

Nickel-catalysed Substitution Reactions of Allylic Carbonates with Aryl- and Alkenyl-borates

Yuichi Kobayashi* and Eitatsu Ikeda

Department of Biomolecular Engineering, Tokyo Institute of Technology, Nagatsuta, Yokohama 227, Japan

Substitution reactions of 1,3-disubstituted allylic carbonates **3** with aryl- and alkenyl-borates **4** are catalysed by $[\text{NiCl}_2(\text{dppf})]$ [dppf = 1,1'-bis(diphenylphosphino)ferrocene], and in the case of the cyclic carbonate **7**, the reaction proceeds with complete inversion.

Transition-metal catalysed substitution reactions of allylic alcohol derivatives with aryl- and alkenyl-metallic reagents is an important carbon-carbon bond forming reaction.¹ Although a number of organometallic reagents based on aluminum,² boron,³ magnesium,⁴ tin,⁵ zinc⁶ and zirconium⁷ have been reported to enter into substitution reactions in the presence of palladium and/or nickel catalysts with varying success, the reaction of 1,3-disubstituted allylic alcohol derivatives, a most important substitution process in organic synthesis, has been examined only with Grignard reagents.^{4,8} Therefore, in an attempt to find a new reagent and catalyst system to enable this reaction to proceed under mild conditions so as to tolerate reactive functional groups, we applied the palladium catalysed reaction of 1- or 3-monosubstituted allylic phenoxides or acetates **1** with organoboron reagents **2** or NaBPh_4 as reported by Suzuki and coworkers^{3a,b} and Legros and Fiaud,^{3c} respectively, (Scheme 1) to 1,3-disubstituted allylic carbonates **3** and organoborates **4**⁹ (Scheme 2), both of which can be readily synthesized.[†] We found that the reaction proceeds in the presence of nickel catalysts, while

palladium catalysts effect formation of the corresponding methyl ether. In this communication, the reactivity and stereochemistry of this new reaction system are presented.

The substitution reactions were examined using the allylic carbonate **3a** ($\text{R}^1 = \text{Ph}$, $\text{R}^2 = n\text{-C}_5\text{H}_{11}$) and 2–3 equiv. of phenylborate (**4a**, $\text{R} = \text{Ph}$) or 2-furylborate (**4d**, $\text{R} = 2\text{-furyl}$) in the presence of 5–10 mol% of a palladium or a nickel catalyst in THF (Scheme 2). The products were analysed by 300 MHz ^1H NMR spectroscopy and the results are summarized in Table 1. When the reaction was carried out with **4a** at 60 °C in the presence of 10 mol% $[\text{Pd}(\text{PPh}_3)_2]$ (prepared *in situ* by mixing $[\text{Pd}_2(\text{dba})_3] \cdot \text{CHCl}_3$ ¹⁰ (dba = dibenzylideneacetone) and 2 equiv. of PPh_3), methyl ether **6** was the major product (66% yield) and the yield of the desired product **5a** ($\text{R}^1 = \text{R} = \text{Ph}$, $\text{R}^2 = n\text{-C}_5\text{H}_{11}$) was <10% (entry 1). Production of **6** was also catalysed by $[\text{Pd}(\text{dppf})]$ ¹¹ (entry 2). We then examined nickel catalysts and found that the desired reaction proceeded in the presence of $[\text{NiCl}_2(\text{PPh}_3)_2]$ ¹² or $[\text{NiCl}_2(\text{dppf})]$ ¹³ giving rise to **5a** in 35 and 83% yield, respectively (entries 3 and 4). As expected from the result of the nickel-catalysed substitution of allylic alcohols with Grignard reagents,^{4a} regio- and stereo-selectivity for **5a** was >99%. In no case was methyl ether **6** detected. The nickel

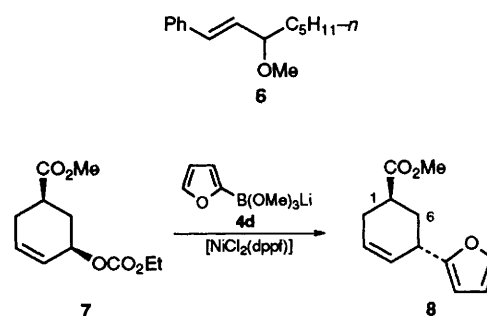
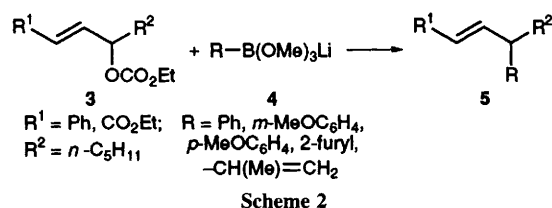
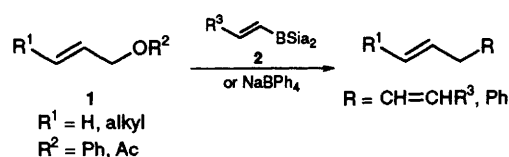


Table 1 Palladium- and nickel-catalysed substitution reactions of carbonates **3** with borates **4**^a

Entry	Catalyst	Carbonate ^b 3 R^1		Borate 4 R		Yield (%)		
						Product ^b		Recovered 3
						5	6	
1	$[\text{Pd}(\text{PPh}_3)_2]^c$	a	Ph	a	Ph	a, <10	66	0
2	$[\text{Pd}(\text{dppf})]^c$	a	Ph	a	Ph	a, 0	54	0
3	$[\text{NiCl}_2(\text{PPh}_3)_2]$	a	Ph	a	Ph	a, 35	0	55
4	$[\text{NiCl}_2(\text{dppf})]$	a	Ph	a	Ph	a, 83	0	0
5	$[\text{NiCl}_2(\text{dppf})]$	a	Ph	b	<i>m</i> -MeOC ₆ H ₄	b, 81	0	0
6	$[\text{NiCl}_2(\text{dppf})]$	a	Ph	c	<i>p</i> -MeOC ₆ H ₄	c, 68	0	0
7	$[\text{NiCl}_2(\text{PPh}_3)_2]$	a	Ph	d	2-Furyl	d, 77	0	0
8	$[\text{NiCl}_2(\text{dppf})]$	a	Ph	d	2-Furyl	d, 65	0	0
9	$[\text{NiCl}_2(\text{dppf})]$	a	Ph	e	CH(Me)=CH ₂	e, 46	0	0
10	$[\text{NiCl}_2(\text{dppf})]$	b	CO ₂ Et	d	2-Furyl	f, 67	^d	0

^a Reaction was carried out with 5–10 mol% of the catalyst in THF at 50–60 °C for 12–15 h. ^b $\text{R}^2 = n\text{-C}_5\text{H}_{11}$. ^c Prepared *in situ* from $[\text{Pd}_2(\text{dba})_3] \cdot \text{CHCl}_3$ and the corresponding phosphine ligand. ^d No corresponding methyl ether was produced.

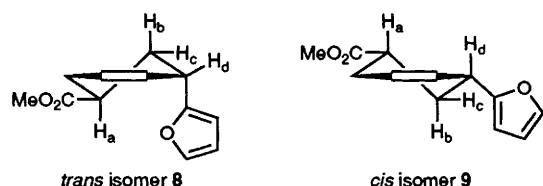


Fig. 1 Structures and plausible conformers of *trans* and *cis*-isomers **8** and **9**

complexes also catalysed substitution of **3a** with the furylborate **4d** to give **5d** selectively in 65–77% yield (entries 7 and 8). For both of the borates **4a** and **4d**, $[\text{NiCl}_2(\text{dppf})]$ was an excellent catalyst.[‡]

The catalytic activity of $[\text{NiCl}_2(\text{dppf})]$ was further investigated to extend the scope of the reaction by using other combinations of organoborates **4b–e** and carbonates **3a,b** and the results are also shown in Table 1. Reaction of **3a** with *m*- and *p*-methoxyphenylborates **4b,c** afforded the substitution products **5b,c** in good yields (entries 5 and 6). Substitution of **3a** with prop-2-enylborate **4e** also proceeded to afford **5e** in 46% yield (entry 9). The last example (entry 10) shows that the ester group can withstand the reaction conditions, for which a further example is presented (reaction of the carbonate **7**, see below). In all cases, examined regio- and/or stereo-isomers were not detected in the NMR spectra, as was seen in the case of the production of **5a** and **5d**.

The stereochemistry of the present reaction was examined by using the *cis* carbonate **7** (*cis*: *trans* >99%), which was prepared from the methyl ester of *cis*-5-hydroxycyclohex-3-enecarboxylic acid¹⁴. The reaction of the carbonate **7** was carried out with 2-furylborate **4d** in the presence of $[\text{NiCl}_2(\text{dppf})]$ (Scheme 3). The substitution product **8** was formed with >99% stereoisomeric purity in 81% yield. Its stereochemistry was established to be *trans* by the 300 MHz ¹H NMR spectrum and by comparison with that of *cis* isomer **9** which was prepared by isomerization of **8** under NaOMe in MeOH. Coupling constants of the C-6 axial hydrogen (H_b) of the *trans* isomer **8** at δ 1.99 are $J_{ab} = 11.3$, $J_{bc} = 12.8$, $J_{bd} = 5.7$ Hz, and those of *cis* isomer **9** at δ 1.77 are $J_{ab} = J_{bc} = 12.6$, $J_{bd} = 11.2$ Hz, indicating the assigned stereochemistry and the conformation shown in Fig. 1. Thus, these data indicate that the present reaction proceeds with inversion.

Based on the facts that $[\text{Ni}(\pi\text{-allyl})(\text{aryl})]$ complexes undergo reductive elimination to afford allyl-aryl products⁸ and that the nickel(o) complexes prepared *in situ* from $[\text{NiCl}_2(\text{dppf})]$ and 2 equiv. of Bu^nLi at room temperature for 1 h also affected the substitution reaction, we propose the present reaction proceeds in the following way: (i) formation of nickel(o) complexes under the reaction conditions, (ii) oxidative addition of the nickel(o) complexes to the allylic carbonate **3** with inversion to produce the allyl-nickel intermediates, (iii) transmetalation with the borate **4** and (iv) reductive elimination with retention of configuration to afford **5**.

Received, 29th April 1994; Com. 4/02550D

Footnotes

[‡] The carbonates **3a,b** and **7** were synthesized from the corresponding allylic alcohols and ethyl chloroformate in the presence of pyridine at 0 °C → room temperature. The borates **4** used here were prepared *in*

situ by addition of a slight excess of trimethyl borate to the corresponding organolithium reagents, which were purchased or generated in THF as follows: PhLi from Aldrich; 2-furyllithium from furan and Bu^nLi (0 °C, 2 h); *m*- and *p*- $\text{MeOC}_6\text{H}_4\text{Li}$ from bromoanisoles and Bu^nLi (–70 °C, 2 h); $\text{CH}_2=\text{CH}(\text{Me})\text{Li}$ from $\text{CH}_2=\text{C}(\text{Me})\text{Br}$ and Bu^nLi (–70 °C, 2 h).

[‡] The following procedure for the synthesis of **5a** is representative. To an ice-cold solution of PhLi (0.81 ml, 1.8 mol dm^{-3} in cyclohexane– Et_2O , 1.45 mmol) in THF (6 ml) was added $\text{B}(\text{OMe})_3$ (0.21 ml, 1.81 mmol) dropwise under nitrogen. After 15 min, the carbonate **3a** (200 mg, 0.72 mmol) and $[\text{NiCl}_2(\text{dppf})]$ (25 mg, 0.036 mmol) were added. The solution was stirred for 12 h at 60 °C and then poured into a mixture of hexane and saturated NH_4Cl aqueous solution. The mixture was filtered through a pad of Celite with hexane. The filtrate was separated and the aqueous layer was extracted with hexane twice. The combined organic layers were concentrated to give **5a** (164 mg) in 83% yield after purification by column chromatography on silica gel.

References

- Reviews: K. Tamao, *Comprehensive Organic Synthesis*, ed. B. M. Trost, I. Fleming and G. Pattenden, Pergamon, 1991, vol. 3, p. 435; G. Consiglio and R. M. Waymouth, *Chem. Rev.*, 1989, **89**, 257.
- H. Matsushita and E. Negishi, *J. Am. Chem. Soc.*, 1981, **103**, 2882; E. Negishi, S. Chatterjee and H. Matsushita, *Tetrahedron Lett.*, 1981, **22**, 3737.
- (a) N. Miyaara, K. Yamada, H. Sugimoto and A. Suzuki, *J. Am. Chem. Soc.*, 1985, **107**, 972; (b) N. Miyaara, T. Yano and A. Suzuki, *Tetrahedron Lett.*, 1980, **21**, 2865; (c) J.-Y. Legros and J.-C. Fiaud, *Tetrahedron Lett.*, 1990, **31**, 7453.
- (a) C. Chuit, H. Felkin, C. Frajerma, G. Roussi and G. Swierczewski, *J. Organomet. Chem.*, 1977, **127**, 371; (b) H. Felkin, E. Jampel-Costa and G. Swierczewski, *J. Organomet. Chem.*, 1977, **134**, 265; (c) B. L. Buckwalter, I. R. Burfitt, H. Felkin, M. Joly-Goudket, K. Naemura, M. F. Salomon, E. Wenkert and P. M. Wovkulich, *J. Am. Chem. Soc.*, 1978, **100**, 6445; (d) G. Consiglio, F. Moradini and O. Piccolo, *J. Am. Chem. Soc.*, 1981, **103**, 1846; (e) T. Hayashi, M. Konishi, K. Yokota and M. Kumada, *J. Organomet. Chem.*, 1985, **285**, 359; (f) T. Hiyama and N. Wakasa, *Tetrahedron Lett.*, 1985, **26**, 3259; (g) H. Urabe, H. Inami and F. Sato, *J. Chem. Soc., Chem. Commun.*, 1993, 1595. Copper(i) salts also catalyse the reaction: (h) T. Sato, M. Takeuchi, T. Ito, M. Kawashima and T. Fujisawa, *Tetrahedron Lett.*, 1981, **22**, 1817; (i) T. Fujisawa, T. Sato, M. Kawashima, K. Naruse and K. Tamai, *Tetrahedron Lett.*, 1982, **23**, 3583; (j) M. Bourgain-Commercon, J. F. Normant and J. Villieras, *J. Chem. Res.*, 1977, (S) 183; (M) 2101.
- F. K. Sheffy and J. K. Stille, *J. Am. Chem. Soc.*, 1983, **105**, 7173; M. Kosugi, K. Ohashi, K. Akuzawa, T. Kawazoe, H. Sano and T. Migita, *Chem. Lett.*, 1987, 1237.
- H. Matsushita and E. Negishi, *J. Chem. Soc., Chem. Commun.*, 1982, 160; E. Keinan and M. Sahai, *J. Chem. Soc., Chem. Commun.*, 1984, 648.
- Y. Hayashi, M. Riediker, J. S. Temple and J. Schwartz, *Tetrahedron Lett.*, 1981, **22**, 2629; J. S. Temple, M. Riediker and J. Schwartz, *J. Am. Chem. Soc.*, 1982, **104**, 1310.
- Stoichiometric reaction of π -allylnickels with ArMgBr (Ar = aromatic) and subsequent reductive elimination has been reported: H. Kurosawa, H. Ohnishi, M. Emoto, N. Chatani, Y. Kawasaki, S. Murai and I. Ikeda, *Organometallics*, 1990, **9**, 3038.
- D. A. Evans, T. C. Crawford, R. C. Thomas and J. A. Walker, *J. Org. Chem.*, 1976, **41**, 3947.
- T. Ukai, H. Kawazura and Y. Ishii, *J. Organomet. Chem.*, 1974, **65**, 253.
- J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill and J. C. Smart, *J. Organomet. Chem.*, 1971, **27**, 241.
- L. M. Venanzi, *J. Chem. Soc.*, 1958, 719.
- T. Hayashi, M. Konishi, K. Yokota and M. Kumada, *Chem. Lett.*, 1980, 767.
- B. M. Trost and T. R. Verhoeven, *J. Am. Chem. Soc.*, 1980, **102**, 4730.