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Organic Syntheses by Means of Metal Complexes. III.[1] Cobalt Carbonyl-catalyzed Carbonylation of β-Propiolactone

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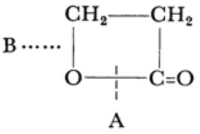
It was found that the carbonylation of β-propiolactone can be carried out in the presence of dicobalt octacarbonyl. Butyrolactone and succinic acid were obtained by the reaction of β-propiolactone with carbon monoxide and hydrogen. Succinic anhydride was obtained by the reaction with carbon monoxide.

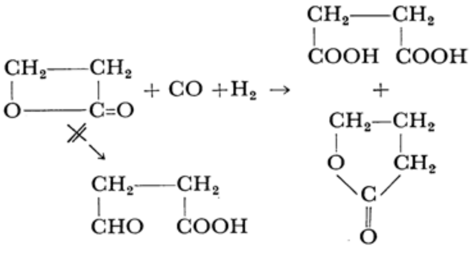
β-Propiolactone (abbreviated as PL) is a reactive compound and undergoes many reactions. Its reactions can be classified into two types. One of them proceeds through the *O*-acyl fission (A) which is possible under basic conditions. On the other hand, under acidic conditions, the *O*-alkyl fission (B) occurs.[2)]



It seemed of interest to us to study the reaction of carbon monoxide with highly reactive PL. Carbon monoxide is also reactive and behaves as nucleophile or radical depending on the reaction conditions. It is known that carbon monoxide is activated most effectively by catalytic action of metal carbonyls, among which dicobalt octacarbonyl is well known catalyst of carbonylation of olefins and other unsaturated compounds. In addition, it catalyzes the carbonylation of epoxide which is a highly strained heterocyclic ring.[3)] In view of the fact that PL is a highly strained reactive cyclic compound, the carbonylation of PL was attempted by the catalytic action of dicobalt octacarbonyl. It is known that active species in the dicobalt octacarbonyl-catalyzed carbonylation is cobalt tetracarbonyl hydride formed from dicobalt octacarbonyl and hydrogen. The cobalt hydride is strongly acidic. Therefore, it is expected that the carbonylation of PL catalyzed by dicobalt cotacarbonyl *via* the cobalt hydride in the presence of hydrogen should proceed through the *O*-alkyl fission, and carbon monoxide should be inserted into the *O*-alkyl bond to give a C_4 dicarbonyl compound.

$$Co_2(CO)_8 + H_2 \longrightarrow 2HCo(CO)_4 \qquad \text{(I)}$$

Based on the above assumption, the reaction of PL with carbon monoxide and hydrogen in the presence of dicobalt octacarbonyl in benzene was attempted. In this reaction, hydrogen reacts with dicobalt octacarbonyl to give cobalt tetracarbonyl hydride (I). Once the acidic hydride is formed, then it is reasonable to assume that the *O*-alkyl fission of PL is possible to form a cobalt-alkyl complex, followed by carbon monoxide insertion to give succinic acid aldehyde as final product. However, contrary to the expectation, the product actually obtained by the reaction of PL with carbon monoxide and hydrogen was not the aldehyde. Instead, butyrolactone and succinic acid were isolated from the reaction mixture in a total yield of about 80% based on PL. The ratio of these two products changed depending on the reaction conditions. It is not easy to define which factor favors the formation of either product. The results are shown in Table 1. The result shows that the alcohol and acid were formed instead of the expected aldehyde by the ring opening reaction of PL with carbon monoxide and hydrogen.



Then the reaction of PL with carbon monoxide in the absence of hydrogen was tried. By the reaction in benzene carried out at 150°C, two products

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[1] Part II: J. Tsuji and Y. Mori, This, Bulletin, in press.

[2] T. L. Gresham, J. E. Jansen, F. W. Shaver and J. T. Gregory, *J. Am. Chem. Soc.*, **70**, 999, 1001, 1003, 1004 (1948).

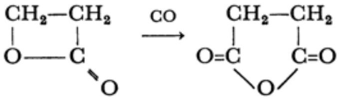
[3] C. Yokokawa, Y. Watanabe and Y. Takegami, This Bulletin, **37**, 667 (1964); J. L. Eisenmann, R. L. Yamartino and J. F. Howard, *J. Org. Chem.*, **26**, 2102 (1961).

TABLE 1. REACTIONS OF PL WITH CARBON MONOXIDE AND HYDROGEN*

Solvent	Pressure		Reaction time hr	Products	
	Carbon monoxide atm	Hydrogen atm		γ-Butyrolactone g(%)	Succinic acid g(%)
Benzene	50	50	18	2.53(36.9)	2.26(23.9)
Benzene	50	100	18	1.93(28.1)	
Benzene	80	40	18	3.16(45.1)	2.30(24.3)
Benzene	80	40	4	3.12(45.5)	3.63(38.4)
Cyclohexane	80	40	4	0.74(10.8)	5.33(56.5)

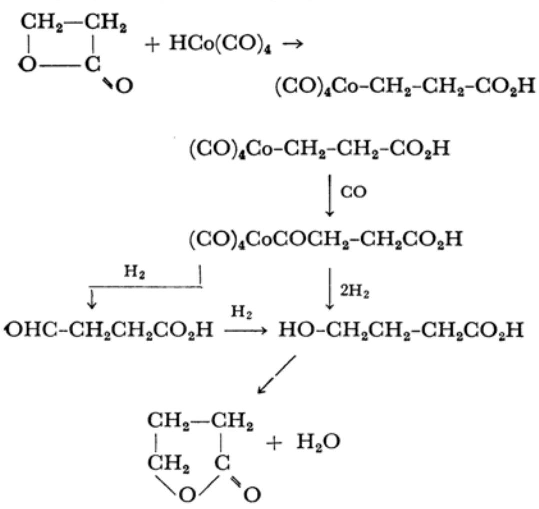
* The reactions were carried out with PL (5.75 g), solvent (30 m*l*) and dicobalt octacarbonyl (0.7 g) at 150°C.

were isolated. One of them was identified as acrylic acid. Apparently acrylic acid was formed by the ring opening of PL without reacting with carbon monoxide. The other product was confirmed to be succinic anhydride. Thus carbon monoxide was inserted into the *O*-alkyl bond.

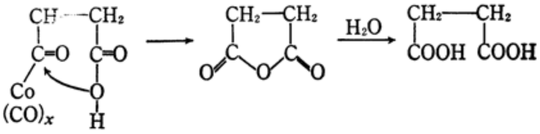


The following mechanisms are proposed for the dicobalt octacarbonyl-catalyzed carbonylation of PL. The reaction of cobalt tetracarbonyl hydride and PL gives the alkyl cobalt complex *via O*-alkyl fission. This is reasonable because cobalt hydride is acidic. The alkyl complex is subjected to carbon monoxide insertion to give the acyl complex. The acyl complex is split with either hydrogen or cobalt tetracarbonyl hydride to give aldehyde and dicobalt octacarbonyl. Alcohol is formed by the hydrogenation of the aldehyde or directly from the acyl complex. Then γ-hydroxybutyric acid is converted into the lactone with the liberation of water.

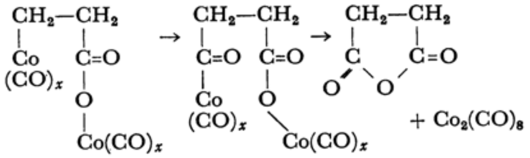
$$Co_2(CO)_8 + H_2 \rightarrow 2HCo(CO)_4$$



The formation of succinic acid can be explained by the cyclization of the acyl complex as shown below. In the presence of water formed by the lactone formation, succinic anhydride is hydrolyzed to give succinic acid.



A possible path of the formation of succinic anhydride in the absence of hydrogen is the following. In this reaction cobalt hydride is not formed and the *O*-alkyl fission reaction of PL with dicobalt octacarbonyl gives the following alkyl complex. The carbon monoxide insertion into the alkyl cobalt bond gives acyl complex which cyclizes to give anhydride and dicobalt octacarbonyl.



The possibility that the reaction proceeds through the intermediate formation of acrylic acid from PL can be ruled out by the fact that an attempted oxo reaction of acrylic acid under the similar reaction conditions did not proceed and unchanged acrylic acid was recovered almost quantitatively. Therefore the selective introduction of carbon monoxide at β-position of PL should be possible through the intermediate complex formed by the *O*-alkyl fission of PL with cobalt catalyst.

Experimental

Materials. Commercially available PL was used without purification. Dicobalt octacarbonyl was synthesized by the known method.

Reaction of PL with Carbon Monoxide and Hydrogen. Benzene (30 m*l*), PL (5.75 g) and dicobalt octacarbonyl (0.7 g) were mixed in a glass vessel equipped with a gas inlet capillary and the glass vessel was placed in an autoclave. Carbon monoxide

(80 atm) and hydrogen (40 atm) were charged and the reaction was carried out at 150°C for 4 hr with shaking. A pressure drop of 35 atm was observed. The solvent was removed by distillation from the reaction mixture, and butyrolactone (3.12 g, 45.5%) was isolated by distillation at 91—94°C/20 mmHg. The residue was recrystallized from ether and succinic acid was isolated (3.63 g, 38.4%). Both products were indentified with authentic samples by IR spectra.

Reaction of PL with Carbon Monoxide. Benzene (30 m*l*), PL (5.75 g) and dicobalt octacarbonyl (0.7 g) were mixed in the autoclave as shown above and allowed to react with carbon monoxide (100 atm) at 150°C for 4 hr and pressure drop of 4 atm was observed. Distillation of the reaction mixture gave acrylic acid (1.08 g, 18.8%) and succinic anhydride (2.37 g, 29%, 99°C/2 mmHg). The latter solidified on standing, mp 117—119°C.