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Copper-Catalyzed Direct Coupling of Unprotected Propargylic Alcohols with P(O)H Compounds: Access to Allenylphosphoryl Compounds under Ligand- and Base-Free Conditions

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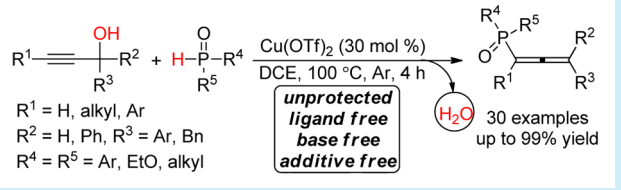
Supporting Information

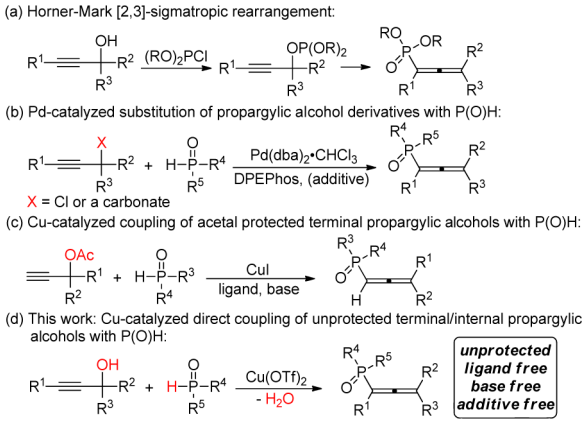
ABSTRACT: The first facile and efficient copper-catalyzed direct C−P cross-coupling of unprotected propargylic alcohols with P(O)H compounds has been developed, providing a general, one-step approach to construct valuable allenylphosphoryl frameworks with operational simplicity and high step- and atom-economy under ligand-, base-, and additive-free conditions.



Allenes are versatile building blocks with broad applications in modern synthetic chemistry,[1] and they are extremely important subunits in a variety of natural products and pharmaceutical molecules. Further, allenes have attracted continuous attention over the past few decades due to their unique cumulene structure and unusual biological activities.[2] Among them, allenylphosphoryl compounds including allenyl phosphonates, phosphinates, and phosphine oxides are an important class of allene-containing, extremely versatile reagents in organic chemistry, especially for the preparation of structurally diverse organophosphorus compounds including useful chiral phosphorus compounds[3] and phosphorus heterocycles of pharmaceutical interest[4] via selective addition with various electrophiles or nucleophiles,[5] selective total or partial hydrogenation,[6] radical reactions,[7] Diels−Alder reaction,[8] or other cycloadditions.[9] In addition, some allenylphosphoryl compounds are endowed with interesting biological activities.[10] However, in contrast to their broad applications, the approach for synthesizing these motifs is scarce.[11] Among all the methods developed, the Horner−Mark [2,3]-sigmatropic rearrangement of propargyl phosphates, which is obtained from the corresponding propargylic alcohols and toxic phosphorus chlorides, is the most commonly used one so far, although it was discovered in the early 1960s, but their general use poses severe limitations due to the requirement of the previous preparation for a rearrangement precursor, poor tolerance of functional groups, low yields, and the use of unstable hazardous phosphorus chlorides (Scheme 1a).[11a−c] To overcome these drawbacks, until recently, the Pd- and Cu-catalyzed propargylic substitution reactions with P(O)H compounds have been developed to afford allenylphosphoryl moieties (Scheme 1b,c).[11d−f] Although they avoided the use of unstable hazardous phosphorus chlorides replaced by readily available and stable P(O)H compounds, it is noteworthy that the propargylic alcohols could not be directly used as coupling substrates in these methods and required previous introduction of the protecting group or derivatization, as well as the internal propargylic substrates were not suitable for the Cu-catalyzed propargylic substitution. Moreover, they also suffered from poor substrate scope, complex or well-defined ligands, or excess bases, thus increasing the cost and limiting their applications. Therefore, the development of convenient, economic, and efficient procedures to various allenylphosphoryl compounds from readily available starting substrates under ligand- and base-free conditions is still highly desirable.

In the past few years, transition-metal-catalyzed direct substitution of propargylic alcohols as a new and powerfully synthetic strategy has aroused great interests among synthetic chemists for the construction of C−C and C−heteroatom

Scheme 1. Synthetic Strategies toward Allenylphosphoryl Compounds



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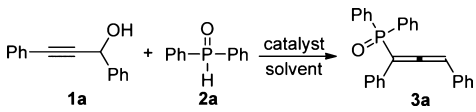
bonds[12] due to its avoidance of the protection of starting substrates and its great potential for step-economy and atom-economy. Thus, as a promising alternative, a more synthetically valuable protocol to allenylphosphoryl compounds would involve direct substitution of unprotected propargylic alcohols with P(O)H compounds since the water is the only byproduct in this transformation and the starting substrates are readily available, as well as it has remarkable advantages of both step- and atom-economy and environmental sustainability in industrial and green chemistry (Scheme 1d). However, to the best of our knowledge, no example of allenylphosphoryl compound synthesis via direct substitution of propargylic alcohols with P(O)H compounds was reported. On the other hand, development of a base-free, ligand-free, and additive-free catalysis system would be highly attractive from both environmental and economic points of view and has become an active topic in modern synthetic chemistry over the past several years.[13] As part of our ongoing endeavors to develop environmentally friendly new protocols for the P−C bond construction,[14] herein, we disclose the first example of a single-step and selective preparation of a wide range of allenylphosphoryl compounds via a facile copper-catalyzed direct substitution of unprotected terminal and internal propargylic alcohols with P(O)H compounds under ligand-free, base-free, and additive-free conditions.

Initially, our efforts focused on the model coupling reaction of 1,3-diphenylprop-2-yn-1-ol **1a** with diphenylphosphine oxide **2a** to optimize the reaction conditions. Gratifyingly, in the presence of 30 mol % of $Cu(OTf)_2$ as catalyst in toluene at 100 °C for 4 h under an argon atmosphere, the desired product **3a** was obtained in a high yield of 85% (Table 1, entry 1). Encouraged by this promising result, other solvents such as dioxane, DMF, and DCE were further investigated, and it was found that DCE was the optimal solvent for this reaction and could enhance the product yield up to 92% (entries 2−4). To advance the process further, a subsequent survey on the role of various copper salts for the aforementioned coupling disclosed $Cu(OTf)_2$ as the most favored catalyst to push the reaction forward, and other catalysts such as $Cu(acac)_2$, CuI, CuO, and $Cu(OAc)_2$ were less effective (entries 4−8). In addition, no product was observed in the absence of $Cu(OTf)_2$ (entry 9). These results illustrated that TfO^- plays a crucial role in achieving a high yield of product **3a**. Note that increasing the reaction temperature to 120 °C led to a lower yield of 83%, and decreasing the temperature to 80 °C also did not increase the yield (entries 10 and 11). Finally, the loading of $Cu(OTf)_2$ was evaluated, yet, using 20 and 10 mol % of $Cu(OTf)_2$ resulted in reduced yield (entries 12 and 13).

With the optimized reaction conditions in hand (footnote *a*, Scheme 2), we investigated the substrate scope of the coupling reaction of diphenylphosphine oxide **2a** with various substituted 1,3-diphenylprop-2-yn-1-ols. As shown in Scheme 2, this protocol was found to be quite general, and a variety of 1,3-diphenylprop-2-yn-1-ols bearing electron-donating groups and electron-withdrawing groups at the aryl ring could be used to generate the desired products (**3a**−**3s**) in good to excellent yields. Thus, various functional groups including MeO, MeS, F, Cl, Br, CF_3, and CH_3 substituents were all well-tolerated for this method. Notably, the *para*-methyl-substituted substrate **1d** and sterically demanding *ortho*-methyl-substituted counterpart **1b** afforded high yields of 86 and 99%, respectively, illustrating that the steric hindrance of substituents on the phenyls is not evident for this reaction. The bulky substrates having a naphthyl group (**1e**) and a biphenyl moiety (**1n**) were also compatible with the present reaction conditions and afforded the corresponding product **3e** and **3n** in 92 and 78% yields, respectively. In addition, some disubstituted 1,3-diphenylprop-2-yn-1-ols (**1r** and **1s**) were also detected and gave the relative products **3r** and **3s** in moderate yields. Fortunately, product **3o** was recrystallized from $CHCl_3/CH_2Cl_2$ as colorless crystals, and the molecular structure of **3o** as a mixture of enantiomers was confirmed by X-ray crystallography. The result clearly showed that the phosphoryl moiety was preferentially installed at the C3-position of propargylic alcohols in the present coupling reaction.

To extend the scope of this reaction, some other kinds of propargylic alcohols and P(O)H compounds were further evaluated. As demonstrated in Scheme 3, the reaction of tertiary

Table 1. Optimization of the Reaction Conditions[a]

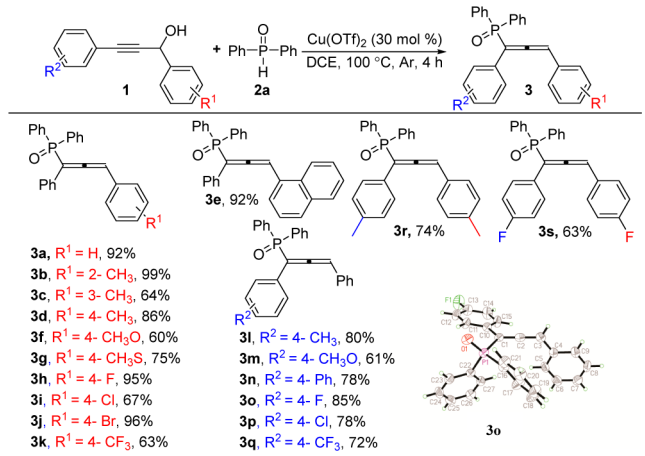


1a 2a 3a

entry	catalyst	solvent	temp (°C)	yield (%)[b]
1	$Cu(OTf)_2$	toluene	100	85
2	$Cu(OTf)_2$	dioxane	100	75
3	$Cu(OTf)_2$	DMF	100	trace
4	**$Cu(OTf)_2$**	**DCE**	**100**	**92**
5	$Cu(acac)_2$	DCE	100	17
6	CuI	DCE	100	trace
7	CuO	DCE	100	trace
8	$Cu(OAc)_2$	DCE	100	20
9		DCE	100	0
10	$Cu(OTf)_2$	DCE	120	83
11	$Cu(OTf)_2$	DCE	80	85
12	$Cu(OTf)_2$	DCE	100	78[c]
13	$Cu(OTf)_2$	DCE	100	52[d]

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.375 mmol), catalyst (30 mol %), and solvent (2.0 mL) at the indicated temperature for 4 h under argon. [b]Isolated yield. [c]Using 20 mol % of $Cu(OTf)_2$. [d]Using 10 mol % of $Cu(OTf)_2$.

Scheme 2. Cu-Catalyzed Direct Coupling of 1,3-Diphenylprop-2-yn-1-ol Derivatives with 2a[a]



[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.375 mmol), $Cu(OTf)_2$ (30 mol %), and DCE (2.0 mL) at 100 °C for 4 h under argon. Isolated yield.

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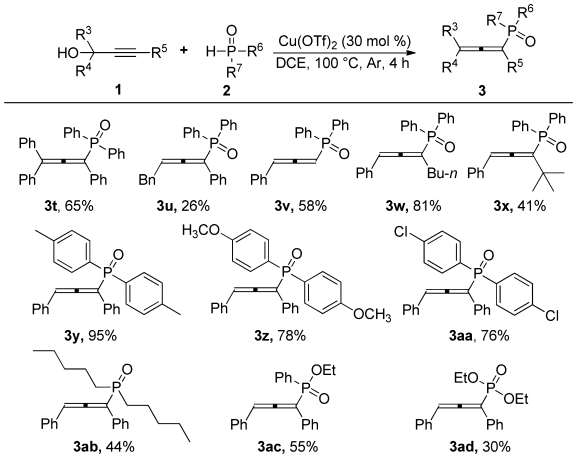
Scheme 3. Cu-Catalyzed Direct Coupling of Propargylic Derivatives with P(O)H Compounds[a]

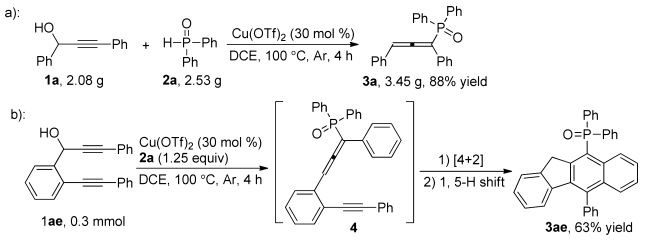


[a]Reaction conditions: **1** (0.3 mmol), **2** (0.375 mmol), $Cu(OTf)_2$ (30 mol %), and DCE (2.0 mL) at 100 °C for 4 h under argon. Isolated yield.

propargylic alcohol **1t** also efficiently gave the expected product **3t** in 65% yield. Interestingly, the terminal propargylic alcohol **1v** was also used as the coupling partner and produced the corresponding product **3v** in moderate yield. The alkyl-substituted substrates (**1w** and **1x**) could all undergo the coupling to provide the desired products (**3w** and **3x**). Yet, the benzyl-containing substrate **1u** only afforded a lower yield of 26%, probably due to poor stability of the carbocation intermediate. With regard to the P(O)H compounds, apart from **2a**, other H-phosphine oxides such as **2b**, **2c**, **2d**, and **2e** were all suitable substrates, and the corresponding products **3y**, **3z**, **3aa**, and **3ab** were obtained in 95, 78, 76, and 44% yields, respectively. In addition, H-phosphinates such as ethyl phenylphosphinate **2f** could also be transformed to the relative product **3ac** in 55% yield. However, diethyl phosphonate **2g** only provided an unsatisfactory yield of 30% in the present catalytic system, indicating that the yields depended primarily upon the electronic properties of P(O)H compounds.

To demonstrate the application of the present method, a gram-scale experiment was performed on **1a** (10 mmol) using **2a** (12.5 mmol) under the optimal reaction conditions (Scheme 4a). The

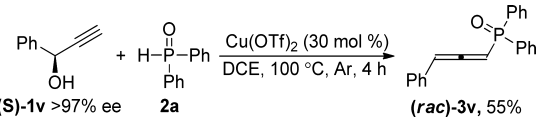
Scheme 4. Application Studies



expected product **3a** was obtained in a high yield of 88%, indicating that this approach could be easily adopted for the large-scale preparations with high efficiency. In addition, to our delight, the reaction of propargylic alcohol **1ae** with **2a** in the presence of $Cu(OTf)_2$ could directly generate a phosphorylated benzo[*b*]fluorene product **3ae** (Scheme 4b), which contains the key fluorene skeleton of importance in intriguing organic materials.[15] In contrast to the known synthetic method,[16] this strategy would open a new avenue for the creation of various unique phosphorylated benzo[*b*]fluorenes through a simple one-pot process without the need to previously prepare the intermediate **4**, improving greatly the reaction efficiency.

To gain insight into the stereochemistry of this coupling, the reaction of enantioenriched propargylic alcohol (*S*)-**1v** with **2a** was carried out under the developed conditions, and the corresponding allenylphosphoryl product **3v** was obtained in a racemic form (Scheme 5). This result demonstrated that center

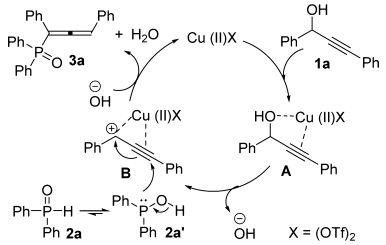
Scheme 5. Control Experiment



to axis chirality transfer exhausted stereochemical features of this allenylphosphoryl compounds synthesis and also revealed that this novel reaction might undergo an S_N1-type reaction mechanism.

Based on the above experimental results and previous reports,[17] a plausible mechanism is proposed (Scheme 6).

Scheme 6. Proposed Reaction Mechanism



Initially, the coordination of copper cation to the triple bond and OH group led to intermediate **A**. Then, the elimination of the OH group easily took place with the assistance of a Lewis acid, $Cu(OTf)_2$, to generate the key propargylic carbocation intermediate **B**.[17a] Finally, the nucleophile **2a** (in the form of the trivalent phosphine oxide **2a′**) attacked the C3-position of **B** via an S_N1-type substitution reaction to afford the desired product **3a** on the basis of the regioselectivity of this coupling.[17b] However, the details of the mechanism are not clear at present.

In conclusion, we have successfully developed the first practical and efficient Cu-catalyzed direct coupling of unprotected terminal and internal propargylic alcohols with P(O)H compounds via an S_N1-type reaction, which represents a new means for the C−P bond construction and provides a powerful synthetic tool for a structurally diverse array of special allenylphosphoryl compounds. Most attractively, only in the presence of simple and inexpensive $Cu(OTf)_2$ without the need for a base, a ligand, and an additive, various valuable allenylphosphoryl products could be conveniently obtained in a simple one-step process. Additionally, the use of inexpensive $Cu(OTf)_2$ as catalyst, directly using easily accessible propargylic alcohols producing H_2O as the only byproduct, the operational simplicity, the remarkable functional group tolerance, and the high step- and atom-economy associated with this method suggest its great potential for widespread application in the construction of important allenylphosphoryl frameworks in organic synthesis and pharmaceutical research. Further mecha-

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nistic investigations and application research are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03028.

General experimental procedures and characterization data of all products (PDF)
Crystallographic data of **3o** (CIF)

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Notes

The authors declare no competing financial interest.

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