Tetrahedron Letters,Vol.27,No.14,pp 1573-1574,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain

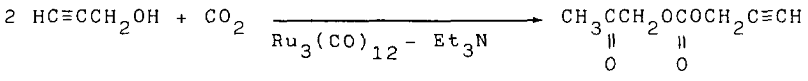
REACTION OF CARBON DIOXIDE WITH PROPARGYL ALCOHOL CATALYZED BY A COMBINATION OF $Ru_3(CO)_{12}$ AND Et_3N

Yoshiyuki Sasaki

National Research Institute for Pollution and Resources, Yatabe Ibaraki 305, Japan.

Summury : The reaction of CO_2 with propargyl alcohol catalyzed by $Ru_3(CO)_{12}$ and Et_3N gives 2-oxo-propyl-2'-propynyl carbonate in an appreciable yield. The similar reaction of 1-butyn-3-ol gives the corresponding carbonate together with 2,3-dioxycarbonyl-1-butene.

Although much interest has been paid to fixation of CO_2 in organic compounds, catalytic reaction is rare. α-Ethynyl-tert-alcohols like 3-methyl-1-butyn-3-ol are known to undergo an addition reaction with CO_2 giving 1:1 adducts (α-methylene-cyclic carbonates) in the presence of CuCl and Et_3N (1), but no catalytic reaction of propargyl alcohol with CO_2 has yet been reported. In this paper it is reported that non-cyclic β-oxo-alkyl carbonates were formed through the 1:2 addition of CO_2 with α-Ethynyl-prim or sec-alcohols catalyzed by $Ru_3(CO)_{12}$ and Et_3N under mild conditions.



$$2\ HC\equiv CCH_2OH + CO_2 \xrightarrow[Ru_3(CO)_{12} - Et_3N]{} CH_3\underset{\substack{\| \\ O}}{C}CH_2O\underset{\substack{\| \\ O}}{C}OCH_2C\equiv CH$$

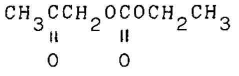
(I)

When a mixture of propargyl alcohol (1 mL), CH_3CN (7 mL), Et_3N (2 mL) and $Ru_3(CO)_{12}$ (0.2 mmol) was stirred at room temperature for 45 h under 50 kg/cm2 pressure of CO_2, 2-oxo-propyl-2'-propynyl carbonate (I) was formed in 27% yield based on propargyl alcohol as shown in Table 1. Small amounts of propargyl carbonate and hydroxyacetone were also detected. The other polymeric products were not analyzed. The yield of (I) based on a ruthenium atom was 368%. Controlled experiments showed that neither $Ru_3(CO)_{12}$ nor Et_3N alone catalyzed the reaction. A combination of CuCl and Et_3N was not a catalyst for this reaction.

When the reaction was carried out in EtOH (7 mL) instead of CH_3CN, ethyl-2-oxo-propyl carbonate (II) was formed in 15% yield through the 1:1:1 addition of CO_2, propargyl alcohol and EtOH.

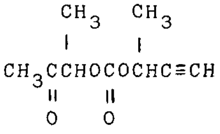
1-Butyn-3-ol also reacted with CO_2 to give 1-methyl-2-oxo-propyl-1'-methyl-2'-propynyl carbonate (III) and 2,3-dioxycarbonyl-1-butene (IV) under similar conditions.

As the cyclic carbonate (IV) reacted smoothly with 1-butyn-3-ol to give (III) in the presence of Et_3N at room température, α-methylene-cyclic carbonate is considered to be a precursor of non-cyclic β-oxo-alkyl carbonate although the corresponding cyclic carbonate was not detected in the case of propargyl alcohol.



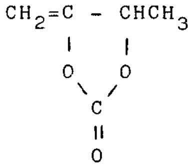
$CH_3\underset{\underset{O}{\|}}{C}CH_2O\underset{\underset{O}{\|}}{C}OCH_2CH_3$

(II)



$CH_3\underset{\underset{O}{\|}}{C}\overset{\overset{CH_3}{|}}{C}HO\underset{\underset{O}{\|}}{C}O\overset{\overset{CH_3}{|}}{C}HC\equiv CH$

(III)



(IV)

TABLE 1 : REACTION OF CO_2 WITH ACETYLENIC ALCOHOLS [(a)]

Cat.	Acetylenic alc.	Solv.	conv. %	β-oxo-alkyl carbonate [(b)]	Yield % [(c)]
$Ru_3(CO)_{12}$	$HC\equiv CCH_2OH$	CH_3CN	69	(I)	27 [(d)]
CuCl	$HC\equiv CCH_2OH$	THF	9	-	0
$Ru_3(CO)_{12}$	$HC\equiv CCH_2OH$	EtOH	66	(II)	15
$RuCl_3 3H_2O$	$HC\equiv C\overset{\overset{CH_3}{\vert}}{C}HOH$	CH_3CN	76	(III)	22 [(e)]

(a) cat. 0.2 mmol, solv. 7 mL, Et_3N 2 mL, acetylenic alc. 1 mL, CO_2 50 kg/cm2; room temp. 45 hrs.

(b) The structures of products were determined by the following data :

(I) : IR. (liquide) 3270 (HC≡), 2140 (C≡C), 1750 (OCOO), 1725 (C=O), 1280 (C-O); ^1H NMR. ($CDCl_3$), 2.24 (3H,s,CH_3), 2.59 (1H,t,HC≡, J=2Hz), 4.79 (2H,s,$OCCH_2O$), 4.87 (2H,d,$OCH_2C\equiv$,H=2Hz); GC-MS 157 $(M+1)^+$.

(II) : IR. (liquid) 1750 (OCOO), 1730 (C=O), 1270 (C-O); ^1H NMR. ($CDCl_3$) 1.35 (3H,t,$\underline{CH_3}CH_2O$-, J=7Hz), 2.20 (3H,s,CH_3CO-), 4.32 (2H,q, CH_3CH_2O-, J=7Hz), 4.75 (2H,s,-OCH_2CO-); GC-MS 147 $(M+1)^+$.

(III) : IR. (liquid) 3270 (HC≡), 2150 (C≡C), 1750 (OCOO), 1730 (C=O), 1260 (C-O); ^1H NMR. ($CDCl_3$) 1.48 (3H,d,CH_3,J=6Hz), 1.63 (3H,d,CH_3, J=6Hz), 2.23 (3H,s,CH_3CO), 2.73 (1H,t,HC≡), 5.15 (1H,q,CH,J=6Hz), 5.45 (1H,q,CH,J=6Hz); GC-MS 185 $(M+1)^+$.

(IV) : IR. (liquid) 1820 (C=O), 1680 (C=C), 855 (CH_2=); ^1H NMR. ($CDCl_3$) 1.60 (3H,d,CH_3,J=6.5Hz), 4.40,4.84 (2H,m,CH_2=), 5.31 (1H,m,CH, J=6.5Hz); GC-MS 115 $(M+1)^+$.

(c) Yield, based on acetylenic alcohol, were determined by g.l.c.

(d) A slight deposition of polymeric product was observed on the wall of autoclave.

(e) (IV) was also formed in 12% yield.

reference

(1) P. Dimroth, H. Pasedach, German Patent 1098953 (1961), BASF; C.A. 56, 2453 (1962).

(Received in France 17 December 1985)