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The Reaction of Cobalt Hydrocarbonyl with Vinylacetate, Crotonate, Styrene, and Acrylates*[1]

Sohei Suga, Hiromitsu Masada and Haruki Suda
Department of Industrial Chemistry, Faculty of Technology, Kanazawa University, Kanazawa

and Yoshihisa Watanabe and Yoshinobu Takegami
Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto

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Ethyl vinylacetate and ethyl crotonate reacted with cobalt hydrocarbonyl at 25°C to give three isomeric acylcobalt carbonyls, α- and γ-carbethoxy-butyrylcobalt carbonyls and β-carbethoxy-isobutyrylcobalt carbonyl. The distribution of these complexes depends greatly on the reaction time (0.5—20 hr). In both cases the β-isomer predominates at shorter reaction times (0.5—1.5 hr), while the γ-isomer predominates at longer reaction times. This shows that isomerization occurs among the complexes and that the equilibrium is very favorable to the γ-isomer. Acrylates and styrene react with cobalt hydrocarbonyl to give two isomeric acylcobalt carbonyls. The isomerization of the acylcobalt complex with a branched structure to that with a straight-chain structure is much promoted by the phenyl and ester groups. The promoting effect of the ester groups is the highest in benzyl, followed by allyl, and ethyl, isopropyl, butyl, and cyclohexyl. Such a promoting effect can reasonably be attributed to the $-I$ effect of these groups.

Some of the present authors have previously shown that acylcobalt carbonyls isomerize under relatively mild conditions.[1-4] In the reaction of cobalt hydrocarbonyl with ethyl acrylate, the α-carbon was selectively carbonylated to give α-carbethoxypropionylcobalt carbonyl.[2] This fact shows that the ester group in the acrylate has a significant effect on the addition of cobalt hydrocarbonyl to the carbon-carbon double bond of the acrylate. The α-isomer, however, isomerized to β-isomer much more readily in non-polar solvents. On the other hand, n- and isobutyrylcobalt carbonyls isomerized with difficulty in non-polar solvents. Thus, the ester group adjacent to the acylcobalt carbonyl group has a promoting effect on the isomerization.

The present study will be concerned with the reaction of cobalt hydrocarbonyl with ethyl crotonate, ethyl vinylacetate, and different acrylates. From the former two olefins, three isomeric acylcobalt carbonyls are possible as reaction products. The effects of the ester groups on the distribution of these complexes and on the isomerization of the

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1) Y. Takegami, C. Yokokawa, Y. Watanabe and Y. Okuda, This Bulletin, **37**, 181 (1964).

2) Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada and Y. Okuda, *ibid.*, **37**, 1190 (1964).

3) Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada and Y. Okuda, *ibid.*, **38**, 787 (1965).

4) Y. Takegami, Y. Watanabe, H. Masada, Y. Okuda, K. Kubo and C. Yokokawa, *ibid.*, **39**, 1495 (1966).

comlexes will be examined. The reaction behavior of different acrylates and styrene will also be examined and compared.

Experimental

Reaction Procedure. The reaction was carried out in the way described in a previous paper, using 50 m*l* of a 0.09 M cobalt hydrocarbonyl solution in hexane in each run.[2)]

Analytical Procedure. The solution of crude products was treated with iodine and ethyl alcohol, and then the excess iodine was removed with crystalline sodium thiosulfate. After the solution had been concentrated, the products were gas-chromatographed on a column, three meters long, 3 mm in diameter, and filled with Apiezon L or Carbowax on Cerite, at 130—220 °C and at the carrier-gas (helium) flow rate of 70 m*l*/min. The infrared spectra were recorded on a Nippon Bunko Model DS-301 spectrophotometer.

Materials. The ethyl acrylate, ethyl crotonate, styrene, ethylmalonate, methylsuccinate, glutarate, succinates, α- and β-phenylpropionates, and methylmalonates were commercial products. The following acrylates were synthesized by the usual ester exchange method: benzyl, allyl, isopropyl, and cyclohexyl acrylates. They have been proved to be sufficiently pure by gas chromatography. The cobalt hydrocarbonyl was prepared in the way described previously.[1)] The ethyl vinylacetate was prepared from allyl chloride.[5)]

Results and Discussion

The Reaction of Ethyl Vinylacetate and Ethyl Crotonate with Cobalt Hydrocarbonyl. The results of the reaction are summarized in Table 1. All of the reactions were carried out in hexane under an atmosphere of carbon monoxide.

The vinylacetate reacted with cobalt hydrocarbonyl at 25°C, with a carbon monoxide absorption, to give three isomeric acylcobalt carbonyls, α- and γ-carbethoxybutyrylcobalt carbonyls and β-carbethoxy-isobutyrylcobalt carbonyl, which then gave the corresponding esters, diethyl ethylmalonate, diethyl methylsuccinate, and diethyl glutarate, upon treatment with an alcoholic iodine solution. The distribution of these complexes depended greatly on the reaction time (Exps. 1—5). When the reaction time was only 0.5 hr, the β-isomer, the methylsuccinate, was predominant (Exp. 1). The percentage of the β-isomer decreased with an increase in the reaction time, but that of the γ-isomer, the glutarate, increased reversely. When the reaction time was more than 1.5 hr, the γ-isomer was predominant and the percentage of the γ-isomer amounted to more than 90%. These facts show that the β-carbon of the vinylacetate is readily carbonylated with cobalt hydrocarbonyl to give the β-carbethoxy-isobutyrylcobalt carbonyl as the major product, then the β-isomer is readily isomerized to the γ-isomer under the conditions employed, and that the equilibrium among the complexes is very favorable to the γ-isomer. On the other hand, such 1-olefins as 1-pentene reacted with cobalt hydrocarbonyl to give *n*-caproylcobalt carbonyl as the major product and also α-methylvalerylcobalt carbonyl,[6)] these complexes were isomerized with much difficulty under the conditions described above.[4)] The results obtained here show that the ester group in the vinylacetate has a great

TABLE 1. THE REACTION OF COBALT HYDROCARBONYL WITH ETHYL VINYLACETATE AND ETHYL CROTONATE

Exp. No.	Reaction conditions* Time (hr)	CO Absorbed mol/mol-$HCo(CO)_4$	Yield of esters** mol/mol-$HCo(CO)_4$	Distribution of esters (%) Ethylmalonate	Methylsuccinate	Glutarate
1a	**Ethyl vinylacetate**					
1	0.5	0	0.05	7	56	37
2	1.5	0.07	0.14	11	30	59
3	3	0.14	0.16	9	26	65
4	4.5	0.20	0.15	3	12	85
5***	5	0.30	0.30	1	7	92
1b	**Ethyl crotonate**					
6	0.5	0	0.02	29	71	0
7	1.5	—	0.07	7	85	8
8	3	—	0.08	12	30	58
9***	5	0.20	0.21	9	30	61
10***	20	0.20	0.15	2	9	89

* Under an atmosphere of carbon monoxide at 25°C. The olefins: 1.5 mol/mol-$HCo(CO)_4$
** Diethyl ethylmalonate, diethyl methylsuccinate and diethyl glutarate
*** The olefins: 3 mol/mol-$HCo(CO)_4$

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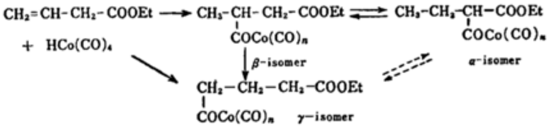
5) E. Rietz, "Organic Syntheses," Coll. Vol. III, p. 851 (1955).

6) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

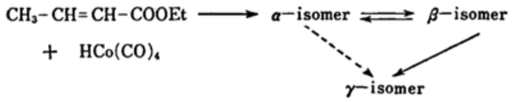
effect on the addition of cobalt hydrocarbonyl to the double bond and on the isomerization of the acylcobalt carbonyls: the ester group promotes the carbonylation of the carbon of the double bond more adjacent to the ester group, while on the contrary, the ester group promotes the isomerization of the acylcobalt carbonyls to that which has an acylcobalt group further from the ester group.

In this reaction, the α-isomer, the ethylmalonate, was obtained in a considerable yield. For the formation of this complex, two routes are possible: one from ethyl crotonate, and the other from the β-isomer. Under the conditions employed, the vinylacetate did not isomerize to ethylcrotonate. Thus, it is safe to conclude that the α-isomer is formed *via* the β-isomer by the isomerization.

On the basis of these results, the reaction seems to follow this reaction scheme:



Ethyl crotonate also gave the three isomeric acylcobalt carbonyls as the reaction products (Exps. 6—10). The distribution of the complexes depended on the reaction time. Longer reaction times were more favorable to the γ-isomer. The percentage of the α- and β-isomers decreased to less than 10%. When the reaction time was only 0.5 hr, the percentage of the α-isomer amounted to about 30%, indicating that, at the initial step of the reaction, the α-carbon of the crotonate was carbonylated relatively readily. The reaction of the crotonate was very slow. At 25°C, after even 20 hr, the yield of the products was only 0.2 mol/mol-$HCo(CO)_4$. On the contrary, the isomerization among the complexes, especially from the α-isomer to the β-isomer, appears to occur more readily. In the light of these results, the reaction of the crotonate may be considered to proceed typically as follows:



The Reaction of Cobalt Hydrocarbonyl with Styrene and Different Acrylates. The results of the reaction are summarized in Tables 2 and 3 and in Fig. 1. All of the reactions under an atmosphere of carbon monoxide were carried out in hexane in two stages: at first for 3 hr at 0°C, and then at 25°C for 0.5—6 hr. The gas absorption ceased completely within 3 hr at 0°C. As we have previously reported in detail, the rate of cobalt hydrocarbonyl consumption may be estimated by means of the rate of carbon monoxide absorption in the system.[2] At a low temperature the acylcobalt carbonyls with a branched-chain structure were almost selectively formed by the direct addition of cobalt hydrocarbonyl to the olefins, while higher temperatures promoted the isomerization of these complexes to those with a straight-chain structure. The complexes were finally converted to the corresponding esters upon treatment with an alcoholic iodine solution. The effects of the structures on the isomerization were examined by means of the distribution of the esters.

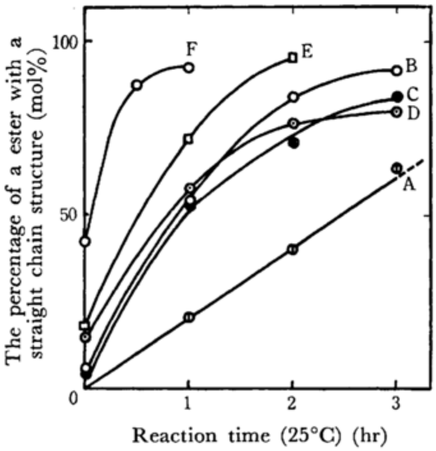


Fig. 1. The percentage of a ester with a straight chain structure *vs.* time plots for the reaction of cobalt hydrocarbonyl with styrene and acrylates.

All of the reaction were carried out in two stages: At 0°C for 3 hr and then at 25°C for 0.5—3 hr.

A: Styrene	D: Cyclohexyl acrylate
B: Ethyl acrylate	E: Allyl acrylate
C: Isopropyl acrylate	F: Benzyl acrylate

A large excess of the olefin was used in order that the cobalt hydrocarbonyl used might be consumed completely and in order that acyl cobalt carbonyls might not be converted to aldehydes. The amount of aldehydes formed was negligible.

Styrene. As Table 2 shows, styrene gave selectively, α-phenylpropionylcobalt carbonyl at 0°C, while at 25°C this isomerized gradually to β-phenylpropionylcobalt carbonyl. The isomerization was slower than that in the case of acrylates (*cf.* Fig. 1). These facts show that the phenyl group activates the α-carbon of the styrene for the carbonylation and that it also promotes the isomerization. On the other hand, in the case of 1-pentene, caproyl- and α-methylvalerylcobalt carbonyls were formed in a 3 : 1 ratio at 0—25°C in non-polar solvents; these complexes were isomerized with much difficulty under these conditions.[4,6] This apparent discrepancy is due to some difference between the effects of the phenyl and propyl groups (CH_2=CH–R, R=Ph and Pr). Two effects appear to operate here. The first,

TABLE 2. THE REACTION COBALT HYDROCARBONYL WITH STYRENE

Exp. No.	Reaction conditions*		CO Absorbed	Yield of esters**	The percentage of β-phenylpropionate (mol%)
	Temp. (°C)	Time (hr)	mol/mol-$HCo(CO)_4$		
11	0	3	0.47	0.51	0
12***	0—25	3+1	0.50	0.40	21
13	0—25	3+2	0.46	0.40	40
14	0—25	3+3	0.47	0.35	64
15	0—25	3+6	0.46	0.35	88

* Under an atmosphere of carbon monoxide. Styrene: 3 mol/mol-$HCo(CO)_4$

** α- and β-Phenylpropionates

*** The reaction was carried out in two stages: at first at 0°C for 3 hr and then at 25°C for 1 hr

TABLE 3. THE REACTION OF COBALT HYDROCARBONYL WITH ACRYLATES

Exp. No.	Reaction conditions*		CO Absorbed	Yield of esters**	The percentage of succinate (mol%)
	Temp. (°C)	Time (hr)			
3a	**Ethyl acrylate**				
16	0	3	0.47	0.57	3
17	0—25	3+1	0.49	0.60	54
18	0—25	3+2	0.51	0.58	84
19	0—25	3+3	0.48	0.59	91
3b	**Cyclohexyl acrylate**				
20	0	3	0.33	0.25	15
21	0—25	3+1	0.35	0.64	56
22	0—25	3+2	0.35	0.73	76
23	0—25	3+3	0.33	0.74	80
3c	**Isopropyl acrylate**				
24	0	3	0.40	0.50	3
25	0—25	3+1	0.44	0.58	54
26	0—25	3+2	0.47	0.61	70
27	0—25	3+3	0.48	0.64	84
3d	**Benzyl acrylate**				
28	0	3	0.33	0.18	42
29	−5	5	0.41	0.10	45
30	0—25	3+0.5	0.36	0.29	87
31	0—25	3+1	0.35	0.45	92
3e	**Allyl acrylate**				
32	0	3	0.47	0.51	17
33	0—25	3+1	0.54	0.56	71
34	0—25	3+2	0.55	0.50	95

* Under an atmosphere of carbon monoxide. Acrylate: 3 mol/mol-$HCo(CO)_4$

** Succinate and methylmalonate

and probably the most important, is an electronic effect. The electron-attracting effect, the $-I$ effect, of the phenyl group is stronger than that of the propyl, and the phenyl group also has a conjugation effect. A second effect concerns a steric factor. The steric effect of the phenyl, however, seems to be almost comparable to that of the propyl. Thus, the large difference in reaction behavior between these groups may be attributed to the electronic effect.

In the α-phenylpropionylcobalt carbonyl, the $-I$ effect of the phenyl group probably decreases the electron density on the cobalt atom; this, in turn, reduces the thermal stability of this complex. This consideration is strongly supported by the fact that acylcobalt carbonyls are safely separated as more stable triphenylphosphine derivatives,[6] in which a stronger basicity of the phosphine increases the electron density on the cobalt atom.[7]

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7) E. R. Tucci, *Ind. Eng. Chem., Product Research and Development,* **7**, 32 (1968).

Accordingly, it is safe to conclude that the promoting effect of the phenyl on the isomerization of the α-phenylpropionylcobalt carbonyl to the β-isomer is due to the $-I$ effect.

Acrylates. As Table 3 shows, different acrylates were used. All of them behave similarly in this reaction. At first at 0°C, acylcobalt carbonyls with a branched-chain structure predominated, and then at 25°C they were isomerized readily to those with a straight-chain structure.

As Fig. 1 shows, the isomerization rate was the highest in benzyl acrylate, followed by allyl and by ethyl, isopropyl, and cyclohexyl acrylates. It is well known that the ester groups have the $-I$ effect. Thus, the promoting effect of the ester groups on the isomerization can be explained by the argument employed in the case of styrene. The fact that even α-carbethoxypropionylcobalt carbonyl triphenylphospine is too unstable to be separated[6] indicates that the ester group greatly reduces the thermal stability of this type of complex. Moreover, the largest promoting effect of the benzyl and allyl ester groups may be attributed to the larger $-I$ effect of the benzyl and allyl groups. The effects of such saturated alkyl groups as ethyl and isopropyl seem to be almost comparable (*cf.* Fig. 1).