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Ni(0)-Triphenylphosphine Complex-Catalyzed Homo-Coupling of 1-Alkenyl Halides with Zinc Powder1)

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Synopsis. The homo-coupling of 1-alkenyl halides was examined in the presence of $NiBr_2(PPh_3)_2$, PPh_3, and excess zinc. The reactions proceed under very mild conditions to give high yields of conjugated dienes. The addition of KI or thiourea was unnecessary for a successful reaction, in contrast with systems without an external phosphine ligand.

It is well known that zerovalent nickel complexes react with aryl and 1-alkenyl halides to afford homo-coupling products, biaryls and conjugated dienes.2—4) Recently, facile catalytic processes have been developed in combination with various reducing agents5—12) or electrochemical reduction13) to overcome the use of stoichiometric amounts of unstable Ni(0) complexes. We previously reported that metallic Ni(0)10,11) or Ni(0) $(PR_3)_2$ (R=Et, Bu)12) were effective for the coupling reactions of 1-alkenyl halides using zinc powder. However, the addition of KI and/or thiourea as a co-catalyst was necessary for successful reactions. In a further investigation, we found that Ni(0) $(PPh_3)_n$ (n=3 or 4) generated in situ from $Ni^{II}Br_2(PPh_3)_2$ and extra PPh_3, catalyzed the homo-coupling of 1-alkenyl bromides and chloride with zinc powder very well without the addition of any co-catalysts.

Result and Discussion

The coupling reaction of (E)-β-bromostyrene (**1**) with zinc powder was examined in the presence of a catalytic amount of $NiBr_2(PPh_3)_2$ and an appropriate amount of PPh_3 under various reaction conditions. As shown in Table 1, the reaction proceeded smoothly upon the addition of two or more molar amounts of PPh_3 to $NiBr_2(PPh_3)_2$ in acetonitrile at room temperature to give the coupling products, 1,4-diphenyl-1,3-butadienes in quantitative yield (Runs 3 and 4). The reaction was highly stereoselective to afford the (E,E)-isomer in 95% selectivity. The presence of the Ni complex and an extra PPh_3 ligand was essential for the successful reaction; additives such as KI and thiourea, which seemed to assist the reduction of Ni(II) by Zn and were frequently used in the catalytic system without extra phosphine ligands,9—12) were unnecessary. Thus, the present catalytic system was most facile and effective for the homo-coupling reaction of 1-alkenyl halides. Other polar solvents, such as hexamethylphosphoric triamide (HMPA), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF), were less effective (Runs 5—7). Eth-

Table 1. Reaction of (E)-β-Bromostyrene (**1**)a)

Run	Solvent	Temp	Yieldb)	Composition (%)c)
		°C	%	$E,E/E,Z/Z,Z$
1	CH_3CN	50	54	94/6/0
2d)	CH_3CN	50	45	88/12/0
3e)	CH_3CN	20	100 (85)	95/5/0 (100/0/0)
4e,f)	CH_3CN	20	91	94/6/0
5	HMPA	50	47	97/3/0
6	DMSO	50	31	98/2/0
7	DMF	50	24	100/0/0
8	EtOH	50	8g)	100/0/0
9	C_6H_6	50	3	100/0/0

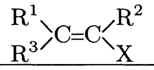
a) The reaction was carried out under following conditions: $NiBr_2(PPh_3)_2$ (1 mmol), Ni/PPh_3/**1**/Zn =1/2/30/30 in 8 cm^3 of the solvent for 8 h. b) Determined by GLC and calculated on the basis of the substrate used. The value in parenthesis is for the isolated one after purification. c) Determined by GLC. The values in the parenthesis are the composition of the purified product. d) $NiBr_2(PBu_3)_2$ (1 mmol) and PBu_3 (2 mmol) was used. e) Twenty cm^3 of solvent was used. f) Ni/PPh_3/**1**/Zn=1/5/30/30. g) Styrene was obtained in 19% yield.

Table 2. Reaction of (Z)-β-Bromostyrene (**2**)a)

Run	Solvent	Temp	Yieldb)	Composition (%)c)
		°C	%	$E,E/E,Z/Z,Z$
10	CH_3CN	20	2	0/63/37
11	CH_3CN	50	71	31/28/41
12	HMPA	50	79	18/42/40
13	DMSO	50	90	20/30/50
14	DMF	50	48	10/15/75
15	DMF	20	92	14/17/68
16d)	DMF	20	98	15/14/71
17e)	DMF	20	96 (55)	10/15/75 (0/0/100)

a) The reaction was carried out under the following conditions: $NiBr_2(PPh_3)_2$ (1 mmol), Ni/PPh_3/**2**/Zn =1/2/30/30 in 8 cm^3 of solvent for 8 h. b) Determined by GLC and calculated on the basis of the substrate used. The value in parenthesis is for the isolated one after purification. c) Determined by GLC. The values in the parenthesis are composition of the purified product. d) Ni/PPh_3/**2**/Zn=1/8/30/30. e) Reaction by using 0.3 mmol of $NiBr_2(PPh_3)_2$ at Ni/PPh_3/**2**/Zn=1/2/100/100 for 24 h.

Table 3. The Reactions of Various 1-Alkenyl Halides[a)]

Run					Solvent		Time	Yield[b)]	Composition (%)[c)]
	R^1	R^2	R^3	X		cm^3	h	%	$E,E/E,Z/Z,Z$
18	p-ClC_6H_4	H	H	Br	CH_3CN	20	8	85	100/0/0
19	p-MeC_6H_4	H	H	Br	CH_3CN	20	8	82	100/0/0
20	Ph	H	Ph	Br	DMF	8	8	90	
21	CH_3	H	CH_3	Br	CH_3CN	8	6	75(88)	
22[d)]	CH_3	H	CH_3	Cl	CH_3CN	8	6	(84)	
23	H	H	CH_3	Br	CH_3CN	20	4	(97)	(0/40/60)
24	H	CH_3	H	Br	CH_3CN	20	4	(79)	
25	n-Bu	H	H	Br	CH_3CN	4	4	(93)	(86/14/0)
26	H	H	n-Bu	Br	CH_3CN	4	4	(89)	(0/30/70)
27	$-(CH_2)_6-$		H	Br	CH_3CN	4	6.5	71(88)	

a) The reaction was carried out under the following conditions: $NiBr_2(PPh_3)_2$, 0.5 mmol, $Ni/PPh_3/Zn/substrate=1/2/30/30$ at 20 °C. b) Isolated yields after purification. The values in parentheses were determined by GLC. c) Isomer composition of isolated products after purification. The values in parentheses are the compositions in the reaction mixture without purification. d) Reaction was carried out at 50 °C.

anol as a solvent afforded styrene as the main product in preference to the coupling products (Run 8).

As shown in Table 2, the reaction of (Z)-β-bromostyrene (**2**) under the same reaction conditions gave only a 2% yield of the coupling products (Run 10). The reaction was therefore reinvestigated under various conditions. HMPA, DMSO, and CH_3CN were effective as solvents for the reaction to give the coupling products in excellent yields, but in low stereoselectivity, at 50 °C (Runs 11—13). Interestingly, the use of DMF as a solvent gave the products in high yield and in excellent Z, Z-diene selectivity at room temperature (Runs 15—17).

As shown in Table 3, a clean coupling reaction of various 1-alkenyl halides proceeded by the catalysis of $NiBr_2(PPh_3)_2/PPh_3/Zn$ system. CH_3CN was the best solvent for most of the reactions, except for 1-bromo-2,2-diphenylethylene, in which DMF was an effective solvent (Run 20), similar to the case of **2**. All substitution patterns, α- or β-monosubstitution (Runs 23—26), α,β- or β,β-disubstitution (Runs 20—22, 27), or p-chloro and p-methyl substituent on the aromatic ring (Runs 18 and 19), did not significantly influence the reactivities. 1-Alkenyl chloride was also reactive at higher temperature (Run 22) though it scarcely reacted when phosphine-free Ni(II) was used as a catalyst.[10—12)] The original configuration of the double bonds in the reactions of (E)-1-alkenyl halides were retained in the products, whereas much isomerization occurred in the (Z)-1-alkenyl halides. These isomerizations have been frequently observed in Ni-promoted homo- and cross-coupling of 1-alkenyl halides,[3,4,10—12,14)] and are a characteristic feature of Ni catalysis. Although we made no effort to establish the origin of the isomerization in this work, it might have occurred in the 1-alkenyl ligand-transfer process, as was proposed in previous studies.[11)]

Experimental

All of the solvents were purified by general methods and stored under dry nitrogen. $NiBr_2(PPh_3)_2$ was prepared by a method described in the literature,[15)] followed by two recrystallizations from 1-butanol. 2-Bromopropene and 1-chloro-2-methylpropene were commercially available and used without further purification. (E)- and (Z)-1-Bromo-1-hexene were prepared according to methods described in the literature.[16,17)] All other 1-alkenyl halides were prepared as previously described.[11,12)]

General Procedure. A mixture of $NiBr_2(PPh_3)_2$ (1 mmol), PPh_3 (2 mmol), and zinc powder (30 mmol) in an appropriate amount of dry solvent was vigorously stirred at the desired temperature under N_2. After stirring for 30 min, a 1-alkenyl halide (30 mmol) was injected into the mixture, and stirring was continued. After the desired time the mixture was poured into 20 cm^3 of 5% aqueous HCl and extracted by 20 cm^3 of dichloromethane or pentane. The extract was washed with 10 cm^3 of 5% HCl and dried over anhydrous sodium sulfate. The resultant mixture was directly subjected to quantitative analysis by GLC. The products were identified by a comparison of the GC retention time and GC/MS with authentic samples.

(E,E)-1,4-Diphenyl-1,3-butadiene. A mixture of **1** (30 mmol), $NiBr_2(PPh_3)_2$ (1 mmol), PPh_3 (2 mmol), and Zn powder (30 mmol) in dry CH_3CN (20 cm^3) was vigorously stirred at 20 °C for 8 h. GLC analysis of the crude product showed a quantitative formation of the title compounds with 95% isomeric purity. Recrystallization from ethanol gave pure E,E-diene in 85% yield. Mp 153 °C (lit,[18)] 149—150 °C). ^1H NMR (200 MHz, $CDCl_3$) $\delta=6.5$—6.8 (m, 4H, olefinic H), 7.1—7.4 (m, 10H, aromatic H).

(Z,Z)-1,4-Diphenyl-1,3-butadiene. The reaction using **2** (30 mmol), $NiBr_2(PPh_3)_2$ (0.3 mmol), PPh_3 (0.6 mmol), and Zn (30 mmol) in dry DMF (8 cm^3) was carried out at 20 °C for 24 h. GLC analysis of dichloromethane extract showed the formation of 94% yield of products with $E,E/E,Z/Z,Z=10/15/75$. Recrystallization from ethanol gave pure Z,Z-diene in 51% yield. Mp 69—70 °C, λ_{max}, 300 nm (lit,[18] Mp 70 °C, $\lambda_{\max}$, 300 nm); ^{1}H NMR (200 MHz, CDCl$_3$) δ=6.5—6.7 (m, 4H, olefinic H), 7.1—7.5 (m, 10H, aromatic H).

(1*E*,3*E*)-1,4-Bis(*p*-chlorophenyl)-1,3-butandiene. The reaction using (*E*)-*p*-chloro-β-bromostyrene (15 mmol), NiBr$_2$(PPh$_3$)$_2$ (0.5 mmol), PPh$_3$ (1.0 mmol), and Zn (15 mmol) in dry CH$_3$CN (20 cm^3) was carried out at 20 °C for 24 h. Recrystallization from ethanol gave pure *E,E*-diene in 85% yield. ^{1}H NMR (200 MHz, CDCl$_3$) δ=6.4—6.7 (m, 4H, olefinic H), 6.8—7.0 (m, 8H, aromatic H).

(1*E*,3*E*)-1,4-Bis(*p*-methylphenyl)-1,3-butadiene. The reaction of (*E*)-*p*-methyl-β-bromostyrene (15 mmol), NiBr$_2$(PPh$_3$)$_2$ (0.5 mmol), PPh$_3$ (1.0 mmol), and Zn (15 mmol) in dry CH$_3$CN (20 cm^3) was carried out at 20 °C for 24 h. Recrystallization from ethanol gave pure *E,E*-diene in 82% yield. Mp 192 °C. ^{1}H NMR (200 MHz, CDCl$_3$) δ=2.4 (s, 6H, CH$_3$), 6.5—6.7 (m, 2H, oldfinic H), 6.8—7.0 (m, 2H, olefinic H), 7.14 (d, 4H, J=8 Hz, aromatic H), 7.34 (d, 4H, J=8 Hz, aromatic H).

1,1,4,4-Tetraphenyl-1,3-butadiene. The reaction of 1-bromo-2,2-diphenylethylene (15 mmol), NiBr$_2$(PPh$_3$)$_2$ (0.5 mmol), PPh$_3$ (1 mmol), and Zn (15 mmol) in dry DMF (4 cm^3) was carried out at 20 °C for 4 h. Recrystallization from ethanol gave a pure product in 90% yield. Mp 203 °C (lit,[19] 207—210 °C); ^{1}H NMR (200 MHz, CDCl$_3$) δ=6.8 (s, 2H, olefinic H), 7.1—7.5 (m, 20H, aromatic H).

1,1′-Bicyclooctenyl. The mixture of 1-bromocyclooctene (15 mmol), NiBr$_2$(PPh$_3$)$_2$ (1 mmol), PPh$_3$ (2 mmol), and Zn powder (15 mmol) in dry CH$_3$CN (4 cm^3) was vigorously stirred at 20 °C for 6.5 h. The crude product was purified by silica-gel column chromatography eluted by hexane and recrystallized from ether-ethanol (1 : 1) to give pure diene in 71% yield. Mp 42 °C (lit,[20] 42—43 °C); ^{1}H NMR (200 MHz, CDCl$_3$) δ=1.2—1.6 (m, 26H, CH$_2$), 5.71 (t, 2H, J=9 Hz, olefinic H).

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