Studies of the Organic Reactions of Metal Carbonyls. VI.* The Isomerization of Acylcobalt Carbonyls—The Effects of Solvents and of the Structure of the Acyl Group

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(Received September 22, 1964)

The previous works in this laboratory have demonstrated that alkyl- and acylcobalt carbonyls readily isomerize and that this isomerization has a significant effect on the distribution of the products which are given by the reaction of olefin with cobalt hydrocarbonyl.[1,2] Heck and Breslow[3] have also observed that a similar isomerization occurs in the reaction of 1-chlorooctane with sodium cobalt carbonylate. Lately, Wakamatsu[4] has reported that this type of isomerization also occurs in the reduction of acylcobalt carbonyl with synthesis gas under Oxo conditions.

In the present program, the isomerization of acylcobalt carbonyls has been studied in detail by examining the effects of solvent, atmosphere, temperature and the structure of the acyl group on this reaction. The data obtained indicate that the solvents as well as the reaction temperature and the atmosphere have a considerable effect on the isomerization reaction, the rate and the equilibrium, and that the isomerization of α-ethylbutyrylcobalt carbonyl to *n*-caproylcobalt carbonyl occurs.

Experimental

The Reaction of Acyl Halides with Potassium Cobalt Carbonylate.—A 100 ml. four-necked flask, fitted with a 50 ml. dropping funnel, a stirrer, and a rubber stopple, was connected with a gas buret and then flushed with carbon monoxide or nitrogen. By the use of a syringe, 50 ml. of 0.09 M cobalt hydrocarbonyl in a toluene solution was put into the flask and then titrated with a 1/2 N ethanol solution of potassium hydroxide in the presence of phenolphthalein. The potassium cobalt carbonylate solution thus obtained was evaporated under a vacuum, and then 50 ml. of various solvents were

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[*] Presented in part at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1964. Presented in part at the Symposium of Organometallic Compounds, Osaka, November, 1964.

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) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, 85, 2779 (1963).

4) H. Wakamatsu, Abstracts of the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, 1964, p. 151.

added. To the solution of potassium cobalt carbonylate, 4.5 mmol. of acyl halide was added; the mixture was then agitated vigorously for several hours at 0 or 25°C. After a desired reaction time, 30 ml. of a saturated solution of iodine in benzene and 4 ml. of alcohol were stirred into the reaction mixture; the agitation was continued until gas ceased to evolve. By this treatment, acylcobalt carbonyl was converted into the corresponding ester of carboxylic acid.5) The solution of this ester was concentrated and then gas chromatographed.

Materials.—Cobalt hydrocarbonyl was prepared according to the method described in a previous paper.1) *n*-Butyryl chloride, isobutyryl bromide and *n*-caproyl chloride were obtained commercially. α-Ethylbutyryl chloride was prepared by the chlorination of α-ethylbutyric acid with thionyl chloride.6) These acyl halides were transformed to the corresponding esters and were proved to be sufficiently pure by gas chromatography. Diethyl ether, ethyl acetate, dioxane, benzene and hexane were dried by the usual methods.

Results and Discussion

The Reaction of Butyryl Halides with Potassium Cobalt Carbonylate. — The results of the reactions of isobutyryl bromide and *n*-butyryl chloride are summarized in Tables I and II respectively. It has been known1) that the isomerization of butyrylcobalt carbonyls is affected by the reaction conditions (temperature, atmosphere and solvent). In tetrahydrofuran, isobutyrylcobalt carbonyl readily isomerizes to *n*-butyrylcobalt carbonyl, but *n*-butyrylcobalt carbonyl seems to be difficult to isomerize. In isopropyl ether, isobutyrylcobalt carbonyl also isomerizes, but the isomerization proceeds more slowly than in tetrahydrofuran.

In this program, the reactions are carried out in various solvents, such as diethyl ether, ethyl acetate, dioxane, benzene, hexane and some mixtures of two kinds of them, in order to study the effect of the solvent in detail.

All of these reactions were carried out at 25°C, since it is relatively difficult for the isomerization reaction of acylcobalt carbonyl to occur at 0°C.1) The percentages in the last columns of the tables indicate the degree of the isomerization, the proportion of isomerized iso- or *n*-butyrylcobalt carbonyl.

In diethyl ether under a carbon monoxide atmosphere, isobutyrylcobalt carbonyl isomerized readily to give a large amount of *n*-butyrate (Exps. 1—5). The degrees of the isomerization were 12, 29 and 41% after one

TABLE I. THE REACTION OF ISOBUTYRYL BROMIDE WITH POTASSIUM COBALT CARBONYLATE AT 25°C

No.	Atmosphere	Solvent*	Time hr.	Yield of esters** [mol./mol. KCo(CO)$_4$]	The degree of isomerization, %***
1	CO	E	1	0.85	12
2	CO	E	3	0.86	18
3	CO	E	7.5	0.93	29
4	CO	E	12	0.64	37
5	CO	E	20	0.69	41
6	N$_2$	E	4	0.96	39
7	N$_2$	E	10	0.48	50
8	CO	EA	2	0.47	13
9	CO	EA	8	0.25	53
10	CO	EA	14	0.49	61
11	CO	EA	28	0.51	69
12	CO	D	1.5	0.27	77
13	CO	D	2.5	0.34	100
14	CO	B	3	0.31	0
15	CO	B	6	0.15	0
16	CO	H	10.5	0.40	0
17	CO	EA 25+B 25	7	0.54	0
18	CO	E 25+B 25	5	0.76	9
19	CO	D 40+B 10	3.5	0.32	82
20	CO	D 40+B 10	10	0.25	100

* E=diethyl ether, EA=ethyl acetate, D=dioxane, B=benzene and H=hexane
EA 25+B 25=a mixed solvent of 25 ml. of ethyl acetate and 25 ml. of benzene

** The reaction products were identified as *n*-propyl *n*-butyrate and *n*-propyl isobutyrate.

*** (*n*-Butyrate/(*n*-Butyrate+Isobutyrate))×100

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5) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **84**, 2499 (1962).

6) W. H. Miller, A. M. Dessert and G. W. Anderson, ibid., **70**, 502 (1948).

TABLE II. THE REACTION OF *n*-BUTYRYL CHLORIDE WITH POTASSIUM COBALT CARBONYLATE AT 25°C

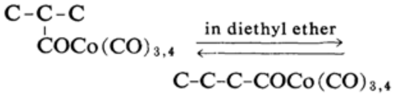
No.	Atmosphere	Solvent*	Time hr.	Yield of esters** [mol./mol. $KCo(CO)_4$]	The degree of isomerization, %***
21	CO	E	2	0.58	12
22	CO	E	5	0.46	31
23	CO	E	10	0.73	41
24	CO	E	15	0.65	44
25	N_2	E	1.5	0.89	31
26	N_2	E	4	0.73	41
27	N_2	E	7	0.60	44
28	N_2	E	10	0.59	39
29	CO	EA	2	0.54	0
30	CO	EA	4	0.67	0
31	CO	EA	8	0.46	0
32	CO	EA	14	0.52	13
33	CO	EA	28	0.17	17
34	CO	D	9	0.13	0
35	CO	B	3.5	0.36	0
36	CO	B	6	0.40	0
37	CO	B	10	0.28	0
38	CO	H	10.5	0.20	0

* Abbreviations have the same meanings as in Table I.

** The reaction products were identified as *n*-propyl *n*-butyrate and *n*-propyl isobutyrate.

*** (Isobutyrate/(*n*-Butyrate+Isobutyrate))×100

hour, 7.5 hr. and 20 hr. of reaction time respectively. Thus, the degree of the isomerization increased with an increase in the reaction time. However, with an increase in the reaction time from 12 to 20 hr., the degree of the isomerization increased from 37 to 41% (Exps. 4, 5), suggesting that the velocity of this isomerization is small near this proportion. On the other hand, *n*-butyrylcobalt carbonyl similarly isomerized to give isobutyrate, and the degree of the isomerization increased with an increase in the reaction time (Exps. 21—28); under a carbon monoxide atmosphere, *n*-butyrylcobalt carbonyl gave 12, 31 and 44% of isobutyrate after 2, 5 and 15 hr. of reaction time respectively, but under nitrogen, it gave 31 and 44% of isobutyrate after 1.5 and 7 hr., indicating that the isomerization proceeded faster under nitrogen than under carbon monoxide. Thus, both *n*- and isobutyrylcobalt carbonyls relatively readily isomerized to give an almost equimolar mixture of two isomers. This seems to indicate that there is the following equilibrium between the isomers:



$$\begin{array}{l}\mathrm{C{-}C{-}C}\\ \quad\mid\\ \ \mathrm{COCo(CO)_{3,4}}\end{array} \xrightleftharpoons{\text{in diethyl ether}} \mathrm{C{-}C{-}C{-}COCo(CO)_{3,4}}$$

The equilibrium proportion of two isomers under the conditions used may be about 50 and 50% respectively. The reaction atmosphere had a great effect on the rate of the isomerization, but it seemed to have no effect on the equilibrium.

Similarly, in ethyl acetate the degree of the isomerization increased with a prolonging of the reaction time. Isobutyrylcobalt carbonyl gave 13% of the isomerized product after 2 hr. and about 70% after 28 hr., but *n*-butyrylcobalt carbonyl gave less than 20% of the isomerized product even after 28 hr. This seems to indicate that it is relatively difficult to isomerize *n*-butyrylcobalt carbonyl in this solvent. Thus, in ethyl acetate, the equilibrium proportion of *n*- and isobutyrylcobalt carbonyl seemed to be about 70 and 30% respectively; ethyl acetate evidently removed this equilibrium toward *n*-butyrylcobalt carbonyl more than diethyl ether did. Moreover, in dioxane, isobutyrylcobalt carbonyl easily isomerized (Exps. 15, 16), but *n*-butyrylcobalt carbonyl did not seem to isomerize under the conditions used (Exp. 34), suggesting that this equilibrium is almost completely favorable to *n*-butyrylcobalt carbonyl.

The relation between the reaction time and the proportion of the isobutyrate included in the products is illustrated in Fig. 1. These isomerization curves evidently show that the rate and the equilibrium of the isomerization are remarkably affected by the solvents, as has been described above.

On the other hand, in nonpolar solvents, benzene and hexane, it seemed difficult for the isomerization of both *n*- and isobutyrylcobalt carbonyl to occur (Exps. 12—14, 35—38).

TABLE III. THE REACTION OF α-ETHYLBUTYRYL AND *n*-CAPROYL CHLORIDE WITH POTASSIUM COBALT CARBONYLATE IN DIETHYL ETHER

No.	Substance	Atmosphere	Temp. °C	Time. hr.	Yield of esters* [mol./mol. $KCo(CO)_4$]	$\frac{n\text{-Ester}\times 100}{\text{Total esters}}$ %
39	α-Ethylbutyryl chloride	CO	0	8	0.73	2
40	α-Ethylbutyryl chloride	CO	25	5	0.80	14
41	α-Ethylbutyryl chloride	CO	25	27	0.60	35
42	α-Ethylbutyryl chloride	N_2	0	8	0.90	2
43	α-Ethylbutyryl chloride	N_2	25	3	0.75	21
44	α-Ethylbutyryl chloride	N_2	25	5	0.73	26
45	*n*-Caproyl chloride	CO	30	14	0.54	58

* The reaction products were identified as ethyl α- ethylbutyrate, ethyl α-methylvalerate and *n*-caproate.

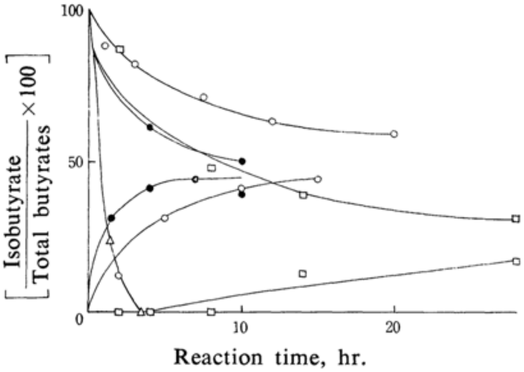


Fig. 1. The proportion of isobutyrate obtained vs. time plots for the reactions of iso- and *n*-butyryl halides with potassium cobalt carbonylate.

- ○ In diethyl ether under carbon monoxide
- ● In diethyl ether under nitrogen
- □ In ethyl acetate under carbon monoxide
- △ In dioxane under carbon monoxide

Potassium cobalt carbonylate relatively readily dissolves in the above-mentioned polar solvents, but it seems difficult for it to dissolve in these nonpolar solvents. However, the expected reaction, the formation of butyrylcobalt carbonyls, was proved to occur even in these solvents.** Thus, the above results with the nonpolar solvents are not due to the insolubility of the potassium cobalt carbonylate in these solvents.

The yields of the expected products, *n*- and isobutyrate, are relatively poor in the reactions in dioxane, benzene and hexane. This may be partly attributed to an instability of intermediates, i. e., *n*- and isobutyrylcobalt carbonyl, in these solvents.

In mixtures of polar and nonpolar solvents, the velocity of the isomerization of isobutyrylcobalt carbonyl was small, as compared with the case using only a polar solvent (Exps. 17—20). Especially in a benzene-dioxane solvent, a relatively small amount of benzene (20%) remarkably decreased the velocity of the isomerization (cf. Exp. 16 and 19).

As has been mentioned above, it is evident that solvents have a great effect on the isomerization of butyrylcobalt carbonyls. The reason for these phenomena can not be definitely established, but these effects may be partly attributed to the coordination of solvents with cobalt carbonyl complex, potassium and organocobalt carbonyls. This consideration seems to be supported by the facts that polar solvents have a great effect on the isomerization and that the sodium cobalt carbonylate forms a coordination compound with diethyl ether.[7]

The Reaction of α-Ethylbutyryl Chloride with Potassium Cobalt Carbonylate.—The isomerization of α-ethylbutyryl cobalt carbonyl (I) was also investigated. The results of this reaction are summarized in Table III. As is shown in the table, I gave an ester with a straight-chain structure, ethyl *n*-caproate (Exps. 39—44), indicating that I isomerized to *n*-caproylcobalt carbonyl (III); at 0°C, I gave only 2% of the isomerized product after 8 hr. under carbon monoxide and nitrogen atmospheres (Exps. 39, 42), but at 25°C under a carbon monoxide atmosphere, I relatively readily isomerized to give 14 and 35% of the isomerized product after 5 and 27 hr. and, under nitrogen, 21 and 26% after 3 and 5 hr. respectively. Thus, nitrogen atmosphere apparently also accelerated this isomerization. The isomerization of I seemed to proceed more slowly than that of butyrylcobalt carbonyl (cf. Exp. 2, 5 and 40).

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

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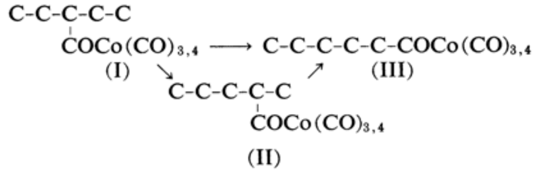
** In the reactions of butyryl halides with potassium cobalt carbonylate in benzene, butyrylcobalt carbonyls were actually formed, since butyrates were given with the gas evolution when the liquid phase of the reaction mixture was treated with iodine and alcohol. The amount of butyrates increased with an increase in the reaction time, suggesting that insoluble potassium cobalt carbonylate could be transformed into soluble butyrylcobalt carbonyls, even in nonpolar solvents.

[7] W. Hieber, O. Vohler and G. Braun, *Z. Naturforsch.*, **13b**, 192 (1958).



course I isomerizes to III via α-methylvalerylcobalt carbonyl (II). In the present case, however, it is impossible to discriminate by gas chromatography between the esters corresponding to I and II. Therefore, it can not be decided which course is taken in this type of isomerization.

The reaction of *n*-caproyl chloride was also carried out in order to check the reverse isomerization from III to I (Exp. 45). The result obtained shows that the isomerization of III to I and/or II occurred. However, it was not decided whether I or II was obtained or whether a mixture of I and II was obtained.

Summary

The reactions of *n*-butyryl chloride, isobutyryl bromide, α-ethylbutyryl chloride and *n*-caproyl chloride with potassium cobalt carbonylate have been studied. The results of this investigation are as follows.

(1) It has been observed that solvents have great effects on the isomerization of butyrylcobalt carbonyls, as do the reaction temperature and the atmosphere. The rate and the equilibrium of this isomerization are remarkably affected by the solvents; in polar solvents, the equilibrium proportion of products (iso/normal) is almost zero in dioxane, 1/3 in ethyl acetate, and 1 in diethyl ether. This isomerization proceeds more rapidly under nitrogen atmosphere than under carbon monoxide. On the other hand, in nonpolar solvents such as benzene this isomerization apparently does not occur.

(2) α-Ethylbutyrylcobalt carbonyl relatively readily isomerizes to *n*-caproylcobalt carbonyl. This isomerization is also accelerated under nitrogen atmosphere.

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