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Palladium-Catalyzed Functionalization of Indoles with 2-Acetoxymethyl-Substituted Electron-Deficient Alkenes

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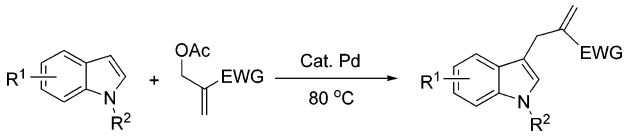

EWG = CO_2Me, COMe, CN, SO_2Ph

New functionalizations of indoles via palladium-catalyzed reaction of indoles and 2-acetoxymethyl-substituted electron-deficient alkenes are reported. It was found that for *N*-protected indoles the reaction proceeded smoothly in the presence of 5 mol % of $Pd(acac)_2$ and 10 mol % of PPh_3 at 80 °C in HOAc, while for *N*-unprotected indoles, the reaction was carried out by using 5 mol % of $Pd(dba)_2$ or 2.5 mol % of $Pd_2(dba)_3{\cdot}CHCl_3$ with 10 mol % of 2,2′-bipyridine as the catalyst in toluene. This strategy allows the selective installation of electron-deficient olefin functionality at the 3-position of indoles, which might be difficult to obtain by other methods and can be further elaborated.

Indoles and their derivatives constitute an important class of biologically active natural products, which play a fundamental role in bioorganic chemistry.[1] For this reason, the efficient synthesis and functionlization of indoles derivatives[2,3] have attracted the interest of many synthetic chemists. The Lewis acid catalyzed alkylation between indoles and electrophiles[4] and palladium-catalyzed Heck-type reactions of 3-halo-substituted indoles[5] are two well-established methods for the functionalization at the 3-position of the indole nucleus. During the past several years, palladium-catalyzed intramolecular or intermolecular direct coupling of indoles with alkenes have also been developed by the utilization of various oxidants to regenerate the catalytically active Pd(II) species in situ.[6] Billups' group reported a palladium-catalyzed nonselective allylation of indoles with allyl acetate, allylic alcohols, or 1,3-dienes, affording a mixture.[7] Recently, the Tamura group has also found that under the catalysis of palladium, Et_3B can promote the C-3-selective allylation of indoles with a variety of allyl alcohols.[8] In both cases, a π-allylpalladium intermediate may be involved. In our previous work,[9] we have demonstrated an efficient metal- and halogen-free route to stereoselective synthesis of benzocycles via TFA-mediated intramolecular Friedel−Crafts reactions of 6-acetoxy-4-alkenylarenes.[9a] Also, a new functionalization of indoles via the $Pd(OAc)_2$-catalyzed reaction of indoles with 2-acetoxymethyl-substituted electron-deficient alkenes to afford 3-(2-methoxycarbonyl-2-propenyl)indoles was reported, in which the β-OAc functional group was used for the regeneration of Pd(II) species.[9c] However, this reaction usually needed a long reaction time and high temperature and suffered from low yield and poor diversity for the starting indoles. Herein, we wish to report our recently developed new catalytic systems for the coupling of indoles with 2-acetoxymethyl-substituted electron-deficient alkenes.

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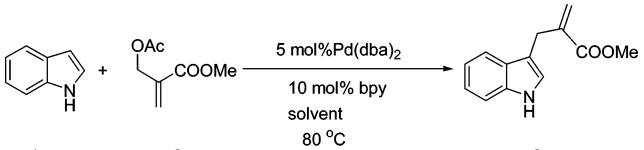
TABLE 1. Optimization of Reaction Conditions for the Pd-Catalyzed Coupling of 1a with Methyl 2-(Acetoxymethyl)acrylate 2a

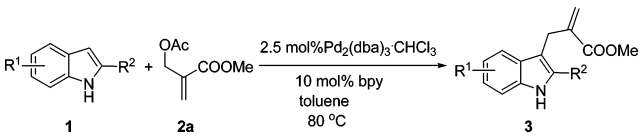


1a **2a** **3aa**

entry	solvent	time (h)	yield[a] (%)
1	*tert*-amyl alcohol	35	17
2	isopropyl alcohol	35	66
3	*tert*-butyl alcohol	35	64
4	toluene	35	96 (81[b])
5	EtOH	19	48
6	1,3-dichloropropane	19	0
7	THF	19	78
8[c]	toluene	12	84[b]

[a] The yield was determined by ^{1}H NMR spectra using CH_2Br_2 as the internal standard. [b] Isolated yield. [c] 2.5 mol % of $Pd_2(dba)_3$·$CHCl_3$ was used as the catalyst.

TABLE 2. Pd-Catalyzed Coupling of Indoles 1 with Methyl 2-(Acetoxymethyl)acrylate 2a



1 **2a** **3**

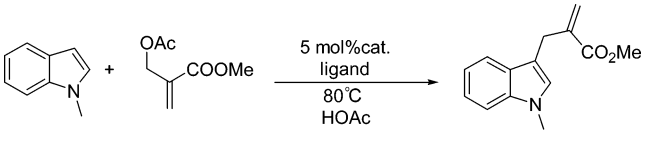
	indoles **1**			
entry	R^1	R^2	time (h)	yield of **3** (%)
1	4-BnO (**1b**)	H	12	76 (**3ba**)
2	5-BnO (**1c**)	H	12	72 (**3ca**)
3	6-BnO (**1d**)	H	12	74 (**3da**)
4	4-Br (**1e**)	H	10	72 (**3ea**)
5	5-Br (**1f**)	H	10	69 (**3fa**)
6	6-Br (**1g**)	H	10	68 (**3ga**)
7	5-Me (**1h**)	H	12	73 (**3ha**)
8	5-MeO (**1i**)	H	10	76 (**3ia**)
9[a]	H (**1j**)	Me	23	67 (**3ja**)

[a] 5 mol % of $Pd(dba)_2$ and 10 mol % of bpy were used.

$Pd(dba)_2$ or $Pd_2(dba)_3$·$CHCl_3$/bpy(2,2′-bipyridine)-Catalyzed Coupling of Indoles with 2-Acetoxymethyl-Substituted Electron-Deficient Alkenes. After trying several combinations of various palladium species and ligands, we examined the reaction of indole (**1a**) with methyl 2-acetoxymethyl acrylate **2a** using $Pd(dba)_2$ or $Pd_2(dba)_3$·$CHCl_3$ and 2,2′-bipyridine[9c] as the catalyst in different solvents (entries 1−8, Table 1). The reactions in *tert*-amyl alcohol, *i*-PrOH, *t*-BuOH, EtOH, and THF afforded the desired coupling product **3aa** in moderate yields (entries 1−3, 5, and 7, Table 1). However, the corresponding reaction in toluene at 80 °C in the presence of $Pd(dba)_2$ or $Pd_2(dba)_3$·$CHCl_3$ afforded **3aa** in good isolated yields (entries 4 and 8, Table 1). Thus, in the following cases, the reaction was conducted at 80 °C in toluene using 5 mol % of $Pd(dba)_2$ or 2.5 mol % of $Pd_2(dba)_3$·$CHCl_3$ and 10 mol % of 2,2′-bipyridine as the catalyst.

A variety of indoles were next examined to generate the desired coupling products **3** under the standard conditions. The results are summarized in Table 2. The yield of this reaction is generally good. It is interesting to note that a bromo substituent is compatible under the cross-coupling conditions (Table 2, entries 4−6).

TABLE 3. Optimization of Reaction Conditions for the Pd-Catalyzed Coupling of *N*-Methylindole 1k with Methyl (2-Acetoxymethyl)acrylate 2a

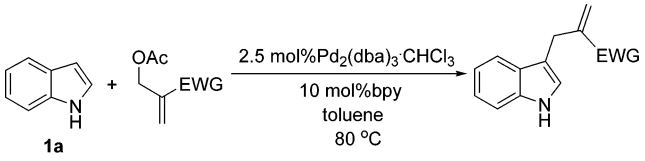


1k **2a** **mol%** **3ka**

entry	cat.	ligand, (mol %)	solvent	time (h)	yield of **3ka**[a] (%)
1	$Pd(acac)_2$	dppp (5)	HOAc	10	53
2	$Pd(acac)_2$	dppe (5)	HOAc	10	46
3	$Pd(acac)_2$	dppb (5)	HOAc	10	28
4	$Pd(PhCN)_2Cl_2$	PPh_3 (10)	HOAc	11	20
5	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	PPh_3 (10)	HOAc	11	64
6	$Pd(acac)_2$	PPh_3 (10)	THF	14	70
7	$Pd(acac)_2$	PPh_3 (10)	DMSO	19	26
8	$Pd(acac)_2$	PPh_3 (10)	DCE	19	73
9	$Pd(acac)_2$	PPh_3 (10)	HOAc	23	84[b]

[a] The yield was determined by ^{1}H NMR spectra using CH_2Br_2 as internal standard. [b] Isolated yield.

SCHEME 1

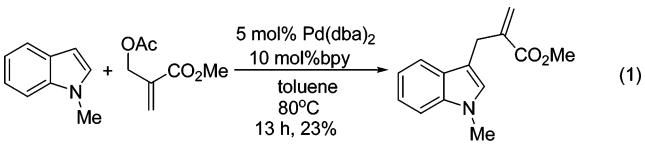


1a

EWG = COMe (**2b**), 9 h, 79% (**3ab**)
EWG = SO_2Ph (**2c**), 15 h, 75% (**3ac**)
EWG = CN (**2d**), 14 h, 71% (**3ad**)

In addition, the reaction is not limited to methyl 2-acetoxymethyl acrylate **2a**. 3-acetoxymethyl-3-buten-2-one **2b**, 2-phenylsulfonyl-2-propenyl acetate **2c**, and 2-acetoxymethyl acrylonitrile **2d** are also effective, affording **3ab**, **3ac**, and **3ad** in 79%, 75%, and 71% yields, respectively (Scheme 1).

However, when 1-methylindole **1k** was reacted with 2-(acetoxymethyl)acrylate **2a** under similar reaction conditions, only a 23% yield of coupling product **3ka** was obtained (eq 1). Thus, a new protocol for the reaction of *N*-protected indoles was desired.



(1)

1k **2a** **3ka**

$Pd(acac)_2$/PPh_3-Catalyzed Coupling of *N*-Protected Indoles with 2-Acetoxymethyl-Substituted Electron-Deficient Alkenes. In an initial attempt, we examined the reaction of **1k** with methyl 2-acetoxymethyl acrylate **2a** in acetic acid under several combinations of $Pd(acac)_2$[7] with monodentate or bidentate phosphine ligands: When bidentate phosphine ligands, such as dppp, dppe, or dppb, were used, the product **3ka** was obtained in 53%, 46%, and 28% yields, respectively (Table 3, entries 1−3). However, to our delight, when 10 mol % of Ph_3P was used, the desired cross-coupled product **3ka** was obtained in 84% isolated yield (Table 1, entry 9). Next, various palladium complexes were screened for the effectiveness in the above transformation. The results showed that $Pd(PhCN)_2Cl_2$ and

SCHEME 2

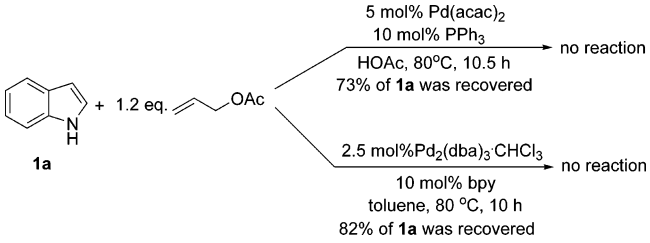
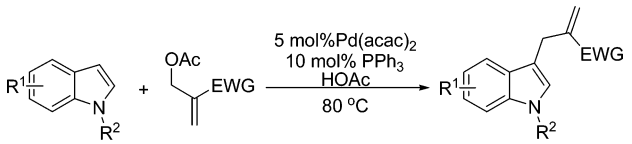


TABLE 4. Pd-Catalyzed Coupling of *N*-Protected Indoles 1 with 2-Acetoxymethyl-Substituted Electron-Deficient Alkenes 2



1 **2** **3**

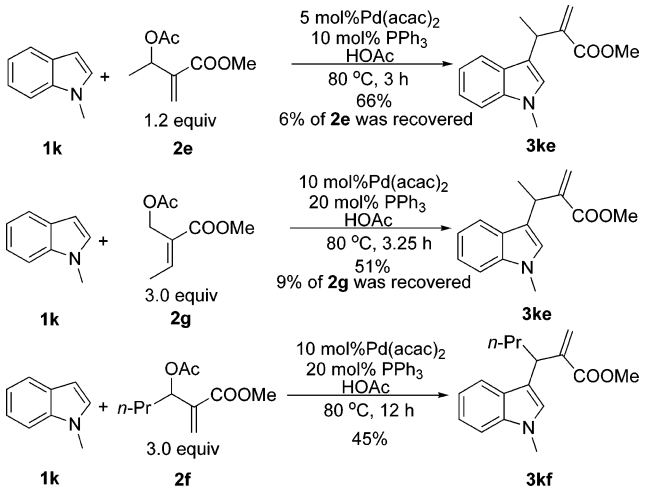
	indole				
entry	R^1	R^2	EWG	time (h)	yield (%)
1	H	Bu (**1l**)	CO_2Me (**2a**)	9	81 (**3la**)
2	H	allyl (**1m**)	CO_2Me (**2a**)	18	74 (**3ma**)
3	H	Bn (**1n**)	CO_2Me (**2a**)	15	82 (**3na**)
4	2-Me	Me (**1o**)	CO_2Me (**2a**)	10	72 (**3oa**)
5	6-BnO	Me (**1p**)	CO_2Me (**2a**)	11	75 (**3pa**)
6	H	Me (**1k**)	COMe (**2b**)	22.5	79 (**3kb**)
7	H	Me (**1k**)	SO_2Ph (**2c**)	11	76 (**3kc**)
8	H	Me (**1k**)	CN (**2d**)	16	75 (**3kd**)

$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ did catalyze the formation of **3ka** but with lower efficiency as compared with $Pd(acac)_2$ (Table 3, entries 4, 5, and 9). Then, the coupling reaction of 1-methylindole **1k** with 2-acetoxymethyl acrylate **2a** in the presence of 5 mol % of $Pd(acac)_2$ and 10 mol % of PPh_3 as the catalyst in different solvents was investigated. Among the solvents tested, toluene, DME, 1,4-dioxane, DMF, and *tert*-amyl alcohol were ineffective for the coupling reaction while THF or 1,2-dichloroethane gave relatively better results (Table 3, entries 6 and 8). The reaction in HOAc afforded **3ka** in the highest yield (Table 3, entry 9). Thus, in following cases, the reaction was conducted at 80 °C in HOAc using 5 mol % of $Pd(acac)_2$ and 10 mol % of PPh_3 as the catalyst. However, it was strange to find that when indole **1a** and allyl acetate were subjected to the similar reaction conditions or the conditions used in Table 2, no reaction occurred, which was different from what was reported (Scheme 2).[7]

The scope of the $Pd(acac)_2/PPh_3$-catalyzed coupling reaction is demonstrated by the reaction of *N*-protected indoles **1k**−**p** with 2-acetoxymethyl-substituted electron-deficient alkenes **2a**−**d**. The results are presented in Table 4. Indoles **1**, in which the nitrogen was protected with various substituents, including butyl, methyl, allyl, and benzyl, reacted with **2a** to give **3** in good yields (entries 1−5, Table 4). In a similar way, 2-acetoxymethyl-3-buten-2-one **2b**, 2-phenylsulfonyl-2-propenyl acetate **2c**, and 2-cyanopropenyl acetate **2d** reacted with **1k** in the presence of 5 mol % of $Pd(acac)_2$ to afford the corresponding products **3kb**, **3kc**, and **3kd** in 79%, 76%, and 75% yields, respectively (entries 6−8, Table 4).

Although no reaction was observed between indole **1a** and 1- or 3-substituted 2-(methoxycarbonyl)allylic acetates **2e** or ***E*-2g**, the reactions of **2e** and **2g** with indole **1k** afforded the same product **3ke** in 66% and 51% yields, respectively (Scheme 3). In addition, it should be noted that no isomerization was observed between **2e** and **2g**. A similar reaction of **1k** with **2f** afforded **3kf** in 45% yield.

SCHEME 3



On the basis of these results, a Pd(0)-catalyzed mechanism is proposed for this reaction (Scheme 4). The oxidative addition reaction of the allylic acetate with Pd(0) forms the π-allylic palladium intermediate **4**.[10] Its reaction with indole via the Heck-type reaction or the direct attack of the nucleophilic 3-position of indole would form the product.

In summary, we have developed two protocols for the Pd-catalyzed C-3 regiospecific functionalization of indoles with 2-acetoxymethyl-substituted electron-deficient alkenes. Although it is still too early to exclude the Pd(II) mechanism completely, this reaction will be useful in organic synthesis due to the potentials of indoles.

Experimental Section

1. $Pd_2(dba)_3\cdot CHCl_3$/bpy-Catalyzed Coupling of Indoles with 2-Acetoxymethyl-Substituted Electron-Deficient Alkenes. Synthesis of 3-(2′-Methoxycarbonyl-2′-propenyl)indole (3aa). Typical Procedure. A dried reaction tube equipped with a magnetic stirring bar was charged with indole **1a** (59 mg, 0.5 mmol), methyl 2-(acetoxymethyl)acrylate (96 mg, 0.6 mmol), $Pd_2(dba)_3\cdot CHCl_3$ (12.9 mg, 2.5 mol %), 2,2′-bipyridine (7.8 mg, 10 mol %), and toluene (1 mL). Then the reaction was heated at 80 °C with stirring for 12 h as monitored by TLC. Filtration of the reaction mixture through a small pad of silica gel (Et_2O), concentration, and purification of the dark oil by flash chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:5) afforded **3aa** as a yellow solid (90 mg, 84%): mp 69−71 °C (hexane); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.04 (bs, 1 H), 7.53 (d, J = 7.5 Hz, 1 H), 7.36 (d, J = 8.1 Hz, 1 H), 7.19 (t, J = 8.4 Hz, 1 H), 7.10 (t, J = 8.1 Hz, 1 H), 7.03 (d, J = 2.4 Hz, 1 H), 6.20 (s, 1 H), 5.49 (s, 1 H), 3.78 (s, 2 H), 3.76 (s, 3 H); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 167.8, 139.3, 136.2, 127.2, 125.6, 122.8, 121.9, 119.2, 119.0, 112.6, 111.1, 51.9, 27.5 ppm; MS (70 eV) *m*/*z* 215 (M^+, 100); IR (neat) ν 3378, 1697, 1628, 1433, 1424, 1310, 1287, 1141, 745 cm^{-1}; HRMS calcd for $C_{13}H_{13}NO_2$ 215.09462, found 215.09223.

2. $Pd(acac)_2/PPh_3$-Catalyzed Coupling of *N*-Protected Indoles with 2-Acetoxymethyl-Substituted Electron-Deficient Alkenes. Synthesis of 3-(2′-Methoxycarbonyl-2′-propenyl)-1-methylin-

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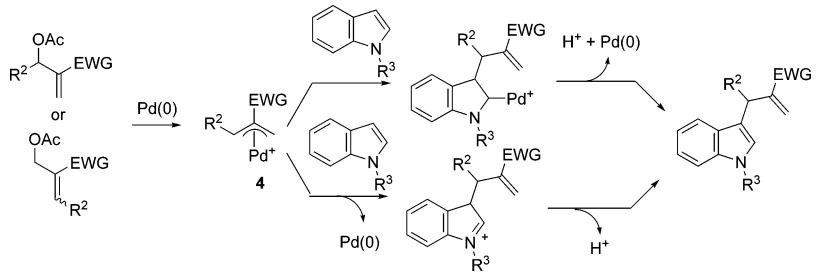
SCHEME 4



dole. Typical Procedure. A dried reaction tube equipped with a magnetic stirring bar was charged with indole **1k** (131 mg, 1.0 mmol), methyl 2-acetoxymethyl acrylate **2a** (160 mg, 1.0 mmol), $Pd(acac)_2$ (15 mg, 5 mol %), PPh_3 (26 mg, 10 mol %), and HOAc (0.5 mL). Then the reaction was heated at 80 °C with stirring for 23 h as monitored by TLC. Filtration of the reaction mixture through a small pad of silica gel (Et_2O), concentration, and purification of the dark oil by flash chromatography on silica gel (eluent: ethyl acetate/petroleum ether = 1:5) afforded 192 mg (84%) of **3ka**: oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 7.8 Hz, 1 H), 7.28 (d, J = 7.8 Hz, 1 H), 7.21 (t, J = 7.8 Hz, 1 H), 7.09 (t, J = 7.8 Hz, 1 H), 6.87 (s, 1 H), 6.18 (s, 1 H), 5.51−5.46 (m, 1 H), 3.75 (s, 5 H), 3.73 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.6, 139.5, 136.9, 127.5, 127.4, 125.3, 121.3, 119.0, 118.6, 110.9, 109.0, 51.6, 32.3, 27.4; IR (neat) 1720, 1631 cm^{-1}; MS m/z 229 (M^+, 100); HRMS m/z (MALDI) calcd for $C_{14}H_{15}NO_2Na^+$(M^+ + Na) 252.0995, found 252.1000.

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Supporting Information Available: Experimental procedures and compound characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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