Applied
Organometallic
Chemistry

Received: 24 April 2012 Revised: 29 May 2012 Accepted: 17 June 2012

(wileyonlinelibrary.com) DOI 10.1002/aoc.2899

PEG-4000-promoted palladium-catalyzed *N*-allylation in water: aminonaphthalene as an example

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An environmentally friendly, efficient catalytic process using palladium associated with ligands in a PEG4000–water system leading to *N*-allylation was described in this study. PEG-4000 was found to improve the palladium-catalyzed allylic amination of allylic acetates with aminonaphthalenes and gave overall good to high yields of the corresponding *N*-allylic aminonaphthalenes.

Supporting information may be found in the online version of this article.

Keywords: palladium-catalyzed; allylation; water; aminonaphthalenes; allylic acetates; polyethylene glycols

Introduction

Allylamines are pivotal building blocks for various biological properties and advanced intermediates in total synthesis of natural products[1] and especially those involving ring-closing metathesis.[2] Therefore their synthesis is still an important area of activity. Palladium-catalyzed transformations of allylic compounds have demonstrated powerful and well-established synthetic procedures for carbon–carbon and carbon–heteroatom (N, O, S) bond formation.[3] With respect to the reaction mechanism, palladium-catalyzed allylation proceeds via π-allyl palladium complexes.[4] Most of the mechanistic studies focus on either the elimination of the leaving group or the attack of the amine.[5]

Aromatic amines have not been used commonly in allylic amination, presumably because they are less nucleophilic than the more commonly used benzylamine or stabilized anionic nitrogen nucleophiles.[6] In this paper, we chose 1-aminonaphthalene as our lead compound, because not only is it the core of the photo-induced electron donor but it was also developed to investigate the electron injection and charge recombination processes in DNA duplex.[7] 1-Aminonaphthalene is also widely used in the organic chemical industry as an intermediate of dye and rubber antioxidants.[8] Moreover, naphthylamine can be oxidized by chromic acid into naphthoquinone, which is a fundamental ring structure related to vitamin K.[9]

With green chemistry processes and concerns over the environmental impacts of using volatile organic solvents, the promising potentials of water and other non-conventional solvents have become highly noteworthy in designing organic syntheses.[10] Water is the cheapest, most abundant solvent available. It also has the highest value for specific heat capacity, enabling more facile control of an exothermic reaction, and has a network of hydrogen bonds which can influence the reactivity of substrates.[11] Palladium-catalyzed *N*-allylation in water had been developed in our lab.[12] On the basis of our previous study, the reactions needed under reflux conditions and reaction time of some derivatives was more than an hour. Other interesting features of water are that additives such as salts can be used, inducing salting-in or salting-out effects, or surfactants and cyclodextrins can be added, the pH can be varied, and co-solvents or biphasic reaction systems can be utilized.[11a] Many successful applications of the aqueous biphasic method have resulted from the use of polyethylene glycol (PEG) as the polymeric support.[13]

PEG employed as soluble supports for biphasic reaction systems must: (i) be commercially available or rapidly and conveniently prepared; (ii) demonstrate good mechanical and chemical stabilities; (iii) provide appropriate functional groups for easy attachment of organic moieties; and (iv) exhibit high solubilizing power in order to dissolve molecular entities with low solubilities and permit the development of a general synthetic methodology independent of the physicochemical properties of target compounds.[13g] PEG is nontoxic and nonvolatile as well as being miscible with water.[14] The use of PEG has been reviewed as a green reaction medium in which its phase-transfer properties and its applications in solutions with water have been highlighted.[13b] It can be isolated by a simple phase separation, if used with organic substrates in a biphasic reaction system. As a logical extension of our previous work,[12] we further find that the palladium-catalyzed *N*-allylation could occur smoothly under a PEG–water system. We wish to present herein the experimental results.

Results and Discussion

In a recent report, we treated a mixture of 1-aminonaphthalene (**1a**) and allyl acetate (**2a**) in the presence of catalytic amounts of $Pd(OAc)_2$ and PPh_3 in 'pure water' under reflux condition for

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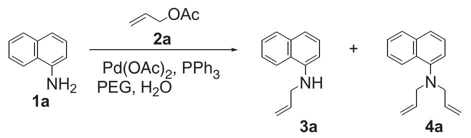
30 min, and overall product yield was 88% (Table 1, entry 1).[12] The reaction temperature was reduced to 70°C and the result was found to be similar to entry 1 (entry 2). Nevertheless, we treated another aminonaphthalene derivative under 'pure-water' conditions to give lower yields. Moreover, the addition of PEG-4000 led to a rapid increase of activity and tended to mono-allylation of 1-aminonaphthalene in the aqueous media (entries 3–11). As far as we know, a number of palladium catalysts are commercially available and their reactivity, stability and selectivity can be tuned by ligands and/or additives.[10a] Herein, we believe PEG was the appropriate additive for mono-selectivity. The optimal ratio of PEG:water was 1.5:3 g (entry 5). The reaction was perfectly stable in air and was carried out in the presence of catalytic amounts of $Pd(OAc)_2$ (0.02 mmol) and PPh_3 (0.08 mmol) at 70°C for 15 min. In addition, the effect of various chain-length PEGs on the reaction was examined under the same reaction conditions (entries 7–10). PEG-4000 was superior to all other PEGs, and therefore PEG-4000 was used as the source of PEG throughout the studies. High efficiency of the $Pd(OAc)_2$–H_2O–PEG system is probably attributed to the properties of PEG as co-solvent and phase transfer catalyst. The reaction at room temperature gave only **3a** in 37% yield (entry 11). As with our observation, *N*-allylation of **1a** may proceed to give the monoallylation product **3a** first, which is then allylated to give diallyated **4a**. Therefore, increasing the relative amount of allyl acetate favored the formation of the diallylated **4a** (entries 12 and 13).

Table 1. Palladium-catalyzed allylation of 1-aminonaphthalene (**1a**) with allyl acetate (**2a**): polyethylene glycols effects[a]



Entry	PEG species	PEG/water (w/w)	Yield (%)[b] (**3a**:**4a**)
1[c]	—	0/5	88 (73:27)[12]
2	—	0/3	84 (90:10)
3	PEG-4000	0.5/3	89 (79:21)
4	PEG-4000	1/3	87 (95:5)
5	PEG-4000	1.5/3	94 (90:10)
6	PEG-4000	2/3	94 (82:18)
7	PEG-600	1.5/3	81 (90:10)
8	PEG-1000	1.5/3	80 (90:10)
9	PEG-2000	1.5/3	79 (94:6)
10	PEG-6000	1.5/3	82 (98:2)
11[d]	PEG-4000	1.5/3	37 (100:0)
12[e]	PEG-4000	1.5/3	97 (68:32)
13[f]	PEG-4000	1.5/3	96 (5:95)

[a] Reaction conditions: **1a** (1 mmol), **2a** (0.8 mmol), $Pd(OAc)_2$ (0.02 mmol), and PPh_3 (0.08 mmol) in PEG–water system were reacted at 70°C for 15 min.

[b] Isolated yield.

[c] Reacted under reflux conditions for 30 min.

[d] Reacted at room temperature.

[e] Compound **2a** (1.2 mmol) was used.

[f] Compound **2a** (4 mmol) was used.

It was confirmed that the reaction did not occur in the absence of palladium species (Table 2, entry 1). The yields were only 19% in the absence of phosphine ligand (entry 2). Among the palladium catalysts were $Pd(OAc)_2$ (entry 3), $Pd(acac)_2$ (entry 4), $Pd(OCOCF_3)_2$ (entry 5), $Pd(propionate)_2$ (entry 6), $PdCl_2$ (entry 7), $PdCl_2(MeCN)_2$ (entry 8), $PdCl_2(PhCN)_2$ (entry 9), $PdCl_2(1,10\text{-}Phen)_2$ (entry 10), $[Pd(allyl)Cl]_2$ (entry 11), $Pd(hfacac)_2$ (entry 12), $Pd(PPh_3)_4$ (entries 13 and 14) and $Pd_2(dba)_3$ (entry 15). $Pd(OAc)_2$, $Pd(acac)_2$, $Pd(OCOCF_3)_2$, $Pd(propionate)_2$, $PdCl_2(MeCN)_2$, $[Pd(allyl)Cl]_2$, $Pd(hfacac)_2$ and $Pd_2(dba)_3$ were found to be superior. $PdCl_2$ and $PdCl_2(1,10\text{-}Phen)_2$ decreased the yield of products (entries 7 and 10). However, using phosphine-based Pd(0) complex $Pd(PPh_3)_4$ with extra PPh_3 as catalyst increased the product yields (entry 13). $[Pd(allyl)Cl]_2$ has been used in another aminonaphthalene derivative and gave lower yields, although it was the most effective Pd catalyst in the reaction of 1-aminonaphthalene with allyl acetate. Considering the above

Table 2. Palladium-catalyzed allylation of 1-aminonaphthalene (**1a**) with allyl acetate (**2a**): palladium catalyst and phosphine ligand effects[a]

Entry	Pd catalyst	Ligand	Yield (%)[b] (**3a**:**4a**)
1	—	PPh_3	0
2	$Pd(OAc)_2$	—	19 (100:0)
3	$Pd(OAc)_2$	PPh_3	94 (90:10)
4	$Pd(acac)_2$	PPh_3	92 (93:7)
5	$Pd(OCOCF_3)_2$	PPh_3	88 (95:5)
6	$Pd(propionate)_2$	PPh_3	87 (97:3)
7	$PdCl_2$	PPh_3	1 (100:0)
8	$PdCl_2(MeCN)_2$	PPh_3	84 (87:13)
9	$PdCl_2(PhCN)_2$	PPh_3	79 (92:8)
10	$PdCl_2(1,10\text{-}Phen)_2$	PPh_3	25 (92:8)
11	$[Pd(allyl)Cl]_2$	PPh_3	99 (97:3)
12	$Pd(hfacac)_2$[c]	PPh_3	86 (95:5)
13	$Pd(PPh_3)_4$	—	78 (94:6)
14	$Pd(PPh_3)_4$	PPh_3	84 (98:2)
15	$Pd_2(dba)_3$	PPh_3	86 (97:3)
16	$Pd(OAc)_2$	$(2\text{-}MeC_6H_4)_3P$	85 (75:25)
17	$Pd(OAc)_2$	$(3\text{-}MeC_6H_4)_3P$	88 (94:6)
18	$Pd(OAc)_2$	$(4\text{-}MeC_6H_4)_3P$	91 (91:9)
19	$Pd(OAc)_2$	$(2\text{-}pyridyl)Ph_2P$	97 (91:9)
20	$Pd(OAc)_2$	$(2\text{-}furyl)_3P$	75 (95:5)
21	$Pd(OAc)_2$	$(4\text{-}ClC_6H_4)_3P$	84 (90:10)
22	$Pd(OAc)_2$	$(4\text{-}FC_6H_4)_3P$	81 (88:12)
23	$Pd(OAc)_2$	$(4\text{-}MeOC_6H_4)_3P$	86 (88:12)
24	$Pd(OAc)_2$	$[2,6\text{-}(MeO)_2C_6H_3]_3P$	9 (100:0)
25	$Pd(OAc)_2$	(±)-BINAP[d]	84 (96:4)
26	$Pd(OAc)_2$	Dppf[e]	87 (97:3)
27	$Pd(OAc)_2$	Dpph[f]	80 (94:6)
28	$Pd(OAc)_2$	Dppb[g]	15 (100:0)

[a] Reaction conditions: **1a** (1 mmol), **2a** (0.8 mmol), Pd catalyst (0.015 mmol), ligand (0.08 mmol) and PEG-4000 (1.5 g) in water (3 g) were reacted at 70°C for 15 min.

[b] Isolated yield.

[c] Palladium hexafluoroacetylacetonate.

[d] (±)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl.

[e] Bis(diphenylphosphino)ferrocene.

[f] 1,6-Bis(diphenylphosphino)hexane.

[g] 1,4-Bis(diphenylphosphino)butane.

Table 3. Reaction of aminonaphthalenes **1** with allyl acetates **2**[a]

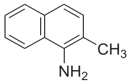
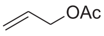
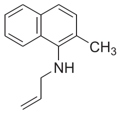
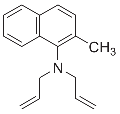
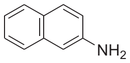
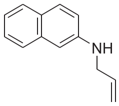
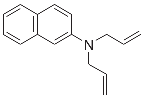
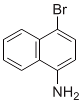
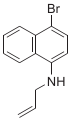
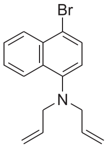
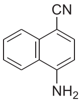
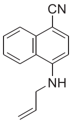
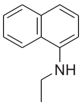
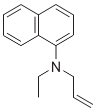
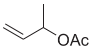
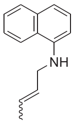
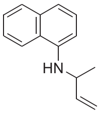
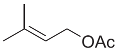
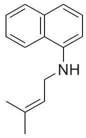
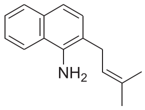
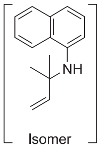
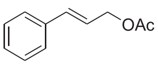
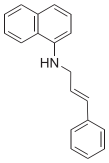
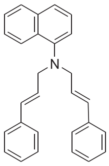
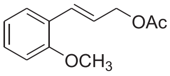
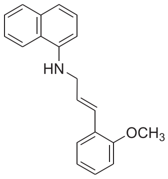
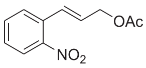
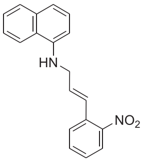
Entry	1	2	Product		Yields (%)[b]
1	 **1b**	 **2a**		**3b**	68
				**4b**	20
2[c]	**1b**	**2a**		**3b** **4b**	57 11
3	 **1c**	**2a**		**3c**	54
				**4c**	21
4	 **1d**	**2a**		**3d**	76
				**4d**	8
5[d]	 **1e**	**2a**		**3e**	40
6	 **1f**	**2a**		**3f**	78
7	**1a**	 **2b**		**5**	28 (*E*/*Z* = 76/24)[d]
				**6**	58

Table 3. *(Continued)*

Entry	**1**	**2**	Product		Yields (%)[b]
8	**1a**	 **2c**		**7**	32
				**8**	64
				**9**	Not obtained
9	**1a**	 **2d**		**10**	81
				**11**	17
10	**1a**	 **2e**		**12**	80
11	**1a**	 **2f**		**13**	71

[a] Reaction conditions: **1** (1 mmol), **2** (0.8 mmol), Pd(OAc)$_2$ (0.02 mmol), PPh$_3$ (0.08 mmol) and PEG-4000 (1.5 g) in water (3 g) were reacted at 70°C for 15 min.

[b] Isolated yield.

[c] Without PEG-4000.

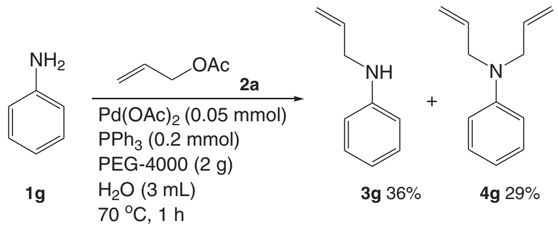
[d] Reacted for 24 h.

[e] Determined by GC.

and cost issues, Pd(OAc)$_2$ has been employed as the palladium source, and a screening of monodentate and bidentate phosphine ligand has been undertaken. In the presence of various monodentate ligands including (2-MeC$_6$H$_4$)$_3$P, (3-MeC$_6$H$_4$)$_3$P, (4-MeC$_6$H$_4$)$_3$P, (2-pyridyl)Ph$_2$P, (2-furyl)$_3$P, (4-ClC$_6$H$_4$)$_3$P, (4-FC$_6$H$_4$)$_3$P, (4-MeOC$_6$H$_4$)$_3$P and [2,6-(MeO)$_2$C$_6$H$_3$]$_3$P (entries 16–24), the results were satisfactory,

]except for [2,6-$(MeO)_2C_6H_3]_3P$ (entry 24). Bidentate ligands such as (±)-BINAP, dpph and dppf could give good yields ranging from 80% to 87% (entries 25–27). Dppb afforded low yields of products (entry 28). Except for $(2\text{-}MeC_6H_4)_3P$ (entry 16), satisfactory selective results were obtained regardless of Pd catalysts or ligands.

To explore the scope of this novel system, *N*-allylation of a series of aminonaphthalenes with allyl acetates using $Pd(OAc)_2$ and PPh_3 in a PEG-4000–water system are summarized in Table 3. Sterically demanding 1-amino-2-methylnaphthalene (**1b**) has afforded monoallylated **3b** and diallylated **4b** in 68% and 20% yields, respectively (entry 1). In the absence of PEG-4000, total yields were decreased to 68% (entry 2). 2-Aminonaphthalene (**1c**) gave mono- and diallylated products in 75% yield overall (entry 3). The electron-deficient 1-amino-4-bromonaphthalene (**1d**) delivered the *N*-allylated products **3d** and **4d** with high yields (entry 4). Using aminonaphthalenes having strong electron-withdrawing groups, such as the cyano group, under reflux for 24 h, only the monoallylated product *N*-allyl-1-(4-cyanonaphthyl)amine (**3e**) was obtained, but in low yield (entry 5). It surprised us that the sterically more demanding secondary *N*-ethyl-1-naphthylamine (**1f**) gave *N*-allyl-*N*-ethyl-1-naphthylamine (**3f**) in 78% yield (entry 6). Encouraged by these results, we studied the allylation of 1-aminonaphthalene (**1a**) with both aliphatic and aromatic allyl acetates (Table 3, entries 7–11). Amination of 1-methylallyl acetate (**2b**) gave mixtures of monoallylated **5** and regioisomeric **6** yields of 28% and 58%, respectively (entry 7). These products may all be derived from the same π-allyl intermediate, which can be attacked at either the C-1 or C-3 position. The 76/24 *E*/*Z* ratio of **5** was determined by gas chromatography (GC). Product *E* alkene arose from the more thermodynamically stable syn π-allyl complex. 3,3-Dimethylallyl acetate (**2c**) gave excellent yields of *N*-allylated product **7** (32%) along with *C*-allylated product **8** (64%), which was formed by aromatic amino-Claisen rearrangement of regioisomer **9** (entry 8). In our previous paper, it was shown that **2c** treated in 'pure water' under reflux conditions gave only moderate yields of 60%.[12] These findings show that PEGs (i) demonstrate good mechanical and chemical stabilities, (ii) provide appropriate functional groups for easy attachment of organic moieties, and (iii) exhibit high solubilizing power in order to dissolve molecular entities with low solubilities and permit the development of a general synthetic methodology independent of the physicochemical properties of target compounds.[13g] The PEG-4000–water system was applicable to various aromatic allyl acetates and tolerant to functional groups such as methoxy and nitro groups. Both electron-rich and electron-withdrawing groups furnished good to excellent yields in this reaction (entries 9–11).



Scheme 1. Allylation of aniline (**1g**) with allylic acetate (**2a**)

Finally, the above process was extended to different kinds of aromatic amine (Scheme 1), providing additional versatility to the reaction process. However, low yields (5% overall) were found. We continued to increase the amount of catalyst system and prolong the reaction time to improve the yield. Although this gave a moderate yield and seemed less product selective, there is potential for further study.

Conclusion

The research has shown that palladium-catalyzed allylation of aminonaphthalenes using allylic acetates in a PEG4000–water system is a simple and efficient route for C–N bond formation. Both selectivity toward mono-alkylated products and reaction yields are improved. Moreover, this method is air-stable, economically viable and environmentally friendly. The major advantages of the PEG-4000–water system are three fold: all reactions are performed in water; no additive other than PEG is required; and the temperature of the reaction is usually lower than 100°C. The products are obtained in excellent yields and tended more to mono-substitution. Further investigations on other applications are in progress.

Experimental

General

All new compounds were characterized by IR spectroscopy, ^1H NMR, ^{13}C NMR and GC-MS analysis. IR absorption spectra were recorded on a PerkinElmer System 2000 FT-IR spectrophotometer. Proton and ^{13}C NMR were measured with a Unity-400 or Mercury Plus-400 spectrometer. Carbon multiplicities were obtained from distortionless enhancement by polarization transfer (DEPT) experiments. Chemical shifts (δ) and coupling constants (Hz) were measured with respect to TMS or chloroform-d_1. Mass spectra and high-resolution mass spectra were taken on a Thermo-Finnigan trace gas chromatograph or Finnigan MAT-95XL instrument with a direct inlet system.

General Procedure for the Palladium-Catalyzed Allylation of Aminonaphthalenes

Reaction with 1-aminonaphthalene (**1a**): in a typical experiment, a stirred mixture of 1-aminonaphthalene (**1a**) (143 mg, 1 mmol), allyl acetate (**2a**) (81 mg, 0.8 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (21 mg, 0.08 mmol) and PEG-4000 (1.5 g) in water (3 g) was heated to 70°C for 15 min. After the mixture was cooled down to room temperature, water and brine were added. The organic materials were extracted with ether, dried over magnesium sulfate and concentrated under vacuum. The crude product was purified by column chromatography on silica gel with chloroform–*n*-hexane (1:2) and afforded **3a** (125 mg, 85%) and **4a** (8 mg, 9%).

Compounds **3a**,[15] **4a**,[15] **3b**,[15] **4b**,[15] **3c**,[15] **4c**,[15] **3d**,[15] **4d**,[15] **3e**,[15] **3f**,[15] **5**,[12] **6**,[12] **7**,[12] **8**,[12] **10**,[15] **11**,[15] and **12**[12] are known.

Supporting Information

Supporting information may be found in the online version of this article, including the data of compound **13**.

Acknowledgments

This work was supported by a grant from the National Science Council of the Republic of China (NSC98-2119-M-037-001-MY3 and NSC101-2113-M-037-008-MY3). Chyi-Jia Wang and Min-Yuan Hung (of the Center for Resources, Research and Development of KMU) are thanked for analytic support.

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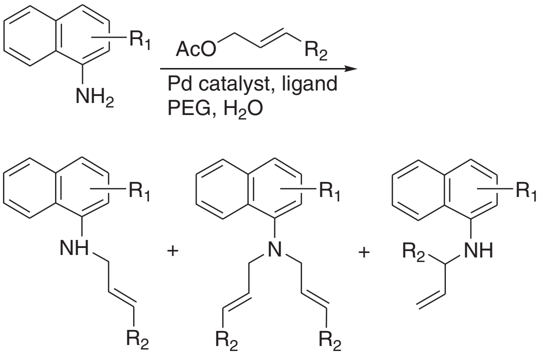
Full Paper

PEG-4000-promoted palladium-catalyzed *N*-allylation in water: aminonaphthalene as an example

Chun-Jen Shih, Yi-Jen Shue, Shiang-Yu Yang and Shyh-Chyun Yang



An eco-friendly method for C-N bond formation of allylic acetates using palladium associated with ligands in PEG-water system leading to *N*-allylation was described.