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Tetrabutylphosphonium 4-ethoxyvalerate as a biomass-originated media for homogeneous palladium-catalyzed Hiyama coupling reactions

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Abstract

The introduction of a biomass-derived ionic liquid into the Hiyama coupling reactions, which has been considered as a powerful tool for the synthesis of symmetrically and non-symmetrically substituted biaryl structures, could further control or even reduce the environmental impact of this transformation. It was shown that tetrabutylphosphonium 4-ethoxyvalerate, a γ-valerolactone-based ionic liquid, can be utilized as an alternative solvent to create carbon–carbon bonds between aryl iodides and functionalized organosilanes in the presence of 1 mol% Pd under typical Hiyama conditions (130 °C, 24 h, tetrabutylammonium fluoride activator). A comparison of different ionic liquids was performed, and the effects of the catalyst precursor and the moisture content of the reaction mixture on the activity of the catalyst system were investigated. The functional group tolerance was also studied, resulting in 15 cross-coupling products (**3a–o**) with isolated yields of 45–72% and excellent purity (>98%).

Keywords Hiyama coupling · Ionic liquids · Homogeneous catalysis · Green chemistry

Introduction

The transition-metal-catalyzed cross-coupling reactions have emerged as one of the most powerful tools for the creative construction of both C–C and C–X (X: heteroatom) bonds, especially in multistep synthesis of biologically active compounds (Yang et al. 2017; Shi et al. 2011; Hosseinian et al. 2018; Jana et al. 2011). From the series of typically applied d^{10} metals, the palladium-catalyzed transformations have

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received outstanding interest, due to their excellent chemoselectivity, functional group tolerance, and mild operation conditions, which are of great importance in the synthesis of pharmaceuticals and agrochemicals (Devendar et al. 2018; Johansson Seechurn et al. 2012; Biajoli et al. 2014; González-Sebastián and Morales–Morales 2019). Among these reactions, the Hiyama coupling represents an excellent protocol for the synthesis of symmetrically and non-symmetrically substituted biaryl structures via coupling of corresponding aryl halides and organosilanes (Hatanaka and Hiyama 1988; Sore et al. 2012; Nakao and Hiyama 2011). The latter, as transmetalation reagents exhibit several advantages over organoboranes or organostannanes, such as low cost, low toxicity, ready availability, and high chemical stability. The protocol exhibits high regio- and stereochemistry, as well (Horn 1995; Nakao and Hiyama 2011). The silicon waste of the reaction can easily be incinerated to harmless SiO_2. All of these points have made the Hiyama coupling an environmentally attractive method; however, it had received limited attention in comparison with Heck, Sonogashira, or Suzuki reaction, before the improved synthetic approaches towards novel organosilane compounds renewed its importance (Denmark and Regens 2008; Denmark and Liu 2010). Depending on the structure and/or nature of organosilanes,

i.e., vinyl silanes (Wolf and Lerebours 2004), alkoxysilanes, silanols (Hirabayashi et al. 1999), and silanolates (Denmark et al. 2008), a huge variety of application scope can be drawn including representation of a key step in the total synthesis of complex structures, for example, the total synthesis of (+)–brasilenyne (Denmark and Yang 2004) and of (+)-papulacandin D (Denmark et al. 2007).

Despite these advantages, the Hiyama couplings are usually performed in common organic solvents, which usually have high toxicity, flammability, and vapor pressure even at low temperatures resulting in serious environmental concerns. As reported by U.S. FDA guidelines (CDER 2017), the commonly used solvents for the Hiyama reactions such as tetrahydrofuran (Miller and Montgomery 2014; Cheng et al. 2013), dioxane (Zhang et al. 2014), *N*,*N*-dimethylformamide (Handy et al. 2005), toluene (Denmark et al. 2008), and 1,2-dichloroethane (Ramgren and Garg 2014) are classified into Class 1 and 2, which utilizations should be avoided or limited, respectively, particularly in the pharmaceutical industry. To eliminate these hazardous auxiliary materials, the reactions have been demonstrated in alternative media, e.g., water (Sakon et al. 2017; Inés et al. 2011; Wolf and Lerebours 2004) or glycerol (Marset et al. 2018). Although, numerous Pd-catalyzed coupling reactions such as Suzuki, Sonogashira, Heck, and Stille were demonstrated in ionic liquids (ILs) (Li et al. 2018; Prechtl et al. 2010; Hallett and Welton 2011), which have been utilized as versatile and easily tunable alternative reaction media, and only a few studies were published on the Hiyama reaction (Mandal et al. 2019). First, Slattery and co-workers demonstrated the applicability of 1-pentyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C$_5$MPyr][Tf$_2$N]) as a reaction media for allyl–aryl coupling under mild conditions (Bäuerlein et al. 2009). Jain developed a phosphane-free protocol for the manufacture of functionalized biaryls with good to excellent yields in 3-(3-cyanopropyl)-1-methyl-1H-imidazol-3-ium hexafluorophosphate ([CN-bmim][PF$_6$]) by the use of in situ generated Pd nanoparticles (Premi and Jain 2013). The effect of the ILs on the stabilization of Pd nanoparticles was also shown. However, acceptable isolated yields were achieved in the presence of a common co-solvent (Planellas et al. 2014).

Although Hiyama coupling is a well-known transformation, according to the best of our knowledge, it has not been carried out in biomass-originated ILs, which could additionally act as a ligand. Therefore, by the introduction of a biomass-based solvent into this synthetically important reaction, the environmental impacts of a Hiyama reaction involved synthesis could be further controlled and reduced.

Herein, we report a study on the palladium-catalyzed Hiyama coupling reactions to synthesize various biaryl structures in biomass-originated γ-valerolactone-based ionic liquid tetrabutylphosphonium 4-ethoxyvalerate ([TBP][4EtOV]) extending its utilization for catalysis.

Experimental

Materials and equipment

The sources of chemicals are listed in the Supplementary Material. The γ-valerolactone-based ionic liquids were prepared by a published method with details presented in Supplementary Material.

The NMR spectra were recorded on a Brucker Avance 250 MHz spectrometer. Water contents of the ionic liquids were determined by Karl Fischer titration performed by HANNA Instruments 904. GC analyses were performed on an Agilent 6890 N instrument with HP-Innowax capillary column (15 m × 0.25 μm × 0.25 μm) using H$_2$ as a carrier gas.

General procedure for Hiyama coupling reactions

In a 4 mL screw-cap vial, 0.5 mmol of the corresponding iodoarene compounds, 1.5 eq of the corresponding silane, 1.5 eq of tetrabutylammonium fluoride (TBAF), 0.01 eq PdCl$_2$(PPh$_3$)$_2$, and 0.8 mL of tetrabutylphosphonium 4-ethoxyvalerate ([TBP][4EtOV]) ionic liquid were mixed and stirred at 130 °C for 24 h. After cooling, the mixture was partitioned between 5 mL of 1 M HCl and 5 mL of pentane. The aqueous phase was extracted subsequently with 3 × 5 mL of pentane. The combined organic phase was washed with brine, dried over MgSO$_4$, and filtered, and the solvent was evaporated under reduced pressure (ca. 1.333 kPa). The residue was purified by chromatography on silica gel (Merck Silicagel 60 (0.063−0.200 mm) for column chromatography (70−230 mesh ASTM)) eluted with *n*-pentane:EtOAc. The detailed experimental procedure, as well as the characterization of isolated compounds are provided in the Supporting Information.

Preparation and characterization of isolated compounds

Preparation and characterization of earlier published compounds (**3a–k** and **3 m–o**) are presented in Supporting Information.

1-Phenyl-2-chloro-4-(trifluoromethyl)benzene (**3 l**) was prepared according to general procedure using 0.5 mmol 2-chloro-1-iodo-4-(trifluoromethyl)benzene, 0.75 mmol triethoxyphenylsilane, 0.75 mmol [N(C$_4$H$_9$)$_4$][F]. Isolated yield: 50%. ^{1}H NMR (250 MHz, CDCl$_3$): δ (ppm) 7.42–7.51 (m, 5H), 7.51–7.54 (m, 1H), 7.56–7.65 (m, 1H), 7.76–7.83 (m, 1H). ^{13}C NMR (62.9 MHz, CDCl$_3$) 123.8 (q, J = 272 Hz), 124.1 (q, J = 3.8 Hz), 127.4 (q, J = 3.8 Hz),

128.7, 128.8, 129.6, 131.3 (q, J = 33.4 Hz), 132.2, 133.6, 138.5. HRMS [M + H]$^+$ Calculated: 257.0345, Measured: 257.0341 (0.5 ppm).

Results and discussion

The applications of ionic liquids into the synthesis protocols have become into the focus of interest due to their versatility and tunability. However, it was shown that the number of chemical steps could be over 20 or even 30, reducing their impact towards green chemistry (Jessop 2011). Using a biomass-originated building block for the synthesis of an IL, this number could be significantly reduced. It was shown that valerate-based ionic liquids could easily be synthesized from γ-valerolactone (Fegyverneki et al. 2010; Orha et al. 2018), which can be obtained by a two-step synthesis via valorization of lignocellulosic biomass wastes (Tukacs et al. 2014 and 2017).

To demonstrate their further applicability, they were first compared to the conventional 1-butyl-3-methylimidazolium cation-based ILs in the coupling of iodobenzene (**1a**) and triethoxyphenylsilane (**2a**) as a model reaction (Scheme 1) under typically used "Hiyama conditions" using tetrabutylammonium fluoride as a F$^-$ source (Ismalaj et al. 2014). As with Sonogashira coupling in ILs (Orha et al. 2019), negligible conversion rates of **1a** were detected in butylmethylimidazolium cation containing ILs (Table 1 entries 1–3). The reaction efficiency could be significantly increased by the introduction of tetrabutylphosphonium 4-ethoxyvalerate [TBP][4EtOV], resulting in the conversion of **1a**. The product biphenyl (**3a**) was isolated with a yield of 58% (Table 1, entry 6), which could be assumed to be higher by subsequent optimization of the reaction parameters.

The selection of a palladium source could have a significant effect on the efficiency of a catalytic transformation (Błaszczyk et al. 2009). When different precursors were compared, it was revealed that using of bis(triphenylphosphine)palladium(II) dichloride (Pd(PPh$_3$)$_2$Cl$_2$) and tris(dibenzylideneacetone)dipalladium(0) (Pd$_2$(dba)$_3$) gave acceptable yields of **3a** (Table 2, entries 1 and 5). A similar observation was reported for the Sonogashira reaction performed in biomass-originated ILs (Orha et al. 2019).
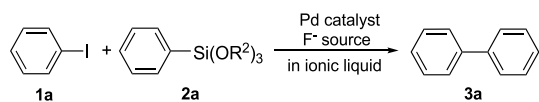
Table 1 Palladium-catalyzed Hiyama coupling reactions of iodobenzene (**1a**) and triethoxyphenylsilane (**2a**)

Entry	Ionic liquids	Isolated yield (%)
1	[BMIM][PF$_6$]	< 5
2	[BMIM][BF$_4$]	< 1
3	[BMIM][OctS]	< 1
4	[TEA][4HV]	10
5	[TBA][4HV]	8
6	[TBP][4EtOV]	58

Reaction conditions: solvent 0.5 mL, 0.5 mmol iodobenzene, 0.75 mmol triethoxyphenylsilane, 1 mol% Pd(OAc)$_2$, 1.5 eq TBAF, T = 130 °C, t = 24 h

The residual moisture content could dramatically affect a transition-metal-catalyzed reaction. In this case, however, the fluoride activator ([N(C$_4$H$_9$)$_4$][F], hereafter TBAF) containing 3 eq water, the water content of the reaction mixtures was ca 10 m/m%. It exceeds the typical residual water content of GVL-based ionic liquids (Strádi et al. 2015, Orha et al. 2018). Consequently, that, the protocol is hardly sensitive to water up to 10%, can be assumed and no special handling of the reaction regarding the exclusion of air and moisture is necessary.

Generally, the organosilane activation with fluoride ion, that is, the formation of the pentavalent silicon center, is considered as a key step. In this way, a facile bond breaking of the carbon–silicon bond during transmetalation is favored. It was demonstrated that alkali metal salt such as NaF or CsF could also act as silane activators for Hiyama coupling reactions (Gurung et al. 2013; Monguchi et al. 2012). In addition, both ammonium- and phosphonium-based ionic liquid have been proved to be good extractants of Pd suggesting their complexing ability (Katsuta et al. 2011; Regel-Rosocka et al. 2015). Because of high water tolerance of

Table 2 Palladium-catalyzed Hiyama coupling reactions of iodoaromatic compounds with triethoxyphenylsilane

Entry	Catalyst precursor	Isolated yield (%)
1	Pd(PPh$_3$)$_2$Cl$_2$	70
2	Pd(OAc)$_2$	58
3	Pd(cod)Cl$_2$	45
4	Pd(dba)$_2$	64
5	Pd$_2$(dba)$_3$	76

Reaction conditions: [TBP][4EtOV] solvent 0.5 mL, 0.5 mmol iodobenzene, 0.75 mmol triethoxyphenylsilane, 1 mol% catalyst, 1.5 eq TBAF, T = 130 °C, t = 24 h

dba benzylideneacetone, cod: 1,5-cyclooctadiene, *OAc* acetate

Scheme 1 Palladium-catalyzed Hiyama cross-coupling of iodobenzene (**1a**) and triethoxyphenylsilane (**2a**) in ionic liquid. F$^-$ source: TBAF

the catalytic reactions, we attempt to convert **1**a and **2** to **3** by the use of cheaper NaF in the presence of the different amount of water. However, no conversion was detected up to 20 wt% water. When 30 wt% of water loading was applied, moderate (39%) conversion of **1a** to **3a** was detected in the presence of 2 eqv NaF, even higher activator concentration at 130 °C for 24 h. To conclude, the fluoride activator cannot be eliminated from the system.
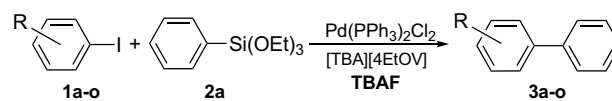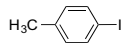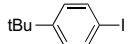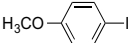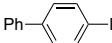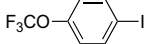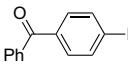
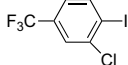Hereafter, to facilitate C–C bond coupling involving several iodoaromatic substances (**1a–o**) and triethoxyphenylsilane (**2**), bis(triphenylphosphine)palladium(II) dichloride was selected as a catalyst precursor by the use of 1.5 eq TBAF in the absence of any additional ligands and auxiliary base in [TBP][4EtOV] at 130 °C for 24 h (Table 3). It was demonstrated that the catalytic system generally could be utilized for the conversion of various iodoaromatic compounds. The substrate reactivity was not affected by the electronic parameters of the aromatic substrates. Thus, no Hammet-sigma (σ_p) correlation can be established for *para*-substituted species. Both electron-donating groups, i.e., methyl, *tert*-butyl, methoxy (Table 3 entries 2–6), and electron-withdrawing groups, i.e., chloro, fluoro or trifluoromethoxy (Table 2, entries 7–12) were tolerated on the aryl iodide. No significant differences of the isolated yields were observed. Under identical conditions, iodopyridine derivatives and 2-iodothiophene were easily converted to the corresponding biphenyls (**3 m–o**). The conversion of 4-chloro-1-iodobenzene did not lead to the formation of 1,4-diphenylbenzene.

The GVL-based [TBP][4EtOV] ionic liquid has been proven as an excellent reaction media for transition-metal-catalyzed C–N (Ullmann type) (Orha et al. 2018) and C–C (Sonogashira) (Orha et al. 2019) coupling reactions previously. In the present work, we demonstrated that its utilization can be extended for Hiyama coupling, as well, which makes it an attractive biomass-based, environmentally friendly alternative for common, fossil-based solvents, and opens the possibility for its application in wider range of chemical transformations.

Conclusions

In conclusion, we have shown that tetrabutylphosphonium 4-ethoxyvalerate [TBP][4EtOV], a γ-valerolactone-based partially biomass-derived ionic liquid, can be applied as an alternative, safer reaction media for palladium-catalyzed Hiyama-type carbon–carbon bond-forming reactions of iodoaromatic compounds with triethoxyphenylsilane. A variety of biphenyl derivatives (**3b–l**) and aromatic heterocycles (**3 m–o**) were obtained with 45–72 % yield. The protocol that can be performed under air showed excellent tolerance to the moisture content of the reaction mixture.

Table 3 Palladium-catalyzed Hiyama coupling reactions of iodoaromatic compounds with triethoxyphenylsilane[a]

#	Iodoaromatic compounds		Product	Yield (%)[b]
1	**1a**	(phenyl iodide)	**3a**	70
2	**1b**	(2-methylphenyl iodide, CH₃)	**3b**	64
3	**1c**	H₃C— (4-methylphenyl iodide)	**3c**	72
4	**1d**	(3-methylphenyl iodide, H₃C)	**3d**	69
5	**1e**	tBu—	**3e**	55
6	**1f**	H₃CO—	**3f**	63
7	**1g**	Ph—	**3g**	45
8	**1h**	Cl—	**3h**	48
9	**1i**	F₃CO—	**3i**	61
10	**1j**	F—	**3j**	68
11	**1k**	(Ph–C(O)–)	**3k**	58
12	**1l**	F₃C— (Cl)	**3l**	50
13	**1m**	(3-iodopyridine, N)	**3m**	55
14	**1n**	(2-amino-3-iodopyridine, N, NH₂)	**3n**	55
15	**1o**	(2-iodothiophene, S)	**3o**	66

[a]Reaction conditions: 0.5 mL [TBP][4EtOV], 0.5 mmol iodoaromatic compounds, 0.75 mmol triethoxyphenylsilane, 1.5 eq TBAF, T = 130 °C, t = 24 h

[b]Isolated yield

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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