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

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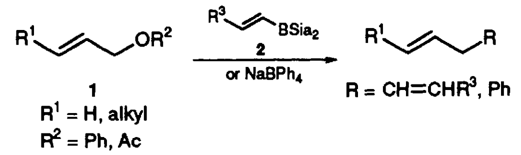
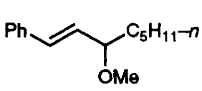
Substitution reactions of 1,3-disubstituted allylic carbonates **3** with aryl- and alkenyl-borates **4** are catalysed by $[NiCl_2(dppf)]$ [dppf = 1,1′-bis(diphenylphosphino)ferrocene], and in the case of the cyclic carbonate **7**, the reaction proceeds with complete inversion.

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] zinc[6] and zirconium[7] 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.



Scheme 1

The substitution reactions were examined using the allylic carbonate **3a** (R^1 = Ph, R^2 = n-C_5H_{11}) and 2–3 equiv. of phenylborate (**4a**, R = Ph) or 2-furylborate (**4d**, R = 2-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% $[Pd(PPh_3)_2]$ (prepared *in situ* by mixing $[Pd_2(dba)_3]\cdot CHCl_3$[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** (R^1 = R = Ph, R^2 = n-C_5H_{11}) was <10% (entry 1). Production of **6** was also catalysed by $[Pd(dppf)]$[11] (entry 2). We then examined nickel catalysts and found that the desired reaction proceeded in the presence of $[NiCl_2(PPh_3)_2]$[12] or $[NiCl_2(dppf)]$[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



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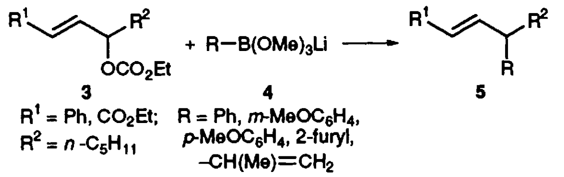
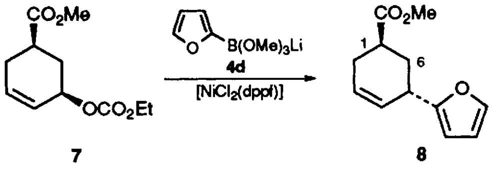


Scheme 2

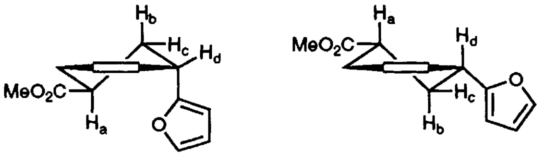


Scheme 3

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

		Carbonate[b]		Borate		Yield (%)		
						Product[b]		
Entry	Catalyst	**3**	R^1	**4**	R	**5**	**6**	Recovered **3**
1	$[Pd(PPh_3)_2]$[c]	**a**	Ph	**a**	Ph	**a**, <10	66	0
2	$[Pd(dppf)]$[c]	**a**	Ph	**a**	Ph	**a**, 0	54	0
3	$[NiCl_2(PPh_3)_2]$	**a**	Ph	**a**	Ph	**a**, 35	0	55
4	$[NiCl_2(dppf)]$	**a**	Ph	**a**	Ph	**a**, 83	0	0
5	$[NiCl_2(dppf)]$	**a**	Ph	**b**	m-$MeOC_6H_4$	**b**, 81	0	0
6	$[NiCl_2(dppf)]$	**a**	Ph	**c**	p-$MeOC_6H_4$	**c**, 68	0	0
7	$[NiCl_2(PPh_3)_2]$	**a**	Ph	**d**	2-Furyl	**d**, 77	0	0
8	$[NiCl_2(dppf)]$	**a**	Ph	**d**	2-Furyl	**d**, 65	0	0
9	$[NiCl_2(dppf)]$	**a**	Ph	**e**	$CH(Me)=CH_2$	**e**, 46	0	0
10	$[NiCl_2(dppf)]$	**b**	CO_2Et	**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] R^2 = n-C_5H_{11}. [c] Prepared *in situ* from $[Pd_2(dba)_3]\cdot CHCl_3$ and the corresponding phosphine ligand. [d] No corresponding methyl ether was produced.



trans isomer **8** *cis* isomer **9**

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**, [NiCl$_2$(dppf)] was an excellent catalyst.‡

The catalytic activity of [NiCl$_2$(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 acid[14]. The reaction of the carbonate **7** was carried out with 2-furylborate **4d** in the presence of [NiCl$_2$(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 ^{1}H 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 [Ni(π-allyl)(aryl)] complexes undergo reductive elimination to afford allyl–aryl products[8] and that the nickel(0) complexes prepared *in situ* from [NiCl$_2$(dppf)] and 2 equiv. of Bu^{n}Li 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(0) complexes under the reaction conditions, (*ii*) oxidative addition of the nickel(0) complexes to the allylic carbonate **3** with inversion to produce the allyl-nickel intermediates, (*iii*) transmetallation with the borate **4** and (*iv*) reductive elimination with retention of configuration to afford **5**.

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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^{n}Li (0 °C, 2 h); *m*- and *p*-MeOC$_6$H$_4$Li from bromoanisoles and Bu^{n}Li (−70 °C, 2 h); CH$_2$=CH(Me)Li from CH$_2$=C(Me)Br and Bu^{n}Li (−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$_2$O, 1.45 mmol) in THF (6 ml) was added B(OMe)$_3$ (0.21 ml, 1.81 mmol) dropwise under nitrogen. After 15 min, the carbonate **3a** (200 mg, 0.72 mmol) and [NiCl$_2$(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$_4$Cl 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.

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