

## The Cobalt Carbonyl-catalyzed Hydroesterification of 3-( $\beta$ -Cyanoethoxy)propene with Carbon Monoxide and Methanol

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The cobalt carbonyl-catalyzed hydroesterification of 3-( $\beta$ -cyanoethoxy)propene with carbon monoxide and methanol occurred in the presence of a small amount of hydrogen at a moderate temperature, methyl 4-( $\beta$ -cyanoethoxy)butyrate being produced in a much larger amount than methyl 2-methyl-3-( $\beta$ -cyanoethoxy)propionate. The double-bond isomerization leading to the formation of propionaldehyde dimethylacetal and ethylene cyanohydrin occurred simultaneously. The selectivity to the double-bond isomerization was very large at a low pressure; it decreased as the pressure was increased, with a corresponding increase in selectivity to the hydroesterification. The reaction rate was not increased by the addition of pyridine, but it was increased about tenfold by the addition of palladium chloride. Thus, the reaction could be carried out at a lower temperature in the presence of palladium chloride. The selectivity to the hydroesterification, however, did not increase upon the addition of palladium chloride, as the double-bond isomerization was also accelerated by its addition.

In a preceding paper on the intramolecular hydroesterification of allyl alcohol with carbon monoxide,<sup>1)</sup> it was reported that the selectivity to the hydroesterification product,  $\gamma$ -butyrolactone, could not exceed 60% because of the simultaneous isomerization of allyl alcohol into propionaldehyde.

In the present study, in this connection, the hydroesterification of 3-( $\beta$ -cyanoethoxy)propene, an etheric derivative of allyl alcohol, is studied with the intention of obtaining methyl 4-( $\beta$ -cyanoethoxy)butyrate in a good yield. The reaction proceeds in the presence of a small amount of hydrogen at a moderate temperature; methyl 4-( $\beta$ -cyanoethoxy)butyrate and methyl 2-methyl-3-( $\beta$ -cyanoethoxy)propionate are produced as the hydroesterification products, there being much more of the former than of the latter. However, an unexpected side-reaction leading to the formation of propionaldehyde dimethylacetal and ethylene cyanohydrin occurs to a considerable extent.

### Experimental

The 3-( $\beta$ -cyanoethoxy)propene was prepared by the cyanoethylation of allyl alcohol with acrylonitrile in the presence of sodium methoxide, and then distilled (73°C/3 mmHg). The propoxypropionitrile and methoxypropionitrile were also prepared by the cyanoethylation of propanol and methanol with acrylonitrile. The propionaldehyde dimethylacetal and isobutyraldehyde dimethylacetal were prepared by the reaction of methanol with propionaldehyde and isobutyraldehyde. The

carbon monoxide and dicobalt octacarbonyl were prepared by a procedure described previously.<sup>2)</sup> The palladium chloride and the other reagents were obtained commercially. The methanol and pyridine were rectified before use.

The reactions were carried out in the same 300-cc stainless-steel autoclave and with the same technique as was described previously;<sup>2,3)</sup> the reaction was started at a desired temperature by dropping in dicobalt octacarbonyl, packed in a stainless-steel saucer, from a wing of the stirrer. The total pressure was kept constant during the reaction by supplying carbon monoxide from a pressure-storage vessel through a pressure regulator; the reaction temperature was controlled within  $\pm 1^\circ\text{C}$ . The product composition was quantitatively determined by the gas-chromatographical method in a manner similar to that already described.<sup>1)</sup>

**Product Identification.** The NMR spectra were measured at 100 Mc in carbon tetrachloride, with tetramethylsilane as the internal standard.

Methyl 4-( $\beta$ -cyanoethoxy)butyrate: bp ca.  $100^\circ\text{C}/10^{-2}$  mmHg. IR spectrum: C=O (ester)  $1735\text{ cm}^{-1}$ ,  $\text{C}\equiv\text{N}$   $2240\text{ cm}^{-1}$ . NMR spectrum:  $\text{CH}_2(-\text{CN})$   $\tau$  7.46 (triplet),  $\text{CH}_2(-\text{COOCH}_3)$   $\tau$  7.63 (triplet),  $\text{CH}_2(-\text{CH}_2\text{COOCH}_3)$   $\tau$  8.13 (quintet),  $\text{OCH}_3$   $\tau$  6.38 (singlet),  $\text{CH}_3\text{OCH}_2$   $\tau$  6.3—6.8 (overlapped multiplet).

Found: C, 55.96; H, 7.10; N, 8.24%. Calcd for  $\text{C}_8\text{H}_{13}\text{NO}_3$ : C, 56.12; H, 7.65; N, 8.18%.

Methyl 2-methyl-3-( $\beta$ -cyanoethoxy)propionate: The sample was obtained by gas-chromatographic separation from the reaction product: the IR and the NMR spectra were compared with those of methyl 4-( $\beta$ -cyanoethoxy)butyrate. In the NMR spectrum there was no absorption due to  $\text{CH}_2\text{CH}_2(-\text{COOCH}_3)$ , but there was a strong

1) A. Matsuda, This Bulletin, **41**, 1876 (1968).

2) A. Matsuda and H. Uchida, *ibid.*, **38**, 710 (1965).

3) A. Matsuda, *ibid.*, **40**, 135 (1967).

TABLE 1. THE EFFECT OF BASES

1/4 mol 3-( $\beta$ -cyanoethoxy)propene, 1/2 mol methanol, 2 mmol  $\text{Co}_2(\text{CO})_8$ ; total pressure 200 kg/cm<sup>2</sup>; hydrogen content of the gas used, 3% (Expt. No. 1–5), 0.8% (Expt. No. 6)

Expt. No.	1	2	3	4	5	6
Reaction temp. (°C)	120	120	120	120	110	120
Base	None	Py	Py	$\text{CH}_3\text{ONa}$	Py	Py
(mmol)	0	2	4	2	2	2
$k \times 10^2$ (min <sup>-1</sup> )	2.3	2.0	1.2	2.7	0.84	0.81
Reaction time (min)	120	120	180	120	180	240
Conversion (%)	99	99	93	98	97	93
Selectivity (%) <sup>a)</sup>						
$\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_3$						
	52	60	63	62	67	70
$\text{OCH}_2\text{CH}_2\text{CN}$						
$\text{CH}_2\text{CH}(\text{CH}_3)\text{COOCH}_3$	1.4	1.5	2.2	1.6	2.0	2.3
$\text{OCH}_2\text{CH}_2\text{CN}$						
$\text{CH}_3\text{CH}_2\text{CH}(\text{OCH}_3)_2$	28	26	28	28	24	27
$\gamma$ -butyrolactone	0.9	3.3	1.7	1.0	1.1	—
$\text{CH}_2\text{CH}_2\text{CH}_3$						
	0.3	0.8	0.6	0.4	0.5	—
$\text{OCH}_2\text{CH}_2\text{CN}$						
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CN}$	—	—	—	0.4	—	—
The residue	17	8	4	6	5	1

a) Each product contained an amount of ethylene cyanohydrin equimolar to propionaldehyde dimethylacetal.

absorption(doublet) due to  $\text{CH}_3(-\text{CH})$ , indicating that this compound was the branched isomer of methyl 4-( $\beta$ -cyanoethoxy)butyrate. IR spectrum:  $\text{C}=\text{O}$  (ester) 1738  $\text{cm}^{-1}$ ,  $\text{C}\equiv\text{N}$  2240  $\text{cm}^{-1}$ . NMR spectrum:  $\text{CH}_2(-\text{CN})$   $\tau$  7.47 (triplet),  $\text{CH}_3(-\text{CH})$   $\tau$  8.82 (doublet),  $\text{CH}(-\text{COOCH}_3)$   $\tau$  7.25 (quartet),  $\text{OCH}_3$   $\tau$  6.35 (singlet),  $\text{CH}_2\text{OCH}_2$   $\tau$  6.3–6.8 (overlapped multiplet),

## Results and Discussion

**The Effect of Bases.** In connection with the previous finding that the rate of the hydroesterification in the presence of a small amount of hydrogen is selectively increased by the addition of pyridine (Py),<sup>1–4)</sup> the effects of such bases as Py and sodium methoxide on the present reaction were first examined.

The results are shown in Table 1. The first-order rate constant,  $k$ , was calculated according to the half-time method by means of this equation:  $k = \ln 2 / t_{1/2}$ . The half-time,  $t_{1/2}$ , was estimated from the gas-supplying curve during the reaction and the final conversion, on the assumption that the amount of gas supplied was proportional to the amount of the reacted olefin. The ratio of methyl 4-( $\beta$ -cyanoethoxy)butyrate to methyl 2-methyl-3-( $\beta$ -cyanoethoxy)propionate was very large (30–40), indicating that the terminal methoxycarbonylation predominated in this case; this trend is the same as that observed in the hydroesterification of propylene and methyl acrylate.<sup>2,4)</sup> The selectivity to  $\beta$ -

propoxypropionitrile resulting from the hydrogenation of 3-( $\beta$ -cyanoethoxy)propene was less than 1%. Propionaldehyde dimethylacetal and ethylene cyanohydrin were produced in equimolar amounts. Propionaldehyde dimethylacetal may result from the double-bond isomerization of 3-( $\beta$ -cyanoethoxy)propene, followed by the reaction with methanol. The other possible route involving the formation of allyl alcohol as an intermediate is not important, since, if such a route were important,  $\gamma$ -butyro-

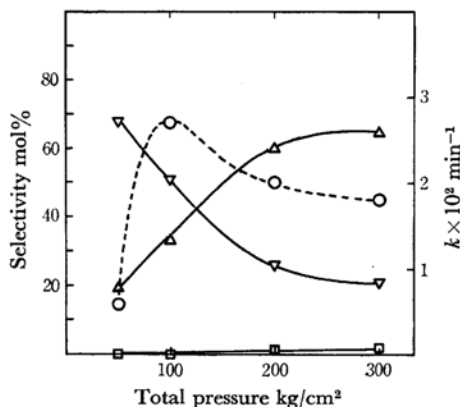
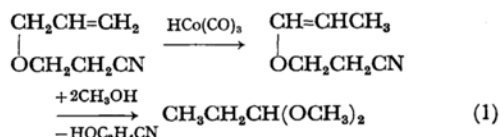


Fig. 1. The effect of total pressure  
 —○— :  $k \times 10^2$  (min<sup>-1</sup>)  
 —△— : methyl 4-( $\beta$ -cyanoethoxy)butyrate (mol%)  
 —□— : methyl 2-methyl-3-( $\beta$ -cyanoethoxy)propionate (mol%)  
 —▽— : propionaldehyde dimethylacetal (mol%)

4) A. Matsuda, *ibid.*, **42**, 571 (1969).

lactone would result from the intramolecular hydroesterification of the intermediate allyl alcohol in a yield comparable with that of propionaldehyde dimethylacetal,<sup>1)</sup> whereas the amount of  $\gamma$ -butyrolactone in the product was very small compared with the amount of propionaldehyde dimethylacetal.

The results of experiments carried out at various pressures, keeping the other conditions equal to those in Expt. No. 2, are shown in Fig. 1. The double-bond isomerization is presumed to be catalyzed by cobalt hydrotricarboxyl, since the selectivity to propionaldehyde dimethylacetal was very large at a low pressure, as had been observed in the previous study.<sup>1)</sup>



As the pressure increased from 50 to 300 kg/cm<sup>2</sup>, the selectivity to propionaldehyde dimethylacetal decreased and the selectivity to the hydroesterification products increased. The rate constant,  $k$ , showed a peak at 100 kg/cm<sup>2</sup>; it began to decline as the pressure increased from 100 to 300 kg/cm<sup>2</sup>. These effects of the total pressure are clearly due to the carbon monoxide partial pressure, since the rate constant,  $k$ , decreases by decreasing the hydrogen partial pressure, while the selectivity to propionaldehyde dimethylacetal remains unchanged (compare Expt. No. 6 with No. 2).

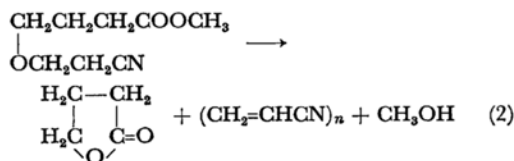
The addition of such bases as Py and sodium methoxide did not affect the reaction rate, but it increased the selectivity to the hydroesterification products. This increase in the selectivity seems to be the direct consequence of the fact that the residue is remarkably reduced by the addition of these bases. The residue is a mixture of unidentified polymers, probably resulting from the hydroformylation of 3-( $\beta$ -cyanoethoxy)propene, followed by the polymerization of the resulting aldehydes; this is in accordance with the fact that the residue is considerably reduced by decreasing the hydrogen content of the gas used (Expt. No. 6), since the selectivity to the hydroformylation decreases upon a decrease in the hydrogen partial pressure.<sup>2)</sup> The residue also decreases upon a decrease in the reaction temperature, resulting in an increased selectivity to the hydroesterification products.

In a preceding study of the hydroesterification of acrylonitrile, it was found that the addition of Py is effective in increasing the rate of the hydroesterification because it accelerates the formation of an acylcobalt carbonyl-intermediate, and that the methanolysis of this intermediate is very fast.<sup>3)</sup> Consequently, the rate-determining step in the present reaction is not the formation of an acylcobalt carbonyl-intermediate, since the reaction rate in

this case does not increase with the addition of pyridine. Therefore, the most probable rate-determining step in the present reaction is the formation of an alkylcobalt carbonyl-intermediate from olefin and cobalt hydrocarbonyl. If the formation of an alkylcobalt carbonyl-intermediate from olefin and cobalt hydrocarbonyl is really the rate-determining step, the reaction rate would probably be affected by weakening the olefinic double-bond by coordination.

**The Effect of Palladium Chloride.** Olefins can be activated by the  $\pi$  complex formation with palladium chloride to undergo reactions with various nucleophiles.<sup>5)</sup> It has also been said that a palladium-complex can catalyze the carbonylation of olefins because it can activate the olefinic double-bond by the  $\pi$  complex formation.<sup>6)</sup> Therefore, it seems probable that the reaction between an olefin and cobalt hydrocarbonyl can also be catalyzed by palladium chloride.

The results of experiments carried out in the presence of palladium chloride are shown in Table 2. Expectedly, the effect of palladium chloride on the rate was very remarkable. The rate constant,  $k$ , increased about tenfold upon the addition of a small amount of palladium chloride. The rate constant,  $k$ , in the presence of a small amount of palladium chloride was further increased by the addition of Py equimolar to dicobalt octacarbonyl. Thus, the reaction could be carried out at 90°C in the presence of small amounts of palladium chloride and Py (Expt. No. 9).<sup>7)</sup> However, the selectivity to the hydroesterification products decreased upon the addition of palladium chloride, while the selectivity to propionaldehyde dimethylacetal increased; this is because palladium chloride accelerates the double-bond isomerization to a larger extent than it does the hydroesterification. The fairly large amount of  $\gamma$ -butyrolactone which is found in the products of the reactions carried out in the presence of palladium chloride probably results from the decomposition of methyl 4-( $\beta$ -cyanoethoxy)butyrate, since the formation of allyl alcohol as an intermediate is unlikely, as has been mentioned before. In fact, such a decomposition took place when the products were distilled at a high temperature:



5) J. Tsuji, *Yukigosei Kagaku Kyokaiishi (J. Synth. Organic Chem., Japan)*, **25**, 984 (1967).

6) K. Bittler, N. Kutepow, D. Neubauer and H. Ries, *Angew. Chem.*, **80**, 352 (1968).

7) In the absence of palladium chloride, almost no reaction occurs at such a low temperature as 90°C.

TABLE 2. THE EFFECT OF PALLADIUM CHLORIDE

1/4 mol 3-( $\beta$ -cyanoethoxy)propene, 1/2 mol methanol, 2 mmol  $\text{Co}_2(\text{CO})_8$ ; total pressure 200 kg/cm<sup>2</sup>; hydrogen content of the gas used, 3%

Expt. No.	1	7	2	8	9
Reaction temp. (°C)	120	120	120	120	90
$\text{PdCl}_2$ (mmol)	0	1	0	1	1
Py (mmol)	0	0	2	2	2
$k \times 10^2$ (min <sup>-1</sup> )	2.3	20	2.0	35	0.91
Reaction time (min)	120	15	120	5	120
Conversion (%)	99	100	99	100	71
Selectivity (%) <sup>a, b)</sup>					
$\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_3$	52	26	60	24	47
$\text{OCH}_2\text{CH}_2\text{CN}$					
$\text{CH}_2\text{CH}(\text{CH}_3)\text{COOCH}_3$	1.4	0.9	1.5	1.0	7.6
$\text{OCH}_2\text{CH}_2\text{CN}$					
$\text{CH}_3\text{CH}_2\text{CH}(\text{OCH}_3)_2$	28	34	26	36	28
$\gamma$ -Butyrolactone	0.9	23	3.3	26	3.6
$\text{CH}_2\text{CH}_2\text{CH}_3$					
$\text{OCH}_2\text{CH}_2\text{CN}$	0.3	0.4	0.8	0.3	0.5
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{CN}$	—	—	—	0.3	0.4
The residue	17	15	8	12	12

a) Cf. Table 1.

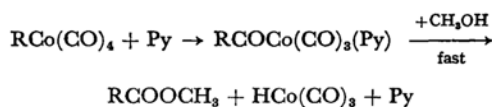
b) The selectivity to isobutyraldehyde dimethylacetal in each run was less than 1%.

That the amount of  $\gamma$ -butyrolactone produced was small in the reaction carried out at 90°C (Expt. No. 9) is understandable, since the decomposition of methyl 4-( $\beta$ -cyanoethoxy)butyrate would be slow at such a low temperature.

Although the reaction rate in the presence of palladium chloride increased upon the addition of Py, this is not because the carbon monoxide-insertion steps are accelerated by Py, for the selectivity to the hydroesterification product is not affected by the addition of Py. The effect of Py on the rate in this case should, therefore, be quite different from those observed in former studies;<sup>1-4)</sup> this effect may be attributable to, for example, the activation of palladium chloride by Py.

In conclusion, it can be said to be certain that the formation of an alkylcobalt carbonyl-inter-

mediate can be accelerated by palladium chloride, but not by Py alone; this is consistent with the former assumption that Py was effective in increasing the rate of the hydroesterification because it accelerated the carbon monoxide-insertion step by forming the acylcobalt carbonyl-Py complex:<sup>3)</sup>



A more extensive study of the effect of palladium chloride is now in progress.

The author is indebted to Professor A. Ozaki, Tokyo Institute of Technology, for his helpful suggestions.