

NOVEL SYNTHESIS OF ENOL ESTERS THROUGH SILVER-CATALYZED REACTION OF  
ACETYLENIC COMPOUNDS WITH CARBOXYLIC ACIDS

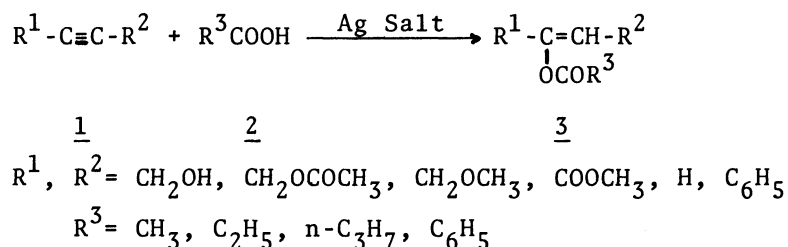
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It was found that the reactions of 1,4-diacetoxy-2-butyne and related acetylenic compounds with carboxylic acids are efficiently catalyzed by silver salts to give the corresponding enol acetates in good yield.

Much attention has been focused on useful application of 2-butyne-1,4-diol and its derivatives to organic synthesis, and on extensive utilization in industry.<sup>1)</sup> For example, we have already reported a facile synthesis of 2,3-diaryl-1,3-butadienes from the reaction of 1,4-dimethoxy-2-butyne with Grignard reagents in the presence of copper(I) salts.<sup>2)</sup>

In this communication, we wish to describe a versatile method for synthesis of enol esters through silver-catalyzed addition of carboxylic acids to 1,4-diacetoxy-2-butyne and related acetylenic compounds.



The hitherto known methods<sup>3-6)</sup> for the addition of carboxylic acid to a carbon-carbon triple bond have not been so useful in organic synthesis owing to low yield, troublesome procedure, or employment of poisonous reagents.

The present method for transformation of acetylenic alcohols to the correspond-

ing enol esters is characterized by simple procedure, unique pattern of the reaction and good yield. A typical procedure is as follows: To a solution of 0.01 mole of 1,4-diacetoxy-2-butyne(1a) in 10ml of acetic acid(2a) was added 0.05 g(0.00018 mole) of silver carbonate in small portions during 1/2 hr at 80 °C with stirring under nitrogen atmosphere. After the addition, the mixture was stirred at 110 °C for 6 hr. Then the solvent was evaporated out under reduced pressure, and distillation or/and column chromatography of the organic residue gave 1,2,4-triacetoxy-2-butene (3a) as a single product in a 80 % yield: bp. 160 °C/27 mmHg. NMR(CCl<sub>4</sub>, ppm)  $\delta$  = 2.00 [d. (J=4.0 Hz), 6H], 2.18[s. 3H], 4.53-4.75[m. 4H], 5.73 and 5.69[t. (J=7.2 Hz), 1H]. MASS: m/e=170(M<sup>+</sup>-HOAc). IR(neat, cm<sup>-1</sup>) 1739.

Catalytic activities of a variety of metal salts in the reaction 1a with 2a are summarized in Table 1. It is interesting that silver carbonate shows the best reactivity among them. While mercury acetate is known as common catalyst for usual electrophilic reactions of ethynyl bond<sup>3-6</sup>), treatment of 1a with mercury acetate under the similar conditions as reported in the literature gave 3a only in a poor yield. Also as is shown in Table I, 0.05 g of silver carbonate(0.0181 eq. mole based on 1a) was enough to promote the present reaction.

Table 1 Catalytic Activities of a Variety of Metal Salts in the Reaction of 1a with 2a

Metal Salt	Amount(g) *	Yield of <u>3a</u> (%)
none	-	0
Ag <sub>2</sub> CO <sub>3</sub>	0.01(0.0036)	65
Ag <sub>2</sub> CO <sub>3</sub>	0.05(0.0181)	80
Ag <sub>2</sub> CO <sub>3</sub>	0.10(0.0363)	73
Ag <sub>2</sub> CO <sub>3</sub>	0.50(0.1813)	72
AgOAc	0.05(0.0300)	53
AgNO <sub>3</sub>	0.05(0.0294)	49
Ag <sub>2</sub> SO <sub>4</sub>	0.50(0.1604)	3
Hg(OAc) <sub>2</sub>	0.50(0.1569)	26
CuCl	0.50(0.0551)	0

\* The numbers in the parentheses show equivalent mole of each metal salt based on 1a.

Under the similar conditions, the addition of a variety of carboxylic acids to 1a and related acetylenic compounds easily took place to give the corresponding enol esters in good yields(Table 2). It may be quite noteworthy that the silver-catalyzed reaction also successfully proceeded with dimethyl acetylenedicarboxylate in which

the ethynyl bond were substituted by typical electron-withdrawing groups. The mixture of enol acetates 4 and 5 (ratio of 4/5 = ca. 2.0) were obtained from the reaction of 1d with acetic acid, indicating some regioselectivity of the reaction.

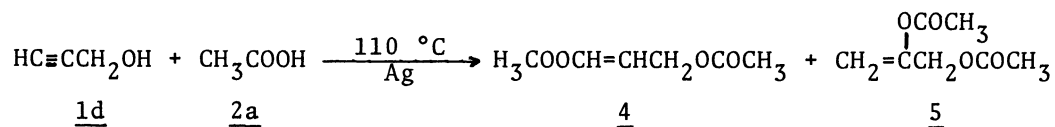


Table 2 The Silver-Catalyzed Reaction of Acetylenic Compounds with Carboxylic Acids

Carboxylic Acids						
	$\begin{matrix} & \text{R}^1 & & \text{R}^2 \\ & \diagup & & \diagdown \\ \text{R}^1 & -\text{C}\equiv\text{C}- & \text{R}^2 \end{matrix}$ (1)		$\begin{matrix} & \text{R}^3 \\ & \diagup \\ \text{R}^3 & \text{COOH} \end{matrix}$ (2)	$\begin{matrix} & \text{OCOR}^3 \\ & \diagup \\ \text{R}^1 & -\text{C}=\text{CH}- & \text{R}^2 \end{matrix}$ (3)	Stereoisomeric ratio <sup>*1</sup>	
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>		isolated yield(%)	
<u>1a</u>	H <sub>3</sub> CCOOCH <sub>2</sub>	H <sub>3</sub> CCOOCH <sub>2</sub>	CH <sub>3</sub> (2a)		80	8/2
			C <sub>2</sub> H <sub>5</sub> (2b)		83	8/2
			n-C <sub>3</sub> H <sub>5</sub> (2c)		94	7/3
			C <sub>6</sub> H <sub>5</sub> (2d)		53	6/4
<u>1b</u>	H <sub>3</sub> COCH <sub>2</sub>	H <sub>3</sub> COCH <sub>2</sub>	CH <sub>3</sub> (2a)		49	9/1
			C <sub>2</sub> H <sub>5</sub> (2b)		55	9/1
			C <sub>6</sub> H <sub>5</sub> (2d)		69	9/1
<u>1c</u>	H <sub>3</sub> COOC	H <sub>3</sub> COOC	CH <sub>3</sub> (2a)		60	9/1
<u>1d</u>	H	HOCH <sub>2</sub>	CH <sub>3</sub> (2a)		63 <sup>*2,3</sup>	6/4 <sup>*7</sup>
<u>1e</u>	C <sub>6</sub> H <sub>5</sub>	HOCH <sub>2</sub>	CH <sub>3</sub> (2a)		54 <sup>*2,4</sup>	9/1
<u>1f</u>	C <sub>6</sub> H <sub>5</sub>	H	CH <sub>3</sub> (2a)		28 <sup>*5</sup>	-
<u>1g</u>	C <sub>6</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub> (2a)		0 <sup>*6</sup>	-

\*1 The stereoisomeric ratio for each product was determined by gas chromatographic technique.<sup>7)</sup>

\*2 All the hydroxyl groups of 3 were acetylated.

\*3 The isomeric mixture of 4 and 5.

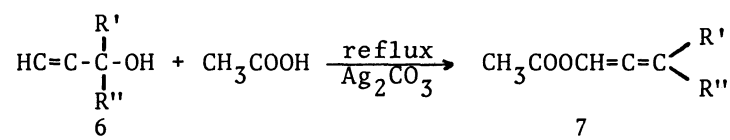
\*4 Based on the consumed starting acetylene (conversion: 53 %).

\*5 Acetophenone was also formed in a 23 % yield.

\*6 Propiophenone was formed in a 60 % yield.

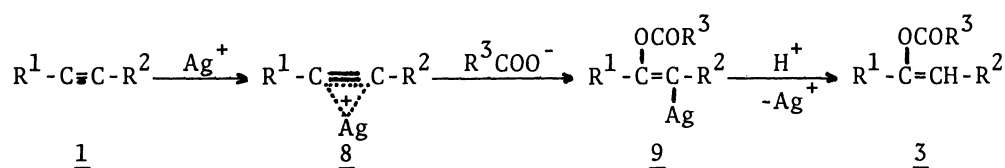
\*7 The ratio for 4.

It has been reported that an acyloxyallene 7 was obtained from the similar silver-catalyzed reaction of an acetylenic tertiary alcohols 6 with acetic acid<sup>9)</sup>, which may give a distinct contrast with the present result.<sup>10)</sup>



Although the detailed mechanism of the present reaction does not seem simple,

it may be proposed as one of the most plausible pathways that initial electrophilic addition of a silver cation to a ethynyl bond gives a  $\pi$ -complex 8, which is successively transformed to the corresponding  $\sigma$ -complex 9 by electrophilic attack of a carboxylate anion. The silver complex 9 may be so reactive as to be decomposed to an enol ester 3 by substitution of the silver atom with a proton, while the corresponding mercury<sup>11)</sup> or thallium complex<sup>12)</sup> was isolated. Therefore, a catalytic amount of a silver salt may be enough effective to promote the esterification of acetylenic compounds, which may be quite significant in organic synthesis.



#### References and Notes

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- 10) Further study on these contrasting behaviours is in progress.
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