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Palladium-Catalyzed Coupling Reactions of Diarylvinylidenecyclopropanes with 2-Iodophenol and *N*-(2-Iodophenyl)-4-methylbenzenesulfonamide

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Keywords: Palladium / Cross-coupling / Annulation / Heterocycles / C–C coupling

A palladium-catalyzed cross-coupling reaction of diarylvinylidenecyclopropanes with 2-iodophenol and *N*-(2-iodophenyl)-4-methylbenzenesulfonamide provided a variety of cyclopropane-containing 2,2-diaryl-3-tetramethylcyclopropylidene-2,3-dihydrobenzofuran and 2,2-diaryl-3-tetramethylcyclopropylidene-1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-indole derivatives in moderate-to-good yields.

Introduction

Cyclopropane subunits are extremely important building blocks for organic chemistry and also occur in many natural products of secondary metabolism.[1,2] Many cyclopropane-containing natural compounds have been isolated from plants, fungi, or microorganisms, and they show biological activity, which may serve as potential drug leads or provide new ideas for the study of enzyme mechanisms. It it also known that cyclopropanes can serve as high-energy intermediates in metabolism (e.g., presqualene), as storage elements to release energy-rich compounds (e.g., ethylene from ACC oxidation), or as trigger components to provide a driving force and ensure irreversibility in mechanism-based inhibition (e.g., CC-1065).[3–6] Therefore, the exploration of a novel synthetic approach for the preparation of cyclopropane-containing compounds is a very attractive field for organic chemists. Annulation reactions of allenes and functionalized aryl halides catalyzed by palladium complexes have been reported by many groups during the last two decades.[7] In this paper, we wish to report a Pd-catalyzed coupling reaction of diarylvinylidenecyclopropanes **1**[8] with 2-iodophenols **2** or *N*-(2-iodophenyl)-4-methylbenzenesulfonamide (**4**) to provide a variety of cyclopropane-containing 2,2-diaryl-3-(tetramethylcyclopropylidene)-2,3-(dihydro)benzofuran or 2,2-diaryl-3-(tetramethylcyclopropylidene)-1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-indole derivatives **3** or **5** in moderate-to-good yields.

Results and Discussion

The initial examination was performed by using diphenylvinylidenecyclopropane (**1a**) and 2-iodophenol (**2a**; 3.0 equiv.) as the substrates upon treatment with $Pd(PPh_3)_2Cl_2$ (5 mol-%) in *N*,*N*-dimethylformamide (DMF) at 100 °C in the presence of potassium carbonate (K_2CO_3, 3.0 equiv.) or cesium carbonate (Cs_2CO_3, 3.0 equiv.), and we found that the reaction proceeded smoothly with 60 or 56% conversion, respectively, and coupling product **3a** was obtained in 41 or 18% yield, respectively, within 64 h (Table 1, entries 1 and 2). The use of Pd^0 such as $Pd(PPh_3)_4$ or $Pd_2(dba)_3$ as the catalyst afforded **3a** in trace amounts under identical conditions. The examination of base effects revealed that by utilizing Et_3N, $(n\text{-}C_7H_{15})_3N$, or $i\mathrm{Pr}_2NEt$ as the base, **3a** could be produced in 67, 56, or 70% yield, respectively, under otherwise identical conditions (Table 1, entries 3–5), although other amino bases are not positive for the reaction outcomes (Table 1, entries 6–10). When $Pd(OAc)_2$ was used as the catalyst and 1,4-bis(diphenylphosphanyl)butane (dppb) or 1,3-bis(diphenylphosphanyl)propane (dppp) was used as a ligand in the presence of Et_3N, **3a** was obtained in 32 or 37% yield after 72 h (Table 1, entries 11 and 12). Interestingly, we found that the use of $Pd(MeCN)_2Cl_2$ and $PdCl_2$ as the palladium sources afforded **3a** in 88 and 76% yields after 72 h, respectively (Table 1, entries 13 and 14). When $PdCl_2$ was used as a palladium source and dppp was employed as a ligand, to our delight, we found that coupling product **3a** was obtained in 94% yield along with 100% conversion of **1a** after 72 h, whereas the phosphane ligand dppb was totally ineffective and Et_3N was not as good a base as $i\mathrm{Pr}_2NEt$ under identical conditions (Table 1, entries 15–17). The structure of **3a** was further confirmed by X-ray diffraction.[9]

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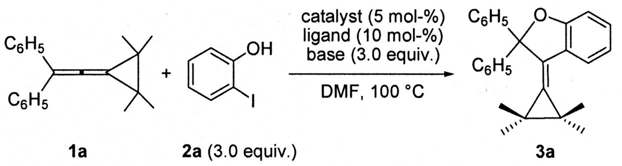
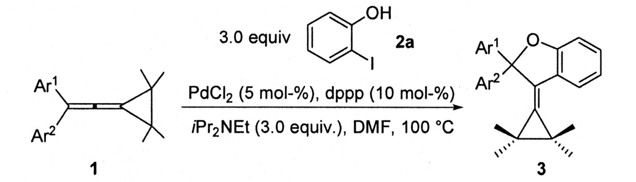
Table 1. Optimization of the coupling reaction conditions catalyzed by palladium complexes.



Entry[a]	Catalyst	Ligand	Base	Time [h]	Conv. [%]	Yield [%][b]
					1a	3a
1	$Pd(PPh_3)_2Cl_2$		K_2CO_3	64	60	41
2	$Pd(PPh_3)_2Cl_2$		Cs_2CO_3	30	56	18
3	$Pd(PPh_3)_2Cl_2$		Et_3N	64	90	67
4	$Pd(PPh_3)_2Cl_2$		$(n\text{-}C_7H_{15})_3N$	64	62	56
5	$Pd(PPh_3)_2Cl_2$		*i*Pr_2NEt	64	100	70
6	$Pd(PPh_3)_2Cl_2$		DABCO	64	complex	
7	$Pd(PPh_3)_2Cl_2$		DMAP	64	no reaction	
8	$Pd(PPh_3)_2Cl_2$		pyridine	64	complex	
9	$Pd(PPh_3)_2Cl_2$		*n*$BuNH_2$	64	complex	
10	$Pd(PPh_3)_2Cl_2$		DBU	72	no reaction	
11	$Pd(OAc)_2$	dppb	Et_3N	72	70	32
12	$Pd(OAc)_2$	dppp	Et_3N	72	62	37
13	$Pd(MeCN)_2Cl_2$		*i*Pr_2NEt	72	92	88
14	$PdCl_2$		*i*Pr_2NEt	72	100	76
15	$PdCl_2$	dppb	*i*Pr_2NEt	72	50	11
16	$PdCl_2$	dppp	Et_3N	72	84	74
17	$PdCl_2$	dppp	*i*Pr_2NEt	72	100	94

[a] General procedure: A solution of **1a** (0.18 mmol), **2a** (0.54 mmol), catalyst (5 mol-%), ligand (10 mol-%), and base (0.54 mmol) in DMF (3 mL) was stirred at 100 °C under an argon atmosphere. [b] Isolated yield.

Table 2. $PdCl_2$-catalyzed coupling reactions of **1** with **2a** under the optimal conditions.



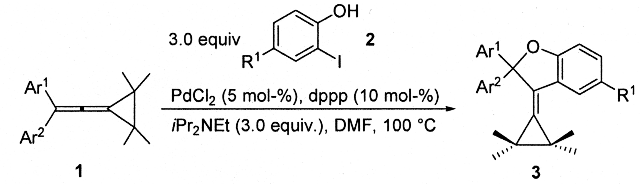
Entry[a]	Ar^1/Ar^2	Time [h]	Yield [%][b]
			3
1	*p*-FC_6H_4/*p*-FC_6H_4 **1b**	96	**3b**, 83
2	C_6H_5/*p*-FC_6H_4 **1c**	96	**3c**, 90
3	C_6H_5/*m*, *p*-$F_2C_6H_3$ **1d**	96	**3d**, 85
4[c]	*p*-ClC_6H_4/*p*-ClC_6H_4 **1e**	120	**3e**, 50
5	C_6H_5/*p*-ClC_6H_4 **1f**	120	**3f**, 51
6	C_6H_5/*m*, *p*-$Cl_2C_6H_3$ **1g**	120	**3g**, 77
7[d]	*p*-MeC_6H_4/*p*-MeC_6H_4 **1h**	120	**3h**, 36

[a] General procedure: A solution of **1** (0.18 mmol), **2a** (0.54 mmol), $PdCl_2$ (5 mol-%), dppp (10 mol-%), *i*Pr_2NEt (0.54 mmol) in DMF (3 mL) was stirred at 100 °C under an argon atmosphere. [b] Isolated yield. [c] $PdCl_2$ (10 mol-%) and dppp (20 mol-%) were used. [d] $[Et_3NH][BF_4]$ (20 mol-%) was added.

With these optimal conditions being identified, we next examined the scope of this interesting coupling reaction. Vinylidene substrates **1** bearing electron-withdrawing groups on their benzene rings underwent the coupling reactions smoothly to provide the corresponding 2,2-diaryl-3-(tetramethylcyclopropylidene)-2,3-(dihydro)benzofuran derivatives **3b–g** in moderate-to-good yields within 4–5 d (Table 2, entries 1–6). As for vinylidene **1e** having a chlorine atom on the benzene ring, $PdCl_2$ (10 mol-%) and dppp (20 mol-%) are required to give **3e** in 50% yield (Table 2, entry 4). However, as for vinylidene **1h** bearing a moderately electron-donating methyl group on the benzene ring, the reaction was sluggish to afford the corresponding coupling product in low yield. After a series of trial-and-error experiments, we found that the addition of $[Et_3NH][BF_4]$ (20 mol-%) as a coadditive could improve the situation to some extent:[10] dihydrobenzofuran derivative **3h** was obtained in 36% yield (Table 2, entry 7).

As for 2-iodophenols **2b** and **2c** bearing a moderately electron-donating methyl group and a moderately electron-withdrawing chloro group at the *para* position of the benzene ring, the corresponding dihydrobenzofuran derivatives **3i–n** were also obtained in moderate-to-good yields under the standard conditions (Table 3, entries 1–6). It should be noted that 2-iodobenzoic acid is totally inactive in this reaction.

Table 3. $PdCl_2$-catalyzed coupling reactions of **1** with **2b** and **2c** under optimal conditions.

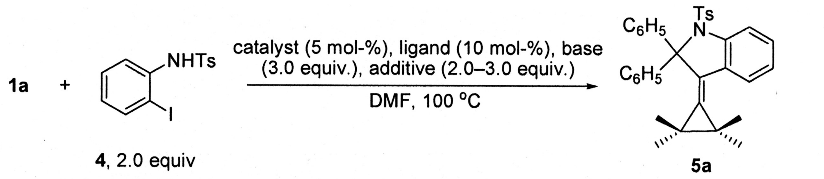


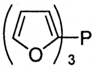
Entry[a]	Ar^1/Ar^2	R^1	Time [h]	Yield [%][b]
				3
1	C_6H_5/C_6H_5 **1a**	Me **2b**	72	**3i**, 71
2	C_6H_5/C_6H_5 **1a**	Cl **2c**	72	**3j**, 75
3	*p*-FC_6H_4/C_6H_5 **1c**	Me **2b**	72	**3k**, 56
4	*p*-FC_6H_4/C_6H_5 **1c**	Cl **2c**	72	**3l**, 76
5	*p*-FC_6H_4/*p*-FC_6H_4 **1b**	Me **2b**	72	**3m**, 60
6	*p*-FC_6H_4/*p*-FC_6H_4 **1b**	Cl **2c**	72	**3n**, 67

[a] General procedure: A solution of **1** (0.18 mmol), **2** (0.54 mmol), $PdCl_2$ (5 mol-%), dppp (10 mol-%), and *i*Pr_2NEt (0.54 mmol) in DMF (3 mL) was stirred at 100 °C under an argon atmosphere. [b] Isolated yield.

Next, on the basis of the above results, we attempted to utilize *N*-(2-iodophenyl)-4-methylbenzenesulfonamide (**4**) as a coupling reagent to react with **1a** under similar conditions. However, it was found that corresponding dihydro-

Table 4. Optimization of the conditions for the reaction of **1a** with **4** catalyzed by palladium complexes.



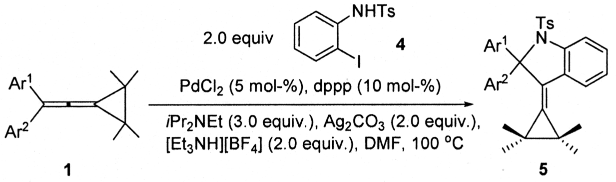
Entry[a]	Catalyst	Ligand	Base	Additive	Time [h]	Conv. [%]	Yield [%][b]
						1a	**5a**
1	Pd(PPh$_3$)$_2$Cl$_2$		*i*Pr$_2$NEt		96	32	9
2	PdCl$_2$	dppp	*i*Pr$_2$NEt		96	56	18
3	PdCl$_2$	dppp	Et$_3$N		96	46	15
4	PdCl$_2$	dppp	Et$_3$N	*n*Bu$_4$NI[c]	72	–[d]	38
5	PdCl$_2$	dppf	*i*Pr$_2$NEt	*n*Bu$_4$NI[c]	72	–[d]	17
6	Pd(OAc)$_2$		*i*Pr$_2$NEt	*n*Bu$_4$NI[c]	72	–[d]	29
7[e]	*PdCl$_2$*	*dppp*	*iPr$_2$NEt*	*Ag$_2$CO$_3$* *[Et$_3$NH][BF$_4$]*	*96*	–[d]	*58*
8[e]	PdBr$_2$	dppp	*i*Pr$_2$NEt	Ag$_2$CO$_3$ [Et$_3$NH][BF$_4$]	96	–[d]	15
9[e]	PdCl$_2$	dppp	*i*Pr$_2$NEt	AgNO$_3$ [Et$_3$NH][BF$_4$]	72	46	11

[a] General procedure: A solution of **1a** (0.18 mmol), **4** (0.36 mmol), catalyst (5 mol-%), ligand (10 mol-%), and base (0.36 mmol) in DMF (3 mL) was stirred at 100 °C under an argon atmosphere. [b] Isolated yield. [c] *n*Bu$_4$NI (3.0 equiv.) was employed. [d] **1a** could not be separated from some impurities. [e] Ag$_2$CO$_3$ or AgNO$_3$ (2.0 equiv.) and [Et$_3$NH][BF$_4$] (2.0 equiv.) were used.

indole **5a** was obtained in low yield (9–18%) under the above standard conditions (Table 4, entries 1–3). The addition of *n*Bu$_4$NI (3.0 equiv.) as a phase-transfer catalyst afforded **5a** in 38% yield (Table 4, entry 4). The use of diphenylphosphanylferrocene (dppf) and tris(2-furyl)phosphane (TFP) as the phosphane ligands to replace dppp did not improve the yield of **5a** (Table 4, entries 5 and 6). After several experiments, we were pleased to find that the use of Ag$_2$CO$_3$ (2.0 equiv.)[11] and [Et$_3$NH][BF$_4$] (2.0 equiv.) as the additives under otherwise identical conditions produced **5a** in 58% yield (Table 4, entry 7). The use of PdCl$_2$ and Ag$_2$CO$_3$ is crucial for this coupling reaction, because if PdBr$_2$ is used as a catalyst or AgNO$_3$ (2.0 equiv.) as the coadditive rather than PdCl$_2$ or Ag$_2$CO$_3$, **5a** was formed in 15 or 11% yield, respectively (Table 4, entries 8 and 9). However, when Ag$_2$CO$_3$ or [Et$_3$NH][BF$_4$] was used separately in this reaction, the achieved yields of **5a** were much lower than that using them together (Table 4, entries 10 and 11). The positive effect of Ag$_2$CO$_3$ is presumably due to the abstraction of a halide from the arylpalladium complex and the formation of a cationic arylpalladium intermediate stabilized by BF$_4^-$ from [Et$_3$NH][BF$_4$], which is assumed to be more reactive toward addition to the C=C=C bond.[12]

The generality of this coupling reaction was also examined by using a variety of vinylidenes **1** under the optimal conditions. The results are summarized in Table 5. The corresponding dihydroindole derivatives **5b–h** were obtained in moderate yields (30–64%) whether electron-donating or -withdrawing groups were introduced in the benzene ring of **1** (Table 5, entries 1–7).

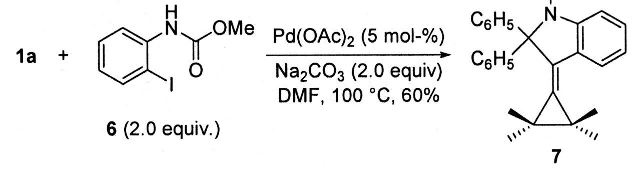
Table 5. PdCl$_2$-catalyzed coupling reactions of **1** with **4** under the optimal conditions.



Entry[a]	Ar^1/Ar^2	Time [h]	Yield [%][b]
			5
1	*p*-FC$_6$H$_4$/*p*-FC$_6$H$_4$ **1b**	96	**5b**, 64
2	C$_6$H$_5$/*p*-FC$_6$H$_4$ **1c**	72	**5c**, 44
3	*p*-ClC$_6$H$_4$/*p*-ClC$_6$H$_4$ **1e**	96	**5e**, 50
4	C$_6$H$_5$/*p*-ClC$_6$H$_4$ **1f**	96	**5f**, 41
5	*p*-MeC$_6$H$_4$/*p*-MeC$_6$H$_4$ **1h**	120	**5h**, 43
6	C$_6$H$_5$/*p*-MeC$_6$H$_4$ **1i**	96	**5d**, 30
7	C$_6$H$_5$/*m*, *p*-Me$_2$C$_6$H$_3$ **1j**	96	**5g**, 41

[a] General procedure: A solution of **1** (0.18 mmol), **4** (0.36 mmol), PdCl$_2$ (5 mol-%), dppp (10 mol-%), *i*Pr$_2$NEt (3.0 equiv.), Ag$_2$CO$_3$ (2.0 equiv.), and *i*Pr$_2$NEt (0.54m mol) inD MF (3 mL) was stirreda t 100 °C under an argon atmosphere. [b] Isolated yield.

When methyl (2-iodophenyl)carbamate (**6**) was used as the coupling reagent, we found that the corresponding dihydroindole derivative **7** was formed in 60% yield by using $Pd(OAc)_2$ as a catalyst and Na_2CO_3 (2.0 equiv.) as a base in DMF at 100 °C (Scheme 1). Its structure was unambiguously determined by X-ray diffraction.[13]



Scheme 1. $Pd(OAc)_2$-catalyzed coupling reaction of **1** with **6**.

Conclusion

We developed efficient methods for the coupling reactions of diarylvinylidenecyclopropanes **1** with 2-iodophenols **2** and *N*-(2-iodophenyl)-4-methylbenzenesulfonamide (**4**) to provide a variety of cyclopropane-containing 2,2-diaryl-3-(tetramethylcyclopropylidene)-2,3-(dihydro)benzofuran and 2,2-diaryl-3-(tetramethylcyclopropylidene)-1-(toluene-4-sulfonyl)-2,3-dihydro-1*H*-indole derivatives **3** and **5** or **7** in moderate-to-good yields catalyzed by various palladium complexes in the presence of bases and other coadditives. A variety of vinylidenes **1** and 2-iodophenols **2** as well as *N*-(2-iodophenyl)-4-methylbenzenesulfonamide and methyl (2-iodophenyl)carbamate are suitable for this coupling reaction to provide the corresponding cyclopropane-containing five-membered heterocycles in a one-step reaction. Efforts are in progress to elucidate further mechanistic details of these reactions and to understand their scope and limitations.

Experimental Section

Representative Procedure for the Preparation of Vinylidenecyclopropanes (VDCPs): The substrates **1a**, **1b**, **1e**, **1f**, **1h**, **1i**, and **1j** were synthesized by following a literature procedure.[7] To a solution of 1,1-dibromocyclopropane (10 mmol) in THF (80 mL) was added 2,3-dimethylbut-2-ene (1.0 M in THF, 20 mL, 20 mmol), NaOH powder (8.0 g, 200 mmol), and $Bu_4N^+HSO_4^-$ (6.8 g, 20 mmol) as a phase-transfer reagent. The resulting mixture was stirred at room temperature for 12 h. After this period, the resulting dark suspension was poured into petroleum ether (100 mL), and the solid was filtered. The organic phase was concentrated under reduced pressure and purified by column chromatography on silica gel.

General Procedure for the Annulation Reaction of 1 with 2-Iodophenol: Under an argon atmosphere, vinylidene **1** (0.18 mmol), 2-iodophenol (119 mg, 0.54 mmol, 3.0 equiv.), $PdCl_2$ (2 mg, 0.01mmol, 5 mol-%), dppp (7 mg, 0.18mmol, 10 mol-%), and $i\mathrm{Pr}_2NEt$ (97 mg, 0.54 mmol, 3.0 equiv.) were dissolved in DMF (3 mL), and the mixture was stirred for 72 h at 100 °C. To the resulting mixture was added H_2O (5 mL), and the solution was extracted with Et_2O (3×10 mL). The combined organic phase was washed with brine (1×10 mL) and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/EtOAc, 80:1).

2,2-Diphenyl-3-(2,2,3,3-tetramethylcyclopropylidene)-2,3-dihydrobenzofuran (3a): A white solid. M.p. 132–134 °C. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.70 (s, 6 H, $2CH_3$), 1.28 (s, 6 H, $2CH_3$), 6.89 (d, *J* = 7.8 Hz, 1 H, Ar), 6.94 (d, *J* = 7.8 Hz, 1 H, Ar), 7.13–7.19 (m, 1 H, Ar), 7.26–7.33 (m, 7 H, Ar), 7.36–7.39 (m, 4 H, Ar) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 20.2, 20.4, 21.2, 23.0, 94.7, 110.3, 121.1, 122.2, 126.6, 127.7, 127.8, 128.1, 129.1, 131.4, 139.2, 142.8, 160.0 ppm. IR (CH_2Cl_2): $\tilde{\nu}$ = 3061, 3034, 2989, 2916, 2863, 1591, 1507, 1490, 1475, 1461, 1447, 1372, 1316, 1288, 1242, 1120, 1033, 1005, 952, 893, 745, 698, 627, 614 cm^{-1}. MS: *m*/*z* (%) = 366 (15) $[M]^+$, 351 (55), 323 (15), 270 (100), 247 (9), 232 (10), 215 (9), 165 (12), 91 (14). $C_{27}H_{26}O$ (366.50): calcd. C 88.48, H 7.15; found C 88.44, H 7.09.

CCDC-666660 (for **3a**) and -682315 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Detailed description of the experimental procedures; full characterization of **3a**–**n**, **5a**–**h**, and **7**; X-ray crystal structure and structure refinement details of **3a** and **7**.

Acknowledgments

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