

Nickel-catalyzed allylation of lithium 1-alkynyl(trialkoxy)borates with 1,3-disubstituted allyl carbonates

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Received 2 December 1999; received in revised form 31 January 2000; accepted 9 March 2000

Abstract

The first Suzuki-type cross-coupling of alkynylborates with 1,3-disubstituted allyl carbonates was studied. It was found that nickel complexes readily catalyzed the reaction giving normal coupling products in good to excellent yields. The nickel complexes of dppe or dppen revealed a higher catalytic activity than that of $\text{NiCl}_2(\text{PPh}_3)_2$ or $\text{NiCl}_2(\text{dppf})$. This is a substrate-controlled reaction with high regioselectivity. The asymmetric cross-coupling reaction of alkynylborates with allyl carbonate enantioselectively produced an allyl substituted alkyne with 13% ee. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Nickel catalysts; Alkynylborates; Allyl carbonate; Cross-coupling

1. Introduction

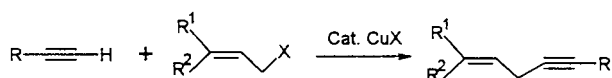
The transition metal-catalyzed allylation of nucleophiles is well-recognized as one of the most powerful synthetic tools for the selective construction of carbon–carbon bonds [1].

The allylation of the terminal alkynes with allyl halides can be accomplished by a direct substitution of allyl halides with 1-alkynylmetal compounds, such as Cu(I), Mg, and Li reagents [2]. Among them the copper-catalyzed allylation of terminal alkynes by allylic halides is the most reliable method [3] (Scheme 1).

Although this type of reaction tolerates functional groups and the procedure is quite convenient, it has been applied limitedly for unsubstituted allyl halides [4]. Moreover, the relatively unreactive allylic alcohol derivatives hardly couple to terminal alkynes under these conditions. The palladium-catalyzed allylation reaction is a prolific area of research, but the reaction of allyl carbonates with the terminal alkynes does not provide normal allylation products [5] (Scheme 2).

It was also reported that alkynes coupled to allyl acetates in the presence of $\text{Ni}(\text{COD})_2$, but the results were unsatisfactory [6]. To the best of our knowledge, very few methods are now available for the synthesis of normal allylation products of terminal alkynes from the substituted allylic alcohol derivatives.

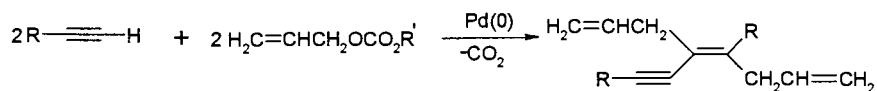
Metal 1-alkynylborates are useful synthetic intermediates, and have been used in many carbon–carbon bond forming reactions, such as 1,2-asymmetric addition to aldehydes [7]; Diels–Alder cycloaddition [8]; and the Suzuki–Miyaura coupling reaction with aryl or alkenyl halides [9]. However, the allylation of alkynylborates with allylic alcohol derivatives have not been reported previously.



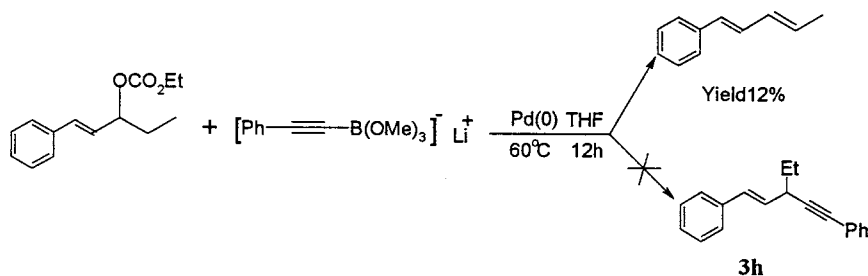
Scheme 1.

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Scheme 2.



Scheme 3.

2. Results and discussion

2.1. The palladium(0)-catalyzed cross-coupling of alkynylborates with (*E*)-3-(ethoxycarbonyloxy)-1-phenyl-1-pentene

Various palladium complexes catalyzed the cross-coupling of alkynylborates with (*E*)-3-(ethoxycarbonyloxy)-1-phenyl-1-pentene; however, the palladium complexes such as PdCl₂(PPh₃)₂, Pd(PPh₃)₄ were ineffective for the coupling reaction due to the formation of the diene instead of desired allylation products **3h** (Scheme 3). The allyl palladium intermediate formed by oxidative-addition of allyl carbonate to palladium, underwent the β-H elimination more quickly than the transmetalation with alkynylborate.

2.2. The nickel-catalyzed cross-coupling of alkynylborates with (*E*)-3-(ethoxycarbonyloxy)-1-phenyl-1-pentene

Nickel complexes were found to be excellent catalysts for activating allyl derivatives [10], such as the NiCl₂(PPh₃)₂ or NiCl₂(dppf)-catalyzed coupling reaction of aryl- or alkenyl-borates with 1,3-disubstituted allyl carbonates [11]. Therefore we investigated the coupling reaction of alkynylborates with allyl carbonates in the presence of a nickel complex as the catalyst. However, the reaction did not provide any coupling products when using NiCl₂(PPh₃)₂ or NiCl₂(dppf) (Entries 1,2). Thus, the effect of the ligands used in nickel catalysts was reinvestigated in details. The results are showed in Table 1.

Table 1 demonstrates that the coupling reaction is readily accomplished by a NiCl₂(dppe) or NiCl₂(dppen) catalyst (Entries 4, 5). The catalytic activity of nickel complexes of dppe or dppen was higher than that of PPh₃, dppf or dppp ligands. The nickel catalyst having a chelating diphosphine dppe or dppen forms a stereo-

chemically nonrigid 18-electron η³-allyl complex, which could undergo reductive elimination leading to the desired allylation product quite readily [12].

In the presence of a NiCl₂(dppe) catalyst, the coupling reaction of various alkynylborates with 1,3-disubstituted allyl carbonates in the different solvents was accomplished successfully. The results are shown in Table 2.

Table 2 illustrates that the addition of MeCN showed minor influence on the reaction, although Kabayashi reported that using the mixture of MeCN and THF in a ratio of 1:1 as the solvent provided somewhat better results in the coupling of 1,3-disubstituted secondary allylic carbonates and lithium aryl- and alkenylborates [11]. This is a substrate-controlled reaction with high regioselectivity to give the normal allylation products of alkynes in good to excellent yields. Considering that the reaction conditions are mild, and alkynylborates can be

Table 1

The effect of ligands in nickel-catalyzed coupling reaction of phenylacetylenylborate with (*E*)-3-(ethoxycarbonyloxy)-1-phenyl-1-pentene^a

Entry	Catalyst	Yield (%) ^b
1	NiCl ₂ (PPh ₃) ₂	Trace
2	NiCl ₂ (dppf)	Trace
3	NiCl ₂ (dppp) ^c	Trace
4	NiCl ₂ (dppe) ^d	68
5	NiCl ₂ (dppe) ^d	64 ^f
6	NiCl ₂ (dppen) ^e	70

^a Phenylacetylenylborate (1.0 mmol), (*E*)-3-(ethoxycarbonyloxy)-1-phenyl-1-pentene (1.2 mmol), 3 mol% nickel catalyst, THF 4 ml (except entry 5) were stirred for 12 h at 60°C under nitrogen atmosphere.

^b Isolated yields.

^c Dppp, 1,2-bis(diphenylphosphino)propane.

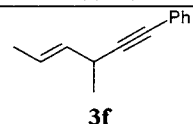
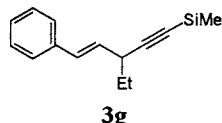
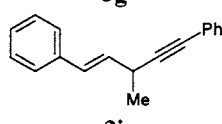
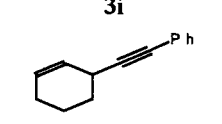
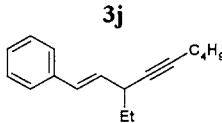
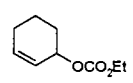
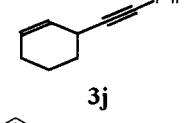
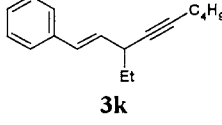
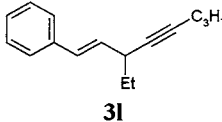
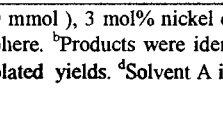
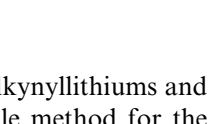
^d Dppe, 1,2-bis(diphenylphosphino)ethane.

^e Dppen, *cis*-1,2-bis(diphenylphosphino)ethylene.

^f The mixture of THF and MeCN (2:2 ml) was used as the solvent.

Table 2

The coupling of 1,3-disubstituted allyl carbonates with alkynylborates^a

Entry	Allyl esters	Alkynes	Product ^b	Solvent ^c	Yield (%) ^d
1	2e	1a		A	59
2	2f	1b		A	92
				B	93
3	2g	1a		A	68
				B	64
4		1a		A	62
5	2f	1d		B	60
				A	78
6	2f	1c		B	78
				A	72

^aAlkynylborates (1.2 mmol), allyl esters (1.0 mmol), 3 mol% nickel catalysts, solvent were stirred for 12–24 hours at 60 °C under nitrogen atmosphere. ^bProducts were identified by ¹H NMR, IR and mass spectral and elemental analysis or HRMS. ^cIsolated yields. ^dSolvent A is the mixture of THF and MeCN (2 mL : 2 mL) and solvent B is THF (4 mL).

easily prepared from corresponding alkynyllithiums and B(OR)₃, the reaction might be a facile method for the allylation of various terminal alkynes with allyl carbonates.

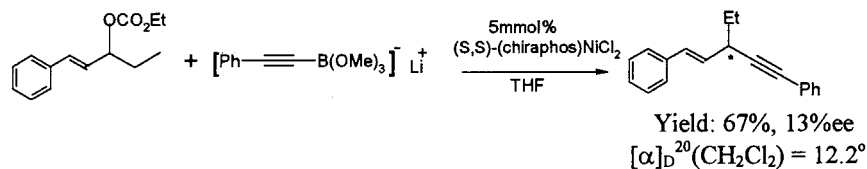
2.3. The asymmetric coupling of phenylacetylenylborate with (*E*)-3-(ethoxycarbonyloxy)-1-phenyl-1-pentene

Preliminary study for the asymmetric reaction of phenylacetylenylborate with (*E*)-3-(ethoxycarbonyloxy)-1-phenyl-1-pentene in the presence of a nickel catalyst having a chiral ligand (*S,S*)-(chiraphos), gave a product with some enantiomeric excess (13%*ee*)

(Scheme 4) (determined by chiral HPLC analysis with OD columns). This fact suggests that the use of nickel catalysts with appropriate chiral ligands could induce the enantioselective cross-coupling reaction of alkynylborates with allyl carbonates. It is the first example of the asymmetric cross-coupling of alkynylborate with allylic carbonate.

2.4. Conclusion

In conclusion, we have demonstrated the first cross-coupling of alkynylborates with 1,3-disubstituted allyl carbonates to give normal allylation products of alkynes. It was found that the nickel complexes are better



Scheme 4.

than palladium complexes as the catalysts, and the nickel catalyst with dppe (or dppen) ligand has higher activity than that of dppp and dppf complexes. The substrate-controlled reaction affords the normal 1,3-disubstituted allylic products of alkynes. We are continuing the study for the asymmetric reaction of alkynylborates with allyl carbonates by using the chiral nickel catalyst and will report the further results accordingly.

3. Experimental

$^1\text{H-NMR}$ spectra were recorded on VXL-300 instruments using TMS as an internal standard in CDCl_3 solution. ^{13}C NMR spectral measurements were performed at 75.4 MHz on a Bruker AMX-300 using CDCl_3 as internal standards. Infrared spectra were recorded on Perkin–Elmer 983 FI-IR spectrometer as liquid films on potassium bromide plates. Mass spectral measurements were performed on Finnigan 4021. Elemental analyses were carried out on a MOD-1606 elemental analyzer. High-resolution mass spectra were recorded on an HP5989A mass spectrometer.

3.1. Chemicals

THF, MeCN were purified and dried by standard techniques just before use. All reactions were monitored by thin layer chromatography (TLC) using GF254. All the alkynes were purchased from Aldrich Chemical Co. and used after distillation except (trimethylsilyl)acetylene. *n*-BuLi was purchased from Aldrich, and allyl carbonates were prepared according to literature procedures [13], and dried before used. The following nicked catalysts were prepared as reported methods: $\text{NiCl}_2(\text{PPh}_3)_2$ [14], $\text{NiCl}_2(\text{dppf})$ [15], $\text{NiCl}_2(\text{dppe})$, $\text{NiCl}_2(\text{dppen})$, $\text{NiCl}_2(\text{dppp})$ [16], and (S,S) -(chiraphos) NiCl_2 [17].

3.2. Representative procedure

The coupling reactions of alkynylborates with 1,3-disubstituted allyl carbonates in the presence of $\text{NiCl}_2(\text{dppe})$.

3.2.1. Synthesis of (*E*)-3-phenylacetynyl-1-phenyl-1-pentene

To a well-stirred solution of phenylacetylene (122.4 mg, 1.2 mmol) in THF (2 ml), *n*-BuLi (0.75 ml, 1.6 M

in hexane, 1.2 mmol) was added dropwise at -78°C . Having stirred for 30 min, $\text{B}(\text{OMe})_3$ (0.134 ml, 1.2 mmol) was added, and the mixture was stirred for 2 h. A second mixture of $\text{NiCl}_2(\text{dppe})$ (15.85 mg, 0.03 mmol) and (*E*)-3-(ethoxycarbonyloxy)-1-phenyl-1-pentene (**2f**) (234 mg, 1 mmol) in THF (2 ml) was added. The reaction mixture was stirred at 60°C for 12 h (monitored by TLC), allowed to cool to room temperature (r.t.) and pentane (30 ml) was then added. The organic phase was washed with water (4×10 ml) and dried over MgSO_4 . After removing the solvent in vacuo, (*E*)-3-phenylacetynyl-1-phenyl-1-pentene (**3h**) (167 mg, 68%) was isolated by silica gel chromatography, eluting with pure pentane.

3.3. Characterization of the products

3.3.1. (*E*)-3-Phenylacetynyl-1-phenyl-1-pentene (**3h**)

Colorless liquid; $^1\text{H-NMR}$ (300 MHz, $\text{CCl}_3\text{D-TMS}$) δ ppm: 7.21–7.46 (m, 10H), 6.74 (d, $J = 16.0$ Hz, 1H), 6.22 (dd, $J = 6.5, 15.7$ Hz, 1H), 3.5 (q, $J = 6.4$ Hz, 1H), 1.78–1.82 (m, 2H), 1.14 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C-NMR}$ δ 131.74, 130.62, 129.88, 128.70, 127.80, 127.37, 126.43, 125.97, 90.61, 83.84, 37.04, 29.07, 15.35; IR (neat) 2232 cm^{-1} ; MS m/e (rel. intensity, %) 246 [M^+ , 33.87], 217 (100), 202 (68.77), 215 (57.57); Anal. Calc. for $\text{C}_{19}\text{H}_{18}$: C, 92.64; H, 7.36. Found: C, 92.52; H, 7.50%.

3.3.2. (*E*)-4-Phenylacetynyl-2-hexene (**3f**)

Colorless liquid, $^1\text{H-NMR}$ (300 MHz, $\text{CCl}_3\text{D-TMS}$) δ ppm: 7.24–7.30 (m, 3H), 7.42–7.49 (m, 2H), 5.75 (dd, $J = 16.3, 8.6$ Hz, 1H), 5.50 (dq, $J = 16.4, 7.2$ Hz, 1H), 3.41 (m, 1H), 1.70 (d, $J = 6.4$ Hz, 3H), 1.22 (d, $J = 7.1$ Hz, 3H); IR (film) 2232 cm^{-1} ; MS m/e (rel. intensity, %) 170 [M^+ , 19.78], 169 (100), 141 (21.93), 115 (20.57); Anal. Calc. for $\text{C}_{13}\text{H}_{14}$: C, 91.71; H, 8.29. Found: C, 91.48; H, 8.73%.

3.3.3. (*E*)-3-Trimethylsilylacetynyl-1-phenyl-1-pentene (**3g**)

Colorless liquid, $^1\text{H-NMR}$ (300 MHz, $\text{CCl}_3\text{D-TMS}$) δ ppm: 7.31–7.42 (m, 5H), 6.70 (d, $J = 15.8$ Hz, 1H), 6.14 (dd, $J = 15.8, 6.5$ Hz, 1H), 3.24 (q, $J = 6.4$ Hz, 1H), 1.70 (m, 2H), 1.19 (t, $J = 6.4$ Hz, 3H), 0.26 (s, 9H); IR (film) 2169 cm^{-1} ; MS m/e (rel. intensity, %) 242 [M^+ , 10.44], 213 (25.45), 169 (21.87), 199 (14.63); HRMS for $\text{C}_{16}\text{H}_{22}\text{Si}$, Anal. Calc: 242.1491. Found: 242.1500.

3.3.4. (*E*)-3-(Hexynyl)-1-phenyl-1-pentene (**3k**)

Colorless liquid, $^1\text{H-NMR}$ (300 MHz, $\text{CCl}_3\text{D-TMS}$) δ ppm: 7.27–7.35 (m, 5H), 6.54 (dd, $J = 15.7$, 1.0 Hz, 1H), 6.24 (dd, $J = 15.7$, 6.5 Hz, 1H), 3.15 (m, 1H), 2.26 (t, $J = 6.4$ Hz, 2H), 1.53–1.70 (m, 6H), 1.09 (t, $J = 7.3$ Hz, 3H), 0.92 (t, $J = 7.2$ Hz, 3H); IR (film) 2210 cm^{-1} ; MS m/e (rel. intensity, %) 226 [M^+ , 20.12], 197 (96.96), 155 (83.50), 153 (40.43); Anal. Calc. for $\text{C}_{17}\text{H}_{22}$: C, 90.20; H, 9.80. Found: C, 90.31; H, 9.60%.

3.3.5. (*E*)-3-(Pentynyl)-1-phenyl-1-pentene (**3l**)

Colorless liquid, $^1\text{H-NMR}$ (300 MHz, $\text{CCl}_3\text{D-TMS}$) δ ppm: 7.26–7.35 (m, 5H), 6.53 (d, $J = 15.7$ Hz, 1H), 6.24 (dd, $J = 15.7$, 6.4 Hz, 1H), 3.17 (m, 1H), 2.27 (t, $J = 6.7$ Hz, 2H), 1.53–1.70 (m, 4H), 1.09 (t, $J = 7.3$ Hz, 3H), 0.91 (t, $J = 7.2$ Hz, 3H); IR (film) 2212 cm^{-1} ; MS m/e (rel. intensity, %) 212 [M^+ , 18.32], 183 (28.99), 155 (40.31), 91 (43.11); Anal. Calc. for $\text{C}_{16}\text{H}_{20}$: C, 90.56; H, 9.44. Found: C, 90.06; H, 9.45%.

3.3.6. (*E*)-3-Phenylacetynyl-1-phenyl-1-butene (**3i**)

Colorless liquid, $^1\text{H-NMR}$ (300 MHz, $\text{CCl}_3\text{D-TMS}$) δ ppm 7.21–7.46 (m, 10 H), 6.77 (d, $J = 16.1$ Hz, 1H), 6.24 (dd, $J = 6.5$, 16.0 Hz, 1 H), 3.5 (m, 1H), 1.45 (d, $J = 7.4$ Hz, 3 H); IR (film) 2230 cm^{-1} ; MS m/e (rel. intensity, %) 232 [M^+ , 95.24], 217 (100), 215 (77.46), 202 (68.94); Anal. Calc. for $\text{C}_{18}\text{H}_{16}$: C, 93.10; H, 6.90. Found: C, 92.97; H, 6.99%.

3.3.7. 1-Phenylacetynyl-2-cyclohexene (**3j**)

Colorless liquid, $^1\text{H-NMR}$ (300 MHz, $\text{CCl}_3\text{D-TMS}$) δ ppm 7.22–7.40 (m, 5H), 5.74 (m, 2H), 3.29 (m, 1H), 1.97–2.10 (m, 2H), 1.56–1.88 (m, 4H); IR (film) 2227 cm^{-1} ; MS m/e (rel. intensity, %) 182 [M^+ , 100], 167 (86.97), 154 (69.93), 181 (52.20); Anal. Calc. for $\text{C}_{14}\text{H}_{14}$: C, 92.30; H, 7.70. Found: C, 92.02; H, 7.90%.

Acknowledgements

We thank the NNSF of China and Laboratory of Organometallic Chemistry, Shanghai Institute of Or-

ganic Chemistry, Chinese Academy of Sciences, for financial support.

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