BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 1495—1498 (1966)

Studies of the Organic Reaction of Metal Carbonyl. VIII.* The Isomerization of Aliphatic C_5- and C_6-Acylcobalt Carbonyls

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(Received September 24, 1965)

The isomerization of C_5-acyl(*n*-valeryl- and α-methylbutyryl-) and C_6-acyl(*n*-caproyl-, α-methylvaleryl- and α-ethylbutyryl-)cobalt carbonyls has been studied and compared with that of C_4- acyl(*n*- and isobutyryl-)cobalt carbonyls previously reported. It has been observed that solvents have great effects on the isomerization (the rate and equilibrium) of the C_5-acylcobalt carbonyls. The equilibrium proportion of the isomers (iso/normal) is almost 1 in diethyl ether and tetrahydrofuran. In solvents such as dioxane, ethyl acetate and benzene it seems difficult for this isomerization to occur. α-Ethylbutyrylcobalt carbonyl appears to isomerize directly to *n*-caproylcobalt carbonyl. However, *n*-caproylcobalt carbonyl isomerizes only to α-methylvalerylcobalt carbonyl; the reverse isomerization also occurs, but it seems very difficult for any other isomerization between the two of them to occur.

The previous studies of this series have shown that acylcobalt carbonyls readily isomerize and that this isomerization is remarkably affected by the various reaction conditions; with the isomerization of *n*- and isobutyrylcobalt carbonyl (C_4-acylcobalt carbonyls), such solvents as diethyl ether and ethyl acetate have a great effect on the rate and the equilibrium.[1-3]

In the present investigation, the isomerization of C_5- and C_6-acylcobalt carbonyls has been studied in detail by examining the effects of solvents on this reaction. In addition, the possible course of the isomerization of α-ethylbutyrylcobalt carbonyl to *n*-caproylcobalt carbonyl has been investigated.

Experimental

The General Procedures.—The reactions were carried out in the way described in previous papers.[1,2]

The Analytical Procedures.—The reaction products were analyzed by means of a study of their infrared spectra, which were measured on a Shimadzu model IR-27 spectrophotometer, and by gas chromatography; a column 4.5 m. long and 3 mm. in diameter, filled with dilauryl phthalate or silicon DC 550 on cerite, was used. The column temperature was 80 to 110°C, and the flow rate was 50 to 75 ml. per minute.

Materials.—Cobalt hydrocarbonyl was prepared

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* Part VII: Y. Takegami, C. Yokokawa, Y. Watanabe and H. Masada, This Bulletin, **38**, 1649 (1965). Presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

1) Y. Takegami, C. Yokokawa, Y. Watanabe, H. Masada and Y. Okuda, This Bulletin, **38**, 787 (1965).

2) Y. Takegami, C. Yokokawa, Y. Watanabe and Y. Okuda, ibid., **37**, 181 (1964).

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

according to the method described in a previous paper.2) Valeryl chloride, α-methylbutyryl chloride, and *n*-caproyl chloride were commercial products. α-Ethylbutyryl chloride and α-methylvaleryl chloride were prepared by the chlorination of α-ethylbutyric acid and α-methylvaleric acid respectively with thionyl chloride. As the authentic samples, methyl, ethyl, and propyl esters of these acids, prepared by the alcoholysis of the acid halides, were used. The solvents used were dried by the usual methods.

Results and Discussion

The Reaction of *n*-Valeryl and α-Methylbutyryl Chloride with Potassium Cobalt Carbonylate.—The results of the reactions of *n*-valeryl chloride and α-methylbutyryl chloride are summarized in Tables I and II.

In the isomerization of *n*- and isobutyrylcobalt carbonyls, equilibrium between the two isomers has been observed to exist and to be remarkably affected by the solvents; the equilibrium proportion of the isomers (iso/normal) is almost zero in dioxane and tetrahydrofuran, 1/3 in ethyl acetate, and about 1 in diethyl ether, but in a nonpolar solvent such as benzene this isomerization does not occur at all.1,2)

In this program, the isomerization of C_5-acylcobalt carbonyls was carried out in various solvents in order to study the effect of solvents in detail. The percentages in the last columns of the tables indicate the degree of the isomerization, the proportion of isomerized *n*-valeryl- or α-methylbutyrylcobalt carbonyls. As the reaction products, about 0.7 to 0.3 mol. of valerate and methylbutyrate per mole of potassium cobalt carbonylate was obtained. The yield of the esters decreased with an increase in the reaction time. This may be partly attributed to a thermal instability of the acylcobalt carbonyls.

In diethyl ether under carbon monoxide or nitrogen, *n*-valerylcobalt carbonyl isomerized readily to α-methylbutyrylcobalt carbonyl (Exps. 1—3). The degree of the isomerization amounted to 43% after 9 hr. On the other hand, α-methylbutyrylcobalt carbonyl also isomerized, to give 30% of *n*-valerate, after 9 hr. (Exp. 13). In these

TABLE I. THE REACTION OF *n*-VALERYL CHLORIDE WITH POTASSIUM COBALT CARBONYLATE

Exp. No.	Reaction conditions*1			Yield of esters*2 mol./mol.-$KCo(CO)_4$	The degree of isomerization*3 %
	Atmosphere	Solvent	Time, hr.		
1	CO	Diethyl ether	4	0.63	32
2	CO	Diethyl ether	9	0.35	43
3	N_2	Diethyl ether	4	0.53	35
4	CO	THF	4	0.40	12
5	CO	THF	8	0.36	20
6	CO	THF	16	0.30	30
7	N_2	THF	4	0.37	22
8	N_2	THF	8	0.35	30
9	CO	Dioxane	4	0.42	2
10	CO	Ethyl acetate	4	0.42	2
11	CO	Benzene	4	0.30	1

*1 At 30°C. THF = tetrahydrofuran

*2 The reaction products were identified as *n*-propyl valerate and *n*-propyl α-methylbutyrate.

*3 (α-Methylbutyrate/(α-Methylbutyrate + Valerate)) × 100

TABLE II. THE REACTION OF α-METHYLBUTYRYL CHLORIDE WITH POTASSIUM COBALT CARBONYLATE

Exp. No.	Reaction condition*1			Yield of esters*2 mol./mol.-$KCo(CO)_4$	The degree of isomerization*3 %
	Atmosphere	Solvent	Time, hr.		
12	CO	Diethyl ether	4	0.41	25
13	CO	Diethyl ether	9	0.30	30
14	N_2	Diethyl ether	4	0.40	25
15	CO	THF	4	0.35	18
16	CO	THF	8	0.27	28
17	CO	THF	16	0.20	35
18	N_2	THF	4	0.46	33
19	N_2	THF	8	0.41	42
20	CO	Dioxane	4	0.50	2
21	CO	Ethyl acetate	4	0.32	6
22	CO	Benzene	4	0.30	7

*1 At 30°C

*2 *n*-Propyl valerate and *n*-propyl α-methylbutyrate

*3 (Valerate/(Valerate + α-Methylbutyrate)) × 100

TABLE III. THE REACTION OF α-METHYLVALERYL AND *n*-CAPROYL CHLORIDE WITH POTASSIUM COBALT CARBONYLATE (at 30°C and CO atmosphere)

Exp. No.	Substance	Reaction condition		Yield of esters[*1] mol./mol.-$KCo(CO)_4$	The percentage of the isomerized products[*2]		
		Solvent	Time, hr.		*n*-Caproate %	α-Methyl-valerate %	α-Ethyl-butvrate %
33	α-Methylvaleryl chloride	Diethyl ether	14	0.30	10	—	0 (trace)
34	α-Methylvaleryl chloride	Ethyl acetate	13	0.37	0	—	0
35	α-Methylvaleryl chloride	Dioxane	13	0.50	2	—	0
36	*n*-Caproyl chloride	Diethyl ether	4	0.45	—	23	0
37	*n*-Caproyl chloride	Diethyl ether	9	0.52	—	26	0
38	*n*-Caproyl chloride	Diethyl ether	14	0.47	—	28	0
39	*n*-Caproyl chloride	Ethyl acetate	9	0.67	—	6	0
40	*n*-Caproyl chloride	Ethyl acetate	14	0.56	—	10	0
41	*n*-Caproyl chloride	Ethyl acetate	23	0.55	—	17	0
42	*n*-Caproyl chloride	Dioxane	20	0.50	—	0	0

[*1] Ethyl *n*-caproate, ethyl α-methylvalerate and ethyl α-ethylbutyrate

[*2] (*n*-Caproate, α-Methylvalerate or α-Ethylbutyrate/Total esters) × 100

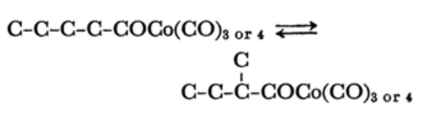
TABLE IV. THE REACTION OF α-ETHYLBUTYRYL CHLORIDE WITH POTASSIUM COBALT CARBONYLATE (at 30°C and CO atmosphere)

Exp. No.	Reaction condition		Yield of esters[*1] mol./mol.-$KCo(CO)_4$	The percentage of the isomerized products[*2]	
	Solvent	Time, hr.		*n*-Caproate %	α-Methylvalerate %
23	Diethyl ether	4	0.66	6	0
24	Diethyl ether	9	0.54	10	~0
25	Diethyl ether	22	0.56	25	~0 (<2)
26	Ethyl acetate	9	0.52	11	~0
27	Ethyl acetate	20	0.30	14	~0
28	Benzene	8	0.41	2	0
29	Toluene	3	0.50	5	0
30	Toluene	10	0.35	24	0
31	Dioxane	10	0.46	0	~0
32	Dioxane	20	0.38	0	0

[*1] Ethyl *n*-caproate, ethyl α-methylvalerate and ethyl α-ethylbutyrate

[*2] (*n*-Caproate or α-Methylvalerate/Total esters) × 100

two cases, the degree of isomerization seemed to increase with an increase in the reaction time. These facts seem to suggest that there is an isomerization equilibrium between the isomers:



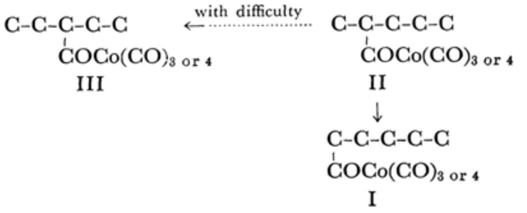
$$\text{C-C-C-C-COCo(CO)}_{3\text{ or }4} \rightleftarrows \text{C-C-}\overset{\text{C}}{\text{C}}\text{-COCo(CO)}_{3\text{ or }4}$$

The equilibrium proportion (iso/normal) may be about 1 under the conditions used. Similarly, in tetrahydrofuran the equilibrium proportion (iso/normal) of the same reaction seemed to be about 1. However, with butyrylcobalt carbonyls the equilibrium is almost completely favorable to *n*-butyrylcobalt carbonyl in tetrahydrofuran.[1] Therefore, the behavior of tetrahydrofuran in the isomerization of the C_5-acylcobalt carbonyls appears to be different from that in the isomerization of the C_4-acylcobalt carbonyls.

In dioxane, ethyl acetate and benzene *n*-valerylcobalt carbonyl isomerized, but they gave only about 2% of α-methylbutyrate after 4 hr. (Exps. 9—11), while α-methylbutyrylcobalt carbonyl gave 2 to 7% of *n*-valerate after 4 hr. (Exps. 20—22), suggesting that the C_5-acylcobalt carbonyls isomerize with much difficulty in these solvents. On the other hand, it has been observed that, in dioxane, isobutyrylcobalt carbonyl readily isomerized to give almost 100% of *n*-butyrylcobalt carbonyl after 2.5 hr. at 25°C, whereas the C_4-acylcobalt carbonyls seem very difficult to isomerize in benzene.[1] Thus, dioxane and benzene also seem to have effects on the isomerization of the C_5-acylcobalt carbonyls apparently different from those on the isomerization of the C_4-acylcobalt carbonyls.

The Reaction of α-Ethylbutyryl Chloride, α-Methylvaleryl Chloride, and *n*-Caproyl Chloride with Potassium Cobalt Carbonylate. —The isomerization of C_6-acylcobalt carbonyls was also investigated. The results of these reactions are summarized in Tables III and IV.

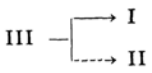
As is shown in Table III, α-methylvalerylcobalt carbonyl (II) isomerized to give some *n*-caproate, but only a trace of α-ethylbutyrate (Exps. 33, 35).



The reverse isomerization of I to II was also observed (Exps. 36—41); in diethyl ether, 23, 26 and 28% of α-methylvalerate was obtained after 4, 9, and 14 hr. respectively, and in ethyl acetate 17% of α-methylvalerate was formed after 23 hr., these facts suggest that the proportion of the isomerized product increases with an increase in the reaction time. However, in ether or ethyl acetate I gave only a trace of α-ethylbutyrate, even after 14 to 23 hr. From this fact, I appears to isomerize to II rather easily, but only with much difficulty to III:

$$\mathrm{II} \longleftarrow \mathrm{I} \dashrightarrow \mathrm{III}$$

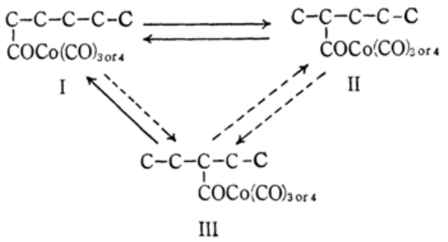
On the other hand, III isomerized to give I in a relatively good yield (Exps. 23—30); in diethyl ether, III gave 6, 10, and 25% of I after 4, 9, and 22 hr. respectively; similarly, in ethyl acetate, benzene or toluene, *n*-caproate was also obtained as the isomerization product. However, α-methylvalerate, which was expected to be one of the isomerization products, was obtained in only a low yield in all of these cases; in these solvents, only a trace or less than 2% of α-methylvalerate was obtained after 4 to 22 hr. These facts seem to indicate that III isomerizes relatively readily to I but only with difficulty to II:



As the course of this isomerization (III to I), two ways are possible: in the first course, III directly isomerizes to I, while in the second course III isomerizes to I via II.

In the present case, the isomerization of III to I seems to proceed through the first course, This conclusion is drawn from the following facts: a) The isomerization of II to I occurred relatively slowly; in diethyl ether, II gave 10% of *n*-caproate, even after 14 hr. but III gave 10% of *n*-caproate after 9 hr. These facts have a strong suggest that the isomerization of II to I occurs more slowly than that of III to I. It is, however, reasonable to consider that the isomerization of III to I via II can not proceed more rapidly than that of II to I. Thus, the isomerization of III to I seems not to take the second course. b) In the isomerization of III, α-methylvalerate, i. e., II, was obtained in only a very low yield. This fact could be explained by the second course as follows: the isomerization of III to II was slower than that of II to I, the isomerization of III to II being the rate-determining step. However, the actual isomerization of III to I proceeds more readily than that of II to I, as has been described in a). Accordingly, in the isomerization of III, II seems to be formed by the successive isomerizations, III to I and then I to II.

On the base of facts mentioned above, the isomerization relation among the C_6-acylcobalt carbonyls (I, II and III) may be summarized as follows:



That is, such isomerizations as I to II, II to I and III to I occur relatively readily, but it appears difficult for the other isomerizations to occur.

The isomerization equilibrium among the three isomers could not be determined since the C_6-acylcobalt carbonyls generally isomerize more slowly than the C_5-acylcobalt carbonyls (for example, cf. Exps. 1 and 36).

As Exps. 32, 35, and 42 show, in dioxane it seems difficult for C_6-acylcobalt carbonyls to isomerize, suggesting that the behavior of a solvent may be different in the isomerization of the C_6-acylcobalt carbonyls and in that of the C_4-acylcobalt carbonyls.[1]