g (13 mmol) of 2,2-dimethyl-1-iodo-5-hexene was added. The reaction mixture was stirred for 60 h at 25 °C, quenched with saturated NH_4Cl (20-mL), and extracted twice with hexane. The combined hexane layers were washed with saturated $NaHCO_3$ followed by five successive washings with water and then dried and concentrated. The residual liquid was chromatographed on silica gel with a hexane–ether eluent (99:1 v/v) to give 1.8 g (57%) of enol ether. Bulb-to-bulb distillation afforded the enol ether as a colorless liquid: ^1H NMR (CCl_4) δ 0.98 (s, 6 H), 1.2–2.2 (m, 4 H), 1.8 (d, 3 H, J = 6.8 Hz), 3.2 (s, 2 H), 4.8–6.2 (m, 4 H), 7.1–7.5 (m, 5 H); IR (film) 3070, 2960, 1655, 1635, 1320, 1065, 910, 760, 700 cm^{-1}; mass spectrum, m/e (relative intensity) 244 (M^+, 4), 202 (8), 135 (28), 134 (100), 133 (75), 117 (19), 105 (41), 91 (9), 77 (15), 69 (59), 55 (46), 41 (48); exact mass calcd for $C_{17}H_{24}O$ 244.1827, found 244.1836.

1-((2,2-Dimethylhexyl)oxy)-1-phenyl-1-propene (10). The enol ether was prepared in 56% yield from 2,2-dimethyl-1-iodohexane by the method described above and after purification gave the following: ^1H NMR (CCl_4) δ 0.97 (s, 6 H), 0.85–1.5 (m, 9 H), 1.8 (d, 3 H, J = 6.8 Hz), 3.2 (s, 2 H), 5.2 (q, 1 H, J = 6.8 Hz), 7.1–7.5 (m, 5 H); IR (film) 3045, 2960, 1650, 1315, 1060, 760, 700 cm^{-1}; mass spectrum, m/e (relative intensity) 246 (M^+, 3), 217 (11), 135 (12), 134 (100), 133 (50), 117 (12), 105 (21), 77 (9), 71 (23), 57 (39), 43 (37); exact mass calcd for $C_{17}H_{26}O$ 246.1984, found 246.1988.

2-(Dicyclohexylphosphino)-1-phenyl-1-propanone. A solution of lithiopropiophenone (9.4 mmol) in HMPA (20 mL) was prepared as described above and 1.2 g (6.3 mmol) of DCPH followed by 1.5 g (6.3 mmol) of 2,2-dimethyl-1-iodo-5-hexene were added. The reaction mixture was stirred for 24 h at 25 °C, quenched with saturated NH_4Cl (10 mL), and extracted twice with hexane. The combined hexane layers were washed 5 times with water, dried, and then concentrated. The residue was chromatographed on silica gel with an ethyl acetate–acetone eluent (1:1 v/v) to give 0.74 g (34%) of the ketone as a viscous oil which was dried in a vacuum dessicator and gave the following: ^1H NMR ($CDCl_3$) δ 1.0–2.1 (br m, 22 H), 1.5 (dd, 3 H), 4.2 (dq, 1 H), 7.3–8.0 (m, 5 H); IR (CCl_4) 3060, 2940, 2860, 1675, 1445, 1170 cm^{-1}; mass spectrum, m/e (relative intensity) 346 (M^+, 8), 264 (28), 263 (30), 182 (27), 133 (14), 117 (100), 105 (30), 83 (24), 77 (25), 55 (57), 43 (27), 41 (50); exact mass calcd for $C_{21}H_{31}O_2P$ 346.2062, found 346.2079.

General Procedure for Alkylation Reactions. Lithiopropiophenone (1.0 mmol) in 5.0 mL of HMPA was prepared as described above and 0.50 mmol of alkyl halide or tosylate was added to the stirring enolate solution at 25 °C. Whenever an additive was employed, the appropriate amount was added to the enolate solution just prior to the addition of the alkyl halide. The alkylation reactions were followed by taking 0.50-mL aliquots from the reaction mixtures at various time intervals and quenching them with saturated NH_4Cl in glass vials containing the necessary internal standards. The organic layer was then extracted (2 × 2.0 mL) with pentane and the combined pentane layers were washed 5 times with H_2O. GLC analyses were then conducted on columns A–D and all products were identified from their GLC retention times and mass spectra by comparison with authentic samples.

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Registry No. 2, 4516-69-2; **4**, 97467-22-6; **5**, 89746-00-9; **6**, 89746-01-0; **9**, 590-73-8; **10**, 97467-24-8; **11**, 97467-25-9; **15**, 97467-23-7; DCPD, 91523-73-8; DCPH, 829-84-5; PDNB, 100-25-4; CH_2=$CH(CH_2)_2C(CH_3)_2CH_2I$, 77400-57-8; CH_2=$CH(CH_2)_2C(CH_3)_2CH_2Br$, 56068-49-6; CH_2=$CH(CH_2)_2C(CH_3)_2CH_2OTs$, 89745-98-2; $(t\text{-Bu})_2NO$, 2406-25-9; CH_2=$CH(CH_2)_2C(CH_3)_2CH_2OH$, 56068-50-9; BuLi, 109-72-8; $CH_3C(O)CH_3$, 67-64-1; $CH_3(CH_2)_3C(OH)(CH_3)_2$, 625-23-0; CH_2=$CH(CH_2)_2C(CH_3)_2CHO$, 52278-99-6; CH_2=$CH(CH_2)_2C(CH_3)_2CH$=$CHC(O)Ph$, 97467-26-0; $PhC(O)CH_3$, 98-86-2; CH_2=$CH(CH_2)_2C(CH_3)_2CH(OH)CH_2C(O)Ph$, 97467-27-1; $PhC(O)CH_2CH_3$, 93-55-0; lithiopropiophenone, 70887-62-6; 1,4-cyclohexadiene, 628-41-1; 2-(dicyclohexylphosphino)-1-phenyl-1-propanone, 97467-28-2.

NAD(P)$^+$–NAD(P)H Models. 55. Transition Metal Catalyzed Reduction of Organic Halides: High Selectivity for Reductive Dehalogenation

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Various types of aryl, benzyl, vinyl, phenacyl, and allyl halides were subjected to reaction with *N*-benzyl-1,4-dihydronicotinamide (BNAH), in the presence of a catalytic amount of chlorotris(triphenylphosphine)rhodium(I) or palladium(II)acetate. The carbon–halogen bonds in these compounds were selectively reduced to the carbon–hydrogen bonds in moderate to excellent yield. This new kind of reduction system has synthetic advantages over many other procedures for reductive dehalogenation: the conditions are mild, nitro, carbonyl, hydroxyl, amino, alkenyl, and ester groups are inert under these conditions, and the halides that can be used are varied. The order of reactivity in a series of organic halides was Cl < Br < I. Substituent effects in the aryl iodides showed that the stronger the electron-withdrawing ability of the substituent, the more reactive the substrate. These results and other evidence suggest that the reaction involves oxidative addition of halides to the transition metal. The reduction of vinyl bromide gave predominantly the thermodynamically more stable isomer, after cis–trans interconversion. In addition, this reduction was accompanied by contamination by deuterium from the deuterated solvent. These facts reveal the intermediacy of vinyl free radicals in the course of the reaction. The free-radical species is probably generated through an electron transfer from BNAH.

Chemoselectivity is of special importance in organic synthesis. It is prerequisite to artificial production of some useful drugs such as antibiotics. Although up to now many types of "selective reactions" have been tried, and some are widely accepted to be useful in synthesis, most organic reactions reported so far are still open to improvement in terms of chemoselectivity.

The selective reduction of a carbon–halogen bond to a carbon–hydrogen one would be of interest to organic

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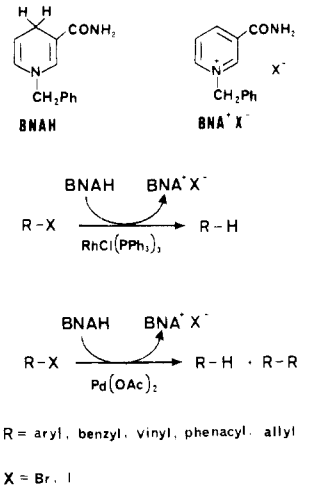
Scheme I



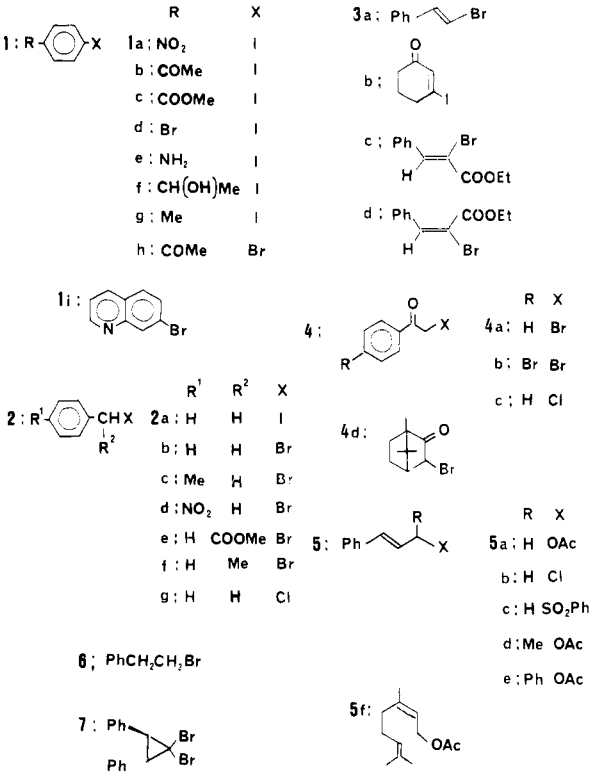
chemists. For example, the reductive deiodination of an organic iodide with a lactone moiety is one of the key steps in the preparation of a prostaglandin.[2,3]

Reductive dehalogenation of several kinds of organic halides were reviewed by Pinder in 1980.[4] Unfortunately, most reducing agents and catalysts listed there are of limited selectivity: that is, functional groups such as nitro, carbonyl, and ester are often changed in the course of the reactions. Although several methods for reductive dehalogenation have been presented since then, these disadvantages remain.[5,6] For these reasons, we have tried to develop a new reduction system in which a particular carbon–halogen bond is reduced selectively to a carbon–hydrogen one.

Since a reagent with high reactivity generally exerts little selectivity for a variety of functional groups, one strategy to obtain higher selectivity is to activate a particular functional group specifically so that it can react with a reagent of poor reactivity. A model of NAD(P)H is an appropriate candidate for this purpose because the reactivity of the model itself is not high. Studies of the mechanism of reduction with a model of NAD(P)H by us and others have revealed that the reduction with a model is catalyzed by some cationic species such as a proton,[7] a Lewis acid,[8] or a magnesium ion.[9] Although these species act as catalysts in an often dramatic and highly selective way, the functional groups to be reduced by their aid are limited to potentially activated ones, such as electron-deficient carbonyl or alkenyl groups. Therefore, the catalysts so far tried are still not appropriate for use in organic synthesis, and so, of course, they are ineffective in reductive dehalogenation.

Transition metals are now being applied to organic synthesis.[10] Successful results in such studies stem from the specificity of a transition metal in activating a particular reagent.

Chart I



With these considerations in mind, we examined the ability of transition metals as catalysts in reduction with a model of NAD(P)H. We found that chlorotris(triphenylphosphine)rhodium(I) specifically catalyzes reductive dehalogenation with one model of NAD(P)H, *N*-benzyl-1,4-dihydronicotinamide (BNAH);[11] a carbon–halogen bond in various types of organic halides is smoothly reduced to a carbon–hydrogen bond, while nitro, carbonyl, hydroxyl, alkenyl, and ester groups are mainly unaffected.

On the other hand, the reactions of organic halides with BNAH in the presence of a catalytic amount of palladium(II) acetate afforded coupling products in addition to the corresponding reduction products.

Scheme I illustrates the reactions. These catalysts have not been used in this way often before.[11-13]

Analyses of this system upon the mechanistic aspects suggest that oxidative addition of a halide to a transition metal is involved. More interestingly, it has been found that BNAH acts as an electron donor in the reaction. Thus, this reaction provides further evidence for the initial one-electron-transfer mechanism previously proposed for NAD(P)H model mediated reductions.[14]

In this report, we wish to emphasize the synthetic utility of this reduction system as well as referring to aspects of the mechanism. This is the first systematic study of ap-

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Table I. $RhCl(PPh)_3$-Catalyzed Reduction of Organic Halides[a]

halide	temp, °C	reacn time, h	conversion, %	yield,[b] %
1a	70	3	100	100
1b	70	3	100	91
1c	70	6	95	95
1d	70	20	91	100[c]
1e	70	23	72	100
1f	70	30	71	96
1g	70	23	60	80
1h	70	26	13	100
1i	70	23	28	100
2a	40	1	100	83
2b	40	2	100	69
2c	40	3	100	79
2d	40	2	100	69
2e	40	1	100	40[d]
2f	40	25	97	15[e]
2g	70	7	76	64
3a	70	1.5	100	90
3b	70	2.5	99	100
3c	70	19	50	90[f]
3d	70	23	67	6[g], 72[h] (72)[h]
4a	40	1.5	100	98
4b	40	2	100	92[i]
4c	40	6.5	34	100
4d	40	7	94	100
6	40	29	0[j]	
7	70	24	0[j]	

[a] Reactions were carried out with 5.0×10^{-2} mmol of a halide, 1.0×10^{-1} mmol of BNAH, and 5.0×10^{-3} mmol of $RhCl(PPh_3)_3$. [b] The yield of the corresponding reduction product is based on the amount of the halide consumed. The value in parentheses denotes isolated yield based on the amount of a halide consumed. [c] The yield of bromobenzene. [d] Dimethyl 1,2-diphenylsuccinate (a mixture of *dl* and *meso* isomers) was given (42%). [e] 2,3-Diphenylbutane (a mixture of *dl* and *meso* isomers) (33%) and styrene (29%) were given. [f] Trace amount of ethyl *cis*-3-phenylpropenoate was detected on VPC. [g] The yield of ethyl *cis*-3-phenylpropenoate. [h] The yield of ethyl cinnamate. [i] The yield of *p*-bromoacetophenone. [j] No reaction.

plications of a model of NAD(P)H to organic synthesis.

Results

Various kinds of dihydropyridine derivatives have been suggested as models of NAD(P)H and employed either in studies of the mechanism of NAD(P)H-mediated reductions[15] or as biological mimics.[16] Wishing to develop a new synthetically useful reduction system, we mainly used BNAH as the reductant, because BNAH can be synthesized most easily and seems to be the most stable of the models synthesized so far when exposed to air and light.[11]

We found that acetonitrile was the best solvent both for reactivity and selectivity among the solvents examined (acetonitrile, methanol, tetrahydrofuran, and benzene). Careful purification of acetonitrile was not essential to obtain satisfactory yield of the product(s) (see Experimental Section). The ease of preparation and the stability of chlorotris(triphenylphosphine)rhodium(I) $RhCl(PPh_3)_3$ and palladium(II) acetate ($Pd(OAc)_2$) contribute to the synthetic utility of our system. The amount of catalyst needed under our conditions was determined. The organic halides subjected to reduction are listed in Chart I.

Organic halides were reacted with BNAH in the presence of a catalytic amount of $RhCl(PPh_3)_3$ at an appropriate temperature in the dark with a nitrogen atmosphere.

Table II. $RhCl(PPh_3)_3$-Catalyzed Reduction of Allyl Derivatives[a]

substrate RX	conversion, %	yield, %[b] RH	yield, %[b] other olefin
5a	100	97	trace[c]
5b	100	96	trace[c], 4[d]
5c	100	79	6[c]
5d	100	71	6[e]
5e	100	77[f]	
5f	0[g]		

[a] *N*-Propyl-1,4-dihydronicotinamide (PNAH) was used as a model in place of BNAH. The reactions were carried out with 1.0×10^{-1} mmol of **5**, 1.5×10^{-1} mmol of PNAH, 1.0×10^{-2} mmol of $RhCl(PPh_3)_3$, and 1.5×10^{-1} mmol of $LiClO_4$ in 2 mL of acetonitrile. Reaction time is 17 h. [b] The yield is based on the amount of **5** consumed. [c] 3-Phenyl-1-propene. [d] *cis*-1-Phenyl-1-propene. [e] *trans*-1-Phenyl-2-butene. [f] Isolated yield. [g] No reaction.

The amount of the product(s) and of the unreacted halide were determined on VPC using an internal standard. Results are summarized in Tables I and II. Reaction time in the Tables denotes the period in which the conversion of the reaction becomes maximum.

Table I shows that an aryl iodide with an electron-withdrawing substituent (**1a–d**) was smoothly reduced to the corresponding arene, whereas that with an electron-releasing substituent (**1e–g**) was reduced with a little difficulty, albeit the yield of the corresponding arene was satisfactory. However, reduction of the corresponding aryl bromides proceeded with difficulty, as exemplified by the reductions of **1h** and **1i**. Therefore, bromobenzene was the only product in the reduction of *p*-bromoiodobenzene (**1d**). This reduction system may also be applicable to heteroaromatic compounds.

The yield from the reduction of benzyl iodide (**2a**) was satisfactory. Benzyl bromide (**2b**) was also satisfactorily reduced to the corresponding hydrocarbon, unlike the aryl bromides. The reduction of α-methylbenzyl bromide (**2f**) afforded styrene as one of the major products along with the reduction product.

Throughout the reduction of aryl and benzyl halides, the nitro, amino, hydroxyl, and ester groups were practically inert, which is of great importance to the utility of this method.

Vinyl (**3a–b**) and phenacryl (**4a–b**) halides as well as α-bromocamphor (**4d**) gave the corresponding reduction products in excellent yield, although the reactivity of phenacyl chloride (**4c**) was not satisfactory. The reactivity of **4a** was much higher than those of the aryl bromides **1h** and **1i**, so *p*-bromophenacyl bromide (**4b**) gave only *p*-bromoacetophenone. The carbon–carbon and carbon–oxygen double bonds in **3** and **4** were not affected by the reduction. The carbon–carbon double bond in 2-cyclohexen-1-one, the reduction product from **3b**, was reduced by *N*-propyl-1,4-dihydronicotinamide (PNAH), a reducing agent slightly more reactive than BNAH, in the presence of a catalytic amount of $RhCl(PPh_3)_3$ in acetonitrile under slightly severer conditions.[13] Therefore, it is clear that the choice of reaction conditions is quite important for specificity. The reduction of the vinyl bromide **3d** was accompanied by cis–trans interconversion (vide infra).

As shown in Table II, acetyloxy, phenylsulfonyl, and even chloro substituents at an allylic position were substituted by a (formal) hydride in excellent yields, provided that the carbon–carbon double bond is conjugated by an aryl group; this is in sharp contrast with the inertness of neryl acetate (**5f**).

In contrast, reductions of 2-phenylethyl bromide (**6**) and *trans*-1,1-dibromo-2,3-diphenylcyclopropane (**7**) gave

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Table III. Deuterium Content in the Reduction Products

halide	solv[a]	product D content, %
1a	M	1
	A	0
1g	M	0
	A	0
2b	A	0
3a	A	5
3b	A	1
3c	A	5
3d	A	3[b], 6[c]

[a] M, CD_3OD; A, CD_3CN. [b] Deuterium content in ethyl *cis*-3-phenylpropenoate. [c] Deuterium content in ethyl cinnamate.

Table IV. $Pd(OAc)_2$-Catalyzed Reduction of Organic Halides[a]

halide RX	temp, °C	reacn time, h	conversion, %	yield, %[b] RH	yield, %[b] R–R
1a[c]	70	4	84	38	44[d]
1a	70	3	100	48	41[d]
1a[e]	70	2	100	23	77[d]
2b	40	4	100	69	8[f]
2f	40	5	52	8	12[g], 10[h], 4[i]
2f[e]	40	6	100	5	19[g], 13[h], 2[i]

[a] The reaction was carried out with 5.0×10^{-2} mmol of the halide, 1.0×10^{-1} mmol of BNAH, and 1.0×10^{-2} mmol of $Pd(OAc)_2$. [b] The yield is based on the amount of halide consumed. [c] 5.0×10^{-3} mmol of $Pd(OAc)_2$ was used. [d] *p,p'*-Dinitrobiphenyl. [e] 5.0×10^{-2} mmol of triethylamine was added. [f] 1,2-Diphenylethane. [g] 1,2-Diphenylbutane (a mixture of *dl* and *meso* isomers). [h] Styrene. [i] α-Phenylethyl acetate.

quantitative recovery of the starting material even after a prolonged reaction period.

Reactions of **1a**, **1g**, **2b**, and **3a–d** with BNAH were carried out in acetonitrile-d_3 or in methanol-d_4 with a catalytic amount of $RhCl(PPh_3)_3$ under the same conditions as above, and the amount of deuterium in the product was analyzed on a GC–MS spectrometer. The results are given in Table III. The reductions of aryl (**1a** and **1g**) and benzyl (**2b**) halides in acetonitrile-d_3 or methanol-d_4 gave no deuterated products, whereas the vinyl halides **3a–d** were reduced in acetonitrile-d_3 with a small but appreciable amount of deuterium incorporated into the products. Hydrogen–deuterium exchange in the product did not occur under these reaction conditions.

Reactions of **1a**, **2b**, and **2f** with BNAH were also carried out in the presence of a catalytic amount of $Pd(OAc)_2$ instead of $RhCl(PPh_3)_3$ (Table IV). Coupling products were obtained in addition to the corresponding reduction products in all cases. Interestingly enough, the yield of the coupling product increased when the proton acceptor triethylamine was added. That is, a fairly good yield of *p,p'*-dinitrobiphenyl was obtained in a practical yield in the reduction of **1a** in the presence of triethylamine. The yield is comparable with that in the conventional Ullmann synthesis.[17] Thus, BNAH can also be used in the synthesis of a biaryl from a halide if $Pd(OAc)_2$ catalyst is added.

Discussion

$RhCl(PPh_3)_3$-Catalyzed Reduction. Most organic reactions catalyzed by transition metals involve a step in which a carbon–metal σ-bond is formed. Although data sets from quantitative examinations are not available in the present study, the results in Table I suggest that in the reduction here of aryl halides, the stronger the electron-withdrawing ability of a substituent, the more reactive the substrate was. This substituent effect is consistent with that in the oxidative addition of aryl halides to a transition metal.[18] Moreover, the order of reactivity in a series of halides is invariably Cl < Br < I, which is again in accordance with the order of the ease of adding a halide oxidatively to a metal.[19] Thus, it seems likely that the reactions in this system involve rate-determining oxidative addition to $RhCl(PPh_3)_3$. That β-elimination from **2f** takes place, giving styrene, supports this hypothesis, because an alkyl halide possessing a β-hydrogen tends to undergo β-elimination to give an olefin when it can react with a transition metal by the mechanism of oxidative addition followed by reductive elimination.[19] Extremely low reactivity observed in the reductions of **6** and **7**, halides that are equivalent to homoallyl halides, may stem from their inertness in oxidative addition to $RhCl(PPh_3)_3$.[20]

Vinyl bromide **3d** was reduced in the presence of $RhCl(PPh_3)_3$ with cis–trans interconversion, giving the thermodynamically more stable trans isomer, predominantly. Since the reductive elimination from a vinyl–metal complex occurs exclusively with retention of configuration,[19,21] this result indicates the involvement of a vinyl-free radical as an intermediate in the reaction:[19] Cis–trans interconversion in the vinyl free radical is much faster than abstraction of hydrogen.[22] It should be noted that the vinyl halides **3a–d** were reduced with contamination by deuterium during the reaction in deuterated solvent. Here, we would like to point out that some metal complexes undergo homolysis in the presence of a reducing agent.[23] Thus, the generation of a vinyl-free radical in our reaction system is quite plausible and suggests that the oxidative addition process precedes other processes such as the reduction of $Rh(PPh_3)_3$ to rhodium metal. In fact, one model of NAD(P)H, PNAH, does not reduce $RhCl(PPh_3)_3$ even under reflux in ethanol.[24]

The reaction sequence described above most likely holds in the $RhCl(PPh_3)_3$-catalyzed reduction of other halides. Although **1a**, **1g**, and **2b** afforded non-deuterated products during reduction in deuterated solvents, these results do not rule out the participation of the free radicals from **1a**, **1g**, and **2b** in the course of the reaction. The free radicals may abstract a hydrogen from a cation radical of BNAH within the cage of solvent before the radical diffuses into the solvent. The extent of hydrogen (deuterium) incorporation from the solvent may depend on the stability of the radical species generated. Similar discussions have appeared in other reports of this series.[14c,25]

Consequently, the most reasonable mechanism for the $RhCl(PPh_3)_3$-catalyzed reaction in our system may be as follows: (i) oxidative addition of a halide to a metal, (ii) an electron transfer from BNAH to the resultant oxidative addition product, (iii) homolytic cleavage of the carbon–metal σ-bond in the complex, generating a free radical, and

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(iv) abstraction of a hydrogen (or a proton and an electron) by the free radical from the cation radical of BNAH or from the solvent.

$Pd(OAc)_2$-Catalyzed Reduction. Since oxidative addition to a metal in a high oxidation state is difficult, an alternative mechanism may operate in $Pd(OAc)_2$-catalyzed reductions. $Pd(OAc)_2$ catalyst tended to result in the coupling product rather than the corresponding reduction product. Coupling products have also been reported to be one of the major products in the reductive dehalogenation of organic halides by sodium methoxide in the presence of a catalytic amount of tetrakis(triphenylphosphine)-palladium(0), where the reaction probably proceeds via the oxidative addition of a halide to the palladium(0) complex.[26] Therefore, in the present reaction, it seems that the reduction of $Pd(OAc)_2$ to the palladium(0) species initially occurs by an electron transfer from BNAH,[27] and, subsequently, oxidative addition of a halide to the palladium(0) species takes place. Indeed, reduction of $Pd(OAc)_2$ to palladium metal with PNAH is very facile process.[24] Unfortunately, the data in our hands now does not help to distinguish the processes leading to reduction and coupling products.

Experimental Section

Materials. Acetonitrile was refluxed on calcium hydride under a nitrogen atmosphere for at least an hour and distilled. Thus freshly purified acetonitrile was used in the reaction. Deuterated solvents were commercially available products (Commissariat a l'Energy Atomique). Chlorotris(triphenylphosphine)rhodium(I) ($RhCl(PPh_3)_3$)[28a] and palladium(II) acetate ($Pd(OAc)_2$)[28b] were prepared with methods described in the literature and stored in a desiccator, where they were stable for several months. The preparation of *N*-benzyl-1,4-dihydronicotinamide (BNAH) was as described previously.[29] Methyl *p*-iodobenzoate (**1c**) and methyl α-bromophenyl acetate (**2e**) were obtained by esterification of the corresponding acids, which were commercially available. α-(*p*-Iodophenyl)ethyl alcohol (**1f**) was synthesized by reduction of *p*-iodoacetophenone (**1b**) with sodium borohydride. 3-Iodo-2-cyclohexen-1-one (**3b**)[30] and *trans*-1,1-dibromo-2,3-diphenylcyclopropane (**7**)[31] were prepared by methods in the literature. A mixture of vinyl bromides **3c** and **3d** was obtained by treatment of commercially available ethyl *erythro*-α,β-dibromohydrocinnamate with triethylamine.[32] The mixture was repeatedly subjected to column chromatography, giving pure **3c** and pure **3d**, and then the configurations of both halides were determined by comparison of NMR chemical shifts with those given elsewhere[32] and those we calculated.[33] Cinnamyl phenyl sulfone (**5c**) was prepared from cinnamyl chloride (**5b**).[34] *trans*-1-Phenyl-1-buten-3-yl acetate (**5d**) was synthesized by methylation of cinnamaldehyde with methylmagnesium bromide, followed by acetylation with acetyl chloride in pyridine. *trans*-1,3-Diphenyl-1-propen-3-yl acetate (**5e**) was prepared from chalcone by reduction with sodium borohydride and subsequent acetylation with acetyl chloride in triethylamine. Neryl acetate (**5f**) was obtained by acetylation of commercially available nerol. Other materials were purchased.

General Procedure. A mixture of 5.0×10^{-2} mmol of a halide and a catalytic amount of a transition metal in 0.5 mL of acetonitrile was stirred at room temperature under a nitrogen atmosphere in the dark for 5–30 min. To the resultant homogeneous solution was added, with a syringe, a solution of 1.0×10^{-1} mmol of BNAH in 0.5 mL of acetonitrile through a silicon–rubber stopper. The mixture was left at an appropriate temperature for an appropriate time; then a 200-μL aliquot of the mixture was pipetted out and quenched with 1 mL of water. The aliquot was extracted with 1 mL of benzene or ether containing an internal standard for VPC analysis. The organic layer was analyzed on a Yanaco G-180 gas chromatograph (OV-17 or SE-30 column). The amounts of the product(s) and the starting material were determined on the basis of calibration curves derived by authentic samples for each run. The total reaction times shown in Tables I and IV were the reaction periods thus monitored to get the maximal yield(s) of the product(s).

Identification of products was done by comparison of IR, NMR, and GC–MS spectra of isolated products with those of the corresponding authentic samples in some cases and in other cases by comparison of GC–MS spectra with those of authentic samples.

The amount of deuterium in the products from the reactions in deuterated solvent was determined by GC–MS spectrometry.

IR, NMR, and GC–MS spectra were recorded on a Hitachi 220 spectrophotometer, a JASCO JNM-FX 100 FT NMR spectrometer, and a Hewlett-Packard 5992 GC–MS spectrometer, respectively.

Registry No. **1a**, 636-98-6; **1a**-*d*, 97351-62-7; **1b**, 13329-40-3; **1c**, 619-44-3; **1d**, 589-87-7; **1e**, 540-37-4; **1f**, 53207-29-7; **1g**, 624-31-7; **1h**, 99-90-1; **1i**, 4965-36-0; **2a**, 620-05-3; **2b**, 28807-97-8; **2c**, 104-81-4; **2d**, 100-11-8; **2e**, 3042-81-7; **2f**, 585-71-7; **2g**, 25168-05-2; **3a**, 588-72-7; **3a**-d_5, 97351-63-8; **3b**, 56671-82-0; **3b**-*d*, 97351-64-9; **3c**, 59106-33-1; **3c**-d_5, 97374-07-7; **3d**, 59106-34-2; **4a**, 70-11-1; **4b**, 99-73-0; **4c**, 532-27-4; **4d**, 76-29-9; **5a**, 21040-45-9; **5b**, 21087-29-6; **5c**, 16212-07-0; **5d**, 74457-38-8; **5e**, 87751-69-7; **5f**, 141-12-8; **6**, 103-63-9; **7**, 952-92-1; BNAH, 952-92-1; PNAH, 35756-49-1; $RhCl(PPh_3)_3$, 14694-95-2; $Pd(OAc)_2$, 3375-31-3; $C_6H_5NO_2$, 98-95-3; $C_6H_5COCH_3$, 98-86-2; $C_6H_5CO_2CH_3$, 93-58-3; C_6H_5Br, 108-86-1; $C_6H_5NH_2$, 62-53-3; $C_6H_5CH(OH)CH_3$, 98-85-1; $C_6H_5CH_3$, 108-88-3; CH_3-*p*-$C_6H_4CH_3$, 106-42-3; CH_3-*p*-$C_6H_4NO_2$, 99-99-0; $C_6H_5CH{=}CH_2$, 100-42-5; (*E*)-$C_6H_5CH{=}CHCO_2Et$, 4192-77-2; (*Z*)-$C_6H_5CH{=}CHCO_2Et$, 4610-69-9; *p*-$BrC_6H_4COCH_3$, 99-90-1; $C_6H_5CH_2CH{=}CH_2$, 300-57-2; (*Z*)-$C_6H_5CH{=}CHCH_3$, 766-90-5; (*E*)-$C_6H_5CH_2CH{=}CHCH_3$, 935-00-2; (*E*)-$C_6H_5CH{=}CHCH_3$, 873-66-5; (*E*)-$C_6H_5CH{=}CHCH_2CH_3$, 1005-64-7; (*E*)-$C_6H_5CH{=}CHCH_2CH_6H_5$, 3412-44-0; *p*-$O_2NC_6H_4C_6H_4NO_2$-*p*, 1528-74-1; $C_6H_5CH_2CH_2C_6H_5$, 103-29-7; *p*-$IC_6H_4CO_2H$, 619-58-9; $C_6H_5CH(Br)CO_2H$, 4870-65-9; quinoline, 91-22-5; *dl*-dimethyl 1,2-diphenylsuccinate, 25169-82-8; *meso*-dimethyl 1,2-diphenylsuccinate, 25169-81-7; *dl*-2,3-diphenylbutane, 2726-21-8; *meso*-2,3-diphenylbutane, 4613-11-0; 2-cyclohexen-1-one, 930-68-7; ehtyl cinnamate, 103-36-6; 1,7,7-trimethylbicyclo[2.2.1]heptane-2-one, 76-22-2; α-phenylethyl acetate, 93-92-5; ethyl *cis*-3-phenylpropenoate-d_3, 97351-65-0; ethyl cinnamate-d_6, 97351-66-1; ethyl *erythro*-α,β-dibromohydrocinnamate, 30983-70-1; cinnamyl chloride, 2687-12-9; cinnamaldehyde, 104-55-2; chalcone, 94-41-7; nerol, 106-25-2.

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