Synthetic Methods

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Palladium-Catalyzed Three-Component Reaction of Allenes, Aryl Iodides, and Diazo Compounds: Approach to 1,3-Dienes**

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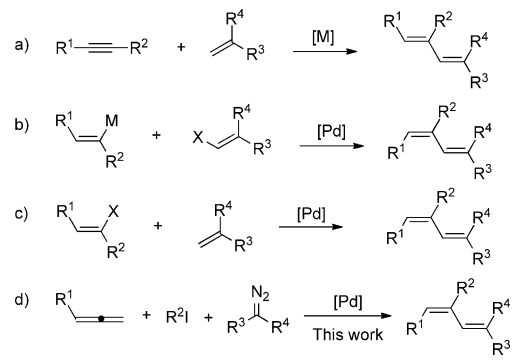
1,3-Dienes are very useful intermediates in organic synthesis because of their rich structural and reaction properties. Consequently, enormous efforts have been devoted to the regio- and stereoselective synthesis of 1,3-dienes. Among the various methods developed in the past decades for the synthesis of 1,3-dienes, the metal-catalyzed intermolecular enyne coupling is a straightforward and atom-efficient approach.[1,2] In 1991, Mitsudo and co-workers reported a ruthenium-catalyzed intermolecular co-dimerization of electron-rich alkynes with α,β-unsaturated alkenes to give 1,3-dienes.[2a] Later on, rhodium-, palladium-, and cobalt-catalyzed 1,3-diene syntheses from alkynes and alkenes were reported (Scheme 1a; M = Ru, Rh, Pd, Co).[2b–e] However, the examples of intermolecular coupling of alkynes with olefins are still limited, in contrast to the corresponding intramolecular enyne isomerization.[1a,3]



Scheme 1. Transition-metal-catalyzed syntheses of 1,3-dienes.

Another powerful method is the coupling of vinyl halides with structurally defined organometallic alkenes (Scheme 1b; M = Zn, B, Sn, Si, Mg).[4] Although the stereochemistry of the reaction is determinate, the substituent pattern is limited by that of the substrates because of the formation of only one C–C single bond. Moreover, it is generally tricky to prepare and handle the organometallic substrates. Another option for the synthesis of conjugated olefins is the palladium-catalyzed coupling of olefins with vinyl halides (Scheme 1c; Mizoroki–Heck reaction).[5] This process does not require a stoichiometric amount of organometallic reagent. However, the stereoselectivity of this type of coupling reaction cannot be easily controlled.

In view of the importance of 1,3-dienes and the limitations and shortcomings of these established methods, it is desirable to develop highly efficient synthetic strategies for rapid construction of complex conjugated olefins. Recently, diazo compounds and N-tosylhydrazones have emerged as new type of cross-coupling partners in palladium-catalyzed reactions, which involves migratory insertion of a palladium carbene.[6] Van Vranken and co-workers pioneered the palladium-catalyzed coupling reactions with trimethylsilyldiazomethane in 2001.[7] Barluenga and Valdés first employed N-tosylhydrazones in palladium-catalyzed cross-coupling reaction with aryl bromides.[8] This type of cross-coupling is general, and the migratory groups include various groups.[9] Three-component reactions based on palladium carbene migratory insertion have also been developed.[10,11] Recently, we have reported palladium-catalyzed three-component coupling of N-tosylhydrazones, aryl bromides, and terminal alkynes.[11] As a continuation of our interest in this area, herein we report a novel method for multisubstituted 1,3-dienes synthesis based on palladium-catalyzed three-component reactions of aryl iodides, allenes, and either diazo compounds or N-tosylhydrazones (Scheme 1d). This multicomponent coupling reaction makes it possible to construct substituted 1,3-diene from simple components.[12]

At the outset of this investigation, we employed the iodobenzene **2a**, propa-1,2-dienylbenzene **1a** and methyl phenyldiazoacetate **3a** as the substrates (Table 1). After some initial experiments (Table 1, entries 1–4), we found that in the presence of K_2CO_3 in MeCN, the palladium-catalyzed coupling of **1a**, **2a**, and **3a** could afford the diene **4a** in 36% yield (Table 1, entry 4). Encouraged by these initial results, we proceeded to optimize the reaction by screening the base (Table 1, entries 5–8). We were delighted to find that Et_3N and TMEDA [1,2-bis(dimethylamino)ethane] could promote the reaction (Table 1, entries 6–8). Then, a series of phosphine ligands were examined (Table 1, entries 9–11), and it was

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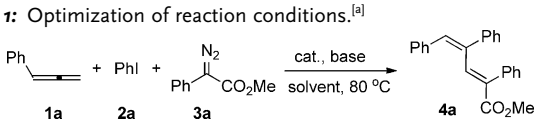
Table 1: Optimization of reaction conditions.[a]



Entry	Pd source (mol%)/ ligand (mol%)	Base	Solvent	Yield [%][b]
1	$[Pd(PPh_3)_4]$ (5)	K_2CO_3	toluene	trace
2	$[Pd(PPh_3)_4]$ (5)	K_2CO_3	DCE	8
3	$[Pd(PPh_3)_4]$ (5)	K_2CO_3	1,4-dioxane	24
4	$[Pd(PPh_3)_4]$ (5)	K_2CO_3	MeCN	36
5	$[Pd(PPh_3)_4]$ (5)	K_3PO_4	MeCN	44
6	$[Pd(PPh_3)_4]$ (5)	Et_3N	MeCN	54
7	$[Pd(PPh_3)_4]$ (5)	iPr_2NH	MeCN	45
8	$[Pd(PPh_3)_4]$ (5)	TMEDA	MeCN	53
9	$Pd(OAc)_2$ (5)/**L1** (20)	Et_3N	MeCN	49
10	$Pd(OAc)_2$ (5)/**L2** (20)	Et_3N	MeCN	65
11	$[Pd_2(dba)_3]$ (2.5)/**L2** (20)	Et_3N	MeCN	48
12[c]	$Pd(OAc)_2$ (5)/**L2** (20)	Et_3N	MeCN	73
13[c,d]	$Pd(OAc)_2$ (5)/**L2** (20)	Et_3N	MeCN	64
14[c,e]	$Pd(OAc)_2$ (5)/**L2** (20)	Et_3N	MeCN	75
15[c,f]	$Pd(OAc)_2$ (5)/**L2** (20)	Et_3N	MeCN	82

[a] Unless otherwise noted, reaction conditions are as follows: **1a** (1.1 equiv), **2a** (0.3 mmol), **3a** (1.1 equiv), base (3 equiv), in 2.0 mL solvent at 80°C for 5 h. [b] Yield of isolated product. [c] Et_3N (200 μL) was used as additives. [d] **1a**/**2a**/**3*a*** = 1.0:1.3:1.3. [e] **1a**/**2a**/**3*a*** = 1.1:1.0:1.5. [f] **1a**/**2a**/**3a** = 1.1:1.0:1.3. **L1** = PPh_3, **L2** = P(2-furyl)$_3$, DCE = 1,2-dichloroethane.

identified that the combination of the ligand P(2-furyl)$_3$ and $Pd(OAc)_2$ provided the optimal result (Table 1, entry 10). We then went on to screen other reaction parameters and observed that the reaction was significantly affected by the amount of Et_3N. After careful experimentation, it was concluded that the reaction carried out in the mixture of MeCN and Et_3N (10:1) afforded the optimal yield (Table 1, entry 12). Finally, the ratio of substrates was examined, and it was found that a **1a**/**2a**/**3a** ratio of 1.1:1.0:1.3 led to the highest yield of **4a** (Table 1, entry 15). Remarkably, the reaction proceeded with high stereoselectivity with both double bonds having *E* configurations. The structure of **4a** was unambiguously confirmed by X-ray crystallographic analysis (Figure 1).

With the optimized reaction conditions in hand, the scope of this transformation was investigated by using a series of aryl iodides, allenes, and diazo compounds. As illustrated in Table 2, the three-component reaction proceeds smoothly over a wide range of substrates to afford the corresponding 1,3-dienes in moderate to good yields. The reaction was found to not be significantly affected by the substituents on the aromatic iodides. Both electron-rich (Table 2, entries 2, 3, 5) and electron-deficient aryl iodides (Table 2, entries 4, 6, 7, 8) were effective. It is noteworthy that alkoxy, nitro, chloro, and ester groups are all tolerated under the reaction conditions.

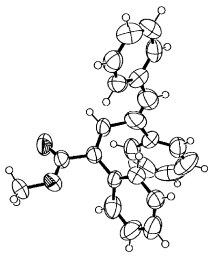
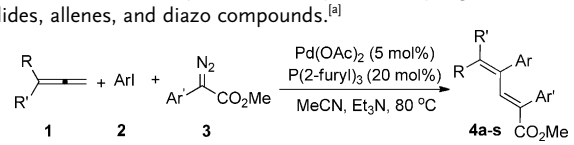


Figure 1. X-Ray structure of **4a**.[19] Thermal ellipsoids shown at 30% probability.

Table 2: Palladium-catalyzed three-component coupling of various aryl iodides, allenes, and diazo compounds.[a]



Entry	**1** R, R′	**2** Ar	**3** Ar′	**4** Yield [%][b]
1	Ph, H	Ph	Ph	**4a**, 82
2	Ph, H	4-MeC_6H_4	Ph	**4b**, 72
3	Ph, H	3-MeC_6H_4	Ph	**4c**, 79
4	Ph, H	4-ClC_6H_4	Ph	**4d**, 67
5	Ph, H	4-$MeOC_6H_4$	Ph	**4e**, 64
6	Ph, H	3-$MeOC_6H_4$	Ph	**4f**, 71
7	Ph, H	4-$MeO_2CC_6H_4$	Ph	**4g**, 81
8	Ph, H	4-$O_2NC_6H_4$	Ph	**4h**, 62
9	Ph, H	Ph	4-MeC_6H_4	**4i**, 81
10	Ph, H	Ph	3-MeC_6H_4	**4j**, 72
11	Ph, H	Ph	4-ClC_6H_4	**4k**, 80
12	Ph, H	Ph	3-ClC_6H_4	**4l**, 74
13	Ph, H	Ph	4-$MeOC_6H_4$	**4m**, 56
14	Ph, H	Ph	3-$MeOC_6H_4$	**4n**,77
15	Ph, H	Ph	2-FC_6H_4	**4o**, 70
16	4-MeC_6H_4, H	4-MeC_6H_4	Ph	**4p**, 71
17	4-ClC_6H_4, H	Ph	Ph	**4q**, 74
18	4-$MeOC_6H_4$, H	Ph	Ph	**4r**, 54
19	Ph, Ph	Ph	Ph	**4s**, 55

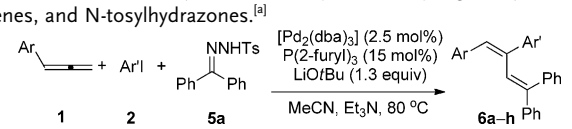
[a] All the reactions were carried out with the aryl iodide **2** (0.30 mmol), allene **1** (1.1 equiv), and diazo compound **3** (1.3 equiv) in 2.0 mL MeCN at 80°C for 1-8 h, Et_3N (200 μL) as additives. The reaction was monitored by TLC. [b] Yield of isolated product.

As for the diazo compound component, the reaction tolerates a relatively small range of substituents and functional groups (Table 2, entries 9–15). In the case when there is a strong electron-withdrawing group, such as *p*-NO_2, only a trace amount of the 1,3-diene product was detected. When there is a strong electron-donating group, the yield of the product was also slightly diminished (Table 2, entry 13). Finally, the reaction scope of the allenes was examined (Table 2, entries 16–20). It was noted that both monosubstituted allenes and 1,1-disubstituted allenes can be employed in this transformation. The reaction is not significantly affected by the electronic effects of the substituents.

N-tosylhydrazones, which are easily prepared from aldehydes or ketones, can generate unstabilized diazo substrates in situ in the presence of a base.[6b–d] Thus, to further expand the scope of the three-component coupling reaction, the N-tosylhydrazone **5a** was employed as model substrate in the coupling under slightly modified reaction conditions (Table 3). Thus, treatment of aryl iodides (**1**) and allenes (**2**) with **5a** in the presence of $[Pd_2(dba)_3]$, P(2-furyl)$_3$, Li*O*t*Bu*, and Et_3N at 80°C furnished the corresponding products dienes in moderate to good yields as a single stereoisomer in each case. The only exception was that when a sterically hindered iodide was used as substrate, only trace amounts of the 1,3-diene product were detected. The reaction resulted in complex mixture (Table 3, entry 2).

Finally, this three-component coupling reaction was applied to the synthesis of ferrocenyl 1,3-butadiene deriva-

Table 3: Palladium-catalyzed three-component coupling of aryl iodides, allenes, and N-tosylhydrazones.[a]



Entry	**1** Ar	**2** Ar′	**6** Yield [%][b]
1	Ph	4-MeC_6H_4	**6a**, 81
2	Ph	2-MeC_6H_4	**6b**, –[c]
3	Ph	4-PhC_6H_4	**6c**, 77
4	Ph	4-$MeOC_6H_4$	**6d**, 69
5	Ph	4-ClC_6H_4	**6e**, 74
6	4-MeC_6H_4	4-MeC_6H_4	**6f**, 76
7	4-$MeOC_6H_4$	4-MeC_6H_4	**6g**, 48
8	4-ClC_6H_4	4-MeC_6H_4	**6h**, 66

[a] All the reactions were carried out with the aryl iodide **2** (0.20 mmol), allene **1** (1.1 equiv), and N-tosylhydrazone **5** (1.1 equiv) in 2.0 mL MeCN at 80 °C for 6 h, Et_3N (200 μL) as additives. The reaction was monitored by TLC. [b] Yield of the isolated product. [c] Trace product was detected by GC-MS. dba = dibenzylideneacetone.

tives. Ferrocenyl 1,3-butadienes have found important applications in various fields, such as special polymers used for coating materials in aerospace transportation.[13] However, the synthetic methods to access such type of compounds are very limited.[14]

We found that under slightly modified reaction conditions (Table 4), the $Pd(OAc)_2$-catalyzed coupling of ferrocenyl allenes, aryl iodides, and aryldiazoacetates led to the formation of (2*E*,4*E*)-ferrocenyl 1,3-butadienes in good yields. Notably, no phosphine ligand is needed in these reactions. Various substitutions on the aromatic ring could be tolerated. In contrast to the results shown in Table 2, the coupling reaction with ferrocenyl allene also afforded (2*E*,4*Z*)-butadienes as minor products in most cases. The structure of the product **8e** was confirmed by X-ray crystallographic analysis (Figure 2).

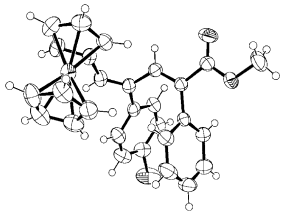
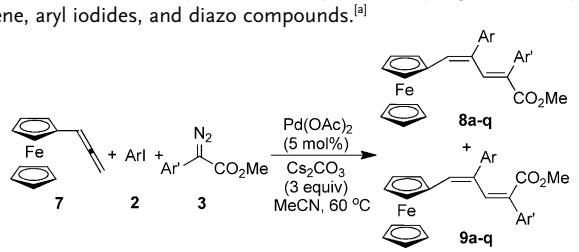


Figure 2. X-Ray structure of **8e**.[19] Thermal ellipsoids shown at 30% probability.

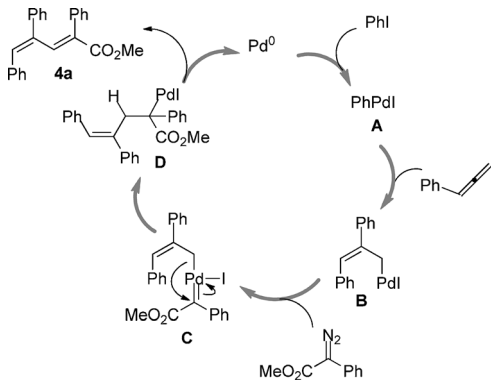
Based on our understanding on the palladium-catalyzed cross-coupling reaction of diazo compounds or N-tosylhydrazones, we propose a plausible mechanism to account for the palladium-catalyzed three-component coupling as shown in Scheme 2. The reaction is initiated by oxidative addition of Pd^0 to the aryl iodide to afford the Pd^{II} intermediate **A**. The π-allyl palladium intermediate **B** is then generated from the carbopalladation of **A** to the allene.[15,16] Decomposition of diazo substrate by the π-allylic Pd^{II} species **B** leads to the palladium carbene intermediate **C**. Migratory insertion of an allyl group to the carbenic carbon atom gives the intermediate **D**, having an *E* configuration of the formed double bond.[17] Finally, β-hydride elimination from **D** affords the diene product **4a** and regenerates the catalyst with the assistance of base.

Table 4: Palladium-catalyzed three-component coupling of ferrocenyl allene, aryl iodides, and diazo compounds.[a]



Entry	**2** Ar	**3** Ar′	**8/9** Yield [%][b]	Ratio
1	Ph	Ph	**8a/9a**, 74	83:17
2	4-MeC_6H_4	Ph	**8b/9b**, 68	90:10
3	4-$MeOC_6H_4$	Ph	**8c/9c**, 79	87:13
4	4-ClC_6H_4	Ph	**8d/9d**,93	88:12
5	4-BrC_6H_4	Ph	**8e/9e**, 93	82:18
6	4-Me(O)CC_6H_4	Ph	**8f/9f**, 73	100:0
7	4-$MeO_2CC_6H_4$	Ph	**8g/9g**, 81	100:0
8	2-$MeO_2CC_6H_4$	Ph	**8h/9h**, 68	82:18
9	3-$MeO_2CC_6H_4$	Ph	**8i/9i**, 67	87:13
10	4-$O_2NC_6H_4$	Ph	**8j/9j**, 90	86:14
11	Ph	4-$MeOC_6H_4$	**8k/9k**, 61	79:21
12	Ph	2-ClC_6H_4	**8l/9l**, 87	86:14
13	Ph	3-ClC_6H_4	**8m/9m**, 89	88:12
14	Ph	4-ClC_6H_4	**8n/9n**, 61	81:19
15	Ph	4-BrC_6H_4	**8o/9o**, 67	84:16
16	Ph	4-$O_2NC_6H_4$	**8p/9p**, 46	84:16

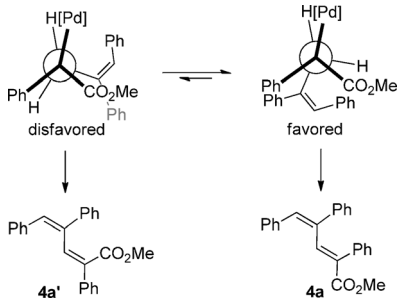
[a] All the reactions were carried out with allene **7** (0.30 mmol), aryl iodide **2** (0.45 mmol), and diazo compound **3** (0.36 mmol) in 2.0 mL MeCN at 60 °C for 3–12 h. The reaction was monitored by TLC. [b] Yield for the isolated and inseparable mixture of **8** and **9**.



Scheme 2. Mechanistic rationale.

The high stereoselectivity for the *E*,*E*-1,3-diene formation might be interpreted by the transition state of the *syn* β-hydride elimination process from **D**, as shown in Scheme 3. Caused by the attractive π–π stacking interaction,[18] the phenyl-substituted alkenyl moiety is preferred to eclipse with the phenyl group, thus leading to the (*E*,*E*)-1,3-diene **4a** as the major product.

In summary, we have developed a new method for the synthesis of 1,3-dienes from aryl iodides, allenes, and either diazo compounds or N-tosylhydrazones. Mechanistically, the reaction involves carbopalladium of allene and migratory



Scheme 3. Rationalization of stereoselectivity.

insertion of palladium carbene. Further exploitation of other types of multicomponent reactions based on the migratory insertion of a palladium carbene to achieve unprecedented organic transformations is currently underway in our laboratory.

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[19] CCDC 948712 (**4a**) and 948713 (**8e**) 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.

