Cobaltocene-Catalyzed Reaction of Carbon Dioxide with Propargyl Alcohols

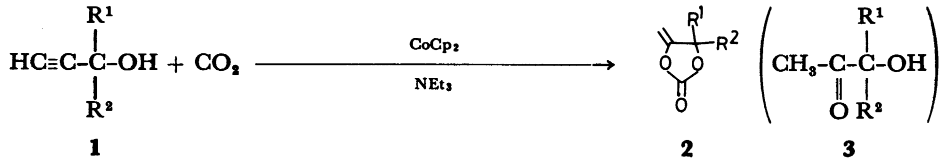
Yoshio Inoue,* Jiro Ishikawa, Masaaki Taniguchi, and Harukichi Hashimoto
Department of Applied Chemistry, Faculty of Engineering, Tohoku University,
Aoba, Aramaki, Sendai 980

(Received September 13, 1986)

Synopsis. The reaction of carbon dioxide with α-ethynyl tertiary alcohols has been catalyzed by cobaltocene to give α-methylene cyclic carbonates in good yields. α-Ethynyl primary or secondary alcohols give noncyclic alkyl carbonates in fair yields.

Considerable attention has been attracted in the fixation of carbon dioxide (CO_2) to organic substrates using transition metals with regard to the use of readily available primary chemicals in organic synthesis.1) Previously we reported a few examples of cooligomerization of acetylenic compounds with CO_2 catalyzed by nickel(0) complexes to produce α-pyrone derivatives.2)

In this paper we describe another example of the reaction of CO_2 with acetylenic alcohols catalyzed by cobaltocene ($CoCp_2$; Cp=cyclopentadienyl). α-Ethynyl tertiary alcohols **1** such as 2-methyl-3-butyn-2-ol underwent cycloaddition with CO_2 yielding α-methylene cyclic carbonates **2** in good yield in the presence of $CoCp_2$ and triethylamine.



a; $R^1=R^2=CH_3$
b; $R^1=CH_3$, $R^2=C_2H_5$
c; $R^1=CH_3$, $R^2=CH_2CH(CH_3)_2$
d; $R^1=R^2=C_2H_5$

Similar types of reaction are also known to be catalyzed by $CuCl$3) or $PdCl_2(MeCN)_2$.4) Very recently $Ru_3(CO)_{12}$ was shown to catalyze the reaction of CO_2 with α-ethynyl primary or secondary alcohols to afford noncyclic 2-oxoalkyl carbonates.5)

The cobalt-mediated reaction was performed in an autoclave under the pressure of CO_2 without employing a solvent usually. In addition to the product **2**, a small amount(<9%) of α-hydroxy ketone of the type **3** was also obtained. This may be formed from the reaction of **1** wih the water concomitant with **1**.

Table 1. Reaction of α-Ethynyl Tertiary Alcohols **1** with CO_2a)

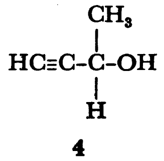
Alcohol 1	Solvent	Reaction temp/°C	Reaction time/h	Product 2	Yieldb) %
1a	—	60	5	**2a**	11
	—	80	0.5		17
	—	80	1		41
	—	80	1.5		83
	—	80	5		87
	—	100	5		87
	—	100	5		84c)
	Benzene	80	5		3
	THF	80	5		5
	DMF	80	5		28
1b	—	80	5	**2b**	87
1c	—	80	5	**2c**	82
1d	—	80	5	**2d**	52
	—	100	5		83

a) **1**, 50 mmol; solvent, 20 cm^3; $CoCp_2$, 1 mmol; Et_3N, 3.6 mmol; CO_2, 50 kg cm^{-2}. b) GLC yield. c) Without NEt_3.

The results are shown in Table 1. At first, 2-methyl-3-butyn-2-ol (**1a**) was employed as a probe to investigate the reaction conditions. The reaction occurred at the temperature above 60 °C and proceeded smoothly at 80 °C. The reaction terminated almost in 1.5 h at this reaction temperature. Normally triethylamine was added as the co-catalyst. However the reaction took place without adding this amine although the yield of **2a** declined slightly. The employment of a solvent such as benzene, tetrahydrofuran (THF), or *N*,*N*-dimethylformamide (DMF) profoundly diminished the yield of the product **2a**.

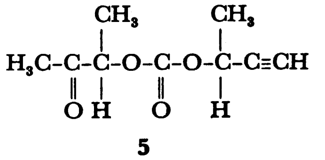
The other α-ethynyl tertiary alcohols such as **1b**—**d** underwent the 1 : 1 cycloaddition reaction giving **2b**—**d**, respectively under similar reaction conditions.

3-Butyn-2-ol (**4**), an α-ethynyl secondary alcohol, did not afford the 1 : 1 cycloaddition product. Instead, a small amount (≈15%) of 1 : 2 addition product, i.e., 1-methyl-2-oxopropyl 1-methyl-2-propynyl carbonate (**5**) was obtained along with the other minor products.



$HC{\equiv}C\text{-}C(CH_3)(H)\text{-}OH$

4

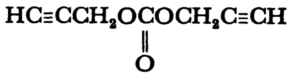


$H_3C\text{-}C(=O)\text{-}CH(CH_3)\text{-}O\text{-}C(=O)\text{-}O\text{-}CH(CH_3)\text{-}C{\equiv}CH$

5

$HC\equiv CCH_2OH$

6

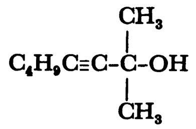


$HC\equiv CCH_2OC(=O)OCH_2C\equiv CH$

7

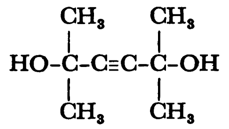
Propargyl alcohol (**6**), an α-ethynyl primary alcohol, afforded dipropargyl carbonate (**7**) in 6% yield together with a small amount of hydroxyacetone (≈0.2%) after the reaction at 80 °C for 5 h. Addition of an equimolar amount of PPh_3 to the catalyst increased the yield of **7** up to 24%.

α-(1-Alkynyl) tertiary alcohols like **8** or **9** did not react with CO_2. Under forced conditions (110 °C, 5 h), **9** afforded an isomerized product **10** in a moderate yield.



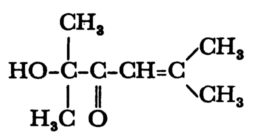
$C_4H_9C\equiv C\text{-}C(CH_3)_2\text{-}OH$

8



$HO\text{-}C(CH_3)_2\text{-}C\equiv C\text{-}C(CH_3)_2\text{-}OH$

9

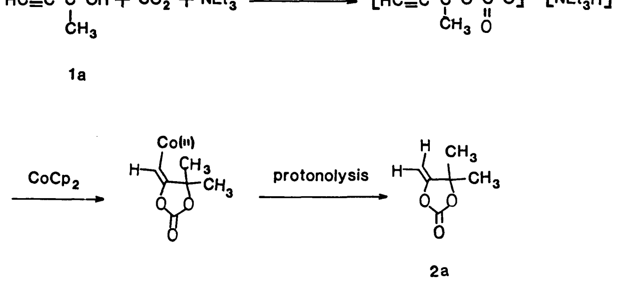


$HO\text{-}C(CH_3)_2\text{-}C(=O)\text{-}CH=C(CH_3)_2$

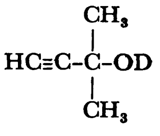
10

It can be presumed that cobaltocene is oxidized to cobaltocenium ion $[CoCp_2]^+$ in the presence of water or alcohol if the air is present.[6] The possible participation of the ion to the present cyclization reaction has been studied. A solution composed of **1a**, triethylamine, and cobaltocene was stirred in the air at an ambient temperature for 0.5 h and then the mixture was submitted to the reaction with CO_2 (80 °C, 5 h) to yield **2a** in only 5%. Another experiment employing $[CoCp_2]Cl$ as catalyst afforded **2a** from **1a** in 15% yield under the standard reaction conditions. So the participation of cobaltocenium ion to this reaction is partial if any.

Although the mechanism is unknown, one possibility will be mentioned at this time. The first step of the reaction is the formation of monoalkyl carbonate ion from **1a** and CO_2. The presence of triethylamine increases the amount of the ion. Then the monoalkyl carbonate undergoes cyclization under the assist of cobaltocene. It has been reported recently that this type of cyclization occurs in a trans fashion in the palladium-catalyzed reaction.

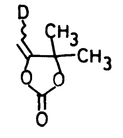


To gain mechanistic information, the deuterio alcohol **1a**-d_1 was employed. This alcohol afforded the cyclic carbonate **2a**-d_1, the deuterium being located almost equally in the exo methylene protons (see the experimental part). This result indicates that exactly the same mechamism as that in the palladium case is not operative.



$HC\equiv C\text{-}C(CH_3)_2\text{-}OD$

1a-d_1



2a-d_1

Experimental

Materials. Cobaltocene[7] and $[CoCp_2]Cl$[8] were prepared according to the literatures. The alcohols, **1a—d**, **4**, and **6**, were obtained commercially and distilled before use. The alcohol **9** was used as received. The alcohol **8** was synthesized according to the reported method[9] from 1-hexyne and acetone.

Reaction of α-Ethynyl Tertiary Alcohols 1 with CO_2. The reaction of 2-methyl-3-butyn-2-ol (**1a**) with CO_2 is typical. A mixture of **1a** (50 mmol), Et_3N (3.6 mmol), and $CoCp_2$ (1 mmol) was stirred at 80 °C for 5 h under the pressure of CO_2 in an autoclave. GLC analysis (FFAP, 10%, 3 m, 160 °C) showed the formation of 4,4-dimethyl-5-methylene-1,3-dioxolan-2-one (**2a**) and 3-hydroxy-3-methyl-2-butanone (**3a**) in 87 and 9% yield, respectively. The product **2a** was isolated by distillation. Liquid; bp 45 °C/3 mmHg (lit,[3] bp 82 °C/18 mmHg); (1 mmHg=133.322 Pa). Mp 26.5—27.5 °C.

4-Ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one (2b). Isolated by distillation. Liquid; bp 55 °C/3 mmHg (lit,[3] bp 95 °C/20 mmHg.).

4-Methyl-5-methylene-4-(2-methylpropyl)-1,3-dioxolan-2-one (2c). Isolated by distillation. Liquid; bp 110—125 °C/3 mmHg. Found: C, 63.36; H, 8.65%. Calcd for $C_9H_{14}O_3$: C, 63.51 H, 8.29%. IR (neat) 1820, 1680, 840 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.89 (d, 6H, J=6 Hz), 1.51 (s, 3H), 2.32—2.60 (m, 1H), 2.60—2.72 (br, 1H), 4.22 (d, 1H, J=4 Hz), 4.72 (d, 1H, J=4 Hz).

4,4-Diethyl-5-methylene-1,3-dioxolan-2-one (2d). Isolated by distilation. Liquid; bp 76 °C/66 mmHg. Found: C, 61.65; H, 7.97%. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74%. IR (neat) 1820, 1680, 845 cm^{-1}. ^1H NMR ($CDCl_3$) δ=0.91 (t, 6H, J=7 Hz), 1.40—2.10 (m, 4H), 4.17 (d, 1H, J=4 Hz), 4.80 (d, 1H, J=4 Hz).

Reaction of 3-Butyn-2-ol (4) with CO_2. The alcohol **4** (64 mmol) was reacted with CO_2 (50 kg cm^{-2}) in the presence of $CoCp_2$ (1 mmol) and Et_3N (3.6 mmol) at 80 °C for 5 h. GLC analysis (Silicone DC-550, 20%, 3 m, 170 °C) showed the formation of 1-methyl-2-oxopropyl 1-methyl-2-propynyl carbonate (**5**)[5] in 15% yield together with several minor products.

Reaction of Propargyl Alcohol (6) with CO_2. The alcohol **6** (86 mmol) was reacted with CO_2 (50 kg cm^{-2}) in the presence of $CoCp_2$ (1 mmol) and NEt_3 (3.6 mmol) at 80 °C for 5 h. GLC analysis (Silicone DC-550, 20%, 3 m, 170 °C) showed the formation of dipropargyl carbonate (**7**) and hydroxyacetone in 6 and 0.2% yield, respectively. Addition of PPh_3 (1 mmol) increased the yield of **7** up to 24%.

Reaction of 2,5-Dimethyl-3-hexyne-2,5-diol (9) with CO_2. The diol **9** (50 mmol) was reacted with CO_2

(50 kg cm^{-2}) in the presence of $CoCp_2$ (1 mmol) and Et_3N (3.6 mmol) at 110 °C for 5 h. GLC analysis (Silicone GE SE-52, 20%, 2 m, 85 °C) showed the formation of 2-hydroxy-2,5-dimethyl-3-hexanone (**10**) in 53% yield. The product **10** was isolated by distillatiuon. Liquid; bp 44 °C/4 mmHg. Found: C, 67.42; H, 10.25%. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93%. IR (neat) 3440, 1675, 1615, 1440, 1360, 1030, 960 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ=1.30 (s, 6H), 1.91 (s, 3H), 2.16 (s, 3H), 4.12 (s, 1H), 6.20 (s, 1H).

Reaction of 2-Methyl-3-butyn-2-ol-*d* (1a-*d*$_1$) with CO_2. A 50 cm^3 flask was flushed with N_2 and was then charged with 28 cm^3 of diethyl ether, 12 cm^3 of **1a**, and 5 cm^3 of D_2O. The flask was shaken vigorously for 5 min. It was placed in a salt/ice bath, the water layer frozen, then the ethereal layer was transferred by a syringe to another flask containg D_2O. This procedure$^{10)}$ was repeated for five times in all. The final ethereal solution was dried over K_2CO_3 and distilled to yield ca. 5 cm^3 of **1a**-*d*$_1$, which was 76% deuterated (by integration of the NMR). The deuterated alcohol **1a**-*d*$_1$ (37 mmol) was reacted with CO_2 (50 kg cm^{-2}) in an autoclave in the presence of $CoCp_2$ (1 mmol) without triethylamine at 80 °C for 1 h. After that time, the resulting reaction mixture was analyzed by ^{1}H NMR. The yield of **2a**-*d*$_1$ was 10%. No H-D scrambling between the alcoholic deuterium and the acetylenic proton was observed during the reaction. The ratio of the exo methylene proton in the position cis to the oxidocarbonyloxy group to that in the position trans was 47:53 for the product **2a**-*d*$_1$.

References

1) For reviews, see; M. E. Volpin and I. S. Kolomnikov, *Organomet. React.*, **5**, 313 (1975); D. J. Darensbourg and R. A. Kudaroski, *Adv. Organomet. Chem.*, **22**, 129 (1983); S. Inoue, "Organic and Bio-organic Chemistry of Carbon Dioxide," Kodan Sha LTD., Tokyo (1981), Chap. 3.

2) Y. Inoue, Y. Itoh, and H. Hashimoto, *Chem. Lett.*, **1977**, 855; **1978**, 633; Y. Inoue, Y. Itoh, H. Kazama, and H. Hashimoto, *Bull. Chem. Soc. Jpn.*, **53**, 3329 (1980).

3) H. Laas, A. Nissen, and A. Nürrenbach, *Synthesis*, **1981**, 958.

4) N. Yanagihara, K. Iritani, and K. Uchimoto, 52nd National Meeting of the Chemical Society of Japan, Kyoto, April 1986, Abstr., No. 4W15.

5) Y. Sasaki, *Tetrahedron Lett.*, **27**, 1573 (1986).

6) E. O. Fischer and R. Jira, *Z. Naturforsch.*, 8B, 1 (1953); *ibid.*, 8B, 327 (1953).

7) G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, **2**, 96 (1956).

8) D. Hartley and M. J. Ware, *J. Chem. Soc. (A)*, **1969**, 138.

9) B. R. Fleck and J. E. Kmiecik, *J. Org. Chem.*, **22**, 90 (1957).

10) T. F. Murray and J. R. Norton, *J. Am. Chem. Soc.*, **101**, 4107 (1979).