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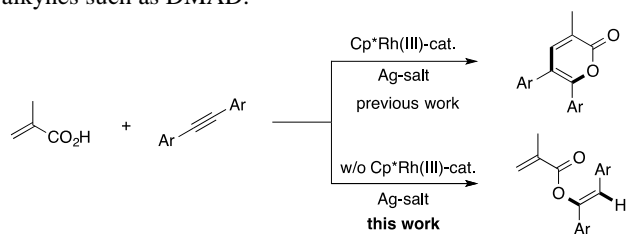
Synthesis of Enol Esters through Silver-Catalyzed or -Mediated Hydroacyloxylation of Internal Alkynes

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The silver-catalyzed hydroacyloxylation of internal alkynes with tertiary alkanoic acids proceeds stereoselectively to produce (*Z*)-enol esters. α,β -Unsaturated carboxylic acids and benzoic acids also undergo silver-mediated addition toward alkynes effectively. Keywords: silver catalyst; hydroacyloxylation, internal alkyne

Carboxylic acids have been recognized as one of the most promising building blocks in modern organic synthesis, because of their ready availability and stability. A variety of their direct transformation methods have been developed.¹ For example, we have reported that α,β -unsaturated carboxylic acids such as methacrylic acid undergo rhodium(III)-catalyzed oxidative coupling with diarylacetylenes in the presence of a silver salt as an oxidant to produce 5,6-diaryl- α -pyrone derivatives (Scheme 1).² During our further study, we unexpectedly found that treatment of the same substrates without the rhodium catalyst induces the stereoselective addition of the carboxylic function across the triple bond of alkynes (hydroacyloxylation) to selectively afford (*Z*)-enol esters. Enol esters are now utilized as important monomers in the polymer industry.³ Furthermore, they are also employed as substrates in various synthetic transformation including cycloaddition and condensation.⁴ Among synthetic approaches toward enol esters, the hydroacyloxylation appears to provide the most promising route from the atom- and step-economical points of view. Although many reports for the transition-metal-catalyzed and -mediated addition of carboxylic acids to dialkylacetylenes and activated internal alkynes have been disclosed,⁵ most of them are not applicable to less reactive diarylacetylenes. The (*Z*)-selective hydroacyloxylation of diarylacetylenes are so far limited to few examples using expensive gold catalysts.^{6,7} Relatively less expensive silver salts have been shown to be effective to promote the hydroacyloxylation of only activated internal alkynes such as DMAD.⁸



Scheme 1.

In an initial attempt, pivalic acid (**1a**, 4 mmol) was treated with diphenylacetylene (**2a**, 0.5 mmol) in the presence of AgOAc (0.5 mmol) under Ar in PhCN at 140 °C for 28 h. As a result, an adduct, (*Z*)-1,2-diphenylethenyl pivalate (**3aa**),

was stereoselectively formed in 75% yield (entry 1 in Table 1). The (*Z*)-geometry was confirmed by X-ray crystal structure analysis (Figure 1). Even in the case using a decreased amount (0.15 mmol, 30 mol%) of AgOAc, **3aa** was obtained in a comparable yield by extending the reaction time (entry 3). Under the catalytic conditions, the addition of tetramethylammonium acetate (0.05 mmol, 10 mol%) was found to promote the reaction: **3aa** was obtained in 75% yield within 68 h (entry 4).⁹ Further decrease of the amount of AgOAc to 20 mol% slightly reduced the reaction efficiency (entry 5). Decreasing the amount of **1a** also resulted in a lower yield of **3aa** (entry 6). At 120 °C, the reaction was sluggish (entry 7).

Table 1. Reaction of Pivalic Acid (**1a**) with Diphenylacetylene (**2a**)

entry	AgOAc (mmol)	Me ₄ N ⁺ (OAc) ⁻	time (h)	yield of 3aa ^b (%)
1	0.5	–	28	75
2	0.25	–	20	76
3	0.15	–	125	73
4	0.15	+	68	75 (56)
5	0.1	+	91	65
6 ^c	0.15	+	63	64
7 ^d	0.15	+	116	46

^a Reaction conditions: **1a** (4 mmol), **2a** (0.5 mmol), (Me₄N⁺(OAc)⁻ (0.05 mmol)) in PhCN (2.5 mL) at 140 °C under Ar, unless otherwise noted. ^b GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification. ^c With **1a** (2 mmol). ^d At 120 °C.

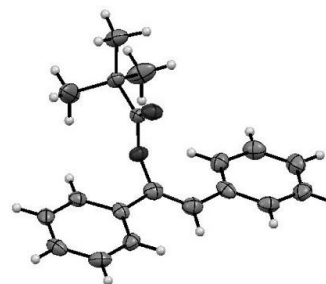


Figure 1. ORTEP drawing of compound **3aa**. Crystal data: C₁₉H₂₀O₂, Mw = 280.37, triclinic, space group *P*-1 (#2), *T* = 123 K, *a* = 5.735(3), *b* = 15.213(9), *c* = 17.848(10), β = 93.908(8), *V* = 1548.9(15), *Z* = 4, 6962 reflections measured, *R* = 0.0558, *R*_w = 0.1516.

We next examined the reactions of **1a** with various alkynes (Table 2). The reaction with *p*-methyl and *p*-chloro substituted diphenylacetylenes **2b** and **2c** selectively gave the corresponding enol esters **3ab** and **3ac**, respectively (entries 1 and 2). The reactions with unsymmetrical alkynes such as 1-phenyl-1-propyne (**2d**) and 1-phenyl-1-hexyne (**2e**) proceeded in good regioselectivities to produce **3ad** and **3ae** predominantly (entries 3 and 4). The acyloxylation by **1a** occurred at the most electrophilic carbon, as in previous gold-catalyzed reactions.^{6a} Expectedly, complete regio- and stereoselectivities were observed in the reaction with ethyl phenylpropiolate (**2f**) to give **3af** exclusively in 80% yield

Table 2. Reaction of Alkanoic Acids **1** with Alkynes **2**

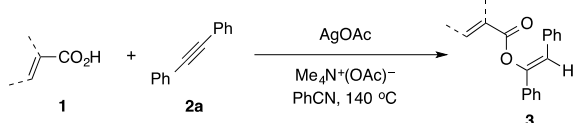

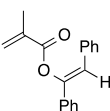
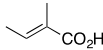
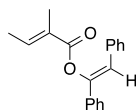

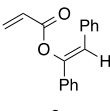
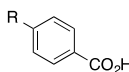
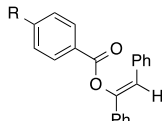
$\text{R}^1\text{-CO}_2\text{H} + \text{R}^2\text{-C}\equiv\text{C-R}^3 \xrightarrow[\text{Me}_4\text{N}^+(\text{OAc})^-, \text{PhCN}, 140^\circ\text{C}]{\text{AgOAc}} \text{R}^1\text{-O-C(=O)-C(R}^2\text{)=C(R}^3\text{)-H}$					
entry	1	2	Time (h)	product	% yield ^b
1	1a	2b : R = Me	72	3ab : R = Me	72 (53)
2	1a	2c : R = Cl	53	3ac : R = Cl	68 (61)
3 ^c	1a	2d : R = Me	23	3ad + 3ad' : ^d R = Me	78 (49)
4 ^c	1a	2e : R = Bu	22	3ae + 3ae' : ^e R = Bu	88 (67)
5 ^c	1a	2f	3	3af	80 (78)
6	1b	2a	96	3ba	81 (63)
7 ^f	1c	2a	75	3ca	51 (45)
8 ^f	1d	2a	44	3da	81 (49)

^a Reaction conditions: **1** (4 mmol), **2** (0.5 mmol), AgOAc (0.15 mmol), Me₄N⁺(OAc)⁻ (0.05 mmol) in PhCN (2.5 mL) at 140 °C under Ar, unless otherwise noted. ^b GC yield based on the amount of **2** used. Value in parentheses indicates yield after purification. ^c With **1a** (2 mmol). ^d **3ad**: **3ad'** = 17 : 1. ^e **3ae**: **3ae'** = 8 : 1. ^f With AgOAc (0.4 mmol).

(entry 5). Alkynes **2d-f** were significantly reactive compared to sterically hindered diarylacetylenes. Thus, their reactions completed within 3-23 h even under conditions using a decreased amount (2 mmol) of **1a**. Other alkanolic acids, 2,2-dimethylbutanoic acid (**1b**), 1-adamantanecarboxylic acid (**1c**), and cyclohexanecarboxylic acid (**1d**) also underwent the hydroacyloxylation of **2a** to afford **3ba**, **3ca**, and **3da** selectively (entries 6-8). In cases with **1c** and **1d**, increased amounts (0.4 mmol) of AgOAc were needed to conduct the reaction smoothly.

In addition to alkanolic acids, α,β-unsaturated carboxylic acids and benzoic acids could also be employed for the hydroacyloxylation of **2a** (Table 3). Treatment of methacrylic acid (**1e**, 4 mmol) with **2a** (0.5 mmol) in the presence of AgOAc (0.4 mmol) and tetramethylammonium acetate (0.1 mmol) under Ar in PhCN at 140 °C for 41 h gave the corresponding (*Z*)-adduct **3ea** in 76% yield (entry 1). As in the cases with **1c** and **1d** (entries 7 and 8 in Table 2), decreasing the amount of AgOAc to 0.15 mmol gave a lower product yield (entry 2). Tiglic acid (**1f**) and acrylic acid (**1g**)

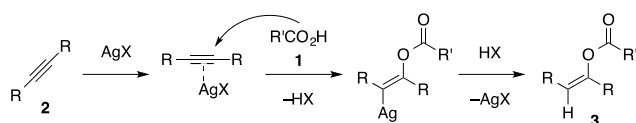
Table 3. Reaction of α,β-Unsaturated and Benzoic Acids **1** with Diphenylacetylene (**2a**)

				
entry	1	Time (h)	product	% yield ^b
1		41		76 (60)
2 ^c	1e	24	3ea	55
3		53		64 (43)
4		19		44 (43)
5		40		86 (57)
6 ^c	1h : R = H	75	3ha : R = H	78
7	1i : R = Me	51	3ia : R = Me	62 (47)
8	1j : R = Br	66	3ja : R = Br	52 (40)

^a Reaction conditions: **1** (4 mmol), **2** (0.5 mmol), AgOAc (0.4 mmol), Me₄N⁺(OAc)⁻ (0.1 mmol) in PhCN (2.5 mL) at 140 °C under Ar, unless otherwise noted. ^b GC yield based on the amount of **2** used. Value in parentheses indicates yield after purification. ^c With AgOAc (0.15 mmol).

could also be used for the hydroacyloxylation to produce **3fa** and **3ga**, respectively (entries 3 and 4). Similarly, benzoic acid (**1h**) reacted with **2a** more efficiently under conditions using 0.4 mmol of AgOAc rather than the catalytic conditions to produce **3ha** in 86% yield (entry 5 versus entry 6). The reactions of 4-toluic acid (**1i**) and 4-bromobenzoic acid (**1j**) with **2a** proceeded in similar manners to give **3ia** and **3ja** (entries 7 and 8).

Although the mechanism for the present reaction has not been extensively investigated yet, the reaction seems to proceed in a similar pathway to that in a gold-catalyzed reaction^{6a} through coordination of alkyne **2** to a silver center, nucleophilic attack by a carboxylic oxygen on the alkyne triple bond in an anti fashion, and subsequent protonation (Scheme 2). The exact role of tetramethylammonium acetate is obscure at the present stage.



Scheme 2.

In summary, we have demonstrated that various carboxylic acids undergo stereoselective addition across internal alkynes under silver-catalyzed or -mediated conditions. This procedure provides a straightforward approach to a variety of (*Z*)-enol esters.

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Supporting Information is available electronically on J-STAGE.

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- With other silver salt catalysts, AgOCOCF₃ and AgOTf, the **3aa** yield decreased to 27 and 2%, respectively.

Graphical Abstract	
Textual Information	
A brief abstract	The silver-catalyzed hydroacyloxylation of internal alkynes with tertiary alkanoic acids proceeds stereoselectively to produce (Z)-enol esters. α,β -Unsaturated carboxylic acids and benzoic acids also undergo silver-mediated addition toward alkynes effectively.
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Authors' Names	Nanae Kikui, Tomoaki Hinoue, Yoshinosuke Usuki, and Tetsuya Satoh
Graphical Information	
<p>Chemical reaction scheme showing the synthesis of enol esters. The reaction involves the silver-catalyzed hydroacyloxylation of internal alkynes with tertiary alkanoic acids. The reactants are $R^1\text{-CO}_2\text{H}$, $R^2\text{-CH=CH-CO}_2\text{H}$ (with R^3 at the α position), and $R^4\text{-C}_6\text{H}_4\text{-CO}_2\text{H}$ (where R^4 is a para-substituent). The alkyne is $R^5\text{-C}\equiv\text{C-R}^6$. The reaction is catalyzed by AgOAc and $\text{Me}_4\text{N}^+(\text{OAc})^-$. The products are three enol esters: 1) $R^1\text{-CO}_2\text{-CH=CH-R}^5$ (with R^6 at the β position), 2) $R^2\text{-CH=CH-CO}_2\text{-CH=CH-R}^5$ (with R^6 at the β position), and 3) $R^4\text{-C}_6\text{H}_4\text{-CO}_2\text{-CH=CH-R}^5$ (with R^6 at the β position).</p>	