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Highly regioselective Heck reactions of heteroaryl halides with electron-rich olefins in ionic liquid

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Dedicated to Professor Eric Derouane on the occasion of his 60th birthday

Abstract

Palladium-catalyzed Heck reactions of the heteroaryl halides, halopyridines, bromoquinoline and bromothiophenes, with the electron-rich olefins vinyl ethers and allyl alcohol were shown to give essentially only the branched olefins in an imidazolium ionic liquid, whereas in molecular solvents a mixture of regioisomers was formed. The method obviates the need for aryl triflates and stoichiometric inorganic salt additives, providing an easy entry to functionalized heteroaromatics incorporating acetyl and 2-allyl alcohol functionalities.

Keywords: Heck reaction; Regioselectivity; Ionic liquid; Heterocycles; Electron-rich olefins; Palladium catalysis

1. Introduction

Heteroaryl compounds have important biological properties and many of their derivatives can be readily accessed by metal catalyzed reactions [1,2]. Among the various reactions catalyzed by metal complexes, the palladium catalyzed Heck reactions of heteroaryl halides and alkenes have demonstrated their utility in a limited number of instances [3]. However, as with most other Heck reactions, these reactions are mainly concerned with electron-deficient olefins [4]. We have recently developed a method that allows electron-rich olefins to be arylated by aryl halides in a highly regioselective manner without recourse to any halide scavengers [5]. We now report results that extend the chemistry to heteroaromatics.

Although a great deal of progress has been made in the Heck coupling reactions in the past several years, the olefinic substrates have so far mostly been limited to electron-deficient olefins [4]. With electron-rich olefins, such as silanes, vinyl ethers, and enol amides, there exits an important issue that has not been fully resolved to date, that is the lack of regioselectivity in normal intermolecular Heck reactions [4a,4d,4e–6]. Such reactions usually give rise to a mixture of regioisomeric olefins and hence are of only limited synthetic utility (Scheme 1). The problem with the regioselectivity can be addressed by using aryl triflates instead of halides or stoichiometric amounts of halide scavengers when aryl halides are used, thallium (I) or silver (I) salts being most popular [6]. The effect of the triflates and halide scavengers on the regioselectivity stems from their effect on the reaction pathway. The Heck reaction is believed to proceed via an ionic pathway leading to the branched product and a neutral variant giving rise to the linear olefin [4–7] (Scheme 2). One can easily envision that

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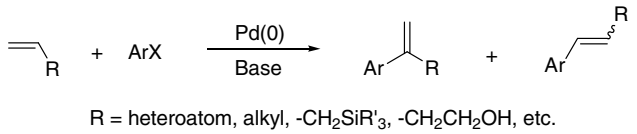


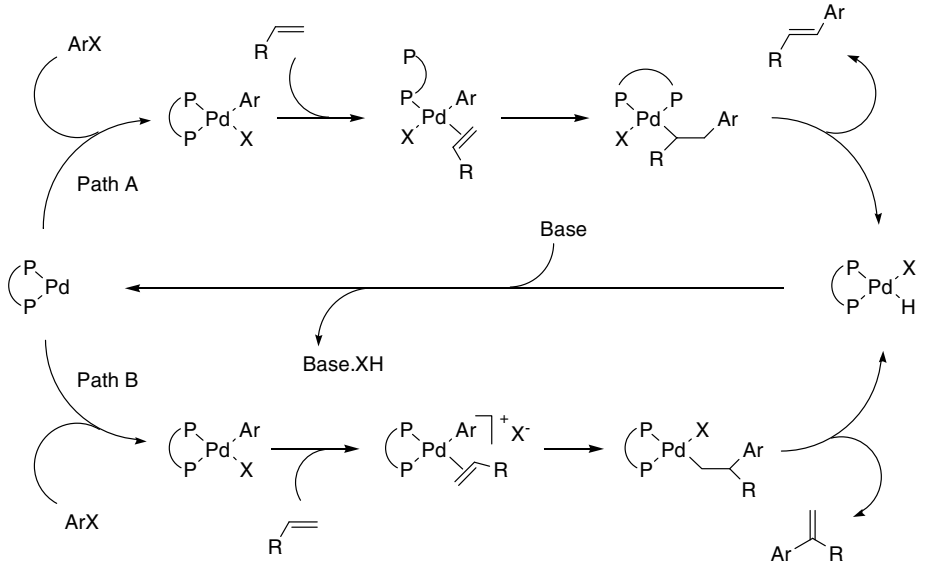
Scheme 1.

the ionic pathway would be rendered favorable when triflates or halide scavengers are chosen.

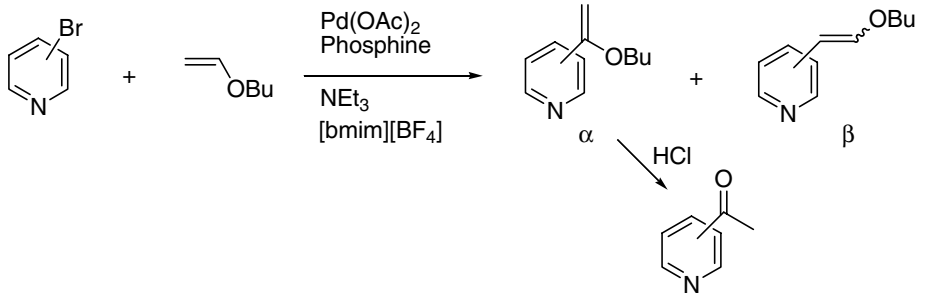
In a program aimed at developing homogeneous catalysis in ionic liquids [5,8], we disclosed that highly regioselective Heck arylation with aryl halides can be accomplished in imidazolium ionic liquids [9], obviating the need for aryl triflates or toxic and costly inorganic additives [5]. The work originated from a hypothesis that because ionic liquids are entirely composed of ions, the ionic Heck pathway (Path B, Scheme 2) would be made favorable when an arylation reaction is performed therein, thus leading to the formation of branched olefins. A similar argument was also invoked by Hallberg, Larhed and coworkers [10,11] in recent studies of the Heck reaction involving electron rich olefins. Following on from the work on normal aryl halides, we extended the chemistry to heteroaryl compounds. The examples presented below fall again in line with this hypothesis.

2. Results and discussion

We first targeted the Heck arylation of bromopyridines with the benchmark electron-rich olefin butyl vinyl ether. Following acidic hydrolysis, the resulting branched olefins should readily lead to acetyl pyridines, a class of compounds that are otherwise difficult to access (Scheme 3). To test out if ionic liquids would offer any advantage over a molecular solvent, the arylation of 3-bromopyridine was conducted in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) alongside five normal solvents. The reaction was carried out by heating a mixture of the bromide (1.0 mmol), butyl vinyl ether (5.0 mmol), triethylamine (1.6 mmol) in the presence of $Pd(OAc)_2$ (4 mol%) and 1,3-bis(diphenylphosphino)propane (DPPP, 8 mol%) in 2 mL of a chosen solvent. The results are summarized



Scheme 2.



Scheme 3.

Table 1
Arylation of butyl vinyl ether by 3-bromopyridine in various solvents[a]

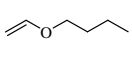
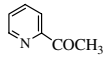
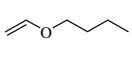
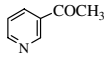
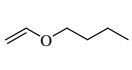
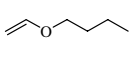
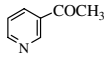
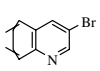
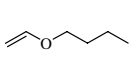
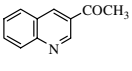
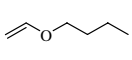
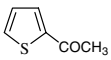
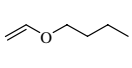
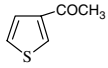
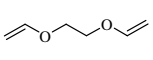
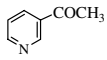
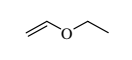
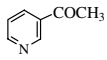
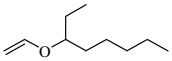
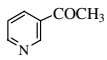
Entry	Solvent	Conversion (%)[b]	Regioselectivity (α/β)[b]
1	[bmim][BF_4]	100	>99/1
2	Toluene	28	61/39
3	Dioxane	36	65/35
4	Acetonitrile	33	62/38
5	DMF	80	71/29
6	DMSO	80	68/32

[a] The reactions were conducted at 125 °C for 30 h in 2 ml of a chosen solvent. See Section 4 for details.
[b] The product was analyzed by ^{1}H NMR. When the β product could not be detected by ^{1}H NMR, a value of >99/1 was assigned.

in Table 1. To our delight, the vinyl ether was completely arylated in [bmim][BF_4] to give essentially exclusively the α substituted product; the ^{1}H NMR spectrum of the reaction mixture after removing the ionic liquid showed no sign of the linear olefin. In contrast, none of the reactions in the five molecular solvents afforded an α/β regioselectivity near to that observed in [bmim][BF_4]. Additionally, in the ionic liquid, the reaction was faster and furnished cleaner product as well, as judged by ^{1}H NMR of the crude products. Theses results are reminiscent of those we obtained in the arylation of vinyl ethers and other electron-rich olefins by various aryl bromides and iodides; several lines of evidence suggested that those arylation reactions proceeded via the ionic pathway [5b]. The high α regioselectivity observed here suggests that the ionic mechanism is also operative in the arylation by heteroaryl halides in the ionic liquid. At the suggestion of one referee, the arylation was also examined in neat water; but a conversion of only ca. 2% was observed under similar conditions. This is at least partly due to the insolubility of the substrates and catalyst in the aqueous phase. However, Hallberg and coworkers [10b] have recently found that a mixture of DMF and water is capable of promoting high regioselectivity in the arylation of vinyl ethers by aryl bromides.

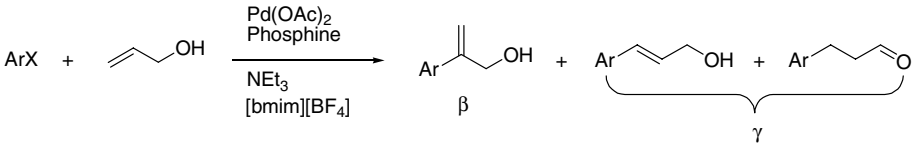
With these results in hand, the arylation of halopyridines, bromoquinoline and bromothiophenes was then carried out. Table 2 summarizes the results obtained. The methyl ketone compounds were obtained by acidic treatment of the Heck coupling products. All the reactions led to exclusive formation of the α arylated olefins, providing the first examples of highly regioselective, intermolecular arylation of electron-rich olefins with heteroaryl halides. The relatively electron-rich 3-bromopyrindines have previously been reported to couple with butyl vinyl ether in acetonitrile to afford a mixture of regioisomeric olefins, with the α substituted being the major component; but 2- and 4-bromopyrindines failed to react [3a]. Exclusive formation of an α product was observed with a 3-pyridyl triflate, consistent with the ionic pathway being facilitated with a good leaving group [12]. In addition to butyl vinyl ether, three other vinyl ethers (entries 8–10) were shown to couple with 3-bromopyrindine equally regioselectively, affording aryl methyl ketones in isolated yields of over 70% after hydrolysis.

Table 2
Heck arylation of vinyl ethers by heteroaryl halides in [bmim][BF_4][a]

Entry	Substrate	Olefin	Product	Yield[b]
1				88
2				81
3				75
4				69
5				91
6				89
7				82
8				77
9				72
10				71

[a] All reactions gave >99% conversion and >99/1 α/β regioselectivity as determined by ^{1}H NMR. See Section 4 for details.
[b] Isolated yield.

To further explore the scope of this highly regioselective Heck arylation method, we applied it to the coupling of allyl alcohol, aiming to prepare heterocyclic allyl alcohol derivatives (Scheme 4). Arylation of allyl alcohols by aryl halides generally leads to carbonyl products via isomerization of the initially formed γ-substituted allyl alcohol [13]. This is also true with bromothiophenes [14]. In fact, there appear to be only two reports in the literature, describing the preferential internal arylation of allyl alcohols and homoallyl alcohol with 1-naphthyl triflate; complex mixtures were formed with the corresponding iodide [15]. Remarkably, under the conditions described above, allyl alcohol coupled with halopyridines, bromoquinoline and bromothiophenes, affording the β-substituted allyl alcohols in excellent regioselectivities and isolated yields, demonstrating again the utility of the current method in controlling regioselectivity in the Heck reaction (Table 3). The similarity between the regioselectivity obtained by Cabri with aryl triflates in DMF [15] and that we obtained with aryl halides in [bmim][BF_4] suggests that this regiocontrol stems from a promoting effect of the ionic



Scheme 4.

Table 3
Heck arylation of allyl alcohol by heteroaryl halides in [bmim][BF_4][a]

Entry	Substrate	Product	Yield[b]
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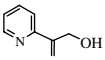
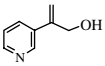
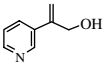
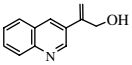
2			89
3			86
4			82
5			75
6			95

[a] All reactions gave >99% conversion and >99/1 β/γ selectivity as determined by ^{1}H NMR. See Section 4 for details.
[b] Isolated yield.

liquid on the dissociation of the halide anion from Pd(II), thus facilitating the ionic pathway. The yield with 3-chloropyridine was relatively low, however.

3. Conclusions

The results presented here demonstrate again that Pd-DPPP in combination with an imidazolium ionic liquid solvent provides an excellent catalytic system, with which highly regioselective Heck arylation of electron rich olefins can be accomplished without recourse to aryl triflates or stoichiometric silver and thallium additives. Specifically, we showed that halopyridines, bromoquinoline and bromothiophenes regioselectively couple with vinyl ethers to give acetyl heterocycles following hydrolysis, and with allyl alcohol to give 2-allyl alcohol-functionalized heteroaromatics. The introduction of these functionalities allow the heterocycles to be further elaborated leading to compounds of potentially interesting bioactivities. Whilst the detailed mechanism of these arylation reactions and those we reported previously [5] remains to be delineated, we believe that the arylation proceeds via the ionic pathway and the ionic liquid solvent plays an essential role in making this possible.

4. Experimental

All reactions were carried out under a nitrogen atmosphere. 1-Butyl-3-methylimidizolium tetrafluoroborate ([bmim][BF_4]) was prepared according to the literature method [16]. Following vacuum-drying at 80 °C for 8 h, the ionic liquid was stored under nitrogen at ambient temperature. Butyl vinyl ethers, halopyridines, bromoquinoline, bromothiophenes, $Pd(OAc)_2$ and 1,3-bis (diphenylphosphino)propane (DPPP) were purchased from Lancaster and Aldrich and were used as received. The products were characterized by ^{1}H and ^{13}C NMR, MS and HRMS, and by comparison of their spectra with the literature data and/or those of authentic samples when available.

4.1. Heck arylation in ionic liquid

An oven-dried, two-necked round-bottom flask containing a stir bar was charged with a heteroaryl halide (1.0 mmol), $Pd(OAc)_2$ (0.04 mmol), DPPP (0.08 mmol), and [bmim][BF_4] (2 mL) under nitrogen at room temperature. Following degassing three times, butyl vinyl ether (5.0 mmol) and triethylamine (1.6 mmol) were added. The mixture was heated and stirred at 125 °C for 30 h. After cooling to room temperature, aqueous HCl (10 mL, 10%) was added and the mixture stirred for 1 h. The solution was then treated with saturated Na_2CO_3 (10 mL) for a few min, without which the subsequent extraction would not work, and extracted with CH_2Cl_2 three times. The combined organic layers were washed with water and brine, dried with $MgSO_4$ and evaporated under reduced pressure. The residue was finally purified by flash chromatography (SiO_2, hexane/EtOAc = 8/2) to give the desired heteroaryl methyl ketone. The Heck arylation of allyl alcohol was performed in a similar manner.

4.2. Compounds isolated

2-Acetylpyridine. ^{1}H NMR ($CDCl_3$): δ = 2.73 (s, 3H), 7.49 (m, 1H), 7.84 (m, 1H), 8.04 (m, 1H), 8.69 (d, 1H); ^{13}C NMR ($CDCl_3$): δ = 26.1, 122.0, 127.4, 137.1, 149.2, 153.9, 200.4; CI-MS, *m/z* (%): 122 [$(M + H)^+$, 100]; HRMS Calcd for C_7H_8NO $(M + H)^+$: 122.0606. Found: 122.0606.

3-Acetylpyridine. ^{1}H NMR ($CDCl_3$): δ = 2.64 (s, 3H), 7.35 (m, 1H), 8.24 (m, 1H), 8.78 (s, 1H), 9.17 (d, 1H);

^{13}C-NMR ($CDCl_3$): δ = 27.1, 124.0, 132.6, 135.8, 150.3, 153.9, 197.1; CI-MS, *m/z* (%): 122 [$(M + H)^+$, 100], 108 (13); HRMS Calcd for C_7H_8NO $(M + H)^+$: 122.0606. Found: 122.0607.

4-Acetylpyridine. ^{1}H NMR ($CDCl_3$): δ = 2.36 (s, 3H), 7.46 (m, 2H), 8.52 (m, 2H); ^{13}C-NMR ($CDCl_3$): δ = 27.0, 121.3, 151.3, 198.2; CI-MS, *m/z* (%): 122 [$(M + H)^+$, 100], 108 (15); HRMS Calcd for C_7H_8NO $(M + H)^+$: 122.0606. Found: 122.0606.

3-Acetylquinoline. ^{1}H NMR ($CDCl_3$): δ = 2.74 (s, 3H), 7.63 (m, 1H), 7.84 (m, 1H), 7.95 (m, 1H), 8.16 (m, 1H), 8.70 (s, 1H), 9.43 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 27.2, 126.9, 128.2, 129.6, 129.8, 132.4, 137.7, 149.6, 150.2, 197.1; CI-MS, *m/z* (%): 172 [$(M + H)^+$, 100], 158 (10), 130 (15); HRMS Calcd for $C_{11}H_{10}NO$ $(M + H)^+$: 172.0762. Found: 172.0761.

2-Acetylthiophene. ^{1}H NMR ($CDCl_3$): δ = 2.57 (s, 3H), 7.14 (m, 1H), 7.64 (m, 1H), 7.71 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 27.3, 128.5, 132.9, 134.2, 145.0, 191.2; CI-MS, *m/z* (%): 127 [$(M + H)^+$, 100], 111 (43); HRMS Calcd for C_6H_7OS $(M + H)^+$: 127.0218. Found: 127.0215.

3-Acetylthiophene. ^{1}H NMR($CDCl_3$): δ = 2.51 (s, 3H), 7.31 (m, 1H), 7.54 (m, 1H), 8.04 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 27.4, 126.8, 127.3, 132.5, 143.1, 192.7; CI-MS, *m/z* (%): 127 [$(M + H)^+$, 100], 111 (50); HRMS Calcd for C_6H_7OS $(M + H)^+$: 127.0218. Found: 127.0216.

2-(Thiophene-2-yl)allyl alcohol. ^{1}H NMR ($CDCl_3$): δ = 1.89 (br, 1H), 4.43 (m, 2H), 5.19 (d, J = 0.3 Hz, 1H), 5.44 (d, 1H), 6.93 (m, 1H), 7.03 (m, 1H), 7.14 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 63.9, 110.2, 122.7, 123.6, 126.4, 139.9; 141.0; CI-MS, *m/z* (%): 141 [$(M + H)^+$, 100], 125 (10); HRMS Calcd for C_7H_9OS $(M + H)^+$: 141.0374. Found: 141.0378.

2-(Thiophene-3-yl)allyl alcohol. ^{1}H NMR($CDCl_3$): δ = 1.59 (br, 1H), 4.51 (m, 2H), 5.31 (d, J = 0.3 Hz, 1H), 5.50 (d, 1H), 7.26-7.33 (m, 3H); ^{13}C NMR ($CDCl_3$): δ = 65.5, 111.7, 126.1, 129.1, 131.1, 132.3, 141.4; CI-MS, *m/z* (%): 141 [$(M + H)^+$, 100], 140 (M^+, 45), 125 (63); HRMS Calcd for C_7H_9OS $(M + H)^+$: 141.0374. Found: 141.0377.

2-(Pyridin-2-yl)allyl alcohol. ^{1}H NMR ($CDCl_3$): δ = 1.54 (br, 1H), 4.58 (m, 2H), 5.51 (d, J = 0.5 Hz, 1H), 5.79 (d, 1H), 7.22 (m, 1H), 7.63 (m, 1H), 7.71 (m, 1H), 8.53 (m, 1H); ^{13}C NMR ($CDCl_3$): δ = 66.6, 116.6, 120.5, 121.2, 123.0, 126.1, 137.1, 148.7; CI-MS, *m/z* (%): 136 [$(M + H)^+$, 100], 121 (45); HRMS Calcd for $C_8H_{10}NO$ $(M + H)^+$: 136.1735. Found: 136.1735.

2-(Pyridin-3-yl)allyl alcohol. ^{1}H NMR($CDCl_3$): δ = 1.68 (br, 1H), 4.56 (m, 2H), 5.31 (d, J = 0.4 Hz, 1H), 5.53 (d, 1H), 7.21 (m, 1H), 7.83 (m, 1H), 8.54 (m, 1H), 8.69 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 66.7, 118.6, 121.3, 124.2, 129.4, 134.8, 139.1, 148.6; CI-MS, *m/z* (%): 136 [$(M + H)^+$, 100], 121 (55); HRMS Calcd for $C_8H_{10}NO$ $(M + H)^+$: 136.1735. Found: 136.1734.

2-(Quinolin-3-yl)allyl alcohol. ^{1}H NMR($CDCl_3$): δ = 1.98 (br, 1H), 4.67 (m, 2H), 5.56 (d, J = 0.6 Hz, 1H), 5.68 (d, 1H), 7.55 (m, 1H), 7.68 (m, 1H), 7.81 (m, 1H), 8.09 (m,1H), 8.19 (s, 1H), 9.01 (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 65.2, 115.3, 127.4, 128.1, 128.5, 129.3, 129.9, 131.6, 132.9, 144.8, 147.7, 149.4; CI-MS, *m/z* (%) (5): 186 [$(M + H)^+$, 100], 170 (15); HRMS Calcd for $C_{12}H_{12}NO$ $(M + H)^+$: 186.0919. Found: 186.0917.

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