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# Synthesis of aryl allyl alkynes via reaction with allyl amine and aryl alkynoic acids through decarboxylation

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#### ABSTRACT

Allyl alkynoic esters were synthesized by the reaction of allyl amines and alkynoic acids via deaminative esterification. The reaction of allyl alkynoic esters with Pd(dba)<sub>2</sub> and Xantphos in digylme at 110 °C for 12 h afforded the desired decarboxylated allyl alkynes in good yields.





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#### **KEYWORDS**

Allyl alkyne; allylation; allyl amine; decarboxylation; intramolecular coupling

### Introduction

Decarboxylative coupling reactions have received considerable attention for the synthesis of key molecules in the pharmaceutical, agricultural, and materials industries.<sup>[1]</sup> Decarboxylative coupling of alkynoic acids has been widely used to introduce alkynyl groups into target molecules.<sup>[2]</sup> This approach affords several advantages compared to the Sonogashira coupling reaction, which employs terminal alkynes as the alkyne source. Aryl alkynoic acid derivatives are readily prepared via direct coupling of propiolic acid and aryl halides (or pseudo halides) and are easily purified and isolated through aqueous workup.<sup>[3]</sup> Alkynoic acids are also stable and the reaction releases only carbon dioxide, which is relatively nontoxic compared to the organometallic waste generated at the end of the coupling reaction. A variety of coupling partners have been employed for the formation of C–C, C–N, and C–P bonds in decarboxylative coupling reactions.<sup>[4]</sup> Transition-metals such as Pd, Ni, Cu, and Ag are generally used as the catalysts, and metal-free conditions have also been reported.<sup>[5]</sup>

Allyl alkynes are one of the useful building blocks in organic synthesis.<sup>[6]</sup> Several methods employing the transition-metal-catalyzed allylation of alkynes have been reported.<sup>[7]</sup> We reported the synthesis of allyl alkynes via nickel-catalyzed decarboxylative coupling of alkynoic acids and allyl acetates.<sup>[8]</sup> While this was the first example of the intermolecular decarboxylative allylation of an alkyne, intramolecular decarboxylation of allyl esters was reported by Tunge and coworkers.<sup>[9]</sup> Although they reported palladium-catalyzed intramolecular decarboxylation, they provided only a few examples

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of the decarboxylation of allyl alkynoic esters. Therefore, general methods of intramolecular decarboxylation for the synthesis of allyl alkynes are in demand.

A variety of synthetic methods for the preparation of esters have been developed. It is well known that allyl and benzyl primary amines react with carboxylic acids to give the corresponding allyl and benzyl esters via deamination in the presence of NaNO<sub>2</sub>.<sup>[10]</sup>

During our studies of decarboxylative coupling reactions, we found that the preparation of allylic alkynoic esters from the reaction with allyl amines has not been reported. In addition, only a few examples of the intramolecular decarboxylative coupling of allylic alkynoic esters have been documented.<sup>[9]</sup> Herein, we report the synthesis of allyl alkynes via the intramolecular decarboxylation of alkynoic esters, which were prepared by deamination.

#### **Results and discussion**

To accomplish this goal, we evaluated the optimal conditions for the formation of allyl esters from allyl amines and phenyl propiolic acid. When allyl amine (1) was reacted with NaNO<sub>2</sub> and phenylpropiolic acid in the presence of several solvents containing water, the desired allyl phenyl propiolate (**3a**) was formed in low yields (entries 1–3). The reactions were carried out in dried solvents, such as dioxane, CH<sub>3</sub>CN, and toluene to give the desired product **3a** in 52, 26, and 31% yield, respectively (entries 4–6). When the amount of phenylpropiolic acid was increased to three equivalents, **3a** was formed in 86% yield (entry 7). By employing HCl instead of additional phenylpropiolic acid, the desired product was obtained in 92% yield when the reaction was conducted with one equivalent of HCl (entry 8). However, the addition of two equivalents of HCl with 1.0 equivalent of phenylpropiolic acid did not provide a satisfactory result (entry 9). The optimal conditions for the preparation of allyl alkynoic esters are as follows: allyl amine (1.0 equiv), HCl (1.0 equiv), and NaNO<sub>2</sub> (2.0 equiv) were reacted at 0 °C for 30 min; alkynoic acid (2.0 equiv) was then added to the reaction mixture and stirred at 25 °C for 6 h (Table 1).

	$NH_2 + NH_2 + HO Ph$	NaNO2 O   Solvent O   0 °C -> 25 °C, 6 h	Ph 3a
	Ratio		
Entry	<b>1a</b> /NaNO <sub>2</sub> / <b>2a</b>	Solvent	Yield (%) <sup>u</sup>
1	1/2/2	Dioxane/H <sub>2</sub> O	19
2	1/2/2	CH <sub>3</sub> CN/H <sub>2</sub> O	12
3	1/2/2	Toluene/H <sub>2</sub> O	Trace
4	1/2/2	Dioxane	52
5	1/2/2	CH₃CN	26
5	1/2/2	Toluene	32
7	1/2/3	Dioxane	86
3 <sup>b</sup>	1/2/2	Dioxane	92
9°	1/2/1	Dioxane	45

Table 1. Optimal conditions for deaminative esterification
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<sup>a</sup>Reaction conditions: **1a** (0.3 mmol) and NaNO<sub>2</sub> were reacted at 0  $^{\circ}$ C for 30 min; **2a** was then added and the reaction proceeded at 25  $^{\circ}$ C for 6 h.

<sup>b</sup>HCI (0.3 mmol) was added.

<sup>c</sup>HCI (0.6 mmol) was added.

<sup>d</sup>Determined by <sup>1</sup>H NMR with internal standard.

	Ph	Pd (10 mol%) Solvent 110 °C, 12 h	Ph/ 4a	
Entry	Pd	Ligand	Solvent	Yield (%) <sup>b</sup>
1	$Pd(PPh_3)_4$	-	Toluene	77
2	Pd(dba) <sub>2</sub>	PPh <sub>3</sub>	Toluene	60
3	$Pd(dba)_2$	Dppb	Toluene	67
4	$Pd(dba)_2$	Xantphos	Toluene	82
5	$Pd(dba)_2$	Xantphos	Diglyme	91
6	$Pd(dba)_2$	Xantphos	DMŚO	24
7	Pd(dba) <sub>2</sub>	Xantphos	DMF	47

Table 2. Optimal conditions for intramolecular decarboxylation <sup>4</sup>	а
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<sup>a</sup>Reaction conditions: **3a** (0.3 mmol), Pd (0.03 mmol), and ligand (0.06 mmol) were reacted in solvent (1.0 mL) at 110 °C for 12 h. <sup>b</sup>Determined by <sup>1</sup>H NMR with internal standard.

Further, the conditions for the intramolecular decarboxylation were optimized. When  $Pd(PPh_3)_4$  was employed and the reaction was allowed to proceed at 100 °C for 12 h, the desired decarboxylated allyl alkyne **4a** was formed in 77% yield (entry 1). The use of  $Pd(dba)_2$  as a palladium source for reaction with ligands like PPh<sub>3</sub>, 1,4-bis(diphenyl-phosphino)butane (dppb), and Xantphos afforded the desired product **4a** in 60, 67, and 82% yields, respectively (entries 2–4). The highest product yield was obtained with digylme as the solvent (entries 5–7) (Table 2).

Under the optimal conditions, various aryl alkynoic acids were evaluated for the formation of allyl alkynoic esters. As expected, when phenylpropiolic acid was employed under the optimal conditions, the desired product **3a** was obtained in 90% isolated yield. The reactions with *ortho-*, *meta-*, and *para-*methyl substituted phenylpropiolic acids afforded the allylated products **3b**, **3c**, and **3d** in 62, 85, and 65% yields. In addition, the reactions with *ortho-*, *meta-*, and *para-*methoxy-substituted phenylpropiolic acids also afforded good yields of the allylated congeners. 4-Biphenyl and 1-naphthyl propiolic acids gave the corresponding products **3h** and **3i** in 63 and 80% yields, respectively. 4-Bromophenylpropiolic acid gave **3j** in 63% yield. Phenylpropiolic acids having ketone and ester groups provided the desired products **3k** and **3l**, respectively, in good yields (Scheme 1).

The intramolecular decarboxylation was conducted with these allyl alkynoic esters. Phenylpropiolic acid provided the desired allyl alkyne **4a** in 90% isolated yield. Methyland methoxy-substituted allyl phenylpropiolates afforded the desired products in good yields. Allyl 4-biphenylpropiolate **3h** gave **4h** in 72% yield. Allyl 4-acetylphenylpropiolate **3k** also provided **4k** in 55% yield. However, the desired products were not obtained in pure form via reactions with other allyl propiolates, such as **3i**, **3j**, and **3l**. They all showed many unidentified spots in TLC (Scheme 2).

#### Conclusion

In summary, allyl alkynoic esters were synthesized via deaminative esterification. The reaction of an allyl amine, NaNO<sub>2</sub>, HCl, and alkynoic acid in a ratio of 1:2:1:2 afforded the desired allyl alkynoic esters in good yields. Pd(dba)<sub>2</sub>/Xantphos was the optimal catalytic system for intramolecular decarboxylation in the synthesis of allyl alkynes.



Scheme 1. Synthesis of allyl alkynoic esters<sup>a</sup>. <sup>a</sup>Reaction conditions: 1 (1.0 mmol), NaNO<sub>2</sub> (2.0 mmol), and HCl (1.0 mmol) were reacted at 0 °C for 30 min and reacted with 2 (2.0 mmol) at 25 °C for 6 h. Numbers in parentheses are isolated yields.

# **Experimental details**

All solvents and reagents were purchased and used without further purification. Thinlayer chromatography (TLC) on precoated plated of silica gel was performed on TLC silica gel 60 F254 with ethyl acetate/n-hexane (2:8) systems. Preparative flash chromatography was performed by elution from columns of silica gel (230–400 mesh size). The TLC plates were visualized by shortwave (254 nm) UV light. Melting points were determined on a capillary melting point apparatus and are uncorrected using electrothermal melting point apparatus. <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (125 MHz) spectra were recorded in CDCl<sub>3</sub> using VARIAN VnmrJ. Chemical shifts are given in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal reference and coupling constants (*J*-values) are in hertz (Hz).

# General procedure for the synthesis of ally alkynoic esters

The aqueous solution of HCl (1.0 mmol) and NaNO<sub>2</sub> (2.0 mmol) was mixed with allyl amine (1.0 mmol) in 1,4-dioxane (5 mL). The resulting mixture was stirred about 30 min at 0 °C. After that, phenylpropiolic acid (2.0 mmol) was added to the mixture and stirred at room temperature for 6 h. The reaction mixture was diluted with EtOAc, and



Scheme 2. Synthesis of allyl alkynes<sup>a</sup>. <sup>a</sup>Reaction conditions: 3 (1.0 mmol), Pd(dba)<sub>2</sub> (0.1 mmol), and Xantphos (0.2 mmol) were reacted in diglyme at 110 °C for 12 h. Numbers in parentheses are isolated yields.

washed with water for three times. The organic layer was dried over  $MgSO_4$  and then the solvent was evaporated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexane:EtOA = 10:1).

Aryl allyl propiolate (1.0 mmol), Pd(dba)<sub>2</sub> (0.1 mmol) and Xantphos (0.2 mmol) were mixed in diglyme at 110 °C for 12 h. The resulting mixture was diluted with EtOAc and washed with water. The organic layer was dried over MgSO<sub>4</sub> and then the solvent was evaporated under reduced pressure. The crude mixture was purified by column chromatography on silica gel (hexane:EtOA = 20:1).

#### **Selected product**

#### Allyl 3-phenylpropiolate (3a)

Propiolic acid (146.0 mg, 1.0 mmol) afforded **3a** (167.4 mg, 0.9 mmol, 90% yield) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61–7.58 (m, 2H), 7.49–7.36 (m, 3H), 5.98 (ddt, *J*=17.1, 10.4, 5.9 Hz, 1H), 5.44–5.38 (m, 1H), 5.34–5.30 (m, 1H), 4.74–4.72 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.8, 133.1, 131.2, 130.7, 128.6, 119.54, 119.49, 86.6, 80.4, 66.6; MS (EI) *m/z*: 186; Anal. Calcd for for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>: C, 77.40; H, 5.41; Found: C, 77.51; H, 5.55.<sup>[11]</sup>

#### Pent-4-en-1-ynyl benzene (4a)

Allyl 3-phenylpropiolate (186.2 mg, 1.0 mmol) afforded **4a** (127.8 mg, 0.9 mmol, 90%) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45–7.40 (m, 2H), 7.31–7.26 (m, 3H),

5.96–5.84 (m, 1H), 5.44–5.38 (m, 1H), 5.19–5.15 (m, 1H), 3.20 (dt, J = 5.3, 1.8 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  132.5, 131.6, 128.2, 127.8, 123.7, 116.3, 86.6, 82.9, 23.7; MS (EI) *m/z*: 142; Anal. Calcd for C<sub>11</sub>H<sub>10</sub>: C, 92.91; H, 7.09; Found: C, 92.88; H, 7.12.<sup>[9b]</sup>

Full experimental detail and <sup>1</sup>H and <sup>13</sup>C NMR spectra have been provided in supporting information. This material can be found via the "Supplementary Content" section of this article's webpage.

# **Disclosure statement**

No potential conflict of interest was reported by the author(s).

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