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Studies of the Organic Reaction of Metal Carbonyl. IX.*[1] The Formation of *o*-Toluylcobalt Carbonyl in the Reaction of Benzyl Chloride with Potassium Cobalt Carbonylate

By Yoshinobu TAKEGAMI, Yoshihisa WATANABE, Hiromitsu MASADA and Chikao YOKOKAWA

Department of Fuel Chemistry, Faculty of Engineering, Kyoto University, Kyoto

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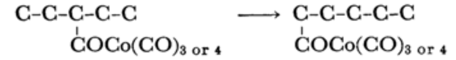
The reaction between benzyl halide and potassium cobalt carbonylate has been studied. *o*-Toluylcobalt carbonyl is found among the reaction products. This carbonyl seems to be formed by the isomerization of benzyl cobalt carbonyl via phenylacetylcobalt tricarbonyl or *o*-tolylcobalt carbonyl. This isomerization occurs only at relatively high temperatures (30—50°C). At 0°C, only phenylacetyl cobalt carbonyl is formed in a good yield. The isomerization is highly promoted by the addition of cobalt hydrocarbonyl. The reaction atmosphere (carbon monoxide and nitrogen) also has a great effect on the isomerization. Such additives as oxalic acid, *p*-toluenesulfonic acid, trichloroacetic acid, and ethyl alcohol-hydrogen chloride have no promoting effect on the isomerization.

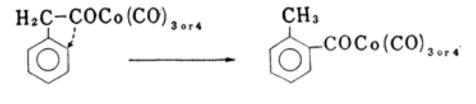
The previous works of this series have shown that α-ethylbutyrylcobalt carbonyl directly isomerizes to *n*-caproylcobalt carbonyl as follows:[1,2]



$$\underset{\mathrm{COCo(CO)_{3\ or\ 4}}}{\mathrm{C\text{-}C\text{-}C\text{-}C\text{-}C}} \longrightarrow \underset{\mathrm{COCo(CO)_{3\ or\ 4}}}{\mathrm{C\text{-}C\text{-}C\text{-}C\text{-}C}}$$

Namely, the acylcobalt carbonyl group bonded to the middle carbon atom of the *n*-C_5 structure appears to rearrange to the terminal carbon atom by leaping one carbon atom at the 2-position.

In this connection, it seems of considerable interest to study whether phenylacetylcobalt carbonyl may analogously isomerize to *o*-toluylcobalt carbonyl:



In the present paper, the reaction between benzyl halide and potassium cobalt carbonylate has been investigated in order to examine the possibility of this isomerization.

Experimental

The Reaction Procedures.—A 100-ml. four-necked flask, equipped 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 a 0.09 M cobalt hydrocarbonyl solution in *n*-hexane was put into the flask; then the solution was titrated with a 1/2 N ethyl alcohol solution of potassium hydroxide, using phenolphthalein as indicator. To the potassium cobalt carbonylate thus formed, 4.5 mmol. of benzyl halide and an appropriate amount of a cobalt hydrocarbonyl solution in *n*-hexane or various organic acids were introduced; then the mixture was stirred at various temperature for 2 to 15 hr.

Analytical Procedure.—After a certain reaction time, about 30 ml. of a saturated solution of iodine in toluene and about 4 ml. of alcohol (methyl, ethyl or propyl alcohol) were stirred into the reaction mixture. By this treatment acylcobalt carbonyl was converted into the corresponding ester of carboxylic acid. The solution of the ester was concentrated to about 5 ml. and then analyzed by means of a study of the infrared spectra, which were measured on a Shimadzu model IR-27 spectrophotometer, and by gas chromatography. A column (3 m. long and 3 mm. in diameter), filled with dilauryl phthalate on cerite, was used; the column temperature was 170°C, and the flow rate of the carrier gas (hydrogen) was 70 ml./min.

Materials.—Cobalt hydrocarbonyl was prepared according to the method described in a previous paper.[3] The benzyl chloride, the bromide and the various organic acid were commercial products.

Results and Discussion

The results of the reactions of benzyl halide with potassium cobalt carbonylate are summarized in Table I.

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*[1] Part VIII: Y. Takegami, Y. Watanabe, H. Masada, Y. Okuda, K. Kobo and C. Yokokawa, This Bulletin, **39**, 1495 (1966). Presented a the 18th Annual Meeting of the Chemical Society of Japan, April, Osaka, 1965.

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

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

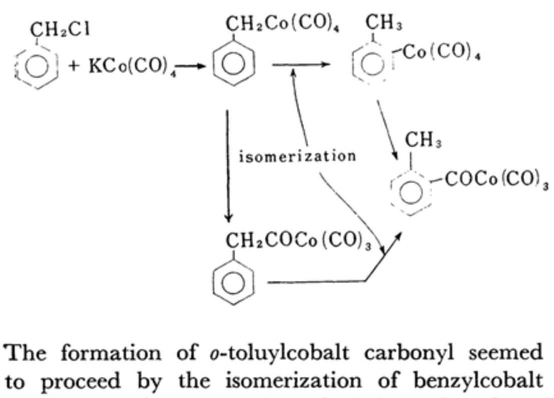
3) Y. Takegami, C. Yokokawa, Y, Watanabe and Y. Okuda, ibid., **37**, 181 (1964).

TABLE I. THE REACTION OF BENZYL CHLORIDE WITH POTASSIUM COBALT CARBONYLATE

Exp. No.	Reaction condition				Gas absorbed[*2] mol./mol.-$KCo(CO)_4$	Yield of esters[*3] mol./mol.-$KCo(CO)_4$	The percentage of o-toluate[*4] %
	Atmos-phere	Temp. °C	Time hr.	Additive[*1] 0.5 mol./mol.-$KCo(CO)_4$			
1	CO	40	11	None	−0.45	0.30	~0
2	N_2	40	3	None	−1.28	0.35	~0
3	N_2	40	15	None	−1.32	0.32	~0
4	CO	20	13	$HCo(CO)_4$	0.70	0.40	0
5	CO	40	5	$HCo(CO)_4$	−1.70	0.46	11
6	CO	40	7	$HCo(CO)_4$	−2.06	0.24	12
7	CO	40	8	$HCo(CO)_4$	−2.68	0.24	17
8	CO	40	11	$HCo(CO)_4$	−3.06	0.1	55
9	N_2	30	8	$HCo(CO)_4$	−1.40	0.55	10
10	N_2	40	2	$HCo(CO)_4$	−1.28	0.59	7
11	N_2	40	4	$HCo(CO)_4$	−1.40	0.51	24
12	N_2	40	5	$HCo(CO)_4$	−1.53	0.25	36
13	N_2	40	7	$HCo(CO)_4$	−2.13	0.1	>95
14	N_2	50	2	$HCo(CO)_4$	−2.15	0.15	40
15[*5]	CO	0, 40	3, 4	$HCo(CO)_4$	0.91—2.03	0.42	0
16[*5]	CO	0, 40	3, 6	$HCo(CO)_4$	0.90—2.33	0.37	3
17	N_2	40	4	Oxalic acid	−0.95	0.51	~0
18	N_2	40	4	p-Toluene-sulfonic acid	−1.00	0.51	~0
19	N_2	40	4	Trichloro-acetic acid	−1.00	0.55	~0
20	N_2	40	4	EtOH-HCl	−0.83	0.30	~0

[*1] Solution in n-hexane.
[*2] The negative sign shows the gas evolution.
[*3] The reaction products were identified as ethyl phenylacetate and ethyl o-toluate.
[*4] (o-Toluate/(o-Toluate + Phenylacetate)) × 100
[*5] Benzyl bromide was used. The reaction was carried out in two stages: at first at 0°C for 3 hr. (0.91 mol. of carbon monoxid was absorbed.) and then at 40°C for 4 hr. (2.03 mol. of gas was evolved.).

As Exp. 1 shows, without additives the reaction of benzyl chloride at 40°C under carbon monoxide proceeded with the evolution of gas[*2] to give ethyl phenylacetate as the main product. Besides this ester, only a small amount of ethyl o-toluate was obtained as an isomerization product. Under nitrogen, a larger amount of gas was evolved, but o-toluate was also obtained in a low yield (Exps. 2 and 3):



The formation of o-toluylcobalt carbonyl seemed to proceed by the isomerization of benzylcobalt carbonyl and/or phenylacetylcobalt carbonyl, as has been shown above. However, it is considered difficult for such an isomerization to occur under these conditions. At a lower reaction temperature (20 to 0°C) under carbon monoxide, the reaction proceeded with the absorption of gas[*3], to give ethyl phenylacetate in a relatively good yield, but no ethyl o-toluate, indicating that under milder conditions the isomerization occurs with much difficulty.

However, this type of isomerization was remarkably promoted by the addition of cobalt hydrocarbonyl. When 0.5 mol. of cobalt hydrocarbonyl per mole of potassium cobalt carbonylate was present, a tolerable amount of o-toluate[*4] was

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[*2] The evolution of gas seemed to be partly attributable to the decomposition of the alkyl- and acylcobalt carbonyls formed.

[*3] The gas absorption seemed to be attributable to the formation of phenylacetylcobalt tetracarbonyl.

[*4] (o-Toluate/(o-Toluate+Phenylacetate)) × 100 Indentified by gas chromatography and by a study of the infrared spectrum of the solution of the products in toluene, which showed absorption bands at 1729 and 1740 cm^{-1}: The retention time of the esters in gas chromatography increased with the molecular weight of the alcohol used in the cleavage of the crude products;

$$RCOCo(CO)_{3\text{ or }4} \xrightarrow{I_2 + R'OH} RCOOR'$$

obtained (Exps. 4—14). Under carbon monoxide at 40°C, the percentage of *o*-toluate amounted to 55% after 11 hr. (Exp. 8). The total yield of esters, i. e., phenylacetate and *o*-toluate, decreased with an increase in the reaction time. Under these conditions, large gas evolution gradually occurred; this amounted to about 3 mole[*5] after 11 hr. On the other hand, at 20°C gas absorption occurred, but no isomerized product was obtained, even after 13 hr. (Exp. 4). These facts indicate that a relatively high temperature, which seems to cause the acyl- and alkylcobalt carbonyls to decompose, may be effective in the isomerization.

Under nitrogen, *o*-toluate was also formed in the presence of cobalt hydrocarbonyl. At 40°C about 7% of *o*-toluate was obtained after only 2 hr. (Exp. 10); this percentage became 36 and more than 95% after 5 and 7 hr. respectively. Thus, the isomerization, the formation of *o*-toluylcobalt carbonyl, occurred under nitrogen more readily than under carbon monoxide, as in the isomerization of aliphatic acylcobalt carbonyls.[1-4] At 50°C, 40% of *o*-toluate was formed after only 2 hr., but at 30°C only 10% of *o*-toluate was obtained, even after 8 hr. Therefore, higher temperatures seem to promote the isomerization. In these cases, a large gas evolution was also observed. The total yield of the esters appeared to decrease with an increase in the amount of gas evolved; when about 2 to 3 mol. of gas were evolved, the yield of the esters amounted to only 0.1—0.2 mol.

As for the course of the isomerization, two ways are possible; in the first course, benzylcobalt carbonyl, which is derived by the reaction of benzyl halide with potassium cobalt carbonylate, isomerizes to *o*-toluylcobalt carbonyl via phenylacetylcobalt carbonyl, while in the second course this isomerization occurs via *o*-tolylcobalt carbonyl. In the present study, it can not be decided which course should be chosen for this type of isomerization. From the fact that a nitrogen atmosphere remarkably promotes the isomerization, however, *o*-tolylcobalt carbonyl and phenylacetylcobalt tricarbonyl, i. e., carbon monoxide-lacking states, appear to be very important as isomerization species, as in the isomerization of aliphatic acylcobalt carbonyls.[1-4] This consideration is supported by the results of Exps. 15 and 16, in which the reaction was carried out in two stages under carbon monoxide, first at 0°C and then at 40°C. At 0°C, about 0.9 mol. of carbon monoxide was absorbed over 3 hr. period, indicating that benzylcobalt carbonyl might be converted into phenylacetylcobalt tetracarbonyl in a good yield; then the reaction temperature was changed to 40°C, which is effective for the isomerization, but only a small amount of the isomerized product was obtained after 6 hr., even in the presence of cobalt hydrocarbonyl. From this fact, it seems that phenylacetylcobalt tetracarbonyl is difficult to isomerize.

It has been known that cobalt hydrocarbonyl is a strong acid.[5] In relation to this character of cobalt hydrocarbonyl, the effects of the addition of various organic acids on the reaction have been examined. Oxalic acid, *p*-toluenesulfonic acid, trichloroacetic acid and ethyl alcohol - hydrogen chloride were used, 0.5 mol. portions of these acids were added to the reaction system instead of cobalt hydrocarbonyl. However, these acids seemed to have no promoting effect on the isomerization, even at 40°C, as Exps. 17—20 show. Thus, the promoting effect of cobalt hydrocarbonyl seems not to be attributable to only its acidic character. The reason why cobalt hydrocarbonyl has this effect could not be determined in the present investigation.

[*5] "Mole" means mole per mole of potassium cobalt carbonylate in this description.

4) Y. Takegami, C. Yokokawa, Y. Watanabe and H. Masada, This Bulletin, **37**, 1190 (1964).

5) W. Hieber and E. Lindner, *Chem. Ber.*, **94**, 1417 (1961); W. Hieber and G. Wagner, *Z. Naturforschung*, **13b**, 339 (1958).