Studies of the Organic Reactions of Metal Carbonyls. I. The Isomerization of Alkyl- and Acylcobalt Carbonyls

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Heck and Breslow[1] obtained two isomeric products by the carbonylation of, for instance, methyl acrylate or 1-pentene with cobalt hydrocarbonyl. This seems to indicate that the addition of the carbonyl group to the olefinic bonds has taken place at both carbon atoms of the C=C double bond. It is possible, however, to assume that the alkyl- and/or acylcobalt carbonyls which are formed in the course of this type of reaction have been isomerized.

In the present program, in order to check the possibility of this isomerization, the reactions of some alkyl (*n*-propyl iodide, ethyl α-bromopropionate) and acyl halides (*n*-butyryl- and iso-butyryl halide) with potassium cobalt tetracarbonyl have been carried out. By means of the results of the structural determination of the products, it has been established that the isomerization mentioned above does indeed take place.

Experimental

The Preparation of Cobalt Hydrocarbonyl. — The aqueous solution of potassium cobalt tetracarbonyl was prepared by Blanchard's method.[2] After the acidification of this solution with hydrochloric acid, cobalt hydrocabonyl was extracted by toluene. Into a 2 l. bottle 250 ml. of an aqueous solution containing 160 g. of potassium hydroxide and 20 g. of potassium cyanide were placed. After the air in the bottle had been replaced with carbon monoxide, the solution containing 50 g. of cobalt(II) chloride hexahydrate and 250 ml. of water was added. The bottle was connected to a reservoir of carbon monoxide and shaken mechanically for 10 to 20 hr. at room temperature under the atmospheric pressure of carbon monoxide. After 17 to 20 l. of the carbon monoxide had been absorbed, a yellow solution of potassium cobalt tetracarbonyl was formed. This solution was stored in a dark and cool place under a carbon monoxide atmosphere. About 250 ml. of this solution and 400 ml. of toluene[3] were then placed in a 1 l. four-necked flask, fitted with a dropping funnel, a stirrer and a rubber stopple, and flashed with carbon monoxide. Seventy to eighty milliliters of concentrated hydrochloric acid were gradually but vigorously stirred in at 0°C. By the use of a hypodermic syringe, the cobalt hydrocarbonyl solution in toluene thus formed was transferred into another bottle, which was then filled with carbon monoxide and kept at −70°C.

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

[2] A. A. Blanchard and P. Gilmont, ibid., **62**, 1192 (1940).

[3] In some cases *n*-heptane was used instead of toluene (cf. Tables).

The concentration of this solution was determined by the analytical method proposed by Sternberg,[4] using 20 ml. of the sample. By diluting it with toluene, a 0.09 M solution was prepared and used for the reaction.

The Reaction of Alkyl Halides with Potassium Cobalt Tetracarbonyl. — 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 the air in the system was replaced with carbon monoxide or nitrogen. By the use of a syringe, 50 ml. of the cobalt hydrocarbonyl solution was put into the flask; then the solution was titrated with a 1/2 N alcohol[5] solution of potassium hydroxide in the presence of phenolphthalein. To the potassium cobalt tetracarbonyl thus formed, a desired amount of alkyl halide was introduced, and the reaction mixture was agitated at various temperatures for several hours. In the course of this reaction, the amounts of carbon monoxide absorbed were determined by following the change in the readings of the buret. In the case of the reaction of ethyl α-bromopropionate under a nitrogen atmosphere, gas formation was observed.

The Reaction of Acyl Halides with Potassium Cobalt Tetracarbonyl.—The solution of potassium cobalt tetracarbonyl, obtained by the procedure mentioned above, was evaporated to dryness[6] under reduced pressure at room temperature, and 50 ml. of anhydrous tetrahydrofuran or isopropyl ether were added. The solution[8] thus formed was mixed with 4.5 mmol. (equi-mole of potassium cobalt tetracarbonyl) of *n*-butyryl chloride or isobutyryl bromide, and the reaction was carried out as in the case of alkyl halides. In every case gas formation was observed.

Analytical Procedures.—After a desired reaction time, 30 ml. of a saturated solution of iodine in toluene[9] and 4 ml. of alcohol[10] were vigorously stirred into the reaction mixture at the same temperature as that for the reaction; the agitation was continued until gas ceased to evolve. By this treatment acylcobalt carbonyl was converted into the corresponding ester of carboxylic acid[1]. The solution of this ester was concentrated under reduced pressure (20 to 30 mmHg) and was then gas chromatographed. A column three meters long, filled with dilauryl phthalate on cerite, was used; the column temperature was varied between 100 to 150°C, depending on the boiling point of the sample, and the flow rate of the carrier gas (hydrogen) was set at 75 ml./min. The identification of the materials was made by means of a mixed melting point test with authentic samples.

Other Materials Used. — Methyl iodide, ethyl iodide, isopropyl bromide, *n*-butyl bromide, benzyl bromide, iodobenzene, bromobenzere, ethyl α-bromopropionate, *n*-butyryl chloride and isobutyryl bromide were commercial products, and all of them were proved to be sufficiently pure by gas chromatography. *n*-Propyliodide and isopropyl iodide were synthesized by the iodination of alcohols with iodide and red phosphor.[11]

Results

The Reactivity of Alkyl Halides with Potassium Cobalt Tetracarbonyl.—The reaction of *n*-propyl iodide with potassium cobalt tetracarbonyl is important in determining the isomerization mentioned at the beginning of this paper. No detailed observation had, however, been reported on the reaction of alkyl halide homologs higher than ethyl halide. Therefore, some alkyl or aryl halides have been reacted with potassium cobalt tetracarbonyl, and the amounts of carbon monoxide absorbed have been determined as the measure of their reactivity. It is believed[12] that the carbon monoxide absorption occurs as a result of the following reactions; the alkylcobalt tetracarbonyl ($RCo(CO)_4$), which is formed at the initial stage of the reaction, is converted to acylcobalt tricarbonyl ($RCOCo(CO)_3$), and the latter absorbs carbon monoxide to form acylcobalt tetracarbonyl ($RCOCo(CO)_4$).

The results for the reactions of ethyl iodide and *n*-propyl iodide illustrated in Fig. 1, in which the amounts of carbon monoxide

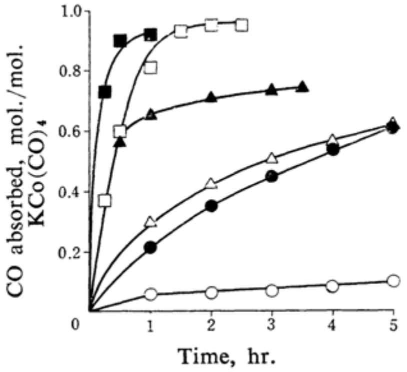

Fig. 1. Carbon monoxide absorption curves of the reaction of some alkyl halides with potassium cobalt tetracarbonyl.

○ *n*-Propyl iodide (0°C)
● *n*-Propyl iodide (25°C)
△ Ethyl iodide (0°C)
▲ Ethyl iodide (25°C)
□ Methyl iodide (0°C)
■ Benzyl bromide (0°C)

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4) H. Sternberg, *Anal. Chem.*, **24**, 174 (1952).

5) Ethyl and *n*-propyl alcohol (cf. Tables).

6) No trace of the alcohol used as a solvent was detected by the xanthate method.[7]

7) F. Feigl, "Spot Tests," Vol. II, Elsvier Publishing Co., Amsterdam (1954), p. 129.

8) Potassium cobalt tetracarbonyl is apparently soluble in tetrahydrofuran, but it is only partly soluble in isopropyl ether.

9) Benzene was used instead of toluene for *n*-propyl esters.

10) *n*-Propyl alcohol was used for acyl halides.

11) L. Gatterman, "Die Praxis des Organischen Chemikers," Walter De Gruyter, Berlin (1958), p. 88.

12) D. S. Breslow and R. F. Heck, *Chem. & Ind.*, **1960**, 467.

TABLE I. REACTIONS OF *n*-PROPYL IODIDE AND ETHYL α-BROMOPROPIONATE WITH POTASSIUM COBALT TETRACARBONYL

No.	Substrate	Atmosphere	Temp. °C	Time hr.	$\frac{\text{Mol. Halide}}{\text{Mol. KCo(CO)}_4}$	Solvent	CO Absorbed $\left(\frac{\text{Mol.}}{\text{Mol. KCo(CO)}_4}\right)$	Yield of ester[*2] $\left(\frac{\text{Mol.}}{\text{Mol. KCo(CO)}_4}\right)$	Ratio of isomeric esters *n*/*iso*[*3]
1	*n*-Propyl iodide	CO	25	5.0	20	*n*-Heptane	0.63	0.41	12
2	*n*-Propyl iodide	CO	0	5.0	20	*n*-Heptane	0.10	—	7
3	*n*-Propyl iodide	N_2	25	5.0	20	*n*-Heptane	—	0.18	2
4	*n*-Propyl iodide	N_2	0	5.0	20	*n*-Heptane	—	—	5
5	Ethyl α-bromopropionate	CO	25	4.3	5.0	Toluene	−1.5[*1]	0.22	2.5
6	Ethyl α-bromopropionate	CO	0	5.3	5.0	Toluene	0.15	0.26	0.4
7	Ethyl α-bromopropionate	CO	−25	4.5	5.0	Toluene	0.23	—	0.0
8	Ethyl α-bromopropionate	N_2	25	4.5	5.0	Toluene	−1.8[*1]	0.12	3.3
9	Ethyl α-bromopropionate	N_2	0	4.5	5.0	Toluene	−1.5[*1]	0.12	0.2

[*1] Gas was evolved.
[*2] The products from *n*-propyl iodide and ethyl α-bromopropionate were identified as *n*-propyl ester and ethyl ester, respectively.
[*3] Cf. Footnote 14.

TABLE II. REACTIONS OF BUTYRYL HALIDES WITH POTASSIUM COBALT TETRACARBONYL

No.	Substance	Reaction condition[*1]			Yield of ester[*2] $\left(\frac{\text{Mol.}}{\text{Mol. KCo(CO)}_4}\right)$	Ratio of isomeric ester, *n*/*iso*[*3]	Amount of gas evolved $\left(\frac{\text{Mol.}}{\text{Mol. KCo(CO)}_4}\right)$
		Atmosphere	Temp., °C	Solvent			
10	*n*-Butyryl chloride	CO	0	Tetrahydrofuran	0.08	∞	0.25
11	*n*-Butyryl chloride	CO	−20	Tetrahydrofuran	0.23	∞	0.17
12	*n*-Butyryl chloride	CO	−40	Tetrahydrofuran	0.27	∞	nil
13	*n*-Butyryl chloride	N_2	0	Tetrahydrofuran	0.15	∞	0.43
14	*n*-Butyryl chloride	N_2	25	Tetrahydrofuran	0.09	∞	0.77
15	*n*-Butyryl chloride	N_2	0	Isopropyl ether	0.49	∞	0.18
16	Isobutyryl bromide	CO	25	Tetrahydrofuran	0.19	4.6	0.40
17	Isobutyryl bromide	CO	0	Tetrahydrofuran	0.10	5.0	0.13
18	Isobutyryl bromide	CO	−20	Tetrahydrofuran	0.13	2.9	0.18
19	Isobutyryl bromide	CO	−40	Tetrahydrofuran	0.03	1.0	0.07
20	Isobutyryl bromide	CO	25	Isopropyl ether	0.32	0.6	0.14
21	Isobutyryl bromide	CO	0	Isopropyl ether	0.38	0.5	nil
22	Isobutyryl bromide	CO	−25	Isopropyl ether	0.37	0.4	0.08
23	Isobutyryl bromide	N_2	25	Tetrahydrofuran	0.27	8.8	0.94
24	Isobutyryl bromide	N_2	0	Tetrahydrofuran	0.13	7.5	0.51

[*1] Reaction time: 3 hr., mol. halide/mol. $KCo(CO)_4$ 1.0
[*2] The reaction products were identified as *n*-propyl esters.
[*3] Cf. Footnote 14.

absorbed are plotted against the reaction time, indicate that these two halides scarcely reacted at 0°C, as it had already been observed,[13] but that they react fairly well at 25°C. For convenience of comparison, the results for methyl iodide and benzyl bromide are also given in Fig. 1.

Besides the halides mentioned above, isopropyl bromide, isopropyl iodide, *n*-butyl bromide, iodobenzene and bromobenzene were subjected to the reaction. It seems that none of them react; there was no absorption of carbon monxide nor any change in the color of the reaction mixtures when five times mole of halides were submitted to the reaction with potassium cobalt tetracarbonyl at 25°C for 2 hr.

The Reaction of *n*-Propyl Iodide and Ethyl *α*-Bromopropionate with Potassium Cobalt Tetracarbonyl.—*n*-Propyl iodide, which is the simplest compound for the study of the isomerization of alkyl- or acylcobalt carbonyls, and ethyl *α*-bromopropionate were subjected to react with potassium cobalt tetracarbonyl; the results are summarized in Table I. The latter was chosen as a sample for the secondary halide, because isopropyl iodide did not react with potassium cobalt tetracarbonyl. Methyl *α*-bromopropionate was submitted to this same type of reaction by Heak and Breslow,[13] but they did not identify the reaction products.

From *n*-propyl iodide only *n*-propyl *n*-butyrate should be produced if no isomerization takes place, but the product contained *n*-propyl isobutyrate besides *n*-butyrate. This formation of the isomeric esters was observed under the atmospheres of both carbon monoxide and nitrogen, but it seems that isobutyrate was formed easily under the nitrogen atmosphere. On the other hand, it was evident that no isomerization of alkyl halide took place in the course of reaction, because no isopropyl iodide was detected in the reaction product, while the amount of *n*-propyl iodide remained unchanged. These findings lead to the conclusion that the isomerization of alkyl- or acylcobalt carbonyls takes place.

In the reaction of ethyl *α*-bromopropionate, carbon monoxide was absorbed at −25°C and 0°C under a carbon monoxide atmosphere, but, on the contrary, gas evolution was observed at 25°C under a carbon monoxide or nitrogen atmosphere. The reaction at −25°C under a carbon monoxide atmosphere gave only diethyl methylmalonate, but at 0°C and 25°C both isomeric products (diethyl methylmalonate and diethyl succinate) were formed. Diethyl methylmalonate (A) was predominant in the reaction product at 0°C, but diethyl succinate (B) was the main product at 25°C. The ratio of B/A was just reversed at 0°C and at 25°C. These tendencies are also observed in a nitrogen atmosphere. Because no ethyl *β*-bromopropionate is formed in these reactions, it can be concluded that the isomerization of alkyl- or acylcobalt carbonyls takes place.

The Reaction of *n*-Butyryl Chloride and Isobutyryl Bromide with Potassium Cobalt Tetracarbonyl.—In order to check the possibility of the isomerization of acylcobalt carbonyls, *n*-butyryl chloride and isobutyryl bromide were made to react with potassium cobalt tetracarbonyl; the results are summarized in Table II. It is evident in all the conditions examined, that *n*-butyryl chloride gave only *n*-propyl *n*-butyrate, but that isobutyryl bromide gave *n*-butyrate besides isobutyrate. It is clear also that *n*-butyrate is predominant when the reactions are carried out in tetrahydrofuran, especially under a nitrogen atmosphere.

These findings seem to indicate that isoacylcobalt carbonyl is easily isomerized to form *n*-acylcobalt carbonyl, but that the reverse isomerization, *n*-acylcobalt carbonyl to isoacylcobalt carbonyl, is extremely difficult.

Comparing the findings concerning acyl halides with those concerning alkyl halides and summarizing the characteristic behavior observed in the course of these two types of reaction, in conclusion it may be said that:

Both isoalkyl- and isoacylcobalt carbonyls are isomerized easily to form large amounts of *n*-structural products,[14] and *n*-alkylcobalt carbonyl is also isomerized to result in a relatively small amount of iso-structural products.[14] On the other hand, *n*-acylcobalt carbonyl gives no iso-structural product. These findings appear to be related to the general tendency for the *n*-structural products to increase as the reaction temperature rises.

In all the experiments described here, the yields of the expected products (esters) are not good; this is because the intermediates, i. e., alkyl- or acylcobalt carbonyls, are very reactive and because some side reactions have taken place. Actually, it is clear that some side reactions occur, because in the reactions of ethyl *α*-bromopropionate in toluene and of acyl halide in tetrahydrofuran, organic crystalline substances were isolated from the concentrated reaction mixtures, and in the case of acyl halides, a relatively large amount of unknown substances was detected in the gas

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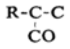
[13] R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **84**, 2499 (1962).

[14] The structures of types A and B are called *n*- and iso-structures respectively:
(A) R-C-C-CO (B)



$$\mathrm{R{-}C{-}\underset{\displaystyle CO}{C}}$$

chromatograms.

As has already been described, the reactions studied in this program are complicated, and their details are not yet solved, but the conclusion, that the isomerization of alkyl- or acylcobalt carbonyl takes place, is unquestionable.

Discussion

It has been postulated by Breslow and Heck[12] that the mechanism of the reaction of organohalides with potassium cobalt tetracarbonyl can be represented as follows:

$$RX + KCo(CO)_4 \rightarrow RCo(CO)_4$$
$$\rightleftarrows RCOCo(CO)_3 \xrightarrow[CO]{} RCOCo(CO)_4$$
$$RCOX + KCo(CO)_4 \rightarrow RCOCo(CO)_4$$

They did not consider any possibility of isomerization during the course of the reaction sequences mentioned above.[15] Our experiments, however, have shown clearly that isomerization does occur at some step of the reaction. On the basis of our finding that the isomerization of acylcobalt carbonyl is accelerated under a nitrogen atmosphere and on the basis of the equilibrium established previously,[16] $RCOMn(CO)_5 \underset{CO}{\overset{\Delta}{\rightleftarrows}} RMn(CO)_5 + CO$, it may reasonably be concluded that [the isomerization species is the carbon monoxide-lacking complex in the reaction sequences described above: i. e., alkylcobalt tetracarbonyl and/or acylcobalt tricarbonyl.

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15) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 651 (1963).

16) T. H. Coffield, J. Kozikowski and R. D. Closson, *J. Org. Chem.*, **22**, 598 (1957).