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Palladium-catalyzed regioselective Heck arylation of electron-rich olefins in a molecular solvent-ionic liquid cocktail

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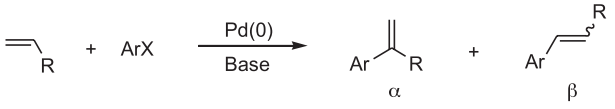
Abstract—We have recently established that highly regioselective Heck arylation of electron-rich olefins can be accomplished with aryl halides without using any halide scavengers in imidazolium ionic liquid solvents. The results presented in this paper show that the benchmark electron-rich olefins vinyl ethers can be readily arylated by aryl bromides in a molecular solvent-ionic liquid cocktail with no compromise on regioselectivity. By introducing a small amount of 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) to DMSO, the arylation reactions of the vinyl ethers **1a–d** by the bromides **2a–j** took place to afford essentially only the α arylated products. The enamide **1e** underwent similar regioselective arylation in the solvent cocktail. In the absence of the ionic liquid, lower regioselectivities were observed. In comparison with the chemistry we have reported so far, the current method reduces considerably the reliance on the volume of ionic liquids used, providing a simpler and more practical synthetic pathway for preparing arylated vinyl ethers and aryl methyl ketones.

1. Introduction

The palladium-catalyzed arylation and vinylation of olefins with aryl halides are well known as the Heck reaction and have proved to be of genuine synthetic utility for carbon–carbon bond formation.[1,2] 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 electronic deficient olefins.[1] 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.[1a,d-f,3] Such reactions usually give rise to a mixture of α and β substituted olefins and hence, are of only limited synthetic utility (Eq. 1). The problem with regioselectivity can be addressed by using aryl triflates instead of halides or stoichiometric amounts of halide scavengers when aryl halides are used, toxic thallium(I) or costly silver(I) salts being most popular.[3] 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 two pathways, one ionic leading to the branched product and the other neutral giving rise to the linear variant (Scheme 1).[3,4] One can easily envision that the ionic pathway will be rendered favorable when triflates or halide scavengers are chosen. However, triflates are thermally labile and in general not commercially available, and the inorganic additives create new problems such as toxicity and high cost. Therefore, it is practically important to develop novel methods, which would allow aryl halides to be used in regioselective arylation of electron-rich olefins with no need for costly or toxic additives.



(1)

In a programme aimed at developing organometallic catalysis in ionic liquids,[5] we disclosed that highly regioselective Heck arylation with aryl halides can be accomplished in imidazolium ionic liquids without recourse to halide scanvegers.[5d,6] In these reactions, pure ionic liquids were used as the bulky solvent. This may create a problem for using the chemistry in various synthetic reactions, as ionic liquid are by no means cheap as solvents and their toxicity and biodegradability are yet to be fully determined.[7] With these concerns in mind, we decided to minimize the amount of ionic liquid used. We now disclose that regioselective arylation of electron-rich olefins can be carried out equally well in a solvent cocktail that contains little ionic liquid. Although molecular solvent-ionic liquid

Keywords: Heck reaction; Electron-rich olefins; Regioselectivity; Ionic liquid; DMSO.
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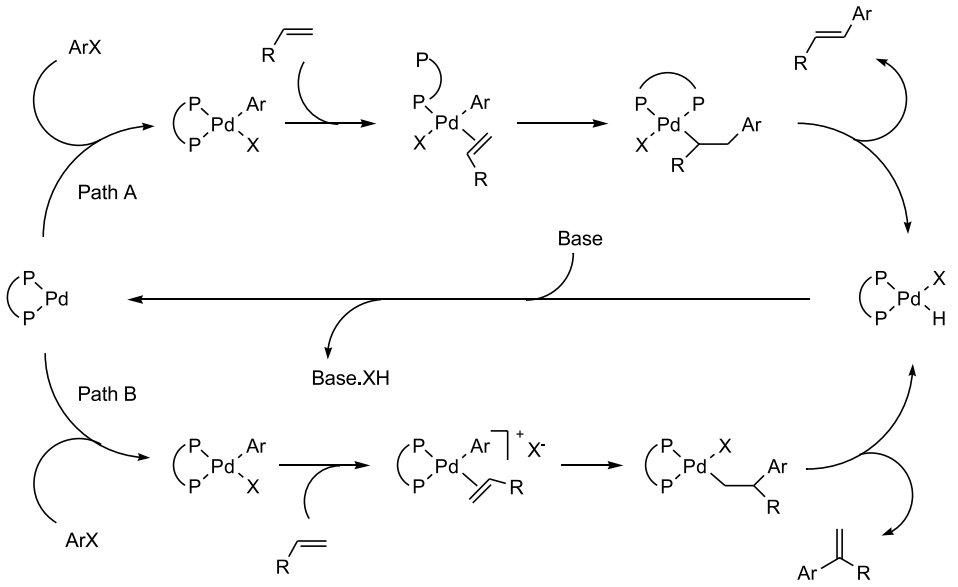


Scheme 1. The neutral and ionic pathways of the Heck reaction.

cocktails have been used in catalysis, ionic liquids act in most instances as the bulky solvents with molecular solvents added mainly to enhance substrate solubilities and/or facilitate catalyst/product separation via phase separation.[8]

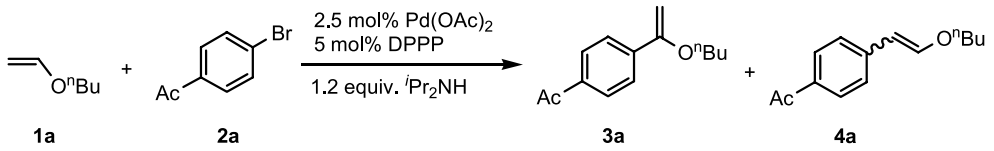
Room temperature ionic liquids such as those based on imidazolium salts have been extensively studied as one of the most promising alternatives to hazardous organic solvents for clean chemical reactions, due to their novel physicochemical properties such as low vapor pressure and tunable solubility for organic or inorganic compounds.[7,9] These solvents are entirely composed of ions; hence, the ionic Heck pathway could be made favorable when an arylation reaction is performed therein. Indeed, shortly after our initial report on the highly regioselective arylation of butyl vinyl ether with aryl bromides in [bmim][BF_4],[5d] Hallberg and co-workers reported similar reactions in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]).[10] High regioselectivities could also be achieved in aqueous DMF, in which water acts as an indispensable polar additive.[11]

2. Results and discussion

In our previous studies into the Heck arylation of electron-rich olefins by palladium catalysis,[5d,6] ionic liquids were used as the sole solvents. A typical arylation reaction at the scale of 1 mmol of substrate would normally require the use of 2 mL of an ionic liquid. To determine if the volume of ionic liquids could be reduced without compromising the regioselectivity at the same time, we examined the arylation of the benchmark electron-rich olefin butyl vinyl ether **1a** by 4-bromoacetophenone **2a** in a DMSO-[bmim][BF_4] solvent cocktail under conditions previously optimized for reactions in neat [bmim][BF_4]. The catalyst was derived in situ from 1 equiv of $Pd(OAc)_2$ and 2 equiv of a diphosphine, 1,3-bis(diphenylphosphino)propane (DPPP). The choice of DMSO as the molecular solvent was based on our observation that it promotes regioselective arylation of enamides in [bmim][BF_4].[6] For comparison, the arylation of **1a** was also carried out in neat DMSO. In a typical reaction, a mixture of **1a**, **2a**, $^{i}Pr_2NH$, $Pd(OAc)_2$, and DPPP was heated in a chosen solvent for 24 h under an inert atmosphere. The products were analyzed by NMR and the results are given in Table 1. As can be seen, in the molecular solvent DMSO, which is often used in the Heck reactions, the reaction afforded an α/β ratio of 86/14 (entry 1). This is consistent with early observations, that is, mixtures of regioisomers result when electron-rich olefins are arylated with aryl halides in molecular solvents.[12] Surprisingly somewhat, when 0.01 ml of [bmim][BF_4] was used as additive, the reaction afforded a better α/β ratio of 91/9 (entry 2). The regioselectivity was further improved when 0.05 ml of [bmim][BF_4] was added (entry 3), and much to our delight, when 0.1 ml of the ionic liquid was introduced to 2 ml of DMSO, **1a** was completely arylated by **2a** to give essentially exclusively the α substituted product **3a** (entry 4); the ^1H NMR spectrum of the reaction mixture after removing the ionic liquid showed no sign of the linear olefin **4a**, indicating that the ionic pathway B becomes overwhelmingly dominated in the presence of even catalytic amount of [bmim][BF_4] (5% volume; ca. 0.5 mmol) in DMSO. Song, Chi and co-worker have recently, reported a method that effects very efficient fluorination of mesylates by KF in a wet mixture of [bmim][BF_4] and CH_3CN, with catalytic amount of ionic liquid being feasible as well albeit less efficient.[8e]

Encouraged by the results above, we extended the scope of additives to other ionic liquids. As is clear, all the additives, [bmim][PF_6], [bmim][NTf_2] and [bdmim][BF_4],[13] promote the regioselectivity in favor of the branched product (entries 5–7). However, the regioselectivity was slightly poorer with these ionic liquids under similar conditions. In contrast, little conversion was observed when the ionic liquid additive was [bmim][Br] (entry 8). This is likely to be due to halide coordination to palladium, which affects the

Table 1. Solvent effect on the Heck arylation of butyl vinyl ether by 4-bromoacetophenone[a]



Entry	Molecular solvent	Ionic liquid (mL)	Conversion (%)[b]	α/β[c]	E/Z[d]
1	DMSO	[bmim][BF_4] (0)	100	84/16	79/21
2	DMSO	[bmim][BF_4] (0.01)	100	91/9	78/22
3	DMSO	[bmim][BF_4] (0.05)	100	98/2	77/23
4	DMSO	[bmim][BF_4] (0.1)	100	>99/1	—
5	DMSO	[bmim][PF_6] (0.1)	100	97/3	63/37
6	DMSO	[bmim][NTf_2] (0.1)	100	95/5	71/29
7	DMSO	[bdmim][BF_4] (0.1)	100	97/3	70/30
8	DMSO	[bmim][Br] (0.1)	5	92/8	—
9	DMSO[e]	None	100	90/10	81/19
10	DMSO[e]	H_2O (0.1)	100	61/39	70/30
11	DMF	[bmim][BF_4] (0)	100	75/25	80/20
12	DMF	[bmim][BF_4] (0.1)	100	94/6	79/21
13	None[f]	[bmim][BF_4] (0.01)	36	>99/1	—
14	None[f]	[bmim][BF_4] (0. 1)	70	>99/1	—
15	DMSO	[$^nBu_4N$][BF_4] (0.2)[g]	100	77/23	80/20
16	DMSO	[$^nBu_4N$][BF_4] (0.5)[g]	100	65/35	76/24

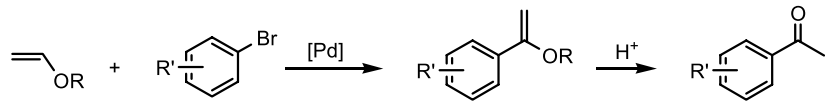
[a] Reaction conditions: 2.0 mmol **1a**, 1.0 mmol **2a**, 2.5 mol% $Pd(OAc)_2$, 5.0 mol% DPPP and 1.2 equiv $^iPr_2NH$ in the solvent cocktail DMSO/DMF (2 mL)+ ionic liquid at 115 °C for 24 h; the product was analyzed by ^1H NMR.
[b] Conversion of **2a** to **3a** and **4a**.
[c] Molar ratio of **3a/4a**; when the product **4a** could not be detected by ^1H NMR, a value of >99/1 was assigned.
[d] Ratio of *trans*/*cis* isomers of **4a**.
[e] Dried DMSO.
[f] 10.0 mmol **1a** and 3.0 mmol $^iPr_2NH$ were used.
[g] The number refers to mmol salt added.

generation of the cationic Pd-olefin species (vide supra), and/or the formation of inactive 1-butyl-3-methylimidazol-2-ylidene complexes of palladium.[14] The DMSO of this study was used as received. Drying the DMSO with molecular sieves resulted in a slightly increased α/β ratio, whilst adding water to the pre-dried DMSO led to its deterioration (entries 9 and 10). In the latter case decomposition of the Pd-DPPP catalyst appeared to occur as judged by the formation of palladium black, which may explain the partial loss of regioselectivity. Significantly improved regioselectivity was also observed when 5% [bmim][BF_4] was introduced into 2 ml of DMF (entries 11 and 12). It was surprising that the reaction proceeded, even without utilizing any molecular solvent, to give rise to exclusively the α substituted product **3a** when 0.01 mL of [bmim][BF_4] was added to the reaction mixture, although it was slow, only affording a 36% conversion (entry 13). However, when the amount of ionic liquid was increased to 0.1 mL, the reaction was accelerated to give a 70% conversion with >99/1 regioselectivity (entry 14). It is noteworthy that in the absence of the ionic liquid, little olefinic product was observed, showing that the ionic liquid plays a pivotal role for the enhanced regioselectivity.

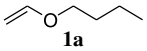
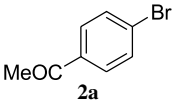
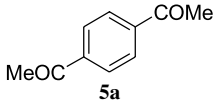
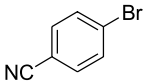
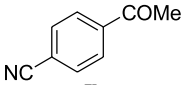
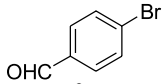
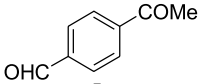
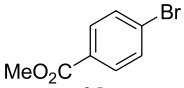
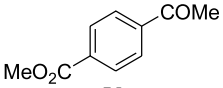
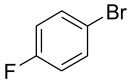
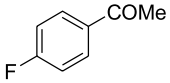
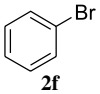
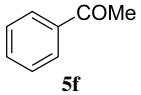
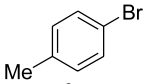
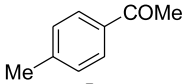
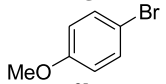
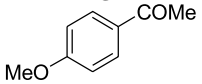
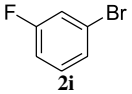
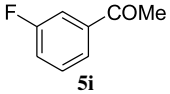
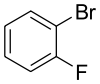
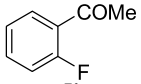
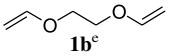
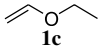
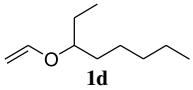
The excellent regioselectivity observed in the DMSO-[bmim][BF_4] solvent cocktail is in line with the arylation proceeding via the ionic pathway that is promoted by the ionic liquid. We have previously shown that amongst various molecular solvents DMSO exerts the best α regiocontrol over the arylation of vinyl ethers; but it could not deliver the same effect as imidazolium ionic liquids.[6] In the present study, DMSO probably plays a role in reinforcing the effect of the ionic liquids, as it is well known to facilitate ligand substitution on square-planar complexes.[15] How the ionic liquids promote the ionic pathway remains unclear, however. Their effects on the α regioselectivity may stem partly from increased ionic strength of the solution, which would be expected to enhance the rate of formation of the ionic palladium species shown in Scheme 1.[16] However, this is somewhat at odds with the observations made when a very small amount of [bmim][BF_4] was added without DMSO (entries 13 and 14), although, one might speculate that those reactions could take place in small droplets of ionic liquid. Furthermore, replacing [bmim][BF_4] with [$^nBu_4N$][BF_4] for the cocktail reaction brought about no improvement in the α/β ratios (entries 15 and 16), suggesting that the primary role of [bmim][BF_4] cannot be ascribed to its effect on the ionic strength. One possibility is the hydrogen bonding of the C^2–H proton with the halide anions,[17,5a] which might facilitate the dissociation of the bromide ion from Pd(II) and hence, the ionic pathway. However, this is not entirely backed by the observation made with [bdmim][BF_4], nor is it consistent with our previous report and that by Dyson.[6,18] Clearly, much remains to be done to delineate the role of the ionic liquids.

On the basis of the above studies, the arylation of **1a** was undertaken in the DMSO-[bmim][BF_4] mixture (20/1 volume ratio) with a variety of aryl bromides in the presence of 2.5 mol% $Pd(OAc)_2$ and 5.0 mol% DPPP. The isolated products were the aryl methyl ketones **5** following acidification of **3**. The results obtained are summarized in Table 2. As can be seen, excellent regioselectivities together with high isolated yields for the ketones **5** were obtained in

Table 2. Heck arylation of vinyl ethers **1a–d** by aryl bromides **2** in DMSO-[bmim][BF_4][a]



1 **2** **3** **5**

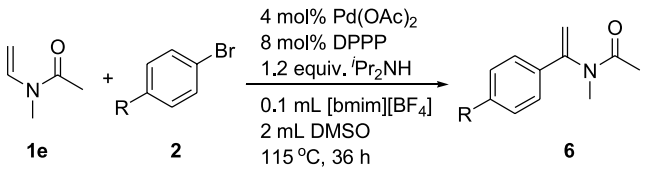
Entry	Olefin	Aryl bromide	Product	Yield (%)[b]
1	 **1a**	 **2a**	 **5a**	92
2	**1a**	 **2b**	 **5b**	88[c]
3	**1a**	 **2c**	 **5c**	89
4	**1a**	 **2d**	 **5d**	94
5	**1a**	 **2e**	 **5e**	96
6	**1a**	 **2f**	 **5f**	95
7	**1a**	 **2g**	 **5g**	87
8	**1a**	 **2h**	 **5h**	84[c]
9	**1a**	 **2i**	 **5i**	82[d]
10	**1a**	 **2j**	 **5j**	81[d]
11	 **1b**[e]	**2a**	**5a**	96
12	 **1c**	**2a**	**5a**	91
13	 **1d**	**2a**	**5a**	85

[a] Reaction conditions: 2.0 mmol **1**, 1.0 mmol **2**, 2.5 mol% $Pd(OAc)_2$, 5.0 mol% DPPP and 1.2 equiv $^iPr_2NH$ in DMSO (2 mL)+[bmim][BF_4] (0.1 mL), at 115 °C for 24 h; all reactions afforded 100% conversion and >99/1 α/β selectivity, as determined by ^1H NMR.
[b] Isolated yield of **5**.
[c] $Pd(OAc)_2$ (4 mol%) and 8 mol% DPPP were used, 36 h.
[d] Thirty six hours.
[e] 0.75 mmol of **1b** was used.

all the reactions in the solvent cocktail, regardless of the nature of the substituents on the aryl rings. Thus, bromobenzenes bearing either strongly electron-withdrawing or electron-donating *p*-substituents, such as –CN or –OMe, all furnished good to excellent isolated yields with α/β ratios of >99/1 (entries 1–8). With either the very electron-withdrawing or donating substituents, –CN or –OMe, the reaction tended to be slower and required a higher catalyst loading, however. With these two substituents, the olefin insertion step or coordination step might be inhibited, leading to slower reactions. Similar arylation reactions can be carried out with *m*- and *o*-substituted bromobenzenes, as demonstrated by the substrates **2i** and **2j** (entries 9 and 10).

The vinyl ethers **1b–d** underwent similar arylation under the same conditions. Examples of arylation of these olefins with **2a** are also seen in Table 2 (entries 11–13). These reactions again furnished >99/1 α/β regioselectivities and over 80% isolated yields for the ketone **5**. Under the given conditions, all the reactions shown in Table 2 went to completion; but shorter times should be possible, since the reaction time was not optimized for each individual reaction. The protocol thus provides a simple, practical supplement to the known methodologies for the synthesis of important aromatic ketones, and particularly to Friedel Crafts acylation, which is neither effective toward electron-deficient arenes nor as regioselective as the current method for the introduction of an acetyl group.[19]

In addition to the vinyl ethers, enamides could also be arylated under the same conditions. A few selected examples concerning the enamide **1e** are given in Eq. 2. The reactions were complete in 36 h, furnishing exclusively the branched product. We have previously shown that **1e** could not be arylated in neat [bmim][BF_4] and the reaction led to a mixture of products when run in neat DMSO.[6] The remarkable regioselectivities observed here suggest that the ionic path B (Scheme 1) is significantly facilitated in the arylation in the presence of even a small quantity of [bmim][BF_4].



2 = **2a** (R = *p*-Ac), **2f** (R = H), **2g** (R = *p*-Me).

100% conversion with α/β >99/1 for all, based on two runs for each.

(2)

3. Conclusions

We have recently developed the ionic liquid method for the highly regioselective Heck arylation of electron-rich olefins with aryl halides by palladium catalysis, circumventing the problems of using halide scavengers, which are often expensive and toxic. We have now shown that the same level of regiocontrol can be delivered for the same reaction by using a molecular solvent-ionic liquid cocktail that contains only a few percent of an ionic liquid, [bmim][BF_4]. This is significant that it substantially reduces the usage of ionic liquids and hence, makes the chemistry more practical for chemical synthesis. The unique regiocontrol observed in the mixed solvent results probably from the promoting effect of the ionic liquid on the ionic pathway, which is generally believed to give rise to the branched olefins. The molecular details of the mechanism remain to be delineated, however.

4. Experimental

All reactions were carried out under a nitrogen atmosphere. 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) was prepared according to the literature method.[20] Following vacuum-drying at 80 °C for 8 h, the ionic liquid was stored under nitrogen at ambient temperature. $AgNO_3$ titration showed the chloride content of the ionic liquid to be below detection limit (<0.2%). Vinyl ethers **1a–d**, aryl halides **2**, $Pd(OAc)_2$, 1,3-bis(diphenylphosphino)propane (DPPP), and diisopropylamine were purchased from Lancaster and Aldrich and were used as received. DMSO was bought from VWR and was used as received (≥99% purity).

An oven-dried, two-necked round-bottom flask containing a stir bar was charged with an aryl halide **2** (1.0 mmol), $Pd(OAc)_2$ (0.025 mmol), DPPP (0.05 mmol), DMSO (2 mL) and [bmim][BF_4] (0.1 mL) under nitrogen at room temperature. Following degassing three times, vinyl ether **1** (2.0 mmol) and $^iPr_2NH$ (1.2 mmol) were injected sequentially. The flask was placed in an oil bath, and the mixture was stirred and heated at the desired temperature. After a reaction time of 24 h, the flask was removed from the oil bath and cooled to room temperature. A small sample was then taken for NMR analysis. To the rest of the mixture, aqueous HCl (5%, 5 mL) was added and following stirring for 0.5 h, CH_2Cl_2 (20 mL) was added. After separation of the organic phase, the aqueous layer was extracted with CH_2Cl_2 (2×20 mL), and the combined organic phase was washed with water until neutrality, dried (Na_2SO_4), filtered, and concentrated in vacuo. The aryl methyl ketone was isolated out of the crude product by flash chromatography on silica gel using a mixture of ethyl acetate and hexane (1/99–10/90) as eluant. The identity and purity of the products were established by comparing their NMR, MS and HRMS spectra with the published data,[6] which are available for all the products in this study.

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