Studies of the Organic Reactions of Metal Carbonyl. II. The Reaction of Olefin Oxide with Cobalt Hydrocarbonyl*

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In connection with the Oxo reaction, the reaction of olefins with cobalt hydrocarbonyl and carbon monoxide has been studied by several workers.[1-5] It has been established[5,6] that alkyl- and acylcobalt carbonyl are formed in this reaction.

Recent papers[7-11] have reported that hydroxy-acids, their derivatives or rearranged carbonyl products are formed in the reaction of olefin oxides with carbon monoxide and water or alcohols using a cobalt salt or cobalt carbonyl as catalyst. With regard to these facts, Heck[13] has established, by isolating β-hydroxyacylcobalt tricarbonyl triphenylphosphine, that β-hydroxyacylcobalt tetracarbonyl is formed in the reaction of olefin oxide with cobalt hydrocarbonyl.

In the present paper, this type of reaction has been studied with an emphasis on the following two points: a) the effect of the reaction conditions on the nature of this reaction and the structure of the products, and b) the relation between the reactivity of olefin oxides and their structures.

Experimental

Reaction Procedures.—The reactions were carried out as described in the previous paper,[14] using 50 ml. of 0.09 M cobalt hydrocarbonyl solution in toluene.

Analytical Procedures.—The solution of crude products was treated with iodine and ethyl alcohol as described previously,[14] and the excess of iodine was reduced with crystalline sodium thiosulfate. After concentration, the reaction products were gas-chromatographed on a column, three meters in length and 3 mm. in diameter, filled with dilauryl phthalate or silicon DC 550 on cerite, at 140∼160°C, and at the flow rate of carrier gas (hydrogen) of 50 ml./min. The identification of ethyl β-hydroxypropionate, ethyl β-hydroxy-*n*-butyrate, β-hydroxy-*n*-butyraldehyde, α- and β-phenylethyl alcohol was made by mixing them with authentic samples in gas chromatography. The infrared spectra of the solution of reaction products in toluene were recorded by a Shimadzu model IR-27 infrared spectrophotometer, after removing iodohydrin* by treating the crude solution with potassium hydroxide.

Materials. — Ethylene oxide, propylene oxide, styrene oxide, epichlorohydrin and pentene-1 were commercial products. Cyclohexene oxide was synthesized by the oxidation of cyclohexene with perbenzoic acid.[15] All of these compounds were proved to be sufficiently pure by gas chromatography. The cobalt hydrocarbonyl solution in toluene was prepared by a method described previously.[14]

Results and Discussion

Propylene Oxide.—A recent paper reported[13] that olefin oxide reacts readily with cobalt hydrocarbonyl, but the effects of the reaction conditions on the reaction and on the products are unknown. The authors found that the reactions of some olefins with cobalt hydrocarbonyl are remarkably influenced by the reaction conditions (temperature, atmosphere, etc.).*

In this study, the reaction of propylene oxide with cobalt hydrocarbonyl has been

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* Believed to have been formed as follows: RCOCo(CO)$_4 \xrightarrow{R'OH+I_2}$ HI + RCOOR′, olefin oxide + HI → iodohydrin.

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TABLE Ia. THE REACTION OF PROPYLENE OXIDE WITH COBALT HYDROCARBONYL

Exp. No.	Reaction Conditions				CO Absorbed (mol./mol.-$HCo(CO)_4$)	Product	
	Atmosphere	Temp. °C	Mole Ratio*3	Time min.		Ester*1 (mol./mol.-$HCo(CO)_4$)	Aldehyde*2
1	CO	0	1.4	180	0.15	0.13	—
2	CO	0	2.7	330	0.57	0.30	—
3	CO	0	4.0	220	0.82	0.44	0.09
4	CO	0	6.2	140	0.90	0.60	—
5	CO	25	4.0	120	0.52	0.15	0.10
6	CO	−30	6.2	200	0.78	0.56	—
7	CO	−45	6.2	180	0.85	0.49	—
8	N_2	0	2.7	30	—	0.14	—
9	N_2	0	2.7	60	—	0.15	—
10	N_2	0	2.7	150	—	0.10	0.05
11	N_2	0	6.2	15	—	0.20	0.04
12	N_2	0	6.2	140	—	0.24	—
13	N_2	0	6.2	330	—	0.18	—
14	N_2	−45	6.2	180	—	0.27	—

TABLE Ib

Exp. No.	Atmosphere	Temp. °C	Mole Ratio*3	Time min.	CO Absorbed (mol./mol.-$HCo(CO)_4$)	Ester*1	Aldehyde*2
15	N_2-CO*4	0	6.2	15, 60	0.20	0.17	0.1
16	N_2-CO	−30	1.2	15, 210	0.71	0.61	0.05
17	CO-N_2*5	0	6.2	70, 240	0.80	0.35	—
18	CO-N_2-CO	0	6.2	18, 15, 70	0.36, 0.16	0.33	—

*1 Ethyl β-hydroxy-*n*-butyrate.

*2 β-Hydroxy-*n*-butyraldehyde.

*3 Mole of propylene oxide per mole of cobalt hydrocarbonyl used.

*4 At first under nitrogen atmosphere and then under carbon monoxide.

*5 At first under carbon monoxide and then under nitrogen.

examined in detail. Two skeletal isomeric products are possible in this case, but the composition of the reaction products has not been studied.[13]

As is shown in Table I, the major product independent of the atmosphere (one atmosphere of carbon monoxide or nitrogen), temperature (25∼−45°C) and mole ratio* of propylene oxide (1.4∼13.5), was ethyl β-hydroxy-*n*-butyrate,** which was evidently derived from β-hydroxy-*n*-butyrylcobalt carbonyl by cleavage with iodine and ethyl alcohol. Besides this ester, a small amount of β-hydroxy-*n*-butyraldehyde was formed, but there was no indication of the presence of ethyl α-methyl-β-hydroxypropionate under the reaction conditions used. The yields of the ester tended to decrease as the reaction temperature rose; i. e., the total yields of the ester and the aldehyde in the reactions at 25, 0, and −30°C were about 30, 55, and 80% respectively, on the basis of the amount of carbon monoxide absorbed. Under nitrogen, the yields of the ester were much less than those under carbon monoxide; at 0°C, in the case of a 2.7 or 6.2 mol. ratio, only about 0.15 or 0.25 mol. of the ester, independent of the reaction time (15∼330 min.), was formed.

The gas absorption curves shown in Fig. 1., in which the amount of carbon monoxide absorbed is plotted against the reaction time, indicate that, at 0°C and under one atmosphere of carbon monoxide, the rate of the gas absorption at the early stage of the reaction is roughly proportional to the square of the mole ratio. The gas absorption at 25, −30

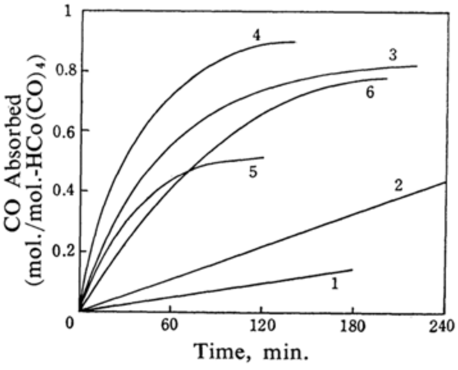

Fig. 1. CO Absorption vs. time plots for the reaction of propylene oxide.
Number: Exp. No.

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* Mole of propylene oxide per mole of cobalt hydrocarbonyl used.

** Identified by gas chromatography and by the infrared spectrum of the solution of products in toluene, which had bands at 3630 cm⁻¹ and 1735 cm⁻¹ corresponding to hydroxy and carbonyl groups.

TABLE II. THE REACTION OF ETHYLENE OXIDE WITH COBALT HYDROCARBONYL

Exp. No.	Reaction Conditions*1		CO Absorbed	β-Hydroxyester*3
	Mole Ratio*2	Time min.	(mol./mol. $HCo(CO)_4$)	(mol./mol. $HCo(CO)_4$)
19	1～2	240	0.16	0.08
20	～4	220	0.80	0.50
21	～5	155	0.96	—

*1 Other reaction conditions: at 0°C and one atmosphere of carbon monoxide.

*2 Mole of ethylene oxide per mole of cobalt hydrocarbonyl used.

*3 Ethyl β-hydroxypropionate.

(and $-45°$C) occurred more slowly than at 0°C. The amount of gas absorbed at 25°C was less than that at 0°C.

In connection with the fact that the reactions under nitrogen gave the ester with a low yield, the reaction was carried out in two stages, the first stage under nitrogen for 15 min. and, then the second stage under carbon monoxide. At 0°C, only 0.2 mol. of the gas was absorbed in the second stage (Exp. 15 and curve 15). This value obviously corresponds with that of the yield of the ester in the corresponding reaction under nitrogen (Exp. 11). This fact seems to indicate that, under nitrogen, some side reaction other than the carbonylation reaction occurred rapidly to consume a large part of the cobalt hydrocarbonyl used. At $-30°$C, however, in the second stage, the gas was absorbed in the usual manner (Exp. 16 and curve 16). The reaction was carried out in two or three stages: at first under carbon monoxide, at the second stage under nitrogen, and then under carbon monoxide. The nitrogen atmosphere had no effect on the reaction when the gas absorption had completely occurred at the first stage (Exp. 17). When, however, the gas absorption was only half-completed at the first stage, the nitrogen atmosphere had the effect on the reaction of decreasing the amount of gas absorbed at the third stage (Exp. 18).

According to Heck and Breslow's suggestion5) that the formation of acylcobalt carbonyl in this type of reaction of olefin is accelerated under nitrogen, it would be expected that the above-mentioned pretreatment under nitrogen would promote the carbonylation reaction of propylene oxide. In reality, however, the amount of gas absorbed and the yields of the ester and the aldehyde were not good, as is demonstrated by Exp. 15; in other words, the nitrogen atmosphere highly promoted some side reaction and then the formation of carbonylated products (ester and aldehyde) was prevented.

In order to compare the reactivity of olefin oxide with that of olefin, the reaction of pentene-1 with cobalt hydrocarbonyl was carried out. The results, shown in Fig. 2(A), indicate that pentene-1 is obviously less reactive than propylene oxide. In general, olefin oxide seems to be more reactive than olefin in this type of reaction. This fact is supported by the authors' observation12) that propylene oxide undergoes the hydroformylation reaction at a lower temperature (80～90°C) than the usual Oxo reaction temperature.

Ethylene Oxide.—Ethylene oxide undergoes this type of reaction in the same manner as propylene oxide. The results are shown in Table II. As the major product, ethyl β-hydroxypropionate was given. In a recent study, Heck13) isolated β-hydroxypropionylcobalt tricarbonyl triphenylphosphine from this reaction.

Cyclohexene Oxide.—Cyclohexene oxide, an internal olefin oxide, reacts readily with cobalt hydrocarbonyl. The results are summarized in Table III. The major product is believed to be ethyl 2-hydroxycyclohexanecarboxylate.* As may be seen from the appearance of the gas absorption, cyclohexene

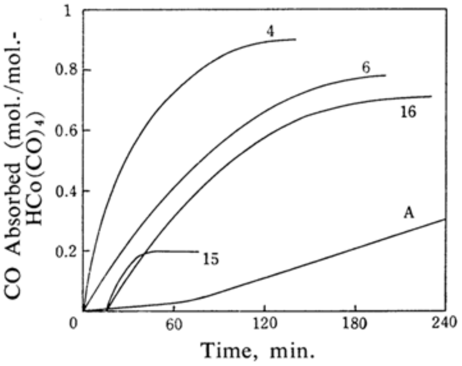

Fig. 2. CO Absorption vs. time plots for the reaction of propylene oxide.
Number: Exp. No.
A: pentene-1 (at 0°C, 10 mole ratio)

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* The infrared spectrum of the reaction products in toluene had bands at 3600 cm^{-1} and 1735 cm^{-1}. As further evidence, the retention time of the major product in gas chromatography increased as the molecular weight of the alcohol used in the cleavage of the crude products increased, and the retention time of the product (ethyl ester) was longer than that of ethyl cyclohexanecarboxylate, so this compound seemed to have some additional functional group.

TABLE III. THE REACTION OF CYCLOHEXENE OXIDE WITH COBALT HYDROCARBONYL

	Reaction Conditions*			CO	Product
Exp. No.	Temp. °C	Mole Ratio	Time min.	Absorbed (mol./mol. $HCo(CO)_4$)	Ester** (mol./mol. $HCo(CO)_4$)
22	0	2.7	155	0.79	0.58
23	0	4.5	95	0.80	0.57
24	25	2.7	60	0.42	0.1
25	−30	2.7	260	0.72	0.63

* Other reaction condition : under one atmosphere of carbon monoxide.

** Ethyl 2-hydroxycyclohexanecarboxylate.

TABLE IV. THE REACTION OF STYRENE OXIDE WITH COBALT HYDROCARBONYL

	Reaction Conditions				CO	Product	
Exp. No.	Atmosphere	Temp. °C	Mole Ratio	Time min.	Absorbed (mol./mol.-$HCo(CO)_4$)	α* (mol./mol. $HCo(CO)_4$)	β** (mol./mol. $HCo(CO)_4$)
26	CO	0	1.0	190	0.20	0.17	0.10
27	CO	25	1.0	80	0.20	0.19	0.12
28	CO	0	2.0	180	0.32	0.19	0.09
29	CO	0	4.0	80	0.49	—	—
30	CO	0	6.0	60	0.52	—	—

* α-Phenylethyl alcohol.

** β-Phenylethyl alcohol.

TABLE V. THE REACTION OF EPICHLOROHYDRIN WITH COBALT HYDROCARBONYL

	Reaction Conditions				CO	Product
Exp. No.	Atmosphere	Temp. °C	Mole Ratio	Time min.	Absorbed (mol./mol.-$HCo(CO)_4$)	Ester* (mol./mol. $HCo(CO)_4$)
31	CO	0	5	270	0	0
32	CO	25	5	240	0	0.15
33	CO	0	30	300	0.60	0.4
34	CO	0	45	330	0.55	0.5

* Ethyl γ-chloro-β-hydroxypropionate.

oxide is obviously more reactive than propylene oxide; for instance, in the case of a 2.7 mol. ratio, cyclohexene oxide absorbs 0.8 mol. of carbon monoxide in 150 min., while propylene oxide absorbs only 0.4 mol. of the gas in 240 min.

The rate of the gas absorption at the early stage of the reaction for cyclohexene oxide is about five times that for propylene oxide. This relation between the reactivity and the chemical structure of two kinds of olefin oxide is the reverse of that for olefins; i. e., in general, the order of the reactivity for olefins is terminal>internal>cyclic.3)

Styrene Oxide.—In the reaction of styrene oxide, a conjugated olefin oxide, with cobalt hydrocarbonyl, exceptional behavior was observed. The mole ratio of styrene oxide had a significant effect on the nature of the reaction. As Table IV shows, when the mole ratio was relatively small (1 and 2) the major products were α- and β-phenylethyl alcohol and the amount of gas absorbed was small. This indicates that the reduction of styrene oxide with cobalt hydrocarbonyl occurred mainly at these mole ratios. As the mole ratio increased (4 and 6), the amount of gas absorbed increased, but it did not exceed 0.6 mol. In these cases, the identification of the products was impossible since a black tarry material was formed in the course of the analysis, but it seemed, mainly because of the relatively large absorption of the gas, that the carbonylation reaction took place. The tarry material may reasonably be attributed to the polymerization of the excess styrene oxide.

Epichlorohydrin.—Epichlorohydrin seems to react with cobalt hydrocarbonyl only with difficulty under the conditions, at 0°C and in a 5 mol. ratio, under which propylene oxide reacts readily; there was, at any rate, no absorption of the gas, as Table V shows. When, however, the mole ratio of epichlorohydrin was increased to 30 and 45, about 0.6 mol. of the gas was absorbed in 5 hr. Therefore, epichlorohydrin is much less reactive than propylene oxide, but it is believed to give ethyl γ-chloro-β-hydroxy-*n*-butyrate,* the structure of which corresponds with that of the products propylene oxide gives.

As may be seen from the appearance of the gas absorption, epichlorohydrin seems to react with cobalt hydrocarbonyl about many times more slowly than propylene oxide. In contrast with this fact, the relative reactivities of these olefin oxides with ammonia and perchloric acid are represented as follows:[16] with ammonia epichlorohydrin 4 > propylene oxide 1; with perchloric acid, epichlorohydrin 1 < propylene oxide 70 (with cobalt hydrocarbonyl epichlorohydrin 1 < propylen oxide 20~40).

Thus, the order of the reactivity of these olefin oxides with cobalt hydrocarbonyl corresponds to that with perchloric acid. This fact seems to support Heck's suggestion,[13] which has been drawn from other evidence, that cobalt hydrocarbonyl reacts as an acid.

Summary

The reactions of olefin oxides with cobalt hydrocarbonyl have been studied.

The effect of the reaction conditions on the nature of the reaction, especially that of propylene oxide, has been examined in detail. Propylene oxide gave only the products with β-hydroxy-*n*-butyryl structure under these reaction conditions: temperature, $25\sim-45°C$; atmosphere; nitrogen or carbon monoxide; and mole ratio of propylene oxide, 1.4~6.2. The inhibitory effect of a nitrogen atmosphere on the formation of carbonylated products (ester and aldehyde) has been observed; under nitrogen, some side reaction was highly promoted, and the formation of carbonylated products was thereby prevented.

The reactions of ethylene oxide, cyclohexene oxide, styrene oxide and epichlorohydrin have also been studied. In the reactions of styrene oxide, the mole ratio of styrene oxide had a significant effect on the nature of the reaction; at a relatively small mole ratio, the reduction gave, mainly two isomeric alcohols, but as the mole ratio increased, the carboxylation reaction seemed to increase. Epichlorohydrin gave a product with a γ-chloro-β-hydroxy-*n*-butyryl structure, which corresponds to that which propylene oxide gave.

The order of the reactivity of these olefin oxides is as follows: cyclohexene oxide (about 5) and styrene oxide > propylene oxide (1) > ethylene oxide $\gg$ epichlorohydrin (1/20~40); (the numbers indicate the relative reactivities).

This fact seems to indicate that, in general, internal (and conjugated) olefin oxides are more reactive than terminal olefin oxides. By analogy with the relative reactivity of propylene oxide and epichlorohydrin with cobalt hydrocarbonyl, perchloric acid and ammonia, it may reasonably be considered that cobalt hydrocarbonyl reacts as an acid.

Pentene-1 appeared to be less reactive than propylene oxide.

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* The infrared spectrum of the product solution in toluene had a band at 1740 cm^{-1}. Further evidence: about 0.5 ml. of the sample solution and about 0.2 g. of potassium hydroxide were placed in a test tube. After the test tube had been shaken, the upper layer was gas-chromatographed. The largest peak of the original gas chromatogram, which is supposed to belong to the ester, vanished, and a new peak, with a comparable area, appeared before the position of the original peak. This fact indicates that the ester has a chlorohydrin structure (γ-chloro-β-hydroxy structure).

[16] R. E. Parker and N. S. Isaacs, *Chem. Revs.*, **59**, 737 (1959).