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Monophenylation accompanied by partial reduction of 1,1-dihalogeno-2-phenyl-1-alkenes in the presence of a nickel-phosphine complex

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Abstract

Reaction of 1,1-dihalogeno-2-phenyl-1-alkenes (I) with phenylmagnesium bromide in the presence of $NiCl_2$(dppp) in THF has been studied. Mono-cross-coupling accompanied by partial reduction gave (*E*)-1,2-diphenyl-1-alkenes (III) as the major products. Use of a large excess of Grignard reagent increased the yields of III and the (*Z*)-isomers (II), with a decrease in the yield of double cross-coupling products, 1,1,2-triphenyl-1-alkenes (IV). The highest ratio of the sum of the yields of the monophenylation products to the yield of the double cross-coupling product, $(II + III)/IV = 36.5$, was found for the reaction of PhMgBr with 1,1-dibromo-2-phenylpropene (Ib) in a 12.0/1 molar ratio. A possible reaction mechanism is described.

Introduction

Transition-metal catalyzed cross-coupling of halogeno-aromatics, halogeno-heteroaromatics, or vinyl halides with Grignard reagents is well known [1]. However, the Grignard cross-coupling of 1,1-dihalogenoethenes has been little studied [1a,1b,2–4]. Minato et al. have recently reported the stereoselective mono cross-coupling of 2-aryl (or heteroaryl)-1,1-dichloroethenes in Et_2O, but not observed formation of any reduction product [4]. Here we describe the interesting and unprecedented observations associated with the nickel-catalysed Grignard cross-coupling reaction.

Results and discussion

We have observed that when 1,1-dihalogeno-2-phenyl-1-alkenes (I) were allowed to react with PhMgBr in the presence of $NiCl_2$(dppp) (dppp = 1,3-bis(diphenyl-

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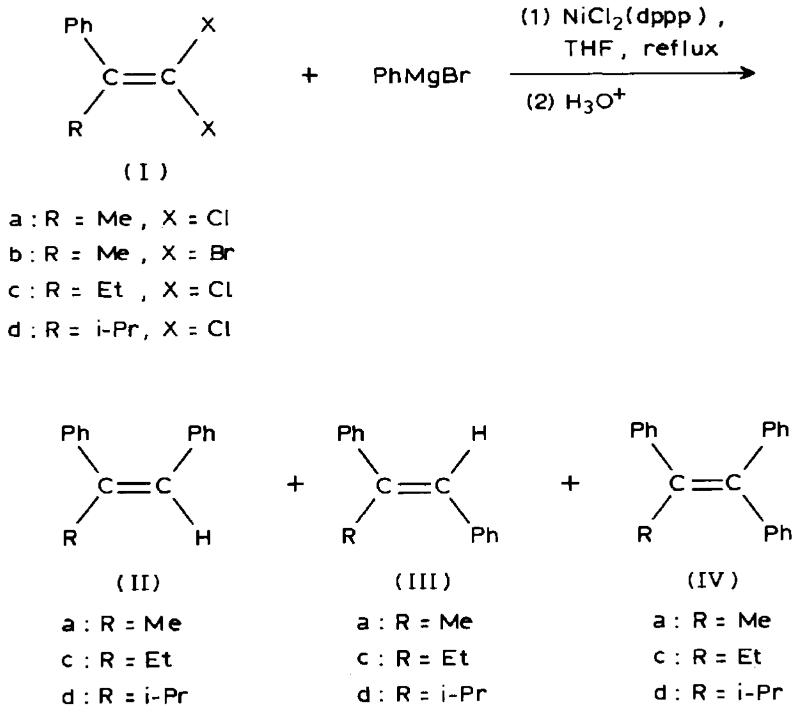


Scheme 1.

phosphino)propane) in THF, and after aqueous work-up the (*Z*)- and (*E*)-1,2-diphenyl-1-alkenes, II and III respectively, were formed together with the expected double cross-coupling products, 1,1,2-triphenyl-1-alkenes (IV) (Scheme 1).

Some results are listed in Table 1. In the reaction of 1,1-dichloro-2-phenylpropene (Ia) with PhMgBr (Grignard/dihaloalkene molar ratio 3.6), monophenylation took place mainly at the position *trans* to the 2-phenyl group, and (*E*)-1,2-diphenylpropene (IIIa) was isolated as the major product in 35% yield (Entry 3). An

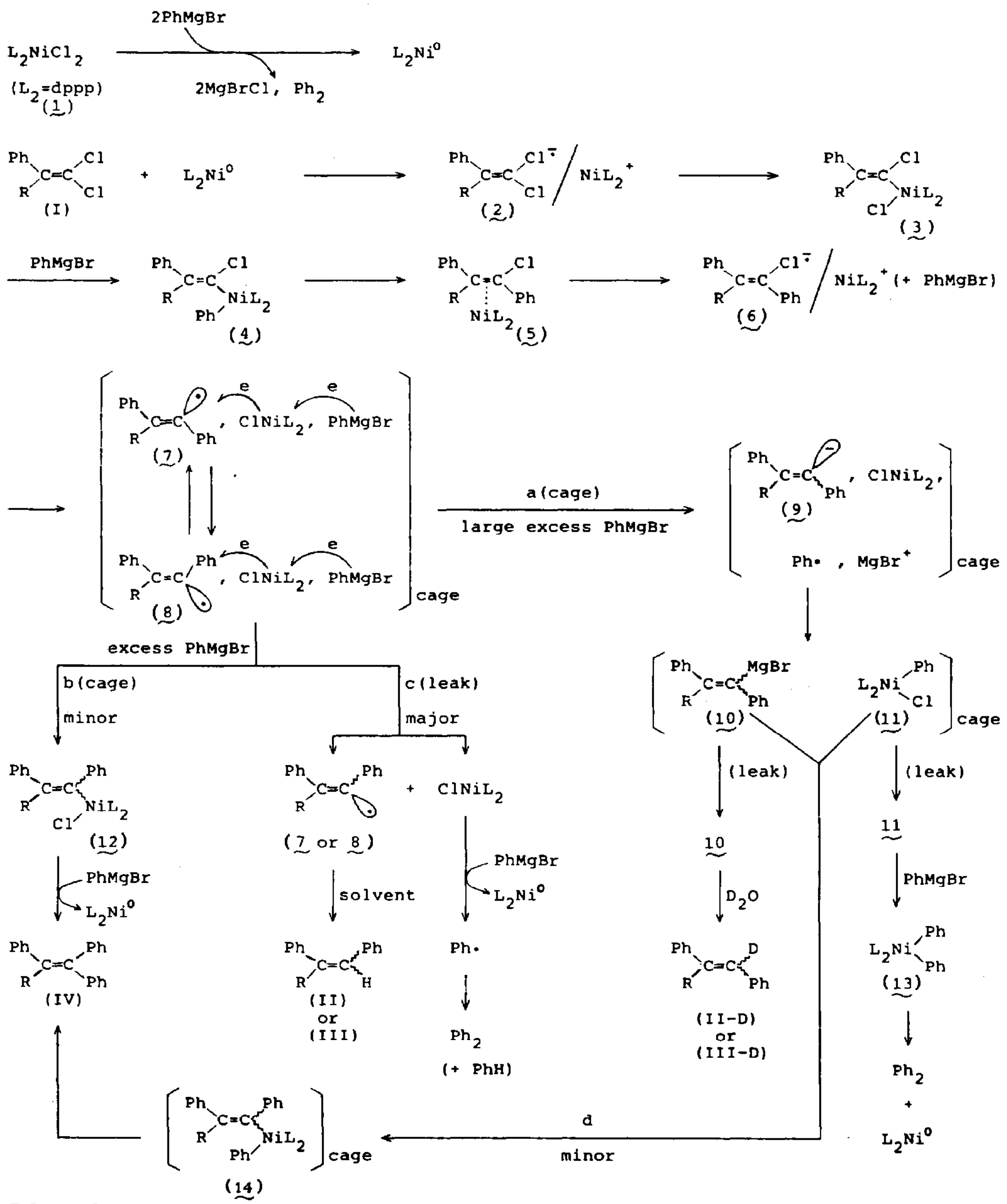
Table 1

Nickel-phosphine complex-catalyzed reaction of 1,1-dihalogeno-2-phenyl-1-alkenes (I) with phenylmagnesium bromide in THF [a]

Entry	Dihaloalkene				PhMgBr (mmol)	Reaction time (h)	Yield (%) [b]			Ratio (II+III)/IV
	I	Ar	R	X			II	III	IV	
1	a:	Ph	Me	Cl	1.2	8	3	14	6	2.8
2					2.4	24	6	26	4	8.0
3					3.6	24	9	35	6	7.3
4					12.0	28	12	59	3	23.7
5	b:	Ph	Me	Be	3.6	0.25	14	26	4	10.0
6					12.0	0.25	20	53	2	36.5
7	c:	Ph	Et	Cl	3.6	28	9	27	3	12.0
8					12.0	28	16	50	2	33.0
9	d:	Ph	i-Pr[c]	Cl	3.6	28	5	12	0	–
10					12.0	28	8	20	0	–

[a] A mixture of I (1 mmol), $NiCl_2$(dppp) (0.02 mmol), and PhMgBr was refluxed in THF (10 ml) for some time under nitrogen, and then worked up with dil. HCl. [b] Determined by GLC. [c] i-Pr = isopropyl.

increase in the molar ratio, of Grignard to dihaloalkene, to 12.0 led to a decreased yield of the expected double cross-coupling product, 1,1,2-triphenylpropene (IVa), and an increased yield of both (*Z*)-1,2-diphenylpropene (IIa) (12%) and IIIa (59%) (Entry 4). Thus, the ratio, (IIa + IIIa)/IVa, of the sum of the yields of the monophenylation products to the yield of the double phenylation product, was augmented markedly by an increase in the molar ratio of Grignard/dihaloalkene (compare Entry 3 with Entry 4). The highest value of (II + III)/IV 36.5 was found in the reaction of PhMgBr with the analogous 1,1-dibromoalkene (Ib) in 12.0 molar



Scheme 2.

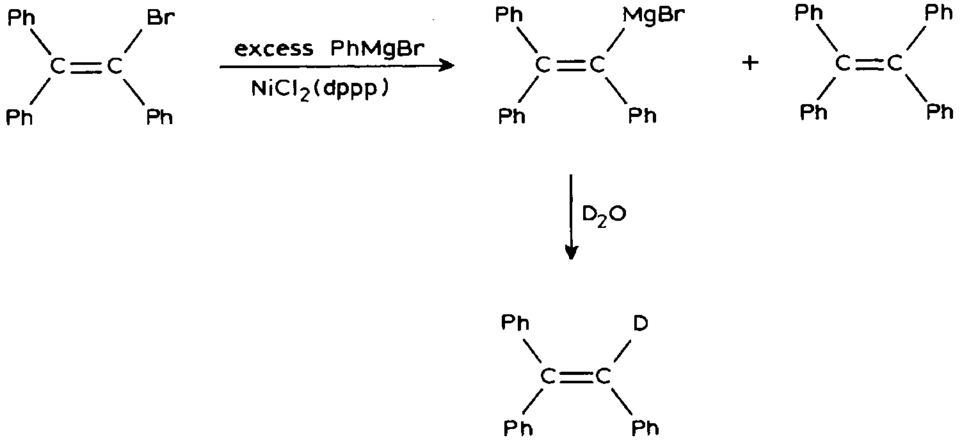
ratio (Entry 6). The reaction of 1,1-dichloro-3-methyl-2-phenyl-1-butene (Id) gave rise to (*E*)-3-methyl-1,2-diphenyl-1-butene (IIId) in the lowest yield because of the steric hindrance by the isopropyl group, and no double cross-coupling product, 3-methyl-1,1,2-triphenyl-1-butene (IVd), was detected (Entries 9, 10). Furthermore, in the absence of the nickel catalyst, I hardly reacted with PhMgBr.

In the initial stages of the reaction with Ia, the formation of a by-product, biphenyl (18% yield), was found to be proportional to the formation of IIa and IIIa (IIa + IIIa 21% yield) during the first one hour period.

When a reaction mixture involving Ia, PhMgBr, and $NiCl_2$(dppp) (Entry 3) was treated with D_2O, (*Z*)-1,2-diphenyl(1-^2H)propene (IIa-D), D 33%, and (*E*)-1,2-diphenyl(1-^2H)propene (IIIa-D), D 68%, were detected by GC-MS. The low D contents of IIa-D and IIIa-D suggest that there is: (i) interference by radical species which abstract hydrogen atoms from the medium, most probably the α-hydrogen atom from THF [5], and (ii) the formation of a new Grignard reagent. On the basis of these results, we consider a possible mechanism of the reaction of I with PhMgBr in the presence of the nickel catalyst (Scheme 2).

In the first step of the reaction, the oxidative addition of the sp^2 carbon-chlorine bond of I to the nickel center of L_2Ni^0, formed in situ from $NiCl_2$(dppp) (**1**) with PhMgBr, gives a (halo)nickel complex (**3**). Reaction of the complex **3** with PhMgBr gives a tricoordinated intermediate (**5**) via the (phenyl)nickel complex (**4**). The intermediate **5** undergoes intramolecular electron-transfer to yield a pair of anion radicals (**6**) and the cation NiL_2^+, which in turn is broken up into an equilibrium mixture of (*E*)- and (*Z*)-1,2-diphenyl-1-alkenyl radicals (**7** and **8**), respectively, with $ClNiL_2$ in the solvent cage.

In the presence of a large excess of PhMgBr, a single electron transfer to **7** and **8** from PhMgBr through $ClNiL_2$ gives an anion, 1,2-diphenyl-1-alkenide (**9**), a Ph radical, and $MgBr^+$ in the cage (path a). The anion **9** and $MgBr^+$ combine to give a new Grignard reagent, 1,2-diphenyl-1-alkenylmagnesium bromide (**10**), while the Ph radical and $ClNiL_2$ form a (chloro)(phenyl)nickel complex (**11**). The reaction of the nickel complex **11** with PhMgBr produces the by-product, biphenyl, via a (diphenyl)nickel complex (**13**). Hydrolysis of the new Grignard reagent **10** with D_2O should give II-D and III-D.



Scheme 3.

In the presence of smaller quantities of PhMgBr, the radicals **7** and **8** leak out of the cage and abstract an α-hydrogen atom from THF probably to give II and III (path c). The radicals **7** or **8** react with $ClNiL_2$ to give a (chloro)(alkenyl)nickel complex (**12**), which reacts less effectively with PhMgBr to produce the minor product IV (path b). Product IV may also be formed from the new Gignard reagent **10** and the nickel complex **11** (path d). These two processes (b and d) may be restricted by the unfavorable formation of sterically crowded trisubsituted alkenylnickel intermediates, **12** or **14**.

When a mixture of PhMgBr, bromotriphenylethene, and $NiCl_2$(dppp) (Grignard/bromoethene/Ni-complex 1.1/1.0/0.025 molar ratio) in THF was treated with D_2O, no triphenyl (1-^2H)ethene could be detected by GC-MS, but from a similar mixture containing a 6.1/1.0/0.025 molar ratio of reactants, triphenyl(1-^2H)ethene, D 44%, was obtained (Scheme 3). These results support the fact that both reactions, paths a and c, proceed concurrently when a large excess of PhMgBr is present.

Experimental

General

All Grignard cross-coupling reactions were carried out under nitrogen. PhMgBr was prepared by a standard procedure from bromobenzene and Mg (20% excess) in THF. $NiCl_2$(dppp) was prepared by a published procedure [6]. THF was distilled over sodium and stored under nitrogen. Quantitative GLC was performed with an SE-30 column using triphenylmethane as the internal standard. ^1H NMR spectra were recorded at 270 MHz. GC-MS spectra were recorded at 70 eV in the region of m/z 80-350.

Preparation of Ia–Id

Ia [7] was prepared by a published procedure [8] from acetophenone, CCl_4, and triphenylphosphine (60 °C, 4 h) and isolated by preparative LC on silica gel. B.p. 76–77 °C/6 Torr; m/z: 190 (6%, $M+4^+$), 188 (37%, $M+2^+$), 186 (58%, M^+), 116 (20%, M^+-2Cl), and 115 (100%, $M^+-2Cl-H$).

Ib [7] was prepared from acetophenone, CBr_4, and triphenylphosphine in dichloromethane (r.t., 1 h) by a published procedure [9]. B.p. 84–84.5 °C/2 Torr; m/z: 278 (32%, $M+4^+$), 276 (65%, $M+2^+$), 274 (33%, M^+), 116 (68%, M^+-2Br), and 115 (100%, $M^+-2Br-H$).

1,1-Dichloro-2-phenyl-1-butene (Ic) was obtained from propiophenone, in a manner similar to that for the preparation of Ia. B.p. 80–81 °C/2 Torr; m/z 204 (5%, $M+4^+$), 202 (30%, $M+2^+$), 200 (46%, M^+), 130 (15%, M^+-2Cl), and 129 (100%, $M^+-2Cl-H$). Anal. Found: C, 59.47; H, 5.05; Cl, 35.03. $C_{10}H_{10}Cl_2$ calc.: C, 59.73; H, 5.01; Cl, 35.26%.

Id was prepared similarly from isobutyrophenone. B.p. 91–92 °C/4 Torr; m/z: 218 (0.8%, $M+4^+$), 216 (5%, $M+2^+$), 214 (8%, M^+), 155 (100%), and 144 (31%, M^+-2Cl). Anal. Found: C, 61.30; H, 5.63; Cl, 33.00. $C_{11}H_{12}Cl_2$ calc.: C, 61.43; H, 5.62; Cl, 32.96%.

Reaction of I with PhMgBr in the presence of $NiCl_2$(dppp)

A typical procedure (Entry 3 in Table 1) was carried out as follows. To a suspension of Ia (0.187 g; 1 mmol) and $NiCl_2$(dppp) (11 mg; 0.02 mmol) in THF

(7.9 ml), was added a 1.70 *M* solution of PhMgBr in THF (2.1 ml; 3.6 mmol). After being refluxed for 24 h, the mixture was quenched with dilute aqueous HCl. The products, IIa, IIIa, IVa, and biphenyl were identified by GLC and characterized by GLC, ^{1}H-NMR, and/or GC-MS. In the absence of the nickel catalyst, Ia scarcely reacted with PhMgBr. IIa [10]: *m/z*: 194 (84%, M^+), 193 (17%, $M^+ - H$), and 179 (100%, $M^+ - CH_3$). IIIa [11]: m.p. 81–82 °C (lit. m.p. 81 °C); ^{1}H NMR ($CDCl_3$): δ 2.27 (d, *J* 1.5 Hz, 3H), 6.83 (unresolved quartet, 1H), and 7.2–7.6 (m, 10H); *m/z* 194 (85%, M^+), 193 (17%, $M^+ - H$), and 179 (100%, $M^+ - CH_3$). IVa [12]: m.p. 83–84 °C (lit. m.p. 86–87 °C); *m/z*: 270 (100%, M^+) and 255 (45%, $M^+ - CH_3$).

The reactions of Ib–Id with PhMgBr were carried out similarly. (*Z*)-1,2-Diphenyl-1-butene (IIc) [10]: *m/z*: 208 (100%, M^+), 207 (15%, $M^+ - H$), 193 (49%, $M^+ - CH_3$), and 179 (50%, $M^+ - C_2H_5$). (*E*) = 1,2-Diphenyl-1-butene (IIIc) [10]: m.p. 59–60 °C (lit. m.p. 56 °C); ^{1}H NMR ($CDCl_3$): δ 1.06 (t, *J* 7.3 Hz, 3H), 2.74 (q, *J* 7.3 Hz, 2H), 6.69 (1H), and 7.2–7.5 (m, 10H); *m/z*: 208 (100%, M^+), 207 (11%, $M^+ - H$), 193 (45%, $M^+ - CH_3$), 179 (47%, $M^+ - C_2H_5$). 1,1,2-Triphenyl-1-butene (IVc) [13]: m.p. 79–80 °C (lit. m.p. 80–81 °C); *m/z*: 284 (100%, M^+), 269 (25%, $M^+ - CH_3$), and 255 (16%, $M^+ - C_2H_5$). (*Z*)-3-Methyl-1,2-diphenyl-1-butene (IId) [14]: *m/z*: 222 (100%, M^+), 221 (6%, $M^+ - H$), 179 (36%, $M^+ - CH(CH_3)_2$), and 130 (74%, $M^+ - C_6H_5 - CH_3$). IIId [14]: *m/z*: 222 (54%, M^+), 221 (3%, $M^+ - H$), 179 (32%, $M^+ - CH(CH_3)_2$), and 130 (100%, $M^+ - C_6H_5 - CH_3$).

Preparation of IIa-D and IIIa-D

After being refluxed for 24 h, the mixture of Ia (1 mmol), PhMgBr (3.6 mmol), and $NiCl_2$(dppp) (0.02 mmol) in THF was quenched with D_2O, extracted with Et_2O, and then dried with Na_2SO_4. The presence of IIa-D and IIIa-D was determined by GC-MS. The H/D ratios of IIa/IIa-D and IIIa/IIIa-D were 67/33 and 32/68, respectively.

Reaction of bromotriphenylethene with PhMgBr

A mixture of the bromoethene [15] (0.17 g; 0.51 mmol), a 1.10 *M* solution of PhMgBr in THF (0.5 ml; 0.55 mmol), and $NiCl_2$(dppp) (7 mg; 0.013 mmol) in THF (4.3 ml) was refluxed for 1 h. After quenching with D_2O, the reaction mixture was treated as described above. The products, triphenylethene and tetraphenylethene, were obtained in 55 and 12% yields, respectively, but no deuterated product could be detected by GC-MS. However, a large excess of the Grignard reagent (Grignard/bromoethene/Ni-complex 6.1/1.0/0.025 molar ratio), gave rise to triphenyl(1-^{2}*H*)-ethene, D 44%, and tetraphenylethene in 80 and 5% yields, respectively. In the absence of the nickel catalyst, the bromoethene scarcely reacted.

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