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Palladium-catalyzed regiospecific tandem allylation of 2-aminophenols using 2-butene-1,4-diol

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Abstract—The direct activation of C–O bonds in 2-butene-1,4-diol by palladium complexes has been accelerated by carrying out the reactions in the presence of a titanium reagent. Palladium-catalyzed regiospecific tandem allylation of 2-aminophenols with 2-butene-1,4-diol leads to 3,4-dihydro-2-vinyl-2*H*-1,4-benzoxazines.
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Morpholine derivatives have aroused increasing interest due to their presence in a large number of therapeutically and biologically active compounds.[1] Numerous 1,4-benzoxazine derivatives have been prepared to lead to biologically active compounds. Research activities in this area continue to generate new compounds having unusual skeletons.[2] A principal goal of organometallic chemistry is the catalytic synthesis of organic compounds by fine tuning the chemistry of organic ligands covalently bound to transition metals. Most organometallic chemistry has focused on complexes with covalent metal–carbon or metal–hydrogen bonds. Transition metal η^3-allyl complexes, as well as transition metal σ-alkyl complexes, play important roles as active species and key intermediates in many reactions catalyzed by transition metal complexes.[3] The platinum group transition metals, in particular palladium and rhodium, have become workhorse elements in many commercialized catalytic processes that include hydrogenations, hydroformylations, acetic acid production, and other C–C and C–H bond forming processes.[4] Although carbon–oxygen, carbon–nitrogen, or carbon–sulfur bonds are found in the majority of important organic molecules, catalytic organometallic reaction chemistry that leads to the formation of carbon–heteroatom bonds is less common than that forming carbon–carbon and carbon–hydrogen bonds. Moreover, the construction of C–N bonds in amines is particularly rare.[5] In large part, routes to the necessary reactive intermediates for such catalysis and the fundamental reactions required of such intermediates are poorly developed. The palladium-catalyzed allylation of nucleophiles is an established, efficient, and highly stereo- and chemoselective method, which has been widely applied to organic chemistry. The catalytic cycle requires the formation of the cationic η^3-allylpalladium(II) complex, an intermediate that is generated by oxidative addition of allylic compounds including allylic halides,[6] acetates,[7] and carbonates[8] to a Pd(0) complex and which can be attacked by nucleophiles at both termini of the allylic system. However, there are few reports on palladium(0)-catalyzed reaction of bifunctional allylic diacetates and dicarbonates with nucleophiles featuring their bifunctionality.[9] Recently, Lhoste reported that (*Z*)-1,4-bis(methoxycarbonyloxy)but-2-ene reacted with *o*-aminophenols in the presence of a palladium catalyst, giving 3,4-dihydro-2-vinyl-2*H*-1,4-benzoxazines.[10] However, there have been only limited and sporadic reports dealing with the direct cleavage of the C–O bond of allylic alcohols on interaction with a transition metal complex.[11] Successful applications using allylic alcohols directly in catalytic processes are even more limited. This apparently stems from the poor capability of a nonactivated hydroxyl to serve as a leaving group.[12] We have recently reported our attempts and some successful applications of a process involving C–O bond cleavage with direct use of allylic alcohols catalyzed by palladium complexes.[13] In this paper, we wish to report the catalytic palladium complex, which mediates regiospecific tandem allylation of 2-aminophenols with 2-butene-1,4-diol directly for the construction of 3,4-dihydro-2-vinyl-2*H*-1,4-benzoxazines.

Initially, we treated a mixture of 2-aminophenol (**1a**, 1.5 mmol) and allyl acetate (**2a**, 1.2 mmol) in the

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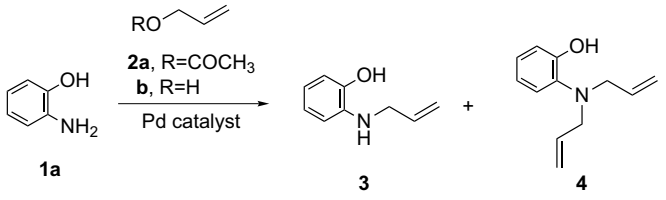
presence of $Pd(OAc)_2$ (1 mol%), PPh_3 (4 mol%), and molecular sieves (MS 4 Å) (200 mg) in refluxing benzene (3 mL) under nitrogen for 3 h. 2-Allylaminophenol (**3**) and 2-diallylaminophenol (**4**) were formed in 68% and 23% yields, respectively (Scheme 1). The ^1H and ^{13}C NMR of NCH_2 appear at δ 3.77 and 47.1 ppm for **3** and at δ 3.51 and 57.5 ppm for **4**. This regiospecificity is in agreement with the fact that the nitrogen nucleophile is generally more reactive than the oxygen nucleophile toward π-allylpalladium complexes.[14] Similarly, direct allylation of **1a** with allyl alcohol (**2b**) in the presence of 25 mol% of $Ti(OPr^i)_4$ gave **3** and **4** in 61% and 31% yields, respectively.

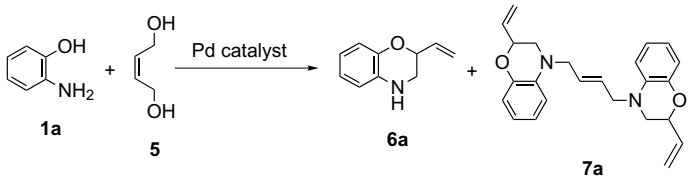
Then, we examined the extension of this reaction to the bifunctional 2-butene-1,4-diol. The palladium-catalyzed cyclization of 2-aminophenol with 2-butene-1,4-diol directly was investigated under various conditions (Scheme 2). When a mixture of 2-aminophenol (**1a**, 1.5 mmol) and 2-butene-1,4-diol (**5**, 1.2 mmol) was heated in the presence of catalytic amounts of $Pd(acac)_2$ (0.075 mmol), PPh_3 (0.3 mmol), $Ti(OPr^i)_4$ (0.75 mmol), and MS 4 Å (200 mg) in benzene (5 mL) under nitrogen at 50 °C for 6 h, 3,4-dihydro-2-vinyl-2*H*-1,4-benzoxazine (**6a**) together with **7a** were formed in 32% and 27%, respectively (entry 1 in Table 1). The ^1H and ^{13}C NMR of OCH appear at δ 4.56 and 74.4 ppm for **6a** and at δ 4.60 and 74.4 ppm for **7a**. In the reaction under reflux for 6 h, the yields of products **6a** and **7a** were increased to 45% and 45%, respectively (entry 2). Increasing the reaction time favored the formation of the cyclic compound **7a** (entries 2–4). The absence of a titanium agent gave only 40% yield of products (entry 5). Decreasing the amount of $Ti(OPr^i)_4$ decreased the yields of products (entry 6). The effect of addition of $Ti(OPr^i)_4$ to promote the palladium-catalyzed allyl-OH bond cleavage remarkably enhanced both the reaction rate and yield. Titanium reagents such as $Ti(OBu)_4$ (entry 7), $Ti(OBu^i)_4$ (entry 8), and $Ti[O(CH_2)_{17}CH_3]_4$ (entry 9) were also effective for the allylation. $TiCl_4$ (entry 10) and $Ti(OEt)_4$ (entry 11) did not promote the reaction to any great extent. In the presence of $Ti(OEt)_4$, increasing the reaction time increased the yields of **6a** and **7a** to 39% and 47%, respectively (entry 12). The reaction is accompanied by formation of water. Without MS 4 Å for water removal, the yields of products were decreased (entry 13). The reaction did not occur in the absence of the phosphine ligand (entry 14). As expected, increasing the relative amount of the 2-aminophenol favored the formation of the desired cyclic compound **6a** (entries 2, 15, and 16). It was known that several factors, such as the solvent and nature of the nucleophile, can alter the product pattern in metal-catalyzed allylation.[15] At 50 °C, eight solvents were investigated, dioxane, HMPA, and DMF gave worst (entries 1 and 17–23). In the reaction under reflux, the yields of products **6a** and **7a** were increased (entries 2 and 24–26). Benzene gave the best results.

A comparative study of different catalysts in benzene was reported (Table 2). As the catalyst precursor, $Pd(acac)_2$ (entry 1), $Pd(OAc)_2$ (entry 2), $Pd(OCOCF_3)_2$ (entry 3), $Pd_2(dba)_3$ (entry 4), and $PdCl_2(MeCN)_2$ (entry 5) showed good catalytic activity. Other palladium complexes such as $PdCl_2$ (entry 6) and $Pd(PPh_3)_4$ (entry 7) were less active and gave lower yields. Many reports have indicated[16] that chloride ions can strongly influence the catalytic activity of palladium catalysts, and it seemed reasonable that this factor might be responsible for the low reactivity of $PdCl_2$ in the present system. However, using $Pd(PPh_3)_4$ with extra PPh_3 as catalyst increased the yield of products (entry 8). Screening of various monodentate ligands (entries 1 and 9–20) showed that PPh_3, $(2\text{-MePh})_3P$, $(2\text{-furyl})_3P$, and $(3\text{-MePh})_3P$ were the most effective ligands. The bidentate ligand including dppm (entry 21), dppe (entry 22), dppp (entry 23), dppb (entry 24), and dpph (entry 25) decreased the yield of products. Dppm and dppe gave only **6a**.

We also studied the influence of substituents on the 2-aminophenol on the reactivity of the amination of 2-butene-1,4-diol (**5**) using $Pd(acac)_2$, PPh_3, and $Ti(OPr^i)_4$. The results collected in Table 3 showed that



Scheme 1.



Scheme 2.

Table 1. Reaction of 2-aminophenol (**1a**) with 2-butene-1,4-diol (**5**)[a]

Entry	Titanium reagent	Solvent	Yield (%)[b] (**6a**:**7a**)
1	$Ti(OPr^i)_4$	Benzene[c]	59 (55:45)
2	$Ti(OPr^i)_4$	Benzene	90 (50:50)
3[d]	$Ti(OPr^i)_4$	Benzene	80 (62:38)
4[e]	$Ti(OPr^i)_4$	Benzene	76 (39:61)
5	—	Benzene	40 (68:32)
6	$Ti(OPr^i)_4$[f]	Benzene	56 (58:42)
7	$Ti(OBu)_4$	Benzene	84 (41:59)
8	$Ti(OBu^i)_4$	Benzene	89 (45:55)
9	$Ti[O(CH_2)_{17}CH_3]_4$	Benzene	78 (49:51)
10	$TiCl_4$	Benzene	3 (100:0)
11	$Ti(OEt)_4$	Benzene	48 (73:27)
12[e]	$Ti(OEt)_4$	Benzene	86 (45:55)
13[g]	$Ti(OPr^i)_4$	Benzene	59 (60:40)
14[h]	$Ti(OPr^i)_4$	Benzene	0
15[i]	$Ti(OPr^i)_4$	Benzene	76 (70:30)
16[j]	$Ti(OPr^i)_4$	Benzene	86 (32:68)
17	$Ti(OPr^i)_4$	Toluene[c]	58 (43:57)
18	$Ti(OPr^i)_4$	THF[c]	59 (60:40)
19	$Ti(OPr^i)_4$	MeCN[c]	56 (71:29)
20	$Ti(OPr^i)_4$	CH_2Cl_2[c]	58 (62:38)
21	$Ti(OPr^i)_4$	Dioxane[c]	18 (0:100)
22	$Ti(OPr^i)_4$	HMPA[c]	9 (0:100)
23	$Ti(OPr^i)_4$	DMF[c]	5 (64:36)
24	$Ti(OPr^i)_4$	Toluene	78 (31:69)
25	$Ti(OPr^i)_4$	THF	71 (57:43)
26	$Ti(OPr^i)_4$	MeCN	83 (47:53)

[a] Reaction conditions: **1a** (1.5 mmol), **5** (1.2 mmol), $Pd(acac)_2$ (0.075 mmol), PPh_3 (0.3 mmol), titanium reagent (0.75 mmol), and molecular sieves 4 Å (200 mg) in a solvent were refluxed for 6 h.
[b] Isolated yield was based on **5**.
[c] Stirred at 50 °C.
[d] Reflux for 3 h.
[e] Reflux for 9 h.
[f] 0.25 mmol of $Ti(OPr^i)_4$ was used.
[g] Without MS 4 Å.
[h] Without PPh_3.
[i] 0.75 mmol of **5** was used.
[j] 1.8 mmol of **5** was used.

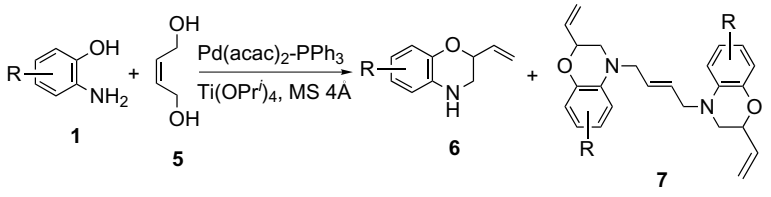
Table 2. Reaction of 2-aminophenol (**1a**) with 2-butene-1,4-diol (**5**): palladium catalyst and phosphine ligand effects[a]

Entry	Palladium	Ligand	Yield (%)[b] (**6a**:**7a**)
1	$Pd(acac)_2$	PPh_3	90 (50:50)
2	$Pd(OAc)_2$	PPh_3	89 (61:39)
3	$Pd(OCOCF_3)_2$	PPh_3	85 (55:45)
4	$Pd_2(dba)_3$	PPh_3	82 (50:50)
5	$PdCl_2(MeCN)_2$	PPh_3	76 (90:10)
6	$PdCl_2$	PPh_3	20 (100:0)
7	$Pd(PPh_3)_4$	—	42 (56:44)
8	$Pd(PPh_3)_4$	PPh_3	77 (54:46)
9	$Pd(acac)_2$	Bu_3P	63 (98:2)
10	$Pd(acac)_2$	$(PhO)_3P$	58 (97:3)
11	$Pd(acac)_2$	$(2\text{-MePh})_3P$	81 (24:76)
12	$Pd(acac)_2$	$(2\text{-Furyl})_3P$	85 (61:39)
13	$Pd(acac)_2$	$(2\text{-Pyridyl})Ph_2P$	37 (97:3)
14	$Pd(acac)_2$	$(3\text{-MePh})_3P$	86 (56:44)
15	$Pd(acac)_2$	$(4\text{-MePh})_3P$	68 (54:46)
16	$Pd(acac)_2$	$(4\text{-MeOPh})_3P$	65 (66:34)
17	$Pd(acac)_2$	$(4\text{-FPh})_3P$	44 (96:4)
18	$Pd(acac)_2$	$(4\text{-ClPh})_3P$	49 (58:42)
19	$Pd(acac)_2$	$(2,6\text{-Di-MeOPh})_3P$	13 (100:0)
20	$Pd(acac)_2$	$(2,4,6\text{-Tri-MeOPh})_3P$	2 (100:0)
21	$Pd(acac)_2$	dppm	21 (100:0)
22	$Pd(acac)_2$	dppe	22 (100:0)
23	$Pd(acac)_2$	dppp	48 (98:2)
24	$Pd(acac)_2$	dppb	56 (85:15)
25	$Pd(acac)_2$	dpph	58 (67:33)

[a] Reaction conditions: **1a** (1.5 mmol), **5** (1.2 mmol), Pd catalyst (0.075 mmol), phosphine ligand (0.3 mmol), $Ti(OPr^i)_4$ (0.75 mmol), and molecular sieves 4 Å (200 mg) in benzene were refluxed for 6 h.
[b] Isolated yield was based on **5**.

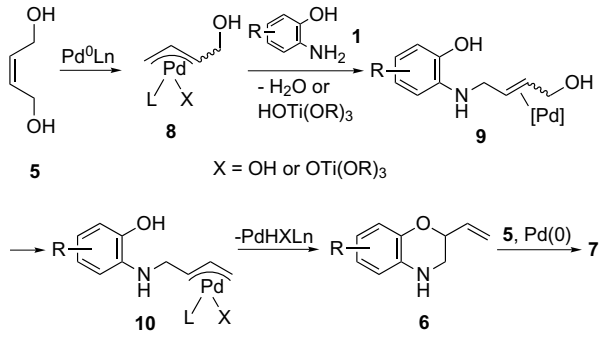
the nature of the substituent had an influence on the reaction rate and the product yield. The amination of 2-butene-1,4-diol (**5**) worked well with 2-aminophenols containing electron-donating groups, giving generally good yields of the corresponding cyclic compounds (entries 1 and 2). Allylation of 2-amino-4-chlorophenol (**1d**) gave 6-chloro-3,4-dihydro-2-vinyl-2*H*-1,4-benzoxazine (**6d**) and (*E*)-1,4-bis(6-chloro-3,4-dihydro-2-vinyl-2*H*-1,4-benzoxazin-4-yl)but-2-ene (**7d**) in 41% and 19% yields, respectively (entry 3). Conversely, 2-aminophenols having strong electron-withdrawing groups, such as

Table 3. Reaction of 2-aminophenols (**1b**–**h**) with 2-butene-1,4-diol (**5**)[a]



Entry	**1**	R	Yields (%)[b]	
1	**1b**	4-Me	**6b** 59	**7b** 27
2	**1c**	5-Me	**6c** 40	**7c** 49
3	**1d**	4-Cl	**6d** 41	**7d** 19
4	**1e**	$4\text{-}NO_2$	**6e** 44	
5	**1f**	$5\text{-}NO_2$	**6f** 32	
6	**1g**	$4\text{-Cl, }5\text{-}NO_2$	**6g** 27	
7	**1h**	$4\text{-}SO_2C_2H_5$	**6h** 37	

[a] Reaction conditions: **1** (1.5 mmol), **5** (1.2 mmol), $Pd(acac)_2$ (0.075 mmol), PPh_3 (0.3 mmol), $Ti(OPr^i)_4$ (0.75 mmol), and molecular sieves 4 Å (200 mg) in benzene were refluxed for 6 h.
[b] Isolated yield was based on **5**.



Scheme 3.

the nitro group (entries 4–6), gave lower chemical yields. These differences in reactivity are likely due to the nucleophilicity of the corresponding 2-aminophenol. 2-Amino-4-chloro-5-nitrophenol (**1g**) gave only product **6g** in 27% yield (entry 5); the lower yield observed may arise from the nature of the nitro group. The more acidic compound is probably less reactive in the attack on the π-allyl complex (entries 4–7).

A plausible reaction pathway for this regiospecific formation is shown in Scheme 3. Diol **5** or an allyl titanate, formed by an alcohol exchange reaction between **5** and titanium reagent, reacts with Pd(0) species generated in situ to afford the π-allylpalladium intermediate **8**. Intermolecular nucleophilic substitution of the amino group of **1** takes place at the less hindered terminus of the π-allyl system to give an allylic amine **9**. Intramolecular nucleophilic attack on the second π-allylpalladium intermediate **10** at the more substituted internal allylic carbon atom produces **6**. Compound **7** is obtained by two successive nucleophilic substitutions of compound **6** on the diol **5** in the presence of palladium.

In summary, we have shown that palladium(0)-catalyzed regiospecific tandem allylation of 2-aminophenols using 2-butene-1,4-diol directly is a simple and efficient route for 3,4-dihydro-2-vinyl-2*H*-1,4-benzoxazines formation. The addition of $Ti(OPr^i)_4$ to promote the palladium-catalyzed allyl-OH bond cleavage remarkably enhanced both the reaction rate and yield. Increasing the relative amount of the 2-aminophenol favored the formation of the desired cyclic compound **6a**.

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