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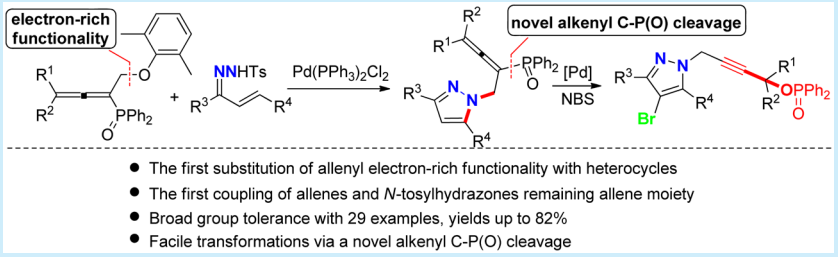
Palladium-Catalyzed Cleavage of α-Allenylic Aryl Ether toward Pyrazolemethylene-Substituted Phosphinyl Allenes and Their Transformations via Alkenyl C−P(O) Cleavage

Jie Zhu,[†,§] Mao Mao,[†,§] Huan-Jing Ji,[†] Jiang-Yan Xu,[†] and Lei Wu*[,†,‡]

[†]Jiangsu Key Laboratory of Pesticide Science and Department of Chemistry, College of Sciences, Nanjing Agricultural University, Nanjing, China

[‡]Beijing National Laboratory for Molecular Sciences and Institute of Chemistry, Chinese Academy of Sciences, Beijing, P. R. China

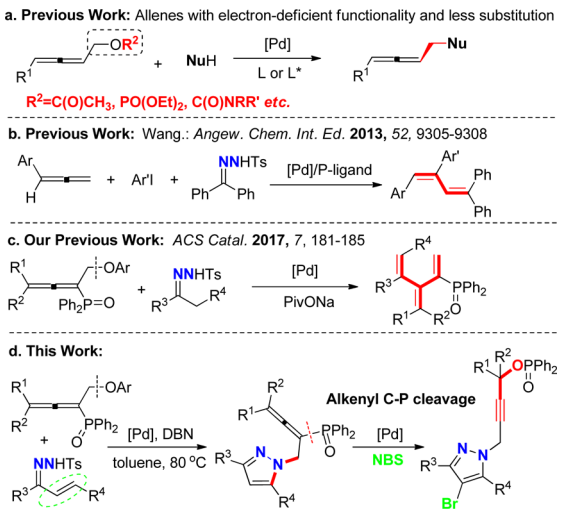
Supporting Information



ABSTRACT: A palladium-catalyzed two-component coupling of allenylphosphine oxides with conjugated *N*-tosylhydrazones is revealed. For the first time, the cleavage of α-allenylic aryl ether toward pyrazolemethylene-substituted phosphinyl allenes enabled facile synthesis of combined motifs with pyrazole and allene. Moreover, the obtained adducts could be easily transformed to potential bioactive multifunctionalized phosphinates via a novel alkenyl C−P(O) cleavage.

Allenes, or 1,2-dienes, are core structures in many naturally occurring biomolecules and synthetic pharmaceuticals.[1] In addition to the cumulated diene structure, the potential for up to four substituents also make them important building blocks in organic synthesis, especially for bioactive compounds. The importance of allenes necessitates extensive explorations on their transformations and synthesis during the past two decades.[2] On one side, various transformations from allenes to other functionalities have been demonstrated including transition-metal catalyzed intermolecular/intramolecular cycloaddition,[3] nucleophilic addition,[4] oxidative carbocyclization,[5] and others.[6−10] The importance of allene moieties has, on the other hand, stimulated substantial interest in constructing versatile allene compounds. Traditional methods to prepare allenes generally lie on monoalkenes, conjugated enynes, alkynes, cyclopropanes, and propargylic fragments as starting materials.[2c,11] Due to the unique activity of cumulate diene, direct functionalization of allenes to obtain allenes is appealing[9a,12,13] but challenging, which would include maintenance of the 1,2-diene moiety against forming alkenes in the presence of a transition-metal catalyst and electrophilic/nucleophilic reagents, generally via the generation of π-allylmetal species followed by a β-hydride elimination process. For elegant studies, Ma's group developed palladium-catalyzed amination of allenyl phosphates and allenyl *N*-tosylcarbamates respectively generating 2,3-allenyl amines with central chirality, in which allenes remained unchanged in the presence of palladium species.[13d,e] Of note, the scope of allene precursors is currently limited to a few substituents with electron-deficient functionalities as good leaving groups, such as acetates, carbonates, halides, and pseudohalides (Scheme 1a).[13] The cleavage of fragments with

Scheme 1. (a) Representative Allenes Synthesis with Electron-Deficient Functionalities; (b and c) Allenes and *N*-Tosylhydrazones involved Catalysis; (d) This Work



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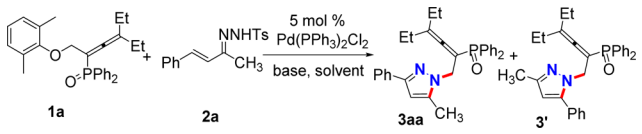
electron-rich functionalities to generate π-allyl-Pd species is challenging but attractive;[14] however, this protocol has not been established in allenes synthesis yet. Considering the importance of allenes, as well as the limitation of reported methods, efficient synthetic strategies for construction of multisubstituted allenes from diverse functionalized allenes, along with their innovative transformations, are still highly desirable.

Over the past decade, *N*-tosylhydrazones, after pioneering work by Barluenga and Valdés,[15] have emerged as versatile building blocks for transition-metal catalyzed coupling reactions, most often with palladium complexes to access alkenes.[16] In general, the reaction intermediates undergo migratory insertion of palladium carbenes, which is unambiguously compatible with allene chemistry. Many achievements have been devoted to converting *N*-tosylhydrazones into allenes,[17] yet the transition-metal catalyzed coupling reactions involving *N*-tosylhydrazones and allenes are rather underdeveloped.[18,19a] Pioneering work was reported by Wang's group in 2013 (Scheme 1b), who discovered the first synthesis of 1,3-dienes through three-component coupling of allenes, aryl-iodides, and *N*-tosylhydrazones, possibly through π-allyl-Pd-carbene intermediates.[18a] Very recently, we advanced the synthesis of a new member of dendralenes family, multisubstituted (*Z*)-selective phosphinyl [3]dendralenes, from the palladium-catalyzed two-component coupling of allenyl-phosphine oxides and *N*-tosylhydrazones (Scheme 1c).[19a] Intriguingly, conjugated *N*-tosylhydrazones changed the coupling pathway against the formation of conjugated alkenes, as illustrated in Scheme 1d. In continuation of our interest in organo-phosphorus and heterocyclic chemistry,[19] herein, we disclose a palladium-catalyzed cleavage of allenyl electron-rich functionality to finalize pyrazolemethylene-substituted phosphinyl allenes. The allene moiety is maintained in the palladium-catalysis system, offering the first synthesis of combined motifs with pyrazole and allene, to our knowledge.[20] Besides, a novel palladium-catalyzed alkenyl C−P(O) bond cleavage of the pyrazolemethylene-substituted phosphinyl allenes to multifunctionalized phosphinates is established (Scheme 1d).

With allenylphosphine oxide (**1a**)[21] and conjugated *N*-tosyl-hydrazone (**2a**) as model substrates, the reaction was initially carried out in the presence of bis(triphenylphosphine) palladium dichloride, K_2CO_3, and refluxing 1,4-dioxane, furnishing **3aa** in 41% yield, along with 38% of **3′** (entry 1). Systematic screenings of the conditions were then performed, as shown in Table 1 (see Supporting Information (SI) for more details). The results indicated that bases played key roles in achieving high regioselectivity when forming the C−N bond between allene and pyrazole. The effect of inorganic bases adversely affected regioselectivity, giving a mixture of **3aa** and **3′** with ratios of around 1:1. Organic bases, on the other hand, prominently inhibited the generation of **3′**, albeit only moderate yields of **3aa** were obtained. Considering both efficiency and regioselectivity, DBN (1,5-diazabicyclonon-5-ene) was chosen for the following optimizations. Further improvements were discovered from screening substrate ratios, reaction temperature, and solvents (in SI). The reaction was found to be significantly affected by the solvents used, where a protic solvent led to no conversion of allenes. To our delight, toluene was found to increase the yield of **3aa** up to 81% without the detection of **3′** (entry 3). Other transition-metal catalysts, including $Pd(OAc)_2$, $Pd(PPh_3)_4$, $Ni(PPh_3)Cl_2$, and $Rh(PPh_3)_3Cl$, were also tested, which were observed to be ineffective with lower yields or less regioselectivity (entries 4−7). Eventually, $Pd(PPh_3)_2Cl_2$ was proven to be the best catalyst to enable the reaction.

Encouraged by the preliminary results, we next investigated the substrate scope of various allenylphosphine oxides (**1a**−**1n**), as listed in Scheme 2. In general, allenylphosphine oxides with terminal alkyl, cyclic, or aromatic substitutions afforded the corresponding adducts (**3aa**−**3la**, **3oa**) with moderate to good yields. Though the cleavage of cyclopropane usually occurred in palladium catalysis,[22] cyclopropane substitution on allenes remains intact in this protocol (**3ca**, **3da**) excluding the possibility of a metal−carbene mechanism. For allenes with aromatic substitutions, both an electron-rich group (such as *p*-MeO) and electron-deficient group (such as *p*-F and *p*-Cl) on the phenyl ring were effective in achieving the reaction, without observation of a distinct electronic effect. Moreover, the existence of the allene moiety in the molecule and the regioselectivity of C−N formation were exemplified by the X-ray crystal structure of *racemic*-**3ka** (see details in the Supporting Information (SI)).[23] It is worthy to mention that dimethyl and cyclohexyl terminated substrates (**1m**, **1n**) became slightly complicated, with only a trace amount of products detected. Quite interestingly, in sharp contrast, cycloheptanone derived allenes proceeded smoothly to furnish a 33% yield of product (**3oa**). This differentiation might be attributed to the competing rates of a side reaction and the desired coupling for specific substrates.

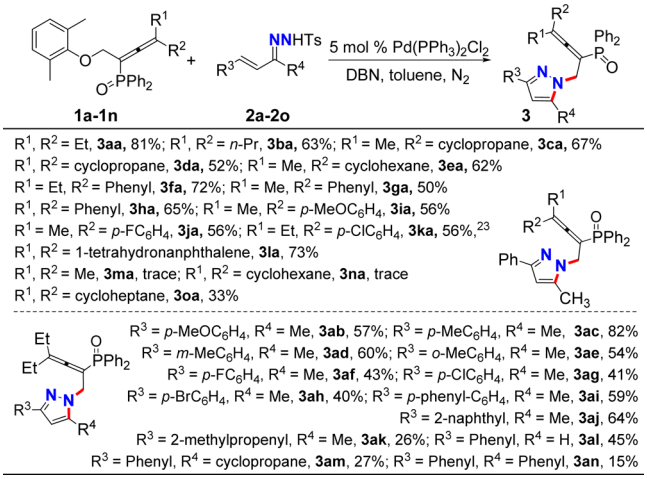
Table 1. Optimization of Reaction Conditions[a,b]



entry	catalyst	base	solvent/temp (°C)	yield (**3aa**/**3′**, %)
1	$Pd(PPh_3)_2Cl_2$	K_2CO_3	1,4-dioxane/110	41/38
2	$Pd(PPh_3)_2Cl_2$	DBN	1,4-dioxane/110	42/0
3	**$Pd(PPh_3)_2Cl_2$**	**DBN**	**toluene/80**	**81/0**
4	$Pd(OAc)_2$	DBN	toluene/80	34/<5
5	$Pd(PPh_3)_4$	DBN	toluene/80	73/0
6	$Ni(PPh_3)_2Cl_2$	DBN	toluene/80	45/<5
7	$Rh(PPh_3)_3Cl$	DBN	toluene/80	42/<5

[a]Reaction conditions: allenylphosphine oxide (**1a**, 0.2 mmol), *N*-tosylhydrazone (**2a**, 0.4 mmol), 5 mol % catalyst, 0.6 mmol of base, N_2, 12 h. [b]Isolated yield by chromatography.

Scheme 2. Substrate Scopes



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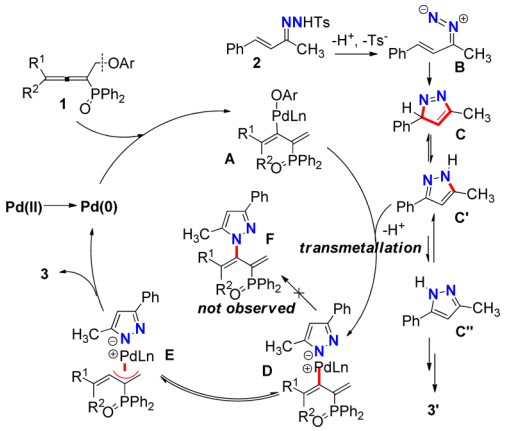
Next, the nature of *N*-tosylhydrazones was examined to verify the generality of this protocol (Scheme 2). *N*-Tosylhydra-zones, bearing OMe, CH_3, NEt_2, F, Cl, or Br groups, were all well tolerated, affording the pyrazole functionalized allenes smoothly. *Para*-substituted halogens (F, Cl, and Br) impaired the reactivity to some extent, giving lower yields compared with electron-donating groups (**3af**–**3ah**). Notably, naphthyl, biphenyl, and aliphatic *N*-tosylhydrazones also proceeded efficiently in this regime with yields of 64%, 59%, and 26% respectively (**3aj**, **3ak**, and **3al**), which further extended the substrate scope greatly. Besides, when R^4 = H, cyclic or aromatic substitutions were also found to be applicable in addition to methyl, with relatively lower yields ranging from 15% to 45%.

Based on the palladium-catalyzed allene chemistry, *N*-tosylhydrazones, and previous reports,[13,19a,24] a tentative mechanism is proposed in Scheme 3. The reaction starts with

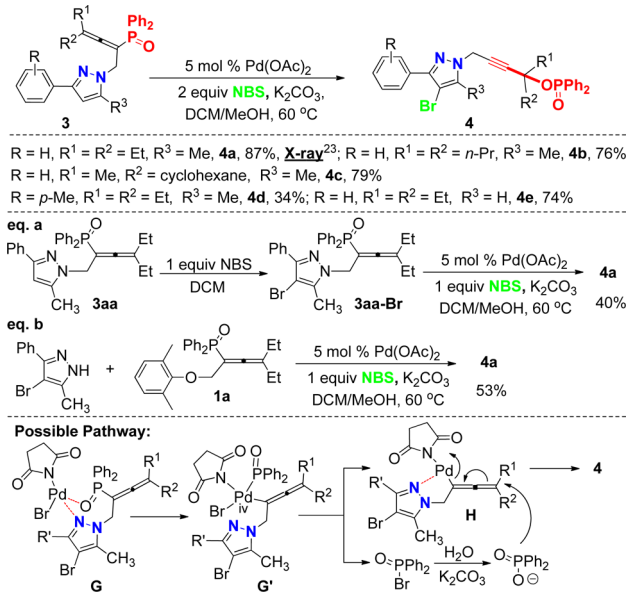
Scheme 3. Tentative Mechanism



the cleavage of the C(sp^3)–O(Ar) bond, which leads to the formation of π-allyl-palladium species **A**. Simultaneously, pyrazole compound **C**/**C′** is formed from the *in situ* generated diazo substrate **B**, with **C′** likley being the major product owing to the larger conjugation. Subsequent transmetalation between **A** and **C′** produces intermediates **D** and **E**. Afterward, reductive elimination of palladium species **E** toward C–N bond formation occurs successfully to finally generate the product **3**, along with recycling of the palladium(0) catalyst. Likewise, the reductive elimination of **D** will furnish a 1,3-diene product (**F**), which is not observed at all. On the other hand, the byproduct **3′** obtained from **C″** is inhibited under the optimized conditions.

To further demonstrate the synthetic applications of our developed protocol, further transformations were performed with pyrazolemethylene-substituted phosphinyl allenes. While the substrates (**3aa**, **3ba**, **3ea**, **3ac**, and **3al**) were treated with 5 mol % palladium acetate and 2 equiv of NBS under air, a series of novel multifunctionalized phosphinates (**4**) formed in "one pot" with acceptable to good yields, ranging from 34% to 87% (Scheme 4). The X-ray crystal structure of **4a** unambiguously displayed an alkenyl C–P(O) cleavage and rearrangement of diphenylphosphine oxide to the endmost carbon of allenes.[23] Although the cleavage of aryl C–P(O) has been sporadically documented,[25] this type of alkenyl C–P(O) bond cleavage is unprecedented and interesting. Control experiments were then conducted to determine the mechanism. In the case of allenes without a pyrazole moiety (**1a**), transformations in the absence of NBS or under anhydrous conditions led to negative results (see more details in the SI). More importantly, sequential bromination and

Scheme 4. Transformations and the Tentative Mechanism



C–P cleavage were conducted as well. As shown in eq a, the first step between **3aa** and NBS became slightly complicated in part because of the addition of Br^+ to the central carbon of allenes.[26a] However, while the crude adducts containing the brominated allene (**3aa-Br**) were treated with 1 equiv of NBS under the standard conditions, a 40% yield of target compound (**4a**) was isolated. Similarly, the coupling of brominated pyrazole and the starting allene (**1a**) afforded **4a** in 53% yield (eq b), which is considerably lower than that from the nonbrominated procedure. This decrease in yield might be attributed to the competing coupling of heterobromide with allenes.[26b] The above-mentioned experimental results collectively indicated two issues: (1) the pyrazole moiety should be involved in the alkenyl C–P(O) cleavage step; (2) NBS plays a dual role in bromination of the pyrazole moiety and generating phosphinates. A possible pathway is described in Scheme 4. The cleavage of the N–Br bond of NBS by a palladium species followed by coordination will form a key intermediate **G**,[27,28] which undergoes an oxidative alkenyl C–P(O) cleavage process to a Pd(IV) species (**G′**). Subsequently, reductive elimination of **G′** gives **H**, with the release of diphenylphosphinic bromide. Spontaneous nucleophilic attack of a diphenylphosphinate anion to the endmost position will lead to the formation of the final product (**4**) and recycling of the palladium catalyst.

In summary, we reported here the first example of two-component coupling between allenes and conjugated *N*-tosyl-hydrazones, in which the allene structure was maintained in the palladium-catalyzed cleavage of the allenyl electron-rich functionality. The reaction tolerated various functional groups and furnished a series of novel pyrazolemethylene-substituted phosphinyl allenes in acceptable to good yields. The obtained adducts can be easily transformed into multifunctionalized phosphinates via a novel alkenyl C–P(O) cleavage. We believe this novel protocol and transformations would enrich the allene chemistry and provide novel scaffolds to constitute bioactive compounds as well.

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00213.

Experimental procedures and spectral data for all new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: rickywu@njau.edu.cn.

ORCID

Lei Wu: 0000-0001-9130-6619

Author Contributions

§J.Z. and M.M. contributed equally.

Notes

The authors declare no competing financial interest.

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