Stereoselective Addition of Alcohol to Acetylenecarboxylate Catalyzed by Silver(I) Salt

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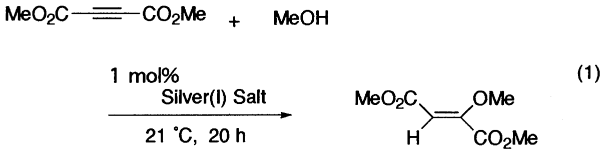
A silver(I) salt catalyzed the stereoselective *trans* addition of alcohol to dimethyl acetylenedicarboxylate smoothly under mild conditions to afford dimethyl methoxyfumarate in a quantitative yield.

It has been widely known that a silver(I) salt catalyzes the formation of heterocycles by intramolecular addition of alcohols,[1] acids and their derivatives,[2] hydroxylamines,[3] or amines[4] to a C-C unsaturated bond. Although several groups showed the intermolecular version by other catalyst,[5-9] the example of a silver salt has not been reported except the addition of carboxylic acids.[10] Herein we report that a silver salt is an efficient catalyst for the stereo- and regioselective addition of alcohols to alkynes activated by ester groups.

The catalytic activity of a silver(I) salt was tested for the reaction of dimethyl acetylenedicarboxylate (DMAD) with MeOH. Reaction of DMAD (5.0 mmol) with MeOH (2.0 mL) in the presence of silver trifluoromethanesulfonate (AgOTf) (0.05 mmol, 1 mol%) at 21 °C for 20 h gave dimethyl methoxyfumarate (**1**) quantitatively (eq 1). The formation of the *Z*-vinyl ether **1** indicated that the reaction proceeded by the *trans* addition of MeOH to DMAD. $AgPF_6$, $AgBF_4$, and $AgClO_4$ showed similar catalytic activity and $AgNO_3$ did a moderate activity (72% yield), but other silver(I) salts, such as Ag_2O, AgCl and Ag_2CO_3, were ineffective. The inefficiency is considered to be partly due to their low solubility in MeOH. The reaction was facilitated by heating at 70 °C and dimethyl methoxyfumarate **1** was obtained quantitatively within 1.5 h. The opposite stereoisomer, dimethyl methoxymaleate (the *E*-vinyl ether), was not detected at all in the reaction mixture.



(1)

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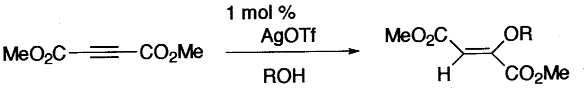
A silver(I) salt, AgOTf, was found to catalyze the addition of a variety of alcohols to DMAD as shown in Table 1. Judging from the consumption of the starting DMAD, almost all of the alcohols examined underwent the addition to DMAD to give the corresponding vinyl ethers, while the addition of phenol did not proceed at all under the present conditions (run 7). Less hindered alcohols such as EtOH, *i*-PrOH, and $PhCH_2OH$ gave *Z*-vinyl ethers exclusively as MeOH did. The addition of bulkier alcohol, *t*-BuOH, was very slow and the resulting tert-butyl vinyl ether was easily hydrolyzed to give dimethyl oxalacetate (run 3).[11] The vinyl ether obtained from allyl alcohol was transformed into the tricarbonyl compound **3** by the following Claisen rearrangement.[12] Reaction of propargyl alcohol with DMAD gave a complex mixture due to polymerization of the product, propargyl vinyl ether.

Table 1. Addition of alcohol to DMAD catalyzed by AgOTf [a]



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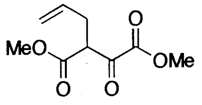
run	ROH	Time / h	Convn. of DMAD / % [b]	Yield / % [c] **2**
1	EtOH	4	100	87
2	*i*-PrOH	7	100	87
3	*t*-BuOH	20	92	10 [d]
4	$PhCH_2OH$	20	100	86
5	Allyl Alcohol	20	100	0 [e]
6	Propargyl Alcohol	20	100	0 [f]
7	PhOH	20	0 [g]	--

[a] The reactions were carried out at 70 °C under Ar atmosphere by employing DMAD (5.0 mmol), alcohol (2.0 mL) and AgOTf (0.05 mmol, 1 mol%).
[b] Conversion was determined by GLC. [c] Isolated yield.
[d] Dimethyl oxalacetate was isolated in 38% yield.
[e] Claisen rearrangement product of the vinyl ether **3** was isolated in 81% yield.
[f] Complex mixture.
[g] DMAD was recovered in 98% isolated yield.



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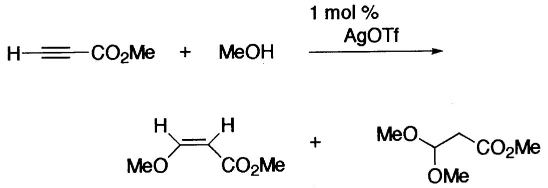
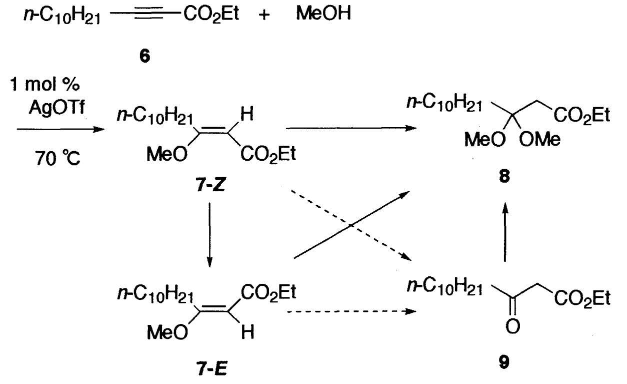


(2)

		4	**5**
21 °C	20 h :	81 % (Z only)	0 %
70 °C	20 h :	78 % (Z only)	4 %

Reaction of a terminal alkyne, methyl propynoate, with MeOH in the presence of 1 mol% AgOTf at 21 °C for 20 h gave *Z*-methyl 3-methoxyacrylate (**4**) in 81% isolated yield, which was also obtained by *trans* addition of MeOH. The reaction at 70 °C for 20 h gave **4** in 78% yield along with an acetal **5** in 4% yield (eq 2). During the first 2 h, the methyl propynoate was completely consumed to give the (*Z*)-vinyl ether but the acetal **5** was not detected at all. The addition of MeOH to the resulting vinyl ether proceeded slowly under these conditions. The addition of MeOH to non-activated alkyne such as 1-dodecyne, phenylacetylene, 6-dodecyne or tolane was not observed under similar conditions employed for DMAD (70 °C, 20 h).[13]

The internal alkyne which has one ester group, ethyl 2-tridecynoate (**6**), however, reacted with MeOH in the presence of a silver(I) salt at 70 °C for 20 h to afford a mixture of vinyl ether **7**, acetal **8** and ketone **9** (Table 2). Although several products were obtained in this reaction, the regioselectivity for the addition of MeOH was completely controlled; that is, the MeO group was introduced only to the β-position of the ester group. The yield of the vinyl ether increased gradually with the reaction time, but decreased after prolonged heating. As the reaction proceeded, the ratio of *E*-isomer increased, and after 20 h the ratio of the *E* and *Z* isomers reached to 81 / 19. These reactions can be explained by Scheme 1; (i) the *trans* addition of MeOH to the alkyne **6** to form *Z*-vinyl ether (ii) the isomerization of the *Z*-vinyl ether to the *E*-vinyl ether and then (iii) the addition of the second molecule of MeOH to the vinyl ether affording the acetal **8**.[14] When a small amount of *p*-TsOH was added to the reaction mixture obtained by the catalytic reaction for 20 h, the ketone **9** was isolated in 99% yield (run 4). Thus, acetylene carboxylate can be transformed to the corresponding β-keto ester by a one-pot reaction.



Scheme 1.

Table 2. Addition of MeOH to ethyl 2-dodecynoate catalyzed by AgOTf[a]

run	Time / h	Convn. of **6** / %	Yield / % **7**	(*E* / *Z*)[b]	**8**	**9**
1	2	34	17	(35 / 65)	4	0
2	8	80	52	(44 / 56)	23	0
3	20	100	32	(81 / 19)	54	4
4[c]	20	100	0	---	0	99

[a] Reaction conditions: See Table 1.
[b] The ratio of *E* and *Z* isomers was determined by ^{1}H NMR.
[c] *p*-TsOH was added before purification.

We are now investigating the role of the silver salts in this catalytic system. This research was supported by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan (#05234217).

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14 In the reaction of DMAD with MeOH, an acetal product prepared from the second addition of MeOH to the vinyl ether **1** was not obtained at all, even if a prolonged reaction time was employed. When propan-1,3-diol was used as an alcohol, DMAD gave only the corresponding γ-hydroxypropyl vinyl ether, but ethyl 2-tridecynoate (**6**) formed a mixture of the corresponding cyclic acetal and ketone. The reason why the second addition of alcohol to vinyl ether **7** occurred smoothly is not clear at present.