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Investigation of the behavior of arenediazonium salts with olefins in $BmimPF_6$

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Abstract—The palladium-catalyzed reactions of olefins with arenediazonium salts in ionic liquids were investigated. For methyl acrylate and methyl acrylonitrile, normal Heck cross-coupling products are obtained in good yields. However, highly selective dimerization products are formed in excellent yields for styrenes. The catalyst system can be recycled.

The palladium-catalyzed Heck reaction is a powerful and versatile tool for carbon–carbon bond formation.[1] For economic reasons, the recovery and recycling of the expensive palladium catalyst is of importance. This issue has been addressed through the use of polymer[2] or inorganic[3] supported palladium complexes in organic solvents and by using special media such as PEG[4] or ionic liquids.[5] Ionic liquids have attracted increasing attention because of their compatibility with transition metal catalysts and their limited miscibility with common organic solvents (which simplifies recycling).

The Heck reactions of aryl halides in ionic liquids have been studied extensively.[6] However, to the best of our knowledge, the reactions of arenediazonium salts in ionic liquids have not been investigated. Diazonium salts have several advantages over aryl halides including the accessibility of precursor anilines and superior reactivity. In continuation of our studies on ionic liquids,[7] we investigated reactions of arenediazonium tetrafluoroborate salts with various olefins in 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$). We wish to report the results of this study.

The reaction of methyl acrylate with phenyldiazonium tetrafluoroborate was investigated first. A variety of ionic liquids were used as solvents and the most effective was found to be 1-butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$). Only traces of product were obtained using either 1-butyl-3-methylimidazolium bromide (BmimBr) or 1-butyl-3-methylimidazolium tetrafluoroborate ($BmimBF_4$).

After establishing the reaction conditions, a number of arenediazonium salts were examined (Table 1, entries 1–9). Both bromo and iodo groups were tolerated. The catalytic system can be recycled at least four times without loss of activity (entries 1–4). The reactions of other olefins with diazonium salts were then examined (entries 10–13). Methyl acrylonitrile gave satisfactory results but higher temperatures and longer reaction times were required (entries 10 and 11). Vinyl ether and vinyl ester derivatives were unreactive (entries 12 and 13).

Surprisingly, when styrene was used as the olefin, the reaction produced the dimerization product, (*E*)-1,3-diphenyl-1-butene, in high yield instead of the expected Heck cross-coupling product. Transition-metal catalyzed dimerizations of aliphatic olefins have been investigated extensively,[8] however, dimerizations of aromatic olefins are not well known and generally give mixtures of *trans*-, *cis*-, and cyclic isomers in low yields.[9] Recently Shirakuwa and co-workers reported the indium triflate promoted, palladium-catalyzed dimerization of styrene.[10] However, the expensive palladium catalyst cannot be recycled and an indium triflate co-catalyst is required.

At first glance, it would appear that the diazonium salt is not involved in the dimerization reaction. However, in

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Keywords: Ionic liquids; Diazonium salts; Heck reaction; Dimerization; Palladium catalyzed.

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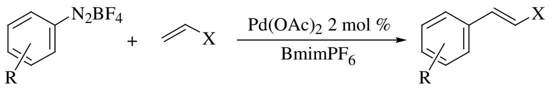
Table 1. Palladium-catalyzed Heck reaction of arenediazonium salts[a]



Entry	R	X	Temperature (°C)	Time (h)	Isolated yield (%)
1	H	CO_2Me	rt	3	76
2[b]	H	CO_2Me	rt	3	76
3[c]	H	CO_2Me	rt	3	73
4[d]	H	CO_2Me	rt	3	72
5	*p*-Br	CO_2Me	rt	3	82
6	*p*-Cl	CO_2Me	rt	3	78
7	*p*-I	CO_2Me	rt	3	32 (75)[e]
8	*o*-CN	CO_2Me	rt	2	80
9	*p*-OCH_3	CO_2Me	rt	3	72
10	*p*-Cl	CN	50	4	70
11	*p*-OCH_3	CN	50	4	68
12	*p*-OCH_3	OBn	50	5	0
13	*p*-OCH_3	OAc	50	5	0

[a] Reaction conditions: methyl acrylate or methyl acetonitrile (1 mmol), arenediazonium salt (1.2 mmol), $Pd(OAc)_2$ (2 mol%) at rt or 50 °C, 2–4 h.

[b] Second cycle of catalyst.

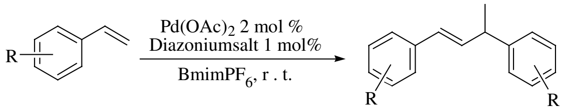
[c] Third cycle of catalyst.

[d] Fourth cycle of catalyst.

[e] GC yield in parenthesis, product decomposed on silica gel.

the absence of the diazonium salt, no trace of dimer was detected. We found that 1 mol% of diazonium salt was sufficient to catalyze the dimerization. The reaction was examined using a variety of substituted styrenes (Table 2). No differences in reactivity with respect to the electronic and steric effects of the substituent were observed. Halogens are tolerated (entries 2–5) and the palladium catalyst can be recycled at least four times (entries 6–9). Though the role of the diazonium salt in the reaction is still not clear, a free radical mechanism has been ruled out by the fact that no dimerization product formed when AIBN was used in place of the diazonium salt.

Table 2. Palladium catalyzed, diazonium salt promoted dimerization reactions of styrenes[a]



Entry	R	Time (h)	Isolated yield (%)
1	H	1.5	94
2	*p*-Cl	1.5	96
3	*o*-Cl	2	93
4	*o*-Br	2	72
5	*m*-Cl	2	89
6	*p*-CH_3	1.5	93
7[b]	*p*-CH_3	1.5	92
8[c]	*p*-CH_3	1.6	92
9[d]	*p*-CH_3	1.6	90

[a] Reaction conditions: styrene (1 mmol), $Pd(OAc)_2$ (2 mol%), *p*-nitrophenyldiazonium tetrafluoroborate (1 mol%), rt, 1.5–2 h.

[b] Second cycle of catalyst.

[c] Third cycle of catalyst.

[d] Fourth cycle of catalyst.

In summary, reactions of olefins with arenediazonium salts in ionic liquids were investigated. The results depend on the olefin used: methyl acrylate and methyl acrylonitrile yield normal Heck cross-coupling products, whereas styrenes produce dimerization products in excellent yields in the presence of a catalytic amount of diazonium salt. The catalytic system can be recycled.

Acknowledgements

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