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First Synthesis of 1-Chlorovinyl Allenes via Palladium-Catalyzed Allenylation of Alkynoates with Propargyl Alcohols

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Vinyl allenes are an important class of highly unsaturated compounds that exhibit interesting reactivity in organic transformations,[1] and have been found in natural products and other biologically active compounds.[2] Contrary to their synthetic significance, procedures for preparing vinyl allenes are unfortunately limited to indirect, multiple and complex ones, which inevitably require prefunctionalized substrates and produce large amounts of byproducts.[3] Moreover, these reactions only provide vinyl allenes without any functional substitution. Thus, a synthetically challenging and yet unachieved work is to design a direct, facile and environmentally benign route to synthesize functional-substituted vinyl allenes,[4] which can be further transformed to more synthetically valuable compounds.

During the last years, organic reactions in water have grown out from their infancy to a comparatively mature level.[5] A crucial discovery in this area is that water can improve and direct the organic process.[6] As a part of this progress, we have recently developed a novel Pd-catalyzed allylation of alkynes in the aqueous phase,[7] in which water improved the regioselectivity of the carbometalation reaction. Inspired by this result, we wished to develop a new type of palladium-catalyzed allenylation reaction[8] to construct 1,2,4-trienes from alkynes and propargyl alcohols under "on water" condition. To the best of our knowledge, this reaction represents the first general synthesis of chloro-substituted vinyl allenes via selective insertion of two different alkynes.

In our catalytic allylation system, water served as a regioselectivity promoter and enhanced the reactivity of alkynes. So, we first examined the allenylation of this reaction in the aqueous phase. However, initial efforts ended up without desired products but very chaotic reaction systems (Table 1, entries 1–4), probably due to the high instability of propargyl alcohol in the presence of both Brønsted acid and Pd salt. To our delight, a replacement of the terminal propargyl alcohol by a phenyl substituted one, which is more stable under the same condition, gave a comparatively clean reaction system and a low yield of desired product with two stereoisomers (1:1) (entry 5). Using HCl as the acid increased the yield to 32 % (entry 6), while less acidic H_3PO_4 decreased the yield to 22 %. Since the combination of phosphine ligand and water was proven to be effective in some catalytic system,[6c, 9] we then added PPh_3 and PBu_3 to this aqueous-phase reaction (entries 8 and 9). Interestingly, the presence of PBu_3 greatly increased the yield, while PPh_3 inhibited the reaction.[10] The Pd^0 catalyst was also employed but afforded lower yields,[11] indicating a Pd^{II}-initiated catalytic circle (entries 9–11). Elevating the temperature to 40 °C led to comparatively low yields probably owing to the instability of vinyl allene (entry 12). To our surprise, the attempt of adding various organic solvents to this "on water" reaction only lowered the yields and led to a Meyer–Schuster rearrangement as the side reaction (entries 13–15).[12] When we tried to create a homogeneous system by adding a large amount of MeOH (entry 16), the reaction was then blocked out. Reactions in pure organic solvent with TfOH as acid (entries 17 and 18) also gave no product but a mixture of dehydration products. These results demonstrate the reaction was accelerated by water as well as the heterogeneity of the catalytic system.

Subsequently, we explored the generality of the reaction under optimized conditions by varying propargylic alcohols and alkynoates (Table 2). Different alkyl substituents on the propargylic position (R^4, R^5), including bulky *tert*-butyl, were effective, providing desired products (entries 1, 4, 6–10). Secondary propargyl alcohol **2 f** also afforded trisubstituted allene (entry 5). Ethyl 3-phenylpropiolate was slightly more reactive than **1 a** (entries 1, 2). Of special interest is the substrate phenylpropiolic acid, which resulted in the introduction of a carboxylic acid moiety directly to the 1,3,4-

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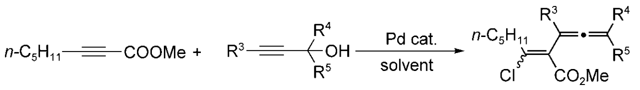
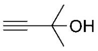
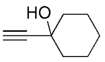
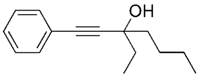
Table 1. Screening of reaction conditions and substrates.

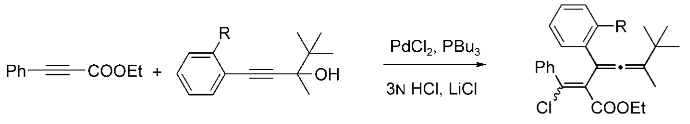


Entry[a]	Cat.	Acid [mL]	Ligand	Progargyl alcohol	Solvent	Yield [%][b] (Z/E)
1	$PdCl_2$	1 mL HOAc	–	 **2a**	neat water	–
2	$PdCl_2$	1 mL HOAc	–	**2a**	neat water	–
3	$PdCl_2$	HCl	–	**2a**	neat water	–
4	$PdCl_2$	1 mL HOAc	–	 **2b**	neat water	–
5	$PdCl_2$	1 mL HOAc	–	 **2c**	neat water	15 (1:1)
6	$PdCl_2$	1 mL 3N HCl	–	**2c**	neat water	32 (1:1)
7	$PdCl_2$	H_3PO_4	–	**2c**	neat water	22 (1:1)
8	$PdCl_2$	1 mL 3N HCl	30% PPh_3	**2c**	neat water	trace
9	$PdCl_2$	1 mL 3N HCl	30% PBu_3	**2c**	neat water	65 (1:1)
10	$Pd(OAc)_2$	1 mL 3N HCl	30% PBu_3	**2c**	neat water	64 (1:1)
11	$Pd_2(dba)_3$	1 mL 3N HCl	30% PBu_3	**2c**	neat water	trace
12[c]	$PdCl_2$	1 mL 3N HCl	30% PBu_3	**2c**	neat water	45 (2:1)
13	$PdCl_2$	1 mL 3N HCl	30% PBu_3	**2c**	0.1 mL CH_2Cl_2	55 (1:1)
14	$PdCl_2$	1 mL 3N HCl	30% PBu_3	**2c**	0.1 mL MeOH	47 (1:1)
15	$PdCl_2$	1 mL 3N HCl	30% PBu_3	**2c**	0.1 mL DMF	43 (1:1)
16	$PdCl_2$	1 mL 3N HCl	30% PBu_3	**2c**	3 mL MeOH	trace
17	$PdCl_2$	3 mmol TfOH	30% PBu_3	**2c**	1 mL CH_2Cl_2	–
18	$PdCl_2$	3 mmol TfOH	30% PBu_3	**2c**	1 mL MeCN	–

[a] Alkynoate (0.5 mmol), propargyl alchohol (1.0 mmol), Pd cat. (10 mol%), 12 h. [b] Isolated yield, Z/E ratio in the parenthesis. [c] Experiment carried out at 40 °C.

trienes without the need for functional group protection/deprotection (entry 11). Various substituents at the *para* or *meta* position were also tolerable in this allenylation process (entries 6–10). It is especially worth mentioning that when but-2-enyl oct-2-ynoate was used as a substrate (entry 12), the allyl unit survived in this Pd^{II}-catalyzed reaction (an analogous condition for intramolecular yne–ene coupling[13]) providing an interesting butenyl trienoate derivative.[14] Unfortunately, reaction of **1a** and **2n** only gave undefined complexes.[15]

An intriguing steric effect on the reactivity and selectivity for this novel allenylation process was also observed during our studies (Scheme 1). When different *ortho*-substituted phenyl propargyl alcohols were reacted with **1b**, fluorine afforded the desired product. Methoxy or chlorine substituents resulted in poor reactivity or no product at all. This obvious dependence on the size of the *ortho* group that is inserted twice in the alkynes to form a 1,3-diene carbometallic intermediate (**I** and **II** in indicates Scheme 2), in which *ortho*-substituted phenyls were trapped at a sterically hindered position. Thus, whatever side the phenyl group rotates to, it will be sterically hindered and end up in high energetic intermediates. But for R = fluorine, an atom that has almost the same radius as hydrogen, the steric hindrance was diminished and the reaction processed faster.

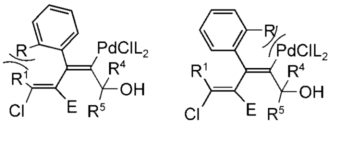


1b

2o: R = OMe
2p: R = Cl
2p: R = F

3bo: no product
3bp: yield < 5 %
3bq: yield = 40 % Z/E 4:6

Scheme 1. Effect of *ortho*-substituents on the allenylation reaction.

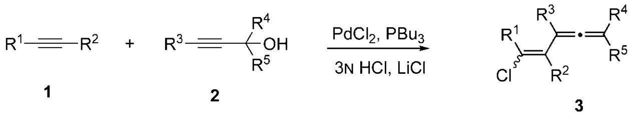


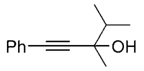
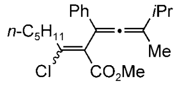
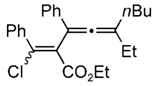
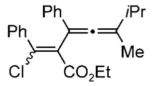
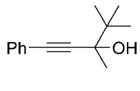
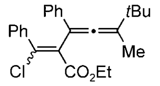
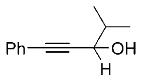
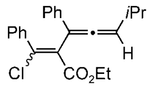
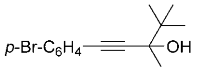
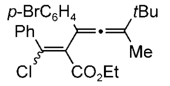
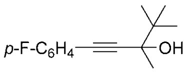
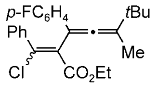
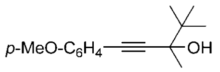
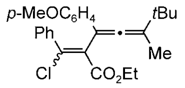
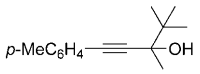
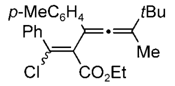
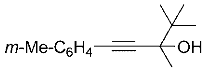
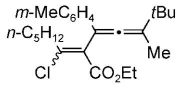
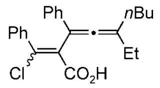
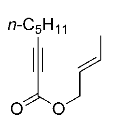
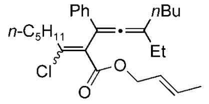
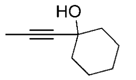
I **II**

Scheme 2. Proposed 1,3-diene carbometallic intermediates.

A tentative mechanism for the water-improved Pd^{II}-catalyzed allenylation of alkynoates is proposed in Scheme 3. Vinylpalladium intermediate **A** is initially formed by chloropalladation of alkyne **1** in aqueous/organic system. Quite different from its allylation counterpart, chloropalladation takes place without stereoselectivity.[16] Propargyl alcohol **2** then inserts into the carbon–palladium bond of vinylpalladium species to form a dienylpalladium intermediate **B**. Meanwhile, the hydroxyl is activated with the aid of acid in water, which made the subsequent β-OH elimination—a well-known challenge for Pd^{II}-catalyzed reaction—easier and smoother. Finally, **B** undergoes β-OH elimination to give

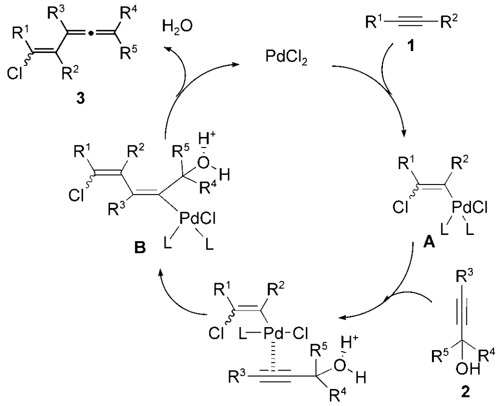
Table 2. Pd^{II}-catalyzed allenylation of alkynoates with propargyl alcohols.



Entry[a]	Alkynoates		Progargyl alcohol		Product		Yield[b] (*Z*/*E*)
1	$n\text{-}C_5H_{11}-\equiv-CO_2Me$	**1a**		**2d**	 **3ad**	**3ad**	63 (50:50)
2	$Ph-\equiv-CO_2Et$	**1b**		**2c**	 **3bc**	**3bc**	70 (50:50)
3		**1b**		**2d**	 **3bd**	**3bd**	64 (45:55)
4		**1b**		**2e**	 **3be**	**3be**	60 (43:57)
5		**1b**		**2f**	 **3bf**	**3bf**	40 (40:60)
6		**1b**		**2g**	 **3bg**	**3bg**	55 (45:55)
7		**1b**		**2h**	 **3bh**	**3bh**	57 (45:55)
8[c]		**1b**		**2k**	 **3bk**	**3bk**	52 (46:54)
9		**1b**		**2l**	 **3bl**	**3bl**	60 (45:55)
10		**1b**		**2m**	 **3bm**	**3bm**	62 (41:59)
11	$Ph-\equiv-CO_2H$	**1c**		**2c**	 **3cc**	**3cc**	59 (45:55)
12		**1d**		**2c**	 **3dc**	**3dc**	41 (95:5)
13[d]		**1a**		**2n**	–		–

[a] Alkynoate (0.5 mmol), propargyl alchohol (1.0 mmol), $PdCl_2$ (10 mol %), PBu_3 (30 %), 1 mL 3 N HCl, 12 h. [b] Isolated yield, *Z*/*E* ratio in parenthesis, determined by ^{1}H NMR. [c] EtOAc (30 mg) was added to smooth the organic phase. [d] Propargyl alchohol (2.0 mmol) was used.

the corresponding product **3** and $PdCl_2$ is regenerated in the presence of chloride source (LiCl) and acid. It is very intriguing that alkynoate and propargyl alcohol insert sequentially to form a 1,3-diene carbometallic intermediate; this affords vinyl allene as the single product and no allenylation product of progargyl alcohol or homocoupling adducts of alkynoate was detected.[17] To the best of our knowledge, selective intermolecular cross-coupling between internal alkynes under transition-metal-catalyzed conditions is very rare,[18,19] though there have been some reports on the sequential insertion of identical alkynes.[20] We assume this unprecedented selectivity was directed by i) different electronic characteristics of alkynoates and propargyl alcohols and ii) the leaving group (-OH) on propargyl alcohols that induced the further transformation of 1,3-diene organometallic intermediates.[21]



Scheme 3. Tentative mechanism for the Pd^{II}-catalyzed allenylation of alkynoates.

In conclusion, we have discovered a novel allenylation reaction of alkynoates by using inactivated propargyl alcohols as allenylating reagents in the presence of water ("on-water") without addition of organic solvent. This water-promoted reaction proceeds via selective sequential insertion of two different alkynes, which might be as a result of the leaving group (-OH) on one of the alkyne molecules. We are now exploring a series of reactions that involve two different alkynes under palladium-catalyzed conditions. Further results will be reported in due course.

Experimental Section

General methods: All reactions were performed at RT under an air atmosphere in a round bottom flask equipped with a magnetic stir bar. ^1H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were recorded using a Bruker Avance 400 MHz NMR spectrometer (100 MHz for carbon) and referenced to 7.27 and 77.0 ppm, respectively, for $CDCl_3$ solvent with TMS as an internal standard. Mass spectra were recorded on a Shimadzu GCMS-QP5050 A at an ionization voltage of 70 eV equipped with a DB-WAX capillary column (internal diameter = 0.25 mm, length = 30 m). IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Bruker Vector 22 spectrometer. TLC was performed using commercially prepared 100–400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. Compounds **2d–m** were produced according to the literature by Sonogashira coupling. All the other chemicals were purchased from Aldrich Chemicals.

General procedure for the preparation of methyl 2-(1-chlorohexylidene)-5-ethyl-3-phenylnona-3,4-dienoate (3ac): A test tube (10 mL) was charged with palladium chloride (10 mg, 0.056 mmol), LiCl (20 mg, 0.5 mmol), propargyl alcohol **2c** (108 mg, 0.5 mmol) and 3 N HCl (0.5 mL). After the mixture was stirred for 2 min, alkynoate **1a** (77 mg, 0.25 mmol) was added, followed by the addition of PBu_3 (12 mg, 0.075 mmol). The reaction was carried out at RT for 12 h (monitored by TLC). The reaction mixture was taken up by in ether (10 mL) and washed with brine (10 mL). The organic layer was dried ($MgSO_4$), concentrated in vacuo and purified by flash silica gel chromatography using petroleum ether/ethyl acetate 10:1 to give (*Z*)-**3ac** (33 mg total, 0.08 mmol, 32 %) and (*E*)-**3ac** (33 mg total, 0.08 mmol, 32 %) as yellow oils.

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Keywords: alcohols · allenes · palladium · water

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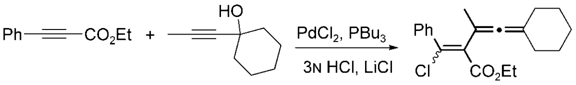

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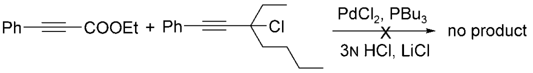

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