Cross-Coupling

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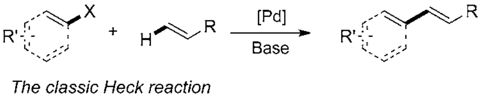
Nickel-Catalyzed Heck-Type Alkenylation of Secondary and Tertiary α-Carbonyl Alkyl Bromides[**]

*Chao Liu, Shan Tang, Dong Liu, Jiwen Yuan, Liwei Zheng, Lingkui Meng, and Aiwen Lei**

Since its development in the early 1970s, the palladium-catalyzed Heck reaction has become a powerful tool for the alkenylation of aryl and alkenyl electrophiles in chemical synthesis [Eq. (1)].[1] Thus far, alkyl halides have had limited application in Heck-type reactions, with only isolated examples available for primary alkyl halides[1b,2] and both secondary and tertiary alkyl halides remaining almost unstudied.[3] This may be because of facile β-hydride elimination on palladium catalysts with such species. To solve this problem, other transition metal catalysts would be potential choices, but very few results have been reported to date. Cobalt and titanocene catalysts were among the few reports to achieve the reaction of alkyl halides with styrenes. However, highly reactive alkyl magnesium reagents were needed as a base in these transformations,[4] thus limiting their potential application. Although nickel catalysts have been applied in various cross-couplings of alkyl halides with organometallic reagents,[5] the application of such catalysts in the Heck-type reaction of alkyl halides is rare.[6] Herein, we report the first nickel-catalyzed Heck-type reaction of secondary and tertiary α-carbonyl alkyl halides with olefins to construct α-alkenyl carbonyls [Eq. (2)].



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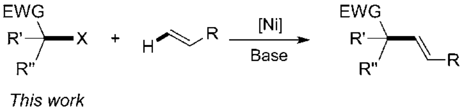

(2)

The α-alkenylation of carbonyls is normally accomplished by palladium-catalyzed cross-coupling of alkenyl halides with metal enolates.[7] Compared to the widely available alkenes, alkenyl halides are normally expensive and not easy to obtain. On the other hand, α-carbonyl alkyl halides are bulk chemicals and readily available. Obviously, the direct utilization of alkenes as coupling partners with α-carbonyl alkyl halides to construct α-alkenyl carbonyls would be an appealing approach.

Recently, the direct coupling of secondary α-carbonyl alkyl halides with arylboronic acids to achieve α-arylation of carbonyls in the presence of a Ni catalyst has been accomplished in our group.[8] To achieve α-alkenylation of carbonyls, we decided to attempt the coupling of alkenes with α-carbonyl alkyl halides. We started our research by applying ethyl 2-bromopropanoate and *p*-methoxystyrene in a model reaction to test different reaction conditions. Selected data from this study is listed in Table 1.

First, various Ni catalyst precursors were screened in toluene at 60 °C in the presence of K_3PO_4 as base. No reaction occurred with Ni^{II} precursors (Table 1, entries 2–5), however, the reaction did proceed with the Ni^0 precursor $[Ni(PPh_3)_4]$ and afforded the coupling product in 4 % yield (Table 1, entry 6). This indicated that Ni^{II} could not be reduced to a lower valent nickel species to initiate the coupling process in those reaction systems. This promising result encouraged us to do further optimization with $[Ni^0(PPh_3)_4]$ as the catalyst precursor. It was interesting to find that the addition of PPh_3 to the $[Ni(PPh_3)_4]$ system improved the yield to 11 % (Table 1, entry 7). We then investigated the influence of several bidentate ligands. Both bis(diphenylphosphino)methane (dppm) and 1,2-bis(diphenylphosphino)ethane (dppe) afforded trace amounts of the coupling product (Table 1, entries 8 and 9). However, the greatest improvement came from 1,3-bis(diphenylphosphino)propane (dppp), which afforded the desired coupling product in 80 % yield (Table 1, entry 1). Further lengthening the carbon chain in the phosphine decreased the yield dramatically, with 1,4-bis(diphenylphosphino)butane (dppb) giving only 7 % yield (Table 1, entry 10). Utilizing the rigid bidentate ligand 1,1′-bis(diphenylphosphino)ferrocene (dppf) afforded the desired product in only 17 % yield (Table 1, entry 11). The influence of the base was also tested. When other potassium salts, such as K_2HPO_4 or K_2CO_3, were used in place of K_3PO_4 the desired product was obtained in low yields (Table 1, entries 12 and 13), and the sodium salt Na_3PO_4 afforded no desired product at all (Table 1, entry 14). Solvent screening showed that the

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[*] C. Liu, S. Tang, D. Liu, J. Yuan, L. Zheng, L. Meng, Prof. A. Lei
College of Chemistry and Molecular Sciences
Wuhan University, Wuhan 430072 (P. R. China)
E-mail: aiwenlei@whu.edu.cn
Homepage: http://www.chem.whu.edu.cn/GCI_WebSite/main.htm
Prof. A. Lei
State Key Laboratory for Oxo Synthesis and Selective Oxidation
Lanzhou Institute of Chemical Physics
Chinese Academy of Sciences, Lanzhou 730000 (P. R. China)

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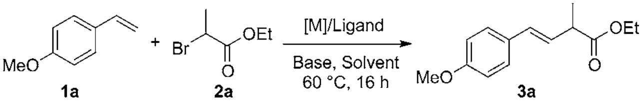
Table 1: Impact of reaction parameters on the Ni-catalyzed Heck-type reaction of ethyl 2-bromopropanoate with *p*-methoxystyrene.[a]

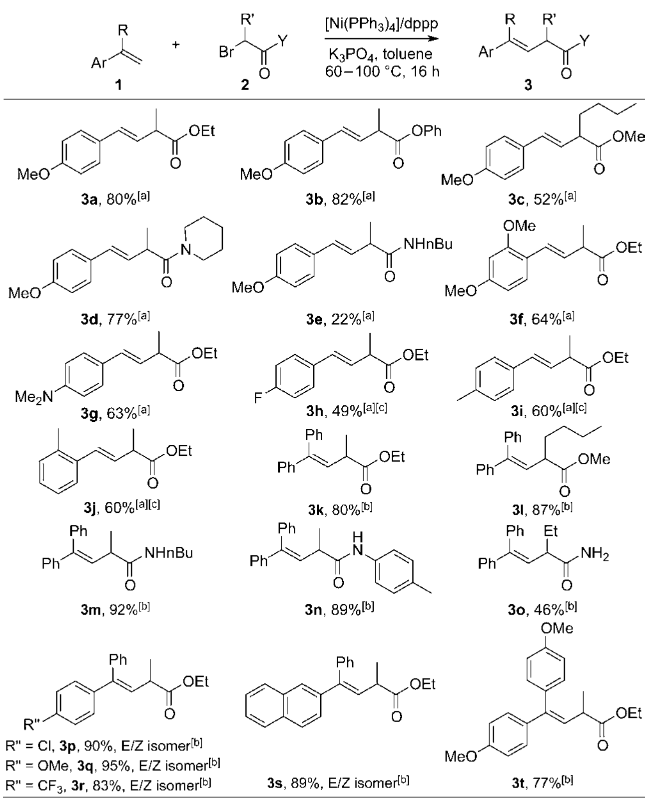


Entry	[M]/Ligand	Base	Solvent	Yield [%][b]
1	**[Ni(PPh$_3$)$_4$]/dppp**	**K$_3$PO$_4$**	**toluene**	**80**
2	[NiCl$_2$(PPh$_3$)$_2$]/dppp	K$_3$PO$_4$	toluene	n.r.
3	[Ni(acac)$_2$]/–	K$_3$PO$_4$	toluene	n.r.
4	[Ni(acac)$_2$]/PPh$_3$	K$_3$PO$_4$	toluene	n.r.
5	[NiCl$_2$(PPh$_3$)$_2$]/–	K$_3$PO$_4$	toluene	n.r.
6	[Ni(PPh$_3$)$_4$]/–	K$_3$PO$_4$	toluene	4
7	[Ni(PPh$_3$)$_4$]/PPh$_3$	K$_3$PO$_4$	toluene	11
8	[Ni(PPh$_3$)$_4$]/dppm	K$_3$PO$_4$	toluene	trace
9	[Ni(PPh$_3$)$_4$]/dppe	K$_3$PO$_4$	toluene	trace
10	[Ni(PPh$_3$)$_4$]/dppb	K$_3$PO$_4$	toluene	7
11	[Ni(PPh$_3$)$_4$]/dppf	K$_3$PO$_4$	toluene	17
12	[Ni(PPh$_3$)$_4$]/dppp	K$_2$HPO$_4$	toluene	35
13	[Ni(PPh$_3$)$_4$]/dppp	K$_2$CO$_3$	toluene	43
14	[Ni(PPh$_3$)$_4$]/dppp	Na$_3$PO$_4$	toluene	n.d.
15	[Ni(PPh$_3$)$_4$]/dppp	K$_3$PO$_4$	THF	21
16	[Ni(PPh$_3$)$_4$]/dppp	K$_3$PO$_4$	dioxane	56
17	[Ni(PPh$_3$)$_4$]/dppp	K$_3$PO$_4$	EtOH	n.d.
18	[Ni(PPh$_3$)$_4$]/dppp	K$_3$PO$_4$	DMF	n.d.
19	[Ni(PPh$_3$)$_4$]/dppp	K$_3$PO$_4$	CH$_3$CN	n.d.
20	[Pd(PPh$_3$)$_4$]/dppp	K$_3$PO$_4$	toluene	n.d.

[a] Unless otherwise noted, the reaction was carried out with **1a** (0.50 mmol), **2a** (0.75 mmol), base (1.0 mmol), catalyst (0.025 mmol), ligand (0.030 mmol), solvent (2 mL), 60 °C, 16 h. [b] The yield was determined by GC analysis with biphenyl as the internal standard. n.r. = no reaction, n.d. = no desired product.

alkenylation product could be obtained in THF or dioxane, but only in low yields (Table 1, entries 15 and 16). No product could be detected in the polar protic solvent EtOH or the polar aprotic solvent DMF (Table 1, entries 17 and 18). Also, no desired product was obtained in CH$_3$CN (Table 1, entry 19). In addition, [Pd(PPh$_3$)$_4$] was tested, but gave no desired product (Table 1, entry 20). From these experiments, we determined the optimized conditions to be: [Ni(PPh$_3$)$_4$] (5 mol %), dppp (6 mol %), K$_3$PO$_4$ (2 equiv), toluene, 60 °C, 16 h.

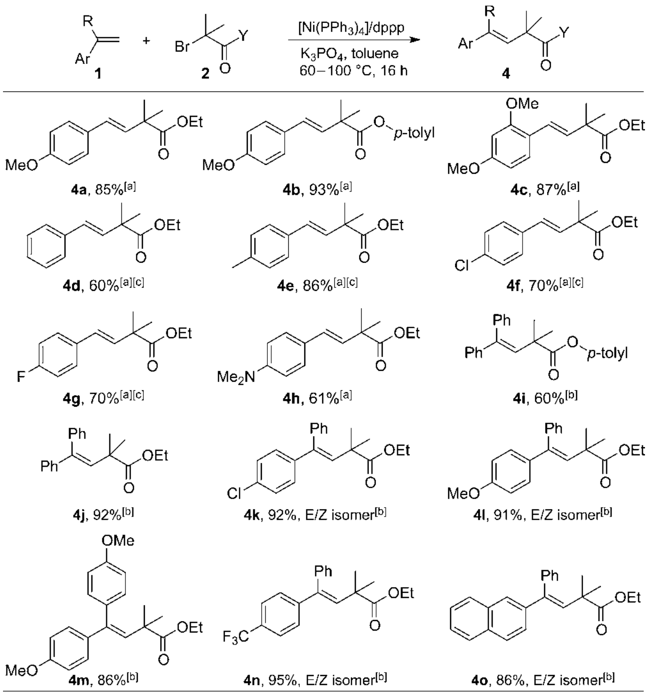
With the optimized conditions in hand, we started employing other substrates in this Ni-catalyzed Heck-type reaction. First of all, various secondary α-carbonyl alkyl bromides were employed to couple with olefins (Scheme 1). Under the optimized conditions, *p*-methoxystyrene coupled with a range of secondary α-carbonyl alkyl bromides in good to excellent yields. A phenyl ester afforded the desired product in 82 % yield (Scheme 1, **3b**). Methyl 2-bromohexanoate also proceeded well, giving the coupling product in 52 % yield (Scheme 1, **3c**). α-Bromoamides were similarly found to be suitable substrates for this transformation and gave the desired products in good yield (Scheme 1, **3d**). In contrast, an amide-bearing substrate with a free NH group afforded only a low yield (Scheme 1, **3e**). However, other substituted styrenes proceeded well. An *ortho*-methoxy substituent has little negative steric effect, affording the coupling product in good yield (Scheme 1, **3f**), and NMe$_2$ was also well tolerated (Scheme 1, **3g**). It is interesting to note that a styrene substituted with an electron-withdrawing group is also a suitable substrate, when acetanilide is used as an additive (Scheme 1, **3h**). *Ortho*- and *para*-methyl substituted styrenes afforded the coupling product in good yields in the presence of acetanilide (Scheme 1, **3i** and **3j**), but *p*-methoxystyrene afforded the alkenylation product **3a** in a lower yield (54 %), even at 100 °C. 1,1-Diaryl substituted ethylenes were also suitable substrates for this alkenylation (Scheme 1, **3k–3t**). 1,1-Diphenyl ethylene proceeded well, coupling with various α-bromoesters and amides in the presence of the Ni catalyst, including amides bearing free NH groups (Scheme 1, **3m** and **3n**), with even an unsubstituted amide offering the desired product in 46 % yield (Scheme 1, **3o**). Normally, Ni reacts with aromatic C–Cl bonds, however, the C–Cl bond was well tolerated in this transformation and the reaction proceeded chemoselectively to afford the desired alkenylation product (Scheme 1, **3p**). Both electron-donating and electron-withdrawing groups were introduced to the 1,1-diaryl substituted ethylenes, providing the alkenylation products in good yields (Scheme 1, **3q**, **3r**, **3t**). A naphthalenyl group was also employed (Scheme 1, **3s**). No isomerized α,β-unsaturated



Scheme 1. Substrate scope for the Ni-catalyzed Heck-type reaction of secondary α-carbonyl alkyl bromides with olefins. [a] The reactions were carried out with **1** (0.50 mmol), **2** (0.75 mmol), [Ni(PPh$_3$)$_4$] (5 mol %), dppp (6 mol %), K$_3$PO$_4$ (1.0 mmol), toluene (2 mL), 60 °C, 16 h. Yields shown are of isolated products. [b] The reactions were carried out with **1** (0.50 mmol), **2** (1.0 mmol), [Ni(PPh$_3$)$_4$] (10 mol %), dppp (12 mol %), K$_3$PO$_4$ (1.0 mmol), toluene (2 mL), 100 °C, 16 h. Yields shown are of isolated products. [c] Acetanilide (1.0 mmol) was added, 100 °C.

ester or amide products have been detected in any of the cases herein reported.

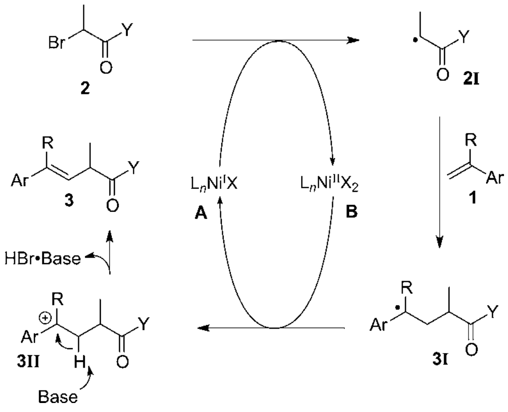
Encouraged by these promising results, we further applied these Ni-catalyzed Heck-type alkenylation conditions to tertiary α-carbonyl alkyl bromides. To our delight, good to excellent yields were obtained with various alkenes (Scheme 2). Both ethyl and *p*-tolyl 2-bromoisobutanoates reacted with *p*-methoxystyrene under the standard conditions to afford the coupling products in good yields (Scheme 2, **4a** and **4b**). Similarly, 2,4-dimethoxystyrene coupled well with ethyl 2-bromoisobutanoates (Scheme 2, **4c**). Acetanilide was again added to promote the alkenylation of tertiary α-carbonyl alkyl bromides with styrene, *p*-methyl styrene, and styrenes substituted with electron-withdrawing groups (Scheme 2, **4d**–**4g**). Various 1,1-diaryl alkenes were also shown to couple with tertiary α-bromo esters in good to excellent yields (Scheme 2, **4i**–**4o**). A range of functional groups were well tolerated, including Cl (**4k**), CF_3 (**4n**), and OMe (**4l** and **4m**).



Scheme 2. Substrate scope for the Ni-catalyzed Heck-type reaction of tertiary α-carbonyl alkyl bromides with olefins. [a] The reactions were carried out with **1** (0.50 mmol), **2** (0.75 mmol), $[\mathrm{Ni(PPh_3)_4}]$ (5 mol%), dppp (6 mol%), K_3PO_4 (1.0 mmol), toluene (2 mL), 60°C, 16 h. Yields shown are of isolated products. [b] The reactions were carried out with **1** (0.50 mmol), **2** (1.0 mmol), $[\mathrm{Ni(PPh_3)_4}]$ (10 mol%), dppp (12 mol%), K_3PO_4 (1.0 mmol), toluene (2 mL), 100°C, 16 h. Yields shown are of isolated products. [c] Acetanilide (1.0 mmol) was added, 100°C.

Alkyl halides have been suggested to react with $\mathrm{Ni^0}$ complexes through a single electron transfer process.[9] $\mathrm{Ni^0}$ offers a single electron to the C–X bond to generate $\mathrm{Ni^I}$ and an alkyl radical. Although condition screening showed that the $\mathrm{Ni^{II}}$ precursor $[\mathrm{NiCl_2(PPh_3)_2}]$ could not initiate the reaction (Table 1, entry 5), the $\mathrm{Ni^0}$ precursor $[\mathrm{Ni(PPh_3)_4}]$ afforded the coupling product (Table 1, entry 6). The univalent Ni complex $[\mathrm{NiX(PPh_3)_3}]$ (X = Cl, Br) is known to be obtained from the reaction of an alkyl halide and $[\mathrm{Ni(PPh_3)_4}]$.[10] To determine whether $\mathrm{Ni^I}$ is present in these transformations, a classic $\mathrm{Ni^I}$ complex $[\mathrm{NiCl(PPh_3)_3}]$ was synthesized.[10a] This $\mathrm{Ni^I}$ complex was used in the reaction of **1a** with **2a** under the standard conditions [Eq. (3)]. To our delight, the reaction proceeded well and afforded the product **3a** in 77% yield, which indicates that the $\mathrm{Ni^I}$ complex could further react with the alkyl bromide to initiate the radical process. Based on this experimental data, we propose the following mechanism for this Ni-catalyzed Heck-type reaction of α-carbonyl alkyl bromides (Scheme 3).

$$\mathbf{1a} + \mathbf{2a} \xrightarrow[\substack{\text{toluene, 60 °C, 16 h}\\ 77\%}]{\substack{5\ \text{mol\%}\ [\mathrm{Ni^ICl(PPh_3)_3}]\ /\ 6\ \text{mol\%}\ \text{dppp}\\ 2\ \text{equiv}\ \mathrm{K_3PO_4}}} \mathbf{3a} \tag{3}$$



Scheme 3. Proposed mechanism.

As the β-hydride elimination from the nickel species and the reductive elimination of nickel hydride have been suggested to be not as facile as for palladium, based on DFT calculations,[11] these two mechanistic steps were not suggested in this transformation. Instead, the following is proposed: First, the reaction of **2** with $[\mathrm{Ni(PPh_3)_4}]$ generates the active $\mathrm{Ni^I}$ species **A**, which then donates an additional electron to **2** to generate the radical species **2I** and a $\mathrm{Ni^{II}}$ species **B**. The radical addition of **2I** to olefin **1** then generates benzyl radical **3I**. The next step is believed to be accomplished through the direct oxidation of radical **3I** by **B** to regenerate a benzyl cation intermediate **3II**.[12] This is followed by deprotonation with the base K_3PO_4 to release the final product **3**, whereupon **B** is reduced to **A** to restart the catalytic cycle. It is for this reason that an electron-donating substituent, which is in favor of cation formation, is beneficial for product formation. Moreover, when amides containing a free NH group were used as substrates, a significant amount of lactam cyclization products were observed (Supporting Information, Scheme S1), which provides further support for the formation of cation **3II**.

In conclusion, we have demonstrated the first nickel-catalyzed Heck-type reaction of secondary and tertiary α-carbonyl alkyl bromides with olefins under mild conditions. Several substituted styrenes and various 1,1-diaryl alkenes were found to be suitable substrates for this α-alkenylation. This work opens up a new approach for the construction of α-alkenyl carbonyl compounds. Tentative mechanistic studies suggest that this reaction is likely to proceed by a single electron transfer mechanism, with a catalytic cycle involving Ni^{I} and Ni^{II} complexes as the catalyst species. Further studies into the use of other alkyl halides and olefins as substrates, as well as more mechanistic investigations, are underway in our laboratory.

Experimental Section

General procedure for the synthesis of **3a**: $[Ni(PPh_3)_4]$ (27.7 mg, 0.025 mmol), dppp (12.4 mg, 0.030 mmol) and K_3PO_4 (212.3 mg, 1.0 mmol) were added to a Schlenk tube in an argon-filled glove box. The tube was then sealed with a septum and taken out of the glove box. Toluene (2 mL) was then injected into the tube by syringe. After stirring for 5 min, **2a** (135.8 mg, 0.75 mmol) and **1a** (0.50 mmol) were consecutively injected into the reaction tube. The reaction was then heated to 60°C and stirred for 16 h. Upon completion, the reaction was quenched with dilute HCl solution (2 M) and extracted with ethyl ether (3 × 10 mL). The organic layers were combined and the pure product was obtained by flash column chromatography on silica gel (petroleum/ethyl acetate = 50:1). The yield of the isolated product was 80%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.30$ (d, $J = 7.8$ Hz, 2H), 6.84 (d, $J = 7.8$ Hz, 2H), 6.42 (d, $J = 15.9$ Hz, 1H), 6.13 (dd, $J = 15.7$, 7.9 Hz, 1H), 4.27–4.01 (m, 2H), 3.80 (s, 3H), 3.40–3.10 (m, 1H), 1.34 (d, $J = 6.6$ Hz, 3H), 1.27 ppm (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 175.36$, 159.73, 131.02, 130.33, 128.05, 127.30, 114.54, 61.25, 55.87, 43.88, 18.15, 14.82 ppm. HRMS (ESI) calcd for $C_{14}H_{18}O_3$ $[M+H]^+$: 235.1334; found: 235.1340.

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