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Pd⁰-Catalyzed Three-Component Tandem Double-Addition–Cyclization Reaction: Stereoselective Synthesis of *cis*-Pyrrolidine Derivatives**

Shengming Ma* and Ning Jiao

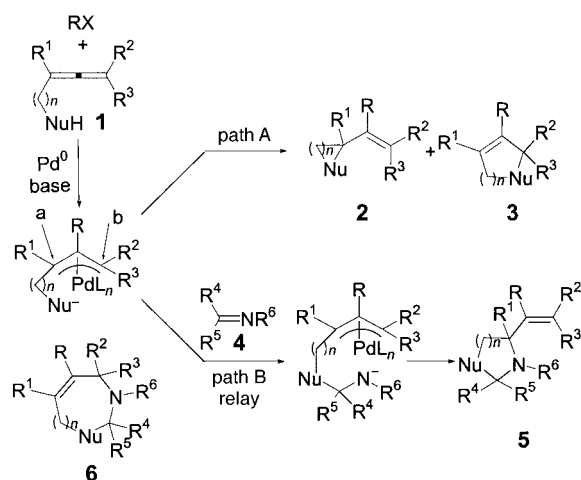
Pd⁰-catalyzed cyclization reactions of functionalized alkenes^[1] leading to carbo- and heterocyclic compounds^[2–4] has been studied extensively. In some of these reactions, the π -allyl palladium intermediate formed in situ^[5] was trapped by an intramolecular nucleophile (path A, Scheme 1). Recently, development of multicomponent reactions to preserve atom economy^[6] and stereoselectively construct an array of several stereogenic centers in one pot is attracting the attention of many chemists.^[7] Therefore, if there is another potential electrophilic receptor such as an imine group in the reaction system, the Pd⁰-catalyzed reaction of organohalides and allenes with a nucleophilic center would allow the formation of pyrrolidine derivatives (path B, Nu = C, Scheme 1). To make this concept synthetically attractive, we must address the issues of matched relay, regioselectivity (by excluding the formation of seven-membered product **6**), and diastereoselectivity (Scheme 1).

The construction of pyrrolidine skeletons, a frequently observed structural unit in various natural products, ligands, etc., is of current interest.^[8,9] Although the transition-metal-catalyzed cyclization of γ -allenic amides to yield 2-substituted

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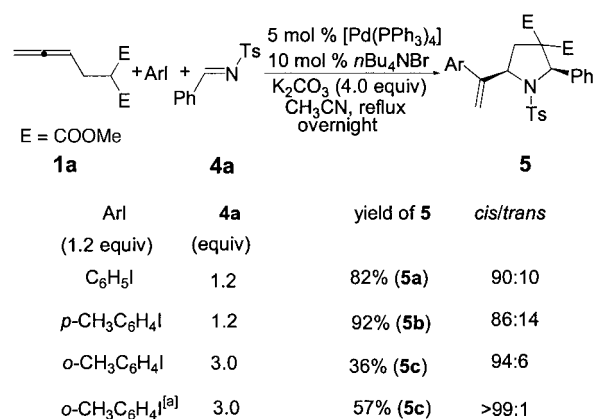
 Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.



Scheme 1. Protocol for the selective synthesis of pyrrolidine derivatives through a three-component reaction.

pyrrolidine has been well-documented,^[10,11] the transition-metal-catalyzed multicomponent reaction of functionalized allenes to form polysubstituted heterocyclic compounds with high stereoselectivity has not been reported. Herein we disclose our recent results on the three-component tandem double-addition–cyclization of 2-(2,3-allenyl)malonates, organohalides, and imines. By tuning the reaction conditions, we have addressed the issues of smooth relay, regio-, and diastereoselectivity.

We recently developed four sets of reaction conditions under which the coupling–cyclization of 2-(2,3-allenyl)malonates with organohalides afforded cyclopropane derivative **2** or cyclopentene derivatives **3** with high regioselectivity (Nu = C, Scheme 1).^[12–14] Fortunately, under the same conditions for path A^[14d] [$\text{Pd}(\text{PPh}_3)_4$ (5 mol %), K_2CO_3 (4 equiv), $n\text{Bu}_4\text{NBr}$ (10 mol %), CH_3CN , reflux), the reaction of 2-(2,3-allenyl)malonates with PhI and N -benzylidene p -toluenesulfonamide (**4a**) afforded pyrrolidine derivative **5a** in 89% yield (*cis/trans* 9:1; Scheme 2). Premature products **2a** and **3a** and seven-membered product **6a** ($n = 1$; Nu = C; $\text{R}^1, \text{R}^2, \text{R}^3, \text{R}^4 = \text{H}$; $\text{R}^5 = \text{Ph}$; $\text{R}^6 = \text{Ts}$) were not observed. The structure of *cis*-**5a** was determined by X-ray diffraction studies (Figure 1).^[15] On the other hand, the corresponding reaction of **1a** and **4a** with



^[a] Na_2CO_3 was used as the base.

Scheme 2. Control of stereoselectivity by the steric effect and base.

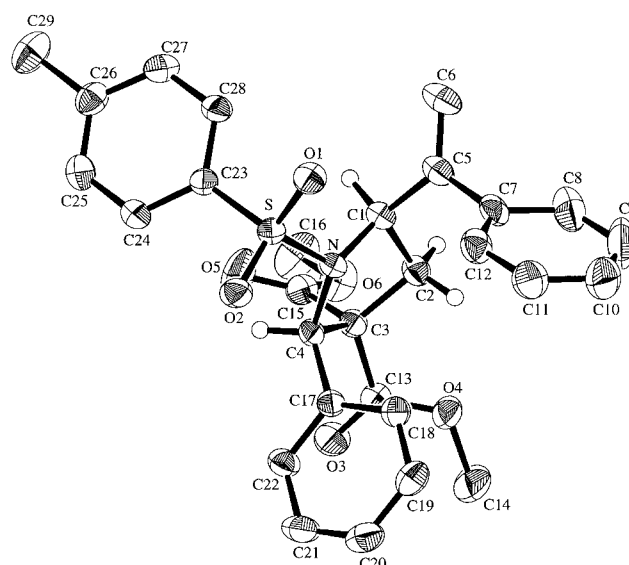
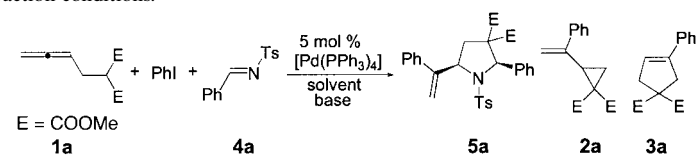


Figure 1. ORTEP representation of *cis*-**5a**.

o-methylphenyl iodide afforded pyrrolidine derivative **5c** in 36% yield (*cis/trans* 94:6; Scheme 2). The use of Na_2CO_3 as base gives higher yield and stereoselectivity. Based on the results shown in Scheme 2, it can be concluded that the base and the steric hindrance of the aryl iodide are two of the major factors that control the stereoselectivity of this tandem coupling–cyclization reaction. Thus, control of the stereoselectivity of the two carbon centers in a general manner would be a new challenge.

The effects of different bases, solvents, and additives for the reaction of Pd^0 -catalyzed reaction of **1a**, iodobenzene, and imine **4a** are shown in Table 1. Of several bases tested, K_2CO_3 and Na_2CO_3 gave higher yields of **5a**, but the *cis/trans* ratio is still not excellent (Table 1, entries 2 and 4). The use of a stronger base (e.g. Cs_2CO_3 , $n\text{Bu}_4\text{NBr}$ (10 mol %), or NaH) in the reaction favors the formation of the premature three-membered cycle **2a** or cyclopentene derivative **3a** (Table 1, entries 3 and 5), indicating a lower relay ability. The use of a phase-transfer catalyst ($n\text{Bu}_4\text{NBr}$, 10 mol %) has no dramatic effect on the stereoselectivity (compare Table 1, entries 1 with 2). Fortunately, the use of THF as the solvent led to the isolation of **5a** in 72% yield with excellent stereoselectivity (*cis/trans* > 99:1), albeit that **2a** was also formed in 26% yield (Table 1, entry 8). Even with 3.0 equivalents of imine, the relay is still not satisfactorily smooth (Table 1, entries 10 and 11). The addition of a Lewis acid did not produce better relaying results; on the contrary, the *cis/trans* ratio decreased (Table 1, entries 12). Furthermore, the effect of the temperature on the reaction is clear: in THF as solvent, the reaction in a sealed screw tube at 85°C overnight afforded pyrrolidine derivative **5a** in 90% yield exclusively, and the ratio is still excellent (Table 1, entry 13; compare entries 10, 11, and 13). A decrease in the amount of imine **4a** from 3.0 to 1.2 equivalents also gave a similar result (Table 1, entry 14). The reaction at 100°C afforded **5a** with a slightly lower stereoselectivity (98:2; Table 1, entry 15). Similar results are also observed in 1,4-dioxane (Table 1, entries 16 and 17). Thus, the solvent (THF or 1,4-dioxane) and reaction temperature

Table 1. [Pd(PPh₃)₄]-catalyzed tandem double-addition–cyclization of **1a** with PhI and imine **4a** under different reaction conditions.^[a]


Entry	Base	Additive ^[b]	Imine [equiv]	Solvent	T [°C]	Time [h]	5a		Yield 2a [%]
							Yield [%]	cis/trans	
1	K ₂ CO ₃	–	1.2	CH ₃ CN	reflux	11	71	86:14	0
2	K ₂ CO ₃	A	1.2	CH ₃ CN	reflux	10	82	90:10	0
3	Cs ₂ CO ₃	A	1.2	CH ₃ CN	reflux	11	trace	–	43 ^[c]
4	Na ₂ CO ₃	A	1.2	CH ₃ CN	reflux	11	89	95:5	0
5	NaH	–	1.2	DMF	85	11	31	86:14	0 ^[d]
6	K ₂ CO ₃	–	1.2	DMF	85	12	73	75:25	0 ^[e]
7	K ₂ CO ₃	A	1.2	toluene	85	12	63	80:20	8
8	K ₂ CO ₃	–	1.2	THF	reflux	11	72	> 99:1	26
9	Na ₂ CO ₃	–	1.2	THF	reflux	36	65	> 99:1	11
10	K ₂ CO ₃	–	3.0	THF	40	58	82	> 99:1	10
11	K ₂ CO ₃	–	3.0	THF	reflux	12	88	> 99:1	8
12	K ₂ CO ₃	B	3.0	THF	reflux	11	89	96:4	5
13	K ₂ CO ₃	–	3.0	THF	85 ^[f]	11	90	> 99:1	0
14	K ₂ CO ₃	–	1.2	THF	85 ^[f]	10	86	> 99:1	0
15	K ₂ CO ₃	–	1.2	THF	100 ^[f]	10	87	98:2	0
16	K ₂ CO ₃	–	1.2	C ^[g]	85	7	86	> 99:1	0
17	K ₂ CO ₃	–	1.2	C ^[g]	reflux	6	75	> 99:1	0

[a] PhI (1.2 equiv), base (4.0 equiv), and NaH (1.1 equiv) were used. [b] A = *n*Bu₄NBr (10 mol %), B = Cu(OTf)₂ (10 mol %); [c] 4% of **3a** was produced. [d] 57% of **3a** was produced. [e] 5% of **3a** was produced. [f] The reaction was carried out in a tube with a screw cap. [g] C = 1,4-Dioxane.

(85 °C) are key to a smooth relay and high stereoselectivity of **5a**.

The results of the [Pd(PPh₃)₄]-catalyzed tandem coupling–cyclization reaction of **1a** with different organohalides and imines in THF or 1,4-dioxane are summarized in Tables 2 and 3. In all other cases, except in the reactions of aryl halides with strongly electron-withdrawing substituents (Table 2,

entries 7–9) the *cis*-pyrrolidine derivatives **5** are formed exclusively with high stereoselectivities by a subtle adjustment of the solvent or the amount of the corresponding imine. From Tables 2 and 3, it is clear that the current reaction can be successfully extended to a variety of organo-

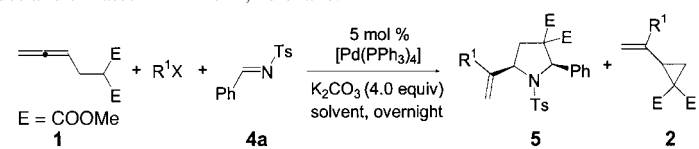
iodides (Table 2, entries 1–14), phenyl bromide (Table 2, entry 15), phenyl triflate (Table 2, entry 16) and imines (Table 3) leading to the formation of the corresponding *cis*-pyrrolidine derivatives in 81–100% yield with excellent stereoselectivities. The electron-withdrawing tosyl group of imine **4** is important for this reaction since the corresponding reaction of **1a** with PhI and *N*-(4-chlorobenzylidene)aniline afforded **2a** as the only product in 92% yield, probably as a result of the lower reactivity of this imine.

The corresponding reaction of dimethyl 2-(2,3-decadienyl)malonate with PhI and **4a** afforded *cis*-**5l** in 85% yield (Scheme 3). The configuration of the C=C bond in **5l** was determined from the ¹H, ¹H NOESY spectra.

In conclusion, we have developed a three-component tandem double-addition–cyclization reaction that provides an efficient route to polysubstituted *cis*-pyrrolidine derivatives with matched relay and excellent regio- and stereoselectivity. As all three building blocks are readily available, this study will open a new area for the transition-metal-catalyzed chemistry of allenes. Further studies on the scope and synthetic applications of this reaction are being pursued in our laboratory.

Experimental Section

Typical procedure: Malonate **1a** (46 mg, 0.25 mmol) and iodobenzene (61 mg, 0.3 mmol, 1.2 equiv) were added consecutively to a sealed tube charged with a mixture of potassium carbonate (138 mg, 1.0 mmol, 4.0 equiv), [Pd(PPh₃)₄] (14.5 mg, 0.0125 mmol, 5 mol %), and **4a** (78 mg, 0.3 mmol, 1.2 equiv) in THF (3 mL) under nitrogen. The resulting mixture was heated at 85 °C overnight and monitored by TLC. After evaporation, the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ether 3:1) to afford pure **5a** (111 mg, 86%; *cis/trans* > 99:1). *cis*-**5a**: white solid, m.p. 146–147 °C (ethyl acetate/hexane); ¹H NMR (300 MHz, CDCl₃): δ = 7.53 (d, *J* = 8.29 Hz, 2H), 7.41–7.30 (m, 5H), 7.28–7.11 (m, 7H), 5.86 (s, 1H), 5.36 (s, 1H), 5.25 (s, 1H), 4.50 (dd, *J* = 11.68, 5.98 Hz, 1H), 3.65 (s, 3H), 3.15 (s, 3H), 2.84 (dd, *J* = 13.70, 11.68 Hz,

Table 2. [Pd(PPh₃)₄]-catalyzed tandem double-addition–cyclization of **1a** with imine **4a** and different organohalides and triflates in THF or 1,4-dioxane.^[a]


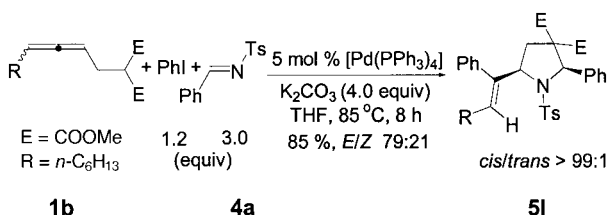
Entry	R ¹ X	Imine [equiv]	Solvent ^[b]	T [°C]	5		Yield of 2 [%]
					Yield	cis/trans	
1	<i>p</i> -CH ₃ C ₆ H ₄ I	3.0	A	reflux	92 (5b)	> 99:1	6 (2b)
2	<i>p</i> -CH ₃ C ₆ H ₄ I	1.2	A	85	92 (5b)	97:3	0
3	<i>p</i> -MeOC ₆ H ₄ I	1.2	A	85	85 (5d)	95:5	3 (2d)
4	<i>p</i> -MeOC ₆ H ₄ I	3.0	A	85	84 (5d)	95:5	0
5	<i>p</i> -MeOC ₆ H ₄ I	1.2	B	85	90 (5d)	> 98:2	0
6	<i>p</i> -MeOC ₆ H ₄ I	1.2	B	reflux	81 (5d)	> 98:2	0
7	<i>p</i> -MeO ₂ CC ₆ H ₄ I	3.0	A	85	92 (5e)	> 99:1	6 (2e)
8	<i>p</i> -MeO ₂ CC ₆ H ₄ I	3.0	B	reflux	92 (5e)	> 99:1	7 (2e)
9	<i>p</i> -MeO ₂ CC ₆ H ₄ I	1.2	B	reflux	64 (5e)	> 99:1	35 (2e)
10	thienyl-I	3.0	A	85	100 (5f)	> 99:1	0
11	(<i>E</i>)-PhC=C-I	3.0	A	85	96 (5g)	97:3	0
12	(<i>E</i>)-PhC=C-I	1.2	B	85	83 (5g)	95:5	0
13	(<i>E</i>)- <i>n</i> BuC=C-I	1.2	A	85	84 (5h)	96:4	0
14	(<i>E</i>)- <i>n</i> BuC=C-I	1.2	B	85	84 (5h)	97:3	0
15	C ₆ H ₅ Br	3.0	A	85	82 (5a)	> 98:2	0
16	C ₆ H ₅ OTf	3.0	A	85	86 (5a)	96:4	0

[a] R¹I (1.2 equiv) was used. [b] A = THF, B = 1,4-dioxane.

Table 3. [Pd(PPh₃)₄]-catalyzed tandem double-addition–cyclization of **1a** with PhI and different imines **4** in THF or 1,4-dioxane.^[a]

Entry	R	Solvent ^[b]	Yield [%] 5	Yield of 2a [%]
			<i>cis/trans</i>	
1	<i>p</i> -O ₂ NC ₆ H ₄ (4b)	THF	89 (5i)	95:5 0
2	<i>p</i> -O ₂ NC ₆ H ₄ (4b)	A	95 (5i)	97:3 0
3	<i>p</i> -MeOC ₆ H ₄ (4c)	THF	52 (5j)	>99:1 42
4 ^[c]	<i>p</i> -MeOC ₆ H ₄ (4c)	THF	99 (5j)	>99:1 0
5	<i>p</i> -MeOC ₆ H ₄ (4c)	A	52 (5j)	97:3 29
6	<i>p</i> -ClC ₆ H ₄ (4d)	THF	95 (5k)	>98:2 0

[a] PhI (1.2 equiv) was used. [b] A = 1,4-dioxane; [c] Imine **4c** (3.0 equiv) was used.

Scheme 3. Synthesis of **5l** from **1b** and imine **4a**.

1H), 2.60 (dd, *J* = 13.70, 5.98 Hz, 1H), 2.39 ppm (s, 3H); ¹³C NMR (75.4 MHz, CDCl₃): δ = 170.04, 167.18, 147.84, 143.71, 139.88, 139.05, 139.04, 135.69, 129.34, 128.55, 128.51, 128.46, 128.38, 128.25, 128.08, 116.63, 68.14, 64.03, 63.83, 53.73, 52.62, 39.28, 21.79 ppm; MS (70 eV): *m/z* (%): 520 (14.32) [M+H]⁺, 364 (100); IR (KBr): $\tilde{\nu}$ = 1749, 1729, 1635, 1597, 1493, 1350, 1165 cm⁻¹; elemental analysis: calcd for C₂₉H₂₉NO₆S (%): C 67.03, H 5.63, N 2.70; found C 67.04, H 5.48, N 2.63.

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Catalytic Electronic Activation: Indirect “Wittig” Reaction of Alcohols**

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Tandem, domino, and cascade reactions have become increasingly popular in recent years, driven by the opportunity to simplify linear sequences and achieve otherwise unfeasible reactions.^[1] Contributions from this group have involved the idea of “catalytic electronic activation”, which temporarily enhances the electronic nature of a functional group to a given reaction. We have recently reported the indirect addition of

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