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Room-temperature palladium(II)-catalyzed N-vinylation of sulfonamides and acylamides with vinyl acetate as vinyl source

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ABSTRACT

Room-temperature N-vinylation of various substituted sulfonamides and acylamides with vinyl acetate was achieved for the first time with a palladium/carbene catalyst system. This reaction provides a useful method for synthesis of enamides under mild conditions.

1. Introduction

Enamides are important structural skeletons in various classes of natural products[1,2] and they are also valuable synthetic intermediates.[3,4] Traditional methods[5–9] for enamide synthesis include: acid-catalyzed condensation of amides and aldehydes,[5] Curtius rearrangement of α,β-unsaturated acyl azides,[6] acylation of imines,[7] and Peterson reaction manifold.[8] More recently, transition metal-catalyzed reactions also provide alternative and convenient approaches for the synthesis of enamides.[10–12] Nowadays, copper-catalyzed coupling[13] of alkenyl halides with amide,[14] a modern variant of the Goldberg reaction,[15] has been the most widely used method as reported by Porco, Buchwald, Ma, and others.[16–20] Although these general methods are often used for enamides formation, they often have limited substrate scope and typically require elevated temperatures, rigorous exclusion of air and water, and two or more equivalents of strong bases. Especially, these methods are not suitable for enesulfonamide formation. There are rare examples for the transition metal-catalyzed enesulfonamide formation, except that Stahl[20] have developed the Pd(II)-catalyzed vinyl transfer reaction from vinyl ethers to nitrogen nucleophiles. Compared to vinyl ethers, the vinyl acetate[21] is more readily available from commercial sources, which is easier to handle in air than the corresponding halides, sulfonates, and phosphates. Besides, an ester is also less dangerous than an ether because the latter may generate explosive peroxides. Considering these advantages, vinyl acetate can be used as a good terminal vinyl source. Herein, we reported the first room-temperature palladium(II)-catalyzed cross-coupling reaction between various amides and vinyl acetate for the formation of terminal enamides. This catalyst system is particularly suitable for enesulfonamide formation.

4-Methyl-*N*-*p*-tolylbenzenesulfonamide (**1a**) was chosen as a model substrate to react with vinyl acetate (**2**) in the initial experiments to optimize the reaction conditions, which had not been used by Stahl[20] in the coupling of vinyl ethers to give the corresponding enamides (Table 1). A blank test, which was conducted only in the presence of K_3PO_4, failed to produce the desired product **3a**, and the starting material was recovered in 95% yield (entry 1). When 10 mol % $Pd(OAc)_2$ was added into the reaction system, the desired N-vinylation product was obtained in 36% yield (entry 2). Various neutral donor ligands were investigated for their effects on palladium(II) center (entries 3–9). Recent results by Stahl and co-workers on vinyl transfer to amide prompted us to test phenanthroline ligand[20] (entry 3), but it did not improve the catalytic activity. The desired cross-coupling barely occurred in the presence of $Pd(OAc)_2$ and bisphosphine ligands that are commonly used for catalytic cross-coupling reactions (entries 4 and 5), which indicated that bis-phosphine ligands may inhibit the desired reaction. However, sterically hindered mono-phosphine ligands (entries 6 and 7) and carbene ligands (entries 8 and 9) improved the catalyst activity efficiently, which give the desired product in moderate to good yield, especially $Pd(OAc)_2$ and IPr catalytic system exhibited higher activity. Considering the high efficiency and availability, 1 mol % $Pd(OAc)_2$ and 2 mol % ligand (IPr) were used in the reaction, which also gave 84% yield (entry 10). Besides, we found that the basicity and solubility of base have significant influence on the reaction efficiency (entries 10–14). A very low yield (28%) was obtained when a strong base *t*-BuOK was used in the reaction (entry 13). However, when K_2CO_3 was used as base in the reaction, the catalytic system displayed the highest activity, which afforded the N-vinylation product in 96% yield (entry 14). Nearly identical activity is obtained when $Pd(OTFA)_2$ was used as Pd(II) catalyst (entry 15). Na_2PdCl_4, which was developed by Geckeler and Baver[22] for N-vinylation of lactams, exhibited no catalytic activity in the reaction (entry 16).

With the optimal catalyst in hand, we examined the scope of this reaction with a series of functionalized aryl amines (Table 2).

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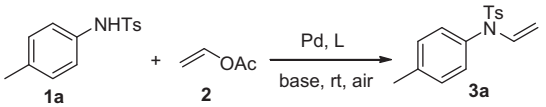
Table 1
Reaction condition screening results[a]



Entry	Pd (mol %)	L (mol %)	Base (1 equiv)	Yield[b] (%)
1	—	—	K_3PO_4	0
2	$Pd(OAc)_2$ (10%)	—	K_3PO_4	36
3	$Pd(OAc)_2$ (10%)	Phen (10%)[c]	K_3PO_4	18
4	$Pd(OAc)_2$ (10%)	dppb (10%)[d]	K_3PO_4	20
5	$Pd(OAc)_2$ (10%)	dppp (10%)[e]	K_3PO_4	<5
6	$Pd(OAc)_2$ (10%)	X-Phos (10%)[f]	K_3PO_4	70
7	$Pd(OAc)_2$ (10%)	Davephos (10%)[g]	K_3PO_4	56
8	$Pd(OAc)_2$ (10%)	IPr (10%)[h]	K_3PO_4	86
9	$Pd(OAc)_2$ (10%)	Mes (10%)[i]	K_3PO_4	80
10	$Pd(OAc)_2$ (1%)	IPr (2%)	K_3PO_4	84
11	$Pd(OAc)_2$ (1%)	IPr (2%)	PivOK	60
12	$Pd(OAc)_2$ (1%)	IPr (2%)	KOAc	74
13	$Pd(OAc)_2$ (1%)	IPr (2%)	*t*-BuOK	28
14	**$Pd(OAc)_2$ (1%)**	**IPr (2%)**	**K_2CO_3**	**96 (90)**
15	$Pd(OTFA)_2$ (1%)	IPr (2%)	K_2C0_3	93
16[j]	Na_2PdCl_4 (1%)	—	—	0

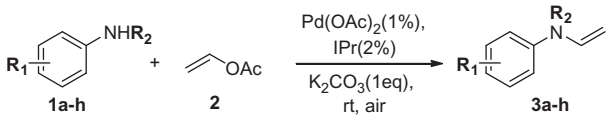
[a] Reaction condition: **1a** (0.5 mmol), 2 (1 mL), Pd catalyst, L, base (1 equiv), rt, open to the air (entries 4–7 was conducted under argon), 6 h.
[b] GC yield (isolated yield in the parentheses).
[c] Phen = 1,10-phenanthroline.
[d] dppb = 1,4-bis(diphenylphosphino)butane.
[e] dppp = 1,3-bis(diphenylphosphino)propane.
[f] X-Phos = 2-dicyclohexyl-phosphino-2′,4′,6′-tri-*i*-propyl-1,1′-biphenyl.
[g] Davephos = 2-(dicyclohexyl-phosphino)-2′-(*N*,*N*-dimethylamino)biphenyl.
[h] IPr = 1,3-bis(2,4,6-tri-isopropyl-phenyl)imidazol-2-ylidene.
[i] Mes = 1,3-bis(2,4,6-methylphenyl)-imidazol-2-ylidene.
[J] The reaction was conducted under reflux for 12 h with exclusion of moisture.

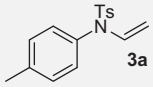
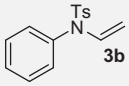
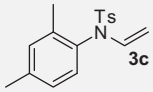
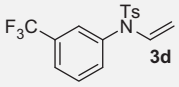
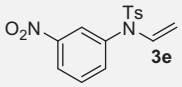
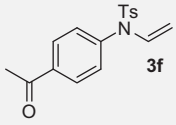
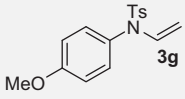
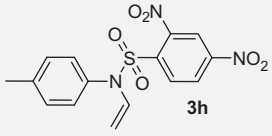
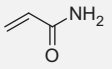
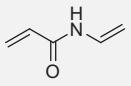
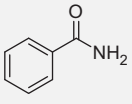
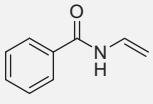
As can be seen, the presence of an *ortho*-methyl group did not diminish the efficiency of the coupling of aniline with vinyl acetate **2** (Table 1, entry 3). Functional groups that are compatible with this Pd-catalyzed N-vinylation protocol include triflourmethyl, nitro, keto, and methoxy groups (entries 4–7). The substrates with those electron-withdrawing groups (entries 4–6) afforded higher yield than those with electron-donating groups (entries 1, 3, 7, and 8). Nearly quantitative conversion was obtained from *N*-(4-acetylphenyl)-4-methylbenzenesulfonamide (**1f**) to desired N-vinylation product (**3f**). 2,4-Dinitrobenzene-1-sulfonyl chloride-protected aryl amine, which is easy to be deprotected, is also compatible for our reaction, giving 82% yield (entry 8). The primary nucleophiles, acrylamide, and benzamide (entries 9 and 10), can also successfully undergo the N-vinylation reaction. The lower reactivity of these substrates led to a longer reaction time, but the product could be obtained in moderate yield. Use of other primary nucleophiles, acetamide, and *p*-toluenesulfonamide, resulted in low conversion (<10%).

Although a detailed mechanistic investigation of the palladium-catalyzed N-vinylation reaction awaits further experimental studies, tentative proposals are outlined in Scheme 1. In the presence of K_2CO_3, compound **1** coordinates to $Pd(OAc)_2$, forming a new Pd–N bond. Then aminopalladation of the vinyl acetate, which undergoes vinyl acetate insertion into the Pd–N bond, affords the intermediate B. Subsequent β-OAc elimination gives the desired amination product.

In summary, our studies have led to the development of a new process for the synthesis of enamides via N-vinylation from vinyl acetate under very mild condition. The $Pd(OAc)_2$ and carbene ligands catalyst are effective with a variety of substituted sulfonamides and acylamide nucleophiles, and this straightforward methodology gives a new sight in palladium(II)-catalyzed C–N bond formation reaction.

Table 2
Examination of the scope of the cross-coupling reaction[a]



Entry	R_1	R_2	Product	Yield[b] (%)
1	4-CH_3	Ts	 **3a**	90
2	H	Ts	 **3b**	92
3	2,4-CH_3	Ts	 **3c**	94
4	3-CF_3	Ts	 **3d**	98
5	3-NO_2	Ts	 **3e**	98
6	4-CH_3CO	Ts	 **3f**	99
7	4-MeO	Ts	 **3g**	87
8	4-CH_3	2,4-DNs	 **3h**	82
9[c]				37
10[c]				36

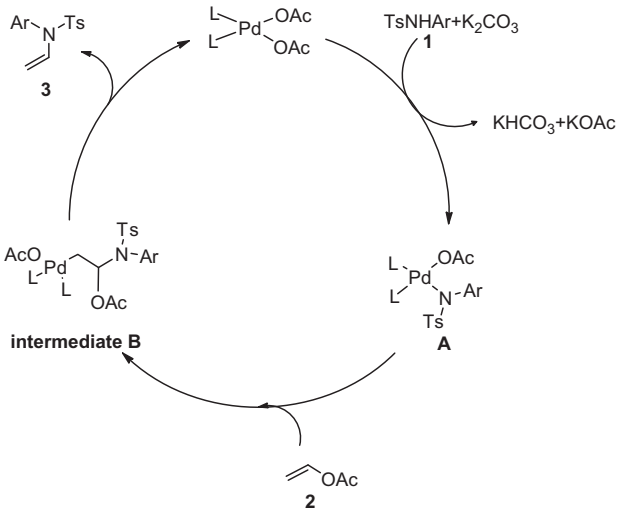
[a] Reaction conditions: 0.5 mmol of **1a**–**h**, 1 mL 2, 1 mol % of $Pd(OAc)_2$, 2 mol % IPr, 1 equiv K_2CO_3, rt, 12 h, open to air.
[b] Isolated yield after flash column chromatography.
[c] K_3PO_4 used as base, reaction time 24 h.

2. Experimental

^1H and ^{13}C NMR spectra were recorded at rt at 400 and 100 MHz, respectively, on an ARX 400 Bruker spectrometer. Chemical shifts are reported in parts per million referenced to the residual proton resonances of the solvents. Coupling constants are expressed in hertz.

2.1. General procedure for the formation of enamides

Aryl amine 1 (0.5 mmol), vinyl acetate 2 (1 mL), $Pd(OAc)_2$ (0.005 mmol, 1.12 mg), and IPr (0.01 mmol, 3.9 mg) were combined in a round-bottomed flask, equipped with a magnetic stir bar. The reaction mixture was stirred at room-temperature, open to air, and monitored for completion by TLC. Upon completion, the solvents were removed via rotary evaporator. Purification of



Scheme 1. Proposed mechanism for palladium(II)-catalyzed N-vinylation of aryl amine.

the residue by column chromatography (silica gel, ethyl acetate/petroleum ether = 1:10) yielded the corresponding products.

2.1.1. 4-Methyl-*N*-*p*-tolyl-*N*-vinyl-benzenesulfonamide (3a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 7.8 Hz, 2H), 7.21 (dd, J = 15.5 Hz, 8.9 Hz, 1H), 7.14 (d, J = 8.1 Hz, 2H), 6.84 (d, J = 8.3 Hz, 2H), 4.23 (dd, J = 8.9 Hz, 0.7, 1H), 3.82 (dd, J = 15.5 Hz, 0.7, 1H), 2.43 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.82, 139.11, 136.02, 134.85, 132.99, 130.13, 129.98, 129.57, 127.52, 93.88, 21.59, 21.23.

2.1.2. 4-Methyl-*N*-phenyl-*N*-vinylbenzenesulfonamide (3b)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.3 Hz, 2H), 7.34 (m, 3H), 7.27 (d, J = 8.3 Hz, 2H), 7.26–7.17 (dd, 1H), 6.98 (m, 2H), 4.25 (dd, J = 8.9 Hz, 0.7, 1H), 3.81 (d, J = 16 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.95, 135.92, 135.79, 134.78, 130.33, 129.61, 129.45, 129.06, 127.52, 94.09, 21.60.

2.1.3. *N*-(2,4-Dimethylphenyl)-4-methyl-*N*-vinyl-benzenesulfonamide (3c)

^{1}H NMR (400 MHz, acetone) δ 7.64 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.23 (dd, J = 15.4 Hz, 8.8 Hz, 1H), 7.17 (s, 1H), 6.96 (d, J = 8.0 Hz, 1H), 6.45 (d, J = 8.0 Hz, 1H), 4.21 (d, J = 8.8 Hz, 1H), 3.59 (d, J = 15.4 Hz, 1H), 2.45 (s, 3H), 2.30 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, acetone) δ 144.22, 139.24, 138.67, 136.90, 134.15, 132.11, 129.80, 129.22, 127.42, 127.37, 92.36, 28.95, 20.59, 20.20, 16.95.

2.1.4. 4-Methyl-*N*-(3-(trifluoromethyl)phenyl)-*N*-vinyl-benzenesulfonamide (3d)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 9.0 Hz, 3H), 7.29 (d, J = 7.9 Hz, 2H), 7.25–7.16 (m, 2H), 7.14 (s, 1H), 4.31 (d, J = 9.0 Hz, 1H), 3.80 (d, J = 15.5 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.51, 136.61, 135.28, 134.45, 134.09, 132.02 (q, J = 32.9 Hz), 130.17, 129.78, 127.49, 127.33 (q, J = 4 Hz), 125.89 (q, J = 3.7 Hz), 124.67, 94.73, 21.58.

2.1.5. 4-Methyl-*N*-(3-nitrophenyl)-*N*-vinyl-benzenesulfonamide (3e)

^{1}H NMR (400 MHz, acetone) δ 8.36 (d, J = 8.3 Hz, 1H), 7.82–7.77 (m, 2H), 7.64 (d, J = 7.5 Hz, 2H), 7.49 (t, J = 9.3 Hz, 3H), 7.29 (dd, J = 15.5 Hz, 9.0 Hz, 1H), 4.41 (d, J = 9.0 Hz, 1H), 3.91 (d, J = 15.5 Hz, 1H), 2.47 (s, 3H) ^{13}C NMR (101 MHz, acetone) δ 148.89, 144.98, 137.30, 136.87, 135.30, 134.61, 130.98, 130.08, 127.48, 125.06, 124.02, 94.72, 20.63.

2.1.6. *N*-(4-Acetylphenyl)-4-methyl-*N*-vinylbenzene sulfonamide (3f)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.9 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 7.20 (dd, J = 15.6, 9.0, 1H), 7.11 (d, J = 8.4, 2H), 4.31 (d, J = 8.8 Hz, 1H), 3.84 (d, J = 15.6 Hz, 1H), 2.62 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.14, 144.33, 140.26, 137.25, 135.56, 134.39, 130.55, 129.79, 129.48, 127.46, 94.81, 26.72, 21.62.

2.1.7. *N*-(4-Methoxyphenyl)-4-methyl-*N*-vinyl-benzenesulfonamide (3g)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 7.3 Hz, 2H), 7.25–7.18 (dd, 1H), 6.90–6.82 (dd, 4H), 4.23 (d, J = 8.8 Hz, 1H), 3.83 (d, J = 14.8 Hz, 1H), 3.81 (s,3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.82, 143.85, 135.89, 134.96, 131.38, 129.58, 127.99, 127.50, 114.65, 93.72, 55.42, 21.59.

2.1.8. 2,4-Dinitro-*N*-*p*-tolyl-*N*-vinyl-benzenesulfonamide (3h)

^{1}H NMR (400 MHz, acetone) δ 8.85 (s, 1H), 8.59 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 8.7 Hz, 1H), 7.30 (d, J = 7.6 Hz, 2H), 7.19 (dd, J = 15.3 Hz, 8.8 Hz, 1H), 7.05 (d, J = 7.2 Hz, 2H), 4.44 (d, J = 8.8 Hz, 1H), 3.89 (d, J = 15.3 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, acetone) δ 150.81, 148.00, 140.20, 135.53, 134.53, 133.41, 131.47, 130.61, 130.27, 126.48, 120.22, 94.37, 20.31.

2.1.9. *N*-Vinylacrylamide

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.14–6.99 (m, 1H), 6.38 (d, J = 16.9 Hz, 1H), 6.17 (dd, J = 17.0 Hz, 10.3, 1H), 5.73 (d, J = 10.3, 1H), 4.71 (d, J = 15.9, 1H), 4.48 (d, J = 8.8, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.89, 130.13, 128.75, 128.18, 96.48.

2.1.10. *N*-Vinylbenzamide

^{1}H NMR (400 MHz, $CDCl_3$) 7.81 (d, J = 7.0 Hz, 2H), 7.75 (br s, 1H), 7.54 (t, J = 7.5 Hz), 7.46 (t, J = 7.6 Hz, 2H), 7.15–7.24 (m, 1H), 4.77 (d, J = 16.0 Hz, 1H), 4.53 (d, J = 9.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 133.7, 132.2, 129.3, 128.9, 127.3, 96.5.

Acknowledgments

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