ethyl acrylate for the small amount (0.05 equiv) of nickel boride catalyst. On the other hand, the increase of nickel boride results in a decrease in the yields in the coupling with methyl crotonate, a hindered unsaturated ester (entry 5). In this case, methyl crotonate is hydrogenated rather slowly under the reaction conditions,[5] and the coupling of the alkyl radical with this hindered enoate must compete with the reduction of the radical to the corresponding alkanes, and thus the increase of nickel boride results in decreased coupling. Excess (20 equiv) unsaturated esters favors the coupling reaction. Indeed, when 10 equiv of unsaturated esters were used, a somewhat lower yield (52 vs 68%) was observed (entry 5). In the case of methyl methacrylate, an increase in nickel boride increased the rate of coupling without affecting the yields substantially (entries 2 and 6). Equally good yields (76−78%) were observed in the couplings of alkyl iodides containing acetal, ester, or nitrile functional group (entries 8, 9, and 10). Finally we studied the reaction of homoallylic iodides. Simple addition products were obtained in moderate yields (70−65%) accompanying 5−15% of the corresponding sequential cyclization products (entries 11 and 12). This will be discussed in the next section (coupling with nitriles).

2. Coupling with α,*β*-Unsaturated Nitriles. Cyclohexyl iodide, 2-hexyl iodide, octyl iodide, *β*-phenethyl iodide, and functionalized alkyl iodides were reacted with representative α,*β*-unsaturated nitriles, namely, crotononitrile, methacrylonitrile, and acrylonitrile in methanol for 1 h at 65 °C. The results are summarized in Table 2. First the reaction was carried out at room temperature, using 0.05 equiv of $Ni(OAc)_2$ and 3 equiv of BER; however, the formation of alkyl radical was too slow as shown in the reaction of cyclohexyl iodide with crotononitrile. Only 25% yield of 3-cyclohexylbutyronitrile was obtained in 12 h, leaving 70% of cyclohexyl iodide unreacted (detected by GC) (entry 1). This slow reaction is probably due to the preferential adsorption[6] and/or reduction of crotononitrile on nickel boride, which hinders the radical formation reaction of cyclohexyl iodide at room temperature since cyclohexyl iodide is reduced with BER−nickel boride (cat.) quantitatively in 1 h at room temperature in the absence of excess (20 equiv) crotononitrile.[3] This problem was resolved simply by carrying out the reaction at 65 °C. Cyclohexyl iodide, 2-hexyl iodide, octyl iodide, and *β*-phenethyl iodide were all smoothly coupled with crotononitrile and methacrylonitrile in methanol in 1 h using 0.05 equiv of $Ni(OAc)_2$ and 3 equiv of BER at 65 °C (condition A) (entries 1, 2, 5, 6, 7, 9, and 12). On the other hand, the reaction of cyclohexyl iodide with acrylonitrile gave only a 65% yield of the addition product, 3-cyclohexylpropiononitrile at condition A, but the yield could be improved to 90% by increasing the amount of $Ni(OAc)_2$ (0.2 equiv) and BER (5 equiv) (condition B, entry 3). Since the radical formation from cyclohexyl

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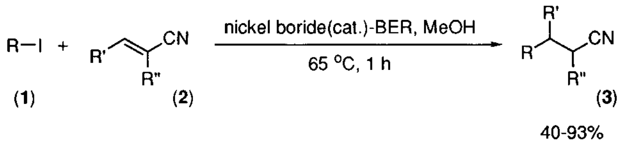
(5) Ethyl acrylate and acrylonitrile can be selectively hydrogenated in the presence of methyl crotonate and crotononitrile by nickel boride−BER in methanol at 0 °C: Choi, J.; Yoon, N. M. *Synthesis* **1996**, 597.

(6) 1-Octene (20 mmol) was hydrogenated over nickel boride (1 mmol) on BER in 1 h; however, it was not hydrogenated in the presence of benzonitrile (5 mmol).

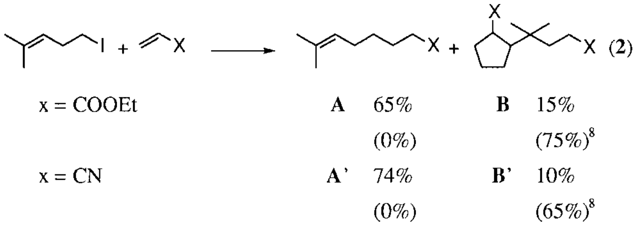
Table 2. Coupling Reaction of Alkyl Halides with α,β-Unsaturated Nitriles Using Nickel Boride (cat.)−BER in Methanol at 65 °C[a]



entry	alkyl halide (**1**)	α,β-unsaturated nitrile (**2**)	condition	yield of **3** (%)[b]
1	cyclo-$C_6H_{11}I$	$CH_3CH{=}CHCN$	A	93, 25,[c] 78[d]
			B	90
2	cyclo-$C_6H_{11}I$	$CH_2{=}C(CH_3)CN$	A	91
3	cyclo-$C_6H_{11}I$	$CH_2{=}CHCN$	A	65
			B	90, 47[f]
4	cyclo-$C_6H_{11}Br$[e]	$CH_3CH{=}CHCN$	A	15 (79)
			B	29 (60)
			C	40 (41)
5	*sec*-$C_6H_{13}I$	$CH_3CH{=}CHCN$	A	92
6	*n*-$C_8H_{17}I$	$CH_3CH{=}CHCN$	A	80
7	*n*-$C_8H_{17}I$	$CH_2{=}C(CH_3)CN$	A	81
8	*n*-$C_8H_{17}I$	$PhCH{=}CHCN$	A	30
			B	77
9	$PhCH_2CH_2I$	$CH_3CH{=}CHCN$	A	68
10	$CH_3(CH_2)_3OCH(OCH_2CH_3)CH_2I$	$CH_2{=}CHCN$	B	81
11	$(CH_3CH_2)_2NOC(CH_2)_4I$	$CH_2{=}CHCN$	B	65
12	*cis*-$CH_3CH_2CH{=}CH(CH_2)_2I$	$CH_2{=}C(CH_3)CN$	A	76
13	$(CH_3)_2C{=}CH(CH_2)_2I$	$CH_2{=}CHCN$	B	74

[a] Alkyl halides (5 mmol) were reacted with α,β-unsaturated nitriles (20 equiv) using (A) $Ni(OAc)_2$ (0.05 equiv) and BER (3 equiv), (B) $Ni(OAc)_2$ (0.2 equiv) and BER (5 equiv), or (C) $Ni(OAc)_2$ (0.5 equiv) and BER (10 equiv) all for 1 h at 65 °C in methanol (20 mL). [b] Isolated yield. [c] Reaction was carried out at room temperature for 12 h, and 70% of cyclohexyl iodide remained. [d] Reaction was carried out under a blanket of purified oxygen, and 5% of cyclohexanol was also obtained. [e] Reaction was carried out for 3 h, and the amount of cyclohexyl bromide unreacted is shown in parentheses. [f] Reaction was carried out with 10 equiv of acrylonitrile.

iodide has to occur on the surface of nickel boride,[7] and acrylonitrile is reduced much more readily by BER−nickel boride than crotononitrile or methacrylonitrile,[5] the radical reaction of cyclohexyl iodide might not proceed successfully in competition with the reduction of acrylonitrile over the small amount of nickel boride produced by 0.05 equiv of $Ni(OAc)_2$. Higher yield was also observed in the reaction of octyl iodide with cinnamonitrile (entry 8). However, the reaction of cyclohexyl iodide with crotononitrile was not influenced by the amount of $Ni(OAc)_2$ or BER (entry 1). In the case of cyclohexyl bromide, the radical reaction of cyclohexyl bromide might not compete successfully with the reduction of crotononitrile even in the presence of $Ni(OAc)_2$ (0.5 equiv)−BER (10 equiv), presumably due to the slow reaction of cyclohexyl bromide compared with cyclohexyl iodide. Considerable amounts of cyclohexyl bromide (41%) remained unreacted even after 3 h (entry 4). Decrease in the amount of α,β-unsaturated nitriles resulted in a significant decrease in the yield. For example, only 47% yield of 3-cyclohexylpropiononitrile was obtained when cyclohexyl iodide was reacted with 10 equiv of acrylonitrile (entry 3). Iodides containing acetal or amide functional group also resulted in good yields (entries 10 and 11). Finally two homoallylic iodides were reacted with unsaturated nitriles. As in the reaction with unsaturated esters, simple addition products were obtained in good yields (76−74%) (entries 12 and 13). The coupling of homoallylic iodides with nickel boride should be valuable for the synthesis of simple addition products (**A** and **A′**), since in the tributyltin hydride method sequential cyclization products (**B** and **B′**) are the major products.[8]



3. Coupling wtih α,β-Unsaturated Ketones. Representative acyclic and cyclic enones were coupled with alkyl iodides. All the reactions were completed in 1 h, using excess (20 equiv) enones in methanol. The results are summarized in Table 3. Enones such as *trans*-4-hexen-3-one and 2-methyl-2-cyclopenten-1-one (entries 1, 2, 8, 11, 13, and 14) were coupled smoothly with alkyl iodides, using 0.1 equiv of $Ni(OAc)_2$ and 3 equiv of BER at room temperature (condition A). As these enones are reduced rather slowly, the reduction does not appear to interfere with the radical formation by the reaction of alkyl iodides and nickel boride−BER. However, enones such as *trans*-4-phenyl-3-buten-2-one, methyl vinyl ketone, ethyl vinyl ketone, 2-cyclopenten-1-one, and 2-cyclohexen-1-one (entries 3, 4, 5, 6, 9, 10, and 12) have rather unhindered carbon−carbon double bonds and/or carbonyl groups and are reduced rapidly by this system. Therefore the radical formation of alkyl iodides might not compete with the reduction of these enones when small amounts of nickel boride were used at room temperature (condition A). For successful coupling of these unhindered enones, increased amounts of $Ni(OAc)_2$ (0.3 equiv) and BER (5.0 equiv) as well as an increase in the reaction temperature to 65 °C were required (condition B). Indeed when some of these reactions were carried out under condition A, most of the alkyl iodides remained unreacted while the hydride was rapidly consumed in the reduction of enones (entries 3, 5, and 7). In the coupling reactions of iodocyclohexane with alkyl vinyl ketones, higher yields

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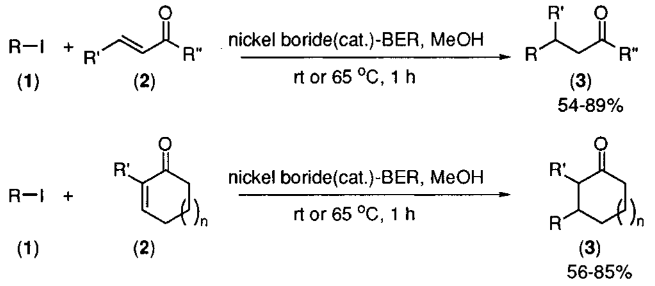
(7) Cyclohexyl iodide was not reduced with BER in the absence of nickel boride.

(8) Cekovic, J.; Saicic, R. S. *Tetrahedron Lett.* **1986**, *27*, 5893.

Table 3. Coupling Reaction of Alkyl Halides with α,*β*-Unsaturated Ketones Using Nickel Boride (cat.)−BER in Methanol[a]



entry	alkyl halide (**1**)	α,*β*-unsaturated ketone (**2**)	condition	yield of **3** (%)[b]
1	cyclo-$C_6H_{11}I$	$CH_3CH{=}CHCOCH_2CH_3$	A	81
2	cyclo-$C_6H_{11}I$	$OC(CH_2)_2CH{=}CCH_3$	A	85,[c] 71[d]
3	cyclo-$C_6H_{11}I$	$CH_2{=}CHCOCH_3$	A	(2)(96[e])
			B	54
4	cyclo-$C_6H_{11}I$	$CH_2{=}CHCOCH_2CH_3$	B	84
5	cyclo-$C_6H_{11}I$	$OC(CH_2)_2CH{=}CH$	A	(17)(75[e])
			B	72
6	cyclo-$C_6H_{11}I$	$OC(CH_2)_3CH{=}CH$	B	66
7	cyclo-$C_6H_{11}Br$	$OC(CH_2)_2CH{=}CCH_3$	A	(6)(88[e])
			B	56
8	*sec*-$C_8H_{17}I$	$CH_3CH{=}CHCOCH_2CH_3$	A	84
9	*sec*-$C_8H_{17}I$	$CH_2{=}CHCOCH_2CH_3$	B	89
10	*sec*-$C_8H_{17}I$	$OC(CH_2)_2CH{=}CH$	B	80
11	*n*-$C_8H_{17}I$	$CH_3CH{=}CHCOCH_2CH_3$	A	73
12	*n*-$C_8H_{17}I$	$PhCH{=}CHCOCH_3$	B	60
13	*n*-$C_8H_{17}I$	$OC(CH_2)_2CH{=}CCH_3$	A	72[f]
14	$NC(CH_2)_4I$	$CH_3CH{=}CHCOCH_2CH_3$	A	68

[a] Alkyl halides (3 mmol) were reacted with enones (20 equiv) in methanol (12 mL) for 1 h using (A) $Ni(OAc)_2$ (0.1 equiv) and BER (3 equiv) at room temperature, (B) $Ni(OAc)_2$ (0.3 equiv) and BER (5 equiv) at 65 °C. [b] Isolated yield, yields in the parentheses were estimated using capillary GC. [c] *Cis/trans* ratio was 28/72 as revealed by capillary GC. [d] Reaction was carried out with 10 equiv of 2-methyl-2-cyclopenten-1-one. [e] Amount of alkyl halide remained. [f] *Cis/trans* ratio was 26/74.

were obtained in the case of ethyl vinyl ketone compared with methyl vinyl ketone (entries 3 and 4). This might be also due to the slower reduction of ethyl vinyl ketone compared with methyl vinyl ketone. The coupling of bromocyclohexane resulted in a much lower yield compared with cyclohexyl iodide as observed in nitrile coupling (entry 7). Similar trends were also reported in the tributyltin hydride reactions.[1b]

Since we obtained practically the same yield of product whether the reaction of cyclohexyl iodide with crotononitrile was carried out with or without nitrogen, we did not endeavor to maintain an inert atmosphere. In the nickel boride (cat.)−BER−methanol system, oxygen free inert atmosphere seems to be automatically obtained by hydrogen evolution due to the decomposition of BER. When the same reaction was carried out under a blanket of purified oxygen, 3-cyclohexylbutyronitrile (78%) was accompanied with 5% of cyclohexanol, produced by oxygen trapping of the cyclohexyl radical (entry 1 in Table 2). Finally we attempted the reaction using $NaBH_4$ instead of BER. When the reaction of cyclohexyl iodide with crotononitrile was repeated using 0.05 equiv of $Ni(OAc)_2$ and 3 equiv of $NaBH_4$ in the presence of charcoal, only 15% yield of 3-cyclohexylbutyronitrile was obtained, accompanied by 55% of unreacted cyclohexyl iodide. Similarly in the coupling reaction of octyl iodide with *trans*-4-hexen-3-one, octyl iodide remained unreacted, and only *trans*-4-hexen-3-one was reduced. Therefore BER is essential for the nickel boride-catalyzed radical coupling reaction.

Conclusion

A new coupling reaction of alkyl iodides with α,*β*-unsaturated esters, nitriles, and ketones has been developed using nickel boride−BER in methanol. This new coupling method allows simpler workup as well as higher yields in the simple coupling of alkyl iodides with α,*β*-unsaturated esters, nitriles, and ketones, although about twice the amount of alkenes are required compared with the tributyltin hydride method. Therefore the heterogeneous catalyst, nickel boride (cat.)−BER in methanol is a good alternative reagent to tributyltin hydride for the coupling of alkyl iodides with α,*β*-unsaturated esters, nitriles, and ketones.

Experimental Section

Preparation of BER. An aqueous solution of sodium borohydride (1 M, 500 mL) was stirred with wet chloride form anion-exchange resin (Amberlite IRA-400 [20 − 50 mesh], 200 g) for 15 min. The resulting resin was washed thoroughly with distilled water until free from excess $NaBH_4$ and once with ethanol. The borohydride form anion-exchange resin[9] was then dried *in vacuo* at 60 °C for 5 h to give 102 g of dried borohydride exchange resin (BER). The dried resin was analyzed for borohydride content by hydrogen evolution on acidification with 2 N HCl, and the average hydride content of BER was found to be 3.0 mmol of BH_4^- per gram. The dried resin was stored under nitrogen in refrigerator (~4 °C). The hydride content was constant over 6 weeks.

Stability of BER. To the two reaction flasks which contain 1 mmol each of BER were added methanol (10 mL) and

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(9) This BER could be directly used without drying. The same yields were obtained with dried BER.

methanol (10 mL) containing 0.02 mmol of $Ni(OAc)_2$, and the rate of decomposition was followed by measuring the hydrogen evolution at room temperature. The measurement was repeated with $NaBH_4$ in the place of BER. BER decomposed 16% in 1 h, 23% in 2 h, and 45% in 1 h, and 56% in 2 h in the presence of $Ni(OAc)_2$. In contrast, $NaBH_4$ decomposed completely in 2 min and 30 min, respectively, in the presence and absence of $Ni(OAc)_2$.

Cyclization of 5-Hexenyl Iodide. BER (1.03 g, 3 mmol) was added to a methanol solution (5 mL) of $Ni(OAc)_2 \cdot 4H_2O$ (0.025 g, 0.1 mmol), and the mixture was stirred slowly at room temperature. Immediately a black coating of nickel boride and a slow hydrogen evolution due to decomposition of BER were observed. After 1 min, a methanol solution (1 mL) of 5-hexenyl iodide (0.21 g, 1 mmol) was added, and the mixture was stirred at room temperature. After 0.5 h, the GC analysis of the mixture on column HP-1 showed 38% of methylcyclopentane and 62% of *n*-hexane.

General Procedure. 1. Ester Coupling. The preparation of methyl 3-cyclohexylbutyrate is representative. BER (5.17 g, 15 mmol) was added to a methanol solution (10 mL) of $Ni(OAc)_2 \cdot 4H_2O$ (0.25 g, 1 mmol), and the mixture was stirred slowly at room temperature. Immediately a black coating of nickel boride and a slow hydrogen evolution due to decomposition of BER were observed. After 1 min, ethyl crotonate (10.01 g, 100 mmol) and a methanol solution (10 mL) of iodocyclohexane (1.05 g, 5 mmol) were added, and the mixture was stirred at room temperature. After 6 h, the resin was removed by filtration, and excess ethyl crotonate, reduction products (cyclohexane and ethyl butyrate), and methanol were evaporated under reduced pressure to yield the pure methyl 3-cyclohexylbutyrate (0.78 g, 85%): IR (neat) 1739 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.82−1.89 (m, 15 H), 2.08 (dd, 1 H, J = 14.6, 11.9 Hz), 2.38 (dd, 1 H, J = 14.6, 5.2 Hz), 3.69 (s, 3 H); MS *m*/*z* (relative intensity) (EI, 70 eV) 153 (18), 141 (5), 111 (100), 101 (67), 87 (37), 74 (60), 69 (37), 55 (66). Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.59; H, 11.03. In some cases, when the reduction products and/or side products were not removed easily by evaporation, flash chromatography was carried out.

2. Nitrile Coupling. The preparation of 3-cyclohexylbutyronitrile is representative. BER (5.0 g, 15 mmol) was added to a methanol solution (10 mL) of $Ni(OAc)_2 \cdot 4H_2O$ (0.13 g, 0.5 mmol) with gentle stirring at room temperature. Immediately a black coating of nickel boride and a slow hydrogen evolution due to decomposition of BER were observed. After 1 min, crotononitrile (6.7 g, 100 mmol) and a methanol solution (10 mL) of iodocyclohexane (1.05 g, 5 mmol) were added, and the mixture was stirred at 65 °C. After 1 h, the resin was removed by filtration, and filtrate was evaporated under reduced pressure. The crude residue was purified by flash chromatography (SiO_2, hexane/EtOAc = 12:1) to yield the pure 3-cyclohexylbutyronitrile (0.70 g, 93%): IR (neat) 2245 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.88−1.18 (m, 2 H), 1.15 (d, 3 H, J = 6.6 Hz), 1.17−1.42 (m, 4 H), 1.68−1.80 (m, 6 H), 2.26 (dd, 1 H, J = 16.8, 7.7 Hz), 2.39 (dd, 1 H, J = 16.8, 5.9 Hz); MS *m*/*z* (relative intensity) (EI, 70 eV) 151 (M^+ 4), 150 (18), 135 (10), 95 (23), 82 (68), 68 (76), 54 (100). Anal. Calcd for $C_{10}H_{17}N$: C, 79.41; H, 11.33; N, 9.26. Found: C, 79.18; H, 11.08; N, 9.37.

3. Ketone Coupling. The preparation of 5-cyclohexyl-3-hexanone is representative. BER (2.90 g, 9 mmol) was added to a methanol solution (6 mL) of $Ni(OAc)_2 \cdot 4H_2O$ (0.08 g, 0.3 mmol), and the mixture was stirred slowly at room temperature. Immediately a black coating of nickel boride and a slow hydrogen evolution due to decomposition of BER were observed. After 1 min, *trans*-4-hexen-3-one (5.89 g, 60 mmol) and a methanol solution (6 mL) of iodocyclohexane (0.63 g, 3 mmol) were added, and the mixture was stirred at room temperature. After 1 h, the resin was removed by filtration, the filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography (SiO_2, hexane/EtOAc = 49:1) to afford 5-cyclohexyl-3-hexanone (0.44 g, 81%): IR (neat) 1736 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.84−1.32 (m, 6 H), 0.85 (d, 3 H, J = 7.1 Hz), 1.07 (t, 3 H, J = 7.3 Hz), 1.61−1.98 (m, 6 H), 2.14−2.55 (m, 4 H); MS *m*/*z* (relative intensity) (EI, 70 eV) 182 (M^+ 1), 153 (10), 135 (31), 110 (100), 99 (47), 81 (46), 69 (49), 57 (44), 55 (38). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.98; H, 12.44.

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Supporting Information Available: Experimental data for IR, NMR, MS, and elemental analyses of new compounds (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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