

## Kinetics of the ring-opening carbonylation of ethyloxirane with hydrido tetracarbonyl cobalt \*

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### Abstract

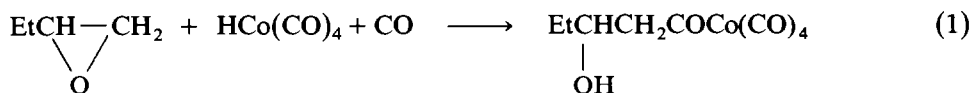
The rate of CO uptake in the reaction of  $\text{HCo}(\text{CO})_4$  with ethyloxirane, which gives (3-hydroxypentanoyl)cobalt tetracarbonyl as the major product in an n-octane/methyl isobutyl ketone solvent mixture at 15 °C, is first order with respect to  $\text{HCo}(\text{CO})_4$  and ethyloxirane, and independent of the concentration of  $\text{Co}(\text{CO})_4$  or CO. The reaction is faster with  $\text{DCo}(\text{CO})_4$ . A preequilibrium ion pair formation and a subsequent rate-determining internal substitution, followed by fast CO insertion, accounts for these results.

### Introduction

The cobalt-catalyzed carbonylation of oxiranes is a potentially useful source of  $\beta$ -hydroxy aldehydes [1] and  $\beta$ -hydroxy carboxylic acid esters [2] since oxiranes are readily available either by classical methods [3] or by transition metal catalyzed epoxidation of olefins [4]. It has been shown that  $\beta$ -hydroxyacylcobalt tetracarbonyl is an intermediate in the synthesis of  $\beta$ -hydroxyaldehydes and  $\beta$ -hydroxycarboxylic acid esters, and these products can be obtained in high yields by the reactions of  $\text{HCo}(\text{CO})_4$  and CO with oxiranes [5]. On the basis of product analyses, an ionic mechanism, in which the acid-opening of the oxirane ring occurs at the least substituted carbon, was suggested for the reaction [5]. In toluene solution the reactivities various oxiranes toward  $\text{HCo}(\text{CO})_4$  and CO were found to be in the order chloromethyloxirane  $\ll$  oxirane < methyloxirane < phenyloxirane < 1,2-epoxycyclohexane [6]. Reactions were faster in the presence of ether, acetonitrile, ketones, or alcohols. The highest relative rate ( $10^2$ ) was obtained with a 2 : 1 molar ratio  $\text{EtOH}/\text{HCo}(\text{CO})_4$  [7]. Up to now, however, there has been no detailed kinetic investigation of the reaction.

\* We dedicate this paper to the late Professor P. Pino in recognition of his major contributions to understanding of the role of organometallics in homogeneous catalysis.

In order to gain more information about the mechanism of the steps involved in the  $\beta$ -hydroxyacylcobalt tetracarbonyl formation we studied the kinetics of CO uptake in reaction 1.



## Results

The reaction of  $\text{HCo}(\text{CO})_4$  with an excess of ethyloxirane under CO resulted in a rapid gas absorption of up to 1 mol CO/mol  $\text{HCo}(\text{CO})_4$  at 15°C. During the reaction, especially at higher initial concentrations of  $\text{HCo}(\text{CO})_4$ , the pale yellow solution became temporarily red, and then yellow again. When the gas uptake was complete the infrared spectrum of the solution in the  $\nu(\text{CO})$  range showed bands (see Experimental) characteristic of an acylcobalt tetracarbonyl [8]. Concentration of the reaction mixture led to isolation of (3-hydroxypentanylo)cobalt tetracarbonyl, the structure of which was verified by spectroscopic methods. Similarly, (3-hydroxybutanylo)cobalt tetracarbonyl was obtained from methyloxirane.

Addition of  $\text{PPh}_3$  in 5% molar excess to the acylcobalt tetracarbonyl solutions resulted in the release of 1 mol gas/mol cobalt, in accord with a rapid and quantitative transformation into the monotriphenylphosphine-substituted derivatives, which were isolated in high yields.

The rate of the ring-opening carbonylation of ethyloxirane by  $\text{HCo}(\text{CO})_4$  and CO was determined by measuring the rate of CO uptake in a gasometric apparatus. In saturated hydrocarbon solution the reaction was very slow, but it could be greatly accelerated by using the oxirane in large excess. The initial rates of CO uptake showed a very strong dependence on the oxirane concentration (Table 1). Similarly, increased reaction rates could be observed if some of the n-octane solvent was replaced by methyl isobutyl ketone, THF, or diisopropyl ether (Table 2).

In order to determine the exact concentration effect of ethyloxirane and  $\text{HCo}(\text{CO})_4$ , the initial rates of CO uptake were measured in a mixture of n-octane and methyl isobutyl ketone at various initial reactant concentrations varying slightly from the stoichiometric ratio. The data in Table 3 reveal that the observed rate is proportional to the concentration of both ethyloxirane and  $\text{HCo}(\text{CO})_4$ , and that the CO concentration has practically no effect on the rate. When  $\text{DCo}(\text{CO})_4$  was used in place of  $\text{HCo}(\text{CO})_4$  there was a 1.7-fold increase in the rate of CO uptake. It is

Table 1

Effect of ethyloxirane (1) concentration on the initial rates of CO uptake ( $r$ ) in the reaction of  $\text{HCo}(\text{CO})_4$  and 1 at 15°C in n-octane solution (total pressure = 740 mmHg,  $[\text{HCo}(\text{CO})_4]_0 = 0.025 M$ )

$[\mathbf{1}]_0$ ( $M$ )	$10^5 r$ ( $M s^{-1}$ )
0.75	0.184
1.25	1.35
2.00	5.71
2.50	11.9

Table 2

Effect of methyl isobutyl ketone (MIBK), tetrahydrofuran and diisopropyl ether on the initial rates of CO uptake ( $r$ ) in the reaction of  $\text{HCo}(\text{CO})_4$  and ethyloxirane at  $15^\circ\text{C}$  in *n*-octane solution ( $[\text{HCo}(\text{CO})_4]_0 = [\text{ethyloxirane}]_0 = 0.025\text{ M}$ , total pressure = 740 mmHg)

[MIBK] ( <i>M</i> )	[THF] ( <i>M</i> )	[ <sup>1</sup> Pr <sub>2</sub> O] ( <i>M</i> )	$10^5 r$ ( <i>M s</i> <sup>-1</sup> )
1.0			0.28
1.5			1.02
2.5			2.98
4.0			7.65
5.0			11.9
	1.0		0.13
	2.0		0.90
	3.0		2.29
	4.0		4.10
	5.5		7.63
		4.0	0.39
		5.0	0.51
		6.9	0.83

noteworthy that the temperature between  $-15$  and  $+30^\circ\text{C}$  does not influence the rate of the CO uptake.

The effect of the  $\text{Co}(\text{CO})_4^-$  concentration was studied in THF solution by starting the reaction at different initial concentrations of  $\text{NaCo}(\text{CO})_4$ . The data in Table 4 show that there is an insignificant increase in the rate even when a large excess of  $\text{NaCo}(\text{CO})_4$  is used. A high concentration of  $\text{NaCo}(\text{CO})_4$  is not in itself

Table 3

Effect of ethyloxirane (**1**),  $\text{HCo}(\text{CO})_4$  and CO concentration on the initial rates of CO uptake ( $r$ ) at  $15^\circ\text{C}$  in the presence of 2.5 *M* methyl isobutyl ketone in *n*-octane solvent at different temperatures

Temp. ( $^\circ\text{C}$ )	[ <b>1</b> ] <sub>0</sub> ( <i>M</i> )	$[\text{HCo}(\text{CO})_4]$ ( <i>M</i> )	$P_{\text{CO}}$ (mmHg)	$10^5 r$ ( <i>M s</i> <sup>-1</sup> )	$10^2 r/[\mathbf{1}]_0[\text{HCo}(\text{CO})_4]_0$ ( <i>M</i> <sup>-1</sup> <i>s</i> <sup>-1</sup> )
-15	0.025	0.025	742	3.00	4.80
0	0.025	0.025	741	3.05	4.88
0	0.025	0.025 <sup>a</sup>	733	5.20	8.32
15	0.012	0.025	725	1.10	3.67
15	0.050	0.025	725	5.15	4.12
15	0.080	0.025	725	8.15	4.08
15	0.120	0.025	725	12.3	4.10
15	0.025	0.010	737	1.19	4.76
15	0.025	0.025	739	2.98	4.77
15	0.025	0.025	368	2.64	4.22
15	0.025	0.050	735	5.84	4.67
15	0.025	0.100	730	12.5	5.00
20	1.25 <sup>b</sup>	0.025	723	3.21	0.103
20	1.25 <sup>b</sup>	0.025 <sup>a</sup>	715	5.50	0.176
25	1.25 <sup>b</sup>	0.025	716	3.28	0.105
30	1.25 <sup>b</sup>	0.025	716	3.13	0.100

<sup>a</sup>  $\text{DCo}(\text{CO})_4$ . <sup>b</sup> *n*-Butyloxirane in isooctane (without added methyl isobutyl ketone).

Table 4

Effect of  $\text{NaCo}(\text{CO})_4$  on the initial rates of CO uptake ( $r$ ) in the reaction of  $\text{HCo}(\text{CO})_4$  and ethyloxirane at  $15^\circ\text{C}$  in THF solution ( $[\text{HCo}(\text{CO})_4]_0 = 0.0050\text{ M}$ ;  $[\text{ethyloxirane}]_0 = 0.0070\text{ M}$ ; total pressure = 740 mmHg)

$[\text{NaCo}(\text{CO})_4]^a$ ( $M$ )	$10^5 r$ ( $M\text{ s}^{-1}$ )
0.00	2.36
0.0015	2.70
0.0030	2.78
0.0075	2.89
0.0450	3.33
0.84	0.00 <sup>b</sup>
0.02	0.22 <sup>b,c</sup>

<sup>a</sup> Added as a 1  $M$  solution in THF. <sup>b</sup> No  $\text{HCo}(\text{CO})_4$  added. <sup>c</sup>  $[\text{methyloxirane}]_0 = 5.8\text{ M}$  in methanol at  $50^\circ\text{C}$ .

enough to bring about the ring-opening and carbonylation of the ethyloxirane at  $15^\circ\text{C}$  in anhydrous THF.

The reaction of oxiranes with  $\text{NaCo}(\text{CO})_4$  could be carried out in protic polar solvents such as methanol, but only at higher temperatures; there was no reaction at  $15^\circ\text{C}$ . At  $50^\circ\text{C}$ , a slow CO uptake was observed in the case of methyloxirane (Table 4), and this continued even when the molar ratio  $\text{CO}/\text{NaCo}(\text{CO})_4$  reached 1:1. The slow formation of methyl 3-hydroxybutyrate rather than of (3-hydroxybutyryl)cobalt tetracarbonyl was revealed by GLC analysis (comparison with authentic sample) and infrared spectroscopy (ester band at  $1740\text{ cm}^{-1}$ ). The infrared spectrum of the reaction mixture showed that the concentration of  $\text{Co}(\text{CO})_4^-$  remained essentially unchanged during the formation of the methyl 3-hydroxybutyrate.

## Discussion

Preparative-scale experiments with ethyloxirane (this work) and with methyl-oxirane (Ref. 5 and this work) showed that the major component ( $\geq 95\%$  and  $\geq 90\%$ ) in the final reaction mixture is (3-hydroxypentenoyl)cobalt tetracarbonyl and (3-hydroxybutanoyl)cobalt tetracarbonyl, respectively, as could be seen from the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the isolated products. The ester obtained by adding sodium methylate to the final reaction solution of methyloxirane and  $\text{HCo}(\text{CO})_4$  is a mixture of 95% methyl 3-hydroxybutyrate and 5% methyl 3-hydroxy-2-methylpropionate, as shown by quantitative GLC analysis. This indicates that the alkyl-cobalt bond is formed predominantly at the more accessible carbon of the substituted oxirane.

$\text{HCo}(\text{CO})_4$  is a strong acid in water or acetonitrile [9] and so it can be assumed that the first step in this reaction is a proton transfer to the weakly basic oxirane [10]. A subsequent  $S_N1$  or  $S_N2$  type nucleophilic substitution could give the alkylcobalt tetracarbonyls, which yield the final acylcobalt tetracarbonyls by CO insertion.

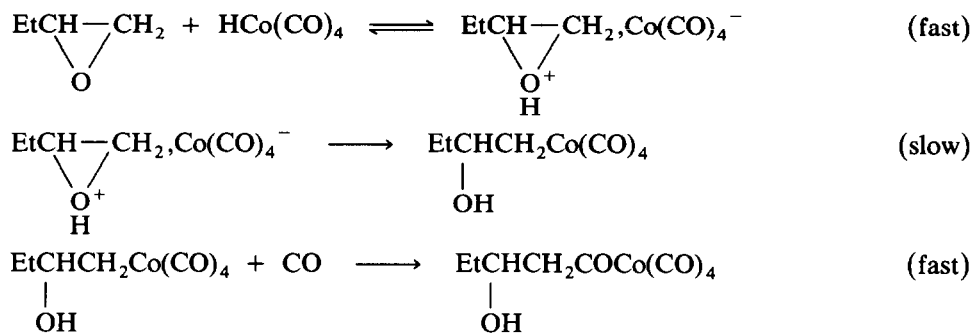
The higher rates observed in solvents with larger dielectric constants are consistent with the involvement of ionic or highly polar intermediates. On the other hand, the fact that the rates are independent of the CO concentration indicates that in the reaction of  $\text{HCo}(\text{CO})_4$  with oxirane (unlike that with certain olefins [11–13]) coordinatively unsaturated intermediates do not influence the rate of CO uptake.

The most important question is which is the rate-determining step. In the well established analogous case involving hydrogen chloride, two distinct sets of kinetic characteristics have been found, depending on the solvent. In water at constant pH the chlorohydrine formation obeys a second-order rate law, first order in methyl-oxirane and first order in chloride ion, and this has been interpreted as a rate-determining borderline  $S_N2$  attack of the chloride ion on the protonated oxirane (in the acid-catalyzed reaction) or on the nonprotonated oxirane (in the uncatalyzed reaction). From the observed rate constant values of  $E_a$  of  $18.3 \pm 0.9$  kcal mol<sup>-1</sup> and  $\Delta S_{40^\circ\text{C}}^\ddagger$  of  $-3.6 \pm 2.7$  e.u. were calculated for the catalyzed reaction, and values of  $E_a$  of  $18.8 \pm 0.9$  kcal mol<sup>-1</sup> and  $\Delta S_{40^\circ\text{C}}^\ddagger$  of  $-22.2 \pm 2.7$  e.u. for the uncatalyzed reaction in the case of the reaction leading to the major product  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{Cl}$  [14]. In anhydrous THF or in 40:60 dioxane–EtOH the kinetics reveal first-order dependence on both oxirane and HCl. The addition of LiCl has no effect on the observed rate, suggesting that in this case an ion pair is involved in the ring opening [15]. The activation parameters in these solvents have not been determined.

The kinetics of the reaction involving  $\text{HCo}(\text{CO})_4$  bear a close resemblance to those for the reaction with HCl in anhydrous solvents, the overall reaction being first order in ethyloxirane and in  $\text{HCo}(\text{CO})_4$ , and the addition of  $\text{NaCo}(\text{CO})_4$  has practically no effect on the rate of CO uptake. This latter result suggests that ion-pairing between the oxirane and  $\text{HCo}(\text{CO})_4$  may be involved in the reaction. On the basis of the kinetic data three possible rate-determining steps can be considered: a slow ion pair formation, an  $S_N1$  type opening of the protonated oxirane in the ion pair, and an intramolecular  $S_N2$  type reaction within the ion pair.

A kinetically slow proton transfer from  $\text{HCo}(\text{CO})_4$  to oxirane is difficult to reconcile with the inverse deuterium isotope effect (see Table 3). Such effect is usually observed in equilibrium protonation of oxiranes [16]. Theoretically an inverse kinetic isotope effect,  $k_H/k_D < 1$ , may arise in a hydrogen transfer step if this goes from a compound with weakly bonded hydrogen to a product with a strongly bonded hydrogen via a very product-like transition state [17]. According to recent opinions [18], however, in most cases in which a slow hydrogen transfer was claimed to account for the observed inverse kinetic isotope effect [19], it can better be interpreted in terms of a reversible preequilibrium hydrogen transfer and a subsequent slow transformation. Although kinetically slow proton transfer from  $\text{HCo}(\text{CO})_4$  to various substituted anilines in acetonitrile solutions is known (e.g. in the case of 4-iodoaniline  $\Delta H_{25^\circ\text{C}}^\ddagger = 2.9 \pm 0.3$  kcal mol<sup>-1</sup> and  $\Delta S_{25^\circ\text{C}}^\ddagger = -27.5 \pm 0.5$  e.u.) [20], the protonation of oxirane by  $\text{HCo}(\text{CO})_4$  probably occurs in a preequilibrium.

A slow  $S_N1$  type reaction is unlikely in light of the activation parameters. From the data in Table 3,  $E_a = 0 \pm 1$  kcal mol<sup>-1</sup> and  $\Delta S_{25^\circ\text{C}}^\ddagger = -66 \pm 3$  e.u. can be calculated for the reaction of ethyloxirane, and  $E_a = 0 \pm 1$  kcal mol<sup>-1</sup> and  $\Delta S_{25^\circ\text{C}}^\ddagger = -75 \pm 5$  e.u. in the case of butyloxirane, which are very different from the high activation energy and the positive activation entropy values found for  $A1$  type hydrolysis of 2,2-dimethyloxirane ( $E_a = 19.34 \pm 0.23$  kcal mol<sup>-1</sup> and  $\Delta S_{25^\circ\text{C}}^\ddagger =$



Scheme 1

+7.9 ± 0.8 e.u.) [21], of acetaldehyde diethylacetal ( $\Delta H_{25^\circ\text{C}}^\ddagger = 21.7 \text{ kcal mol}^{-1}$  and  $\Delta S_{25^\circ\text{C}}^\ddagger = +15 \text{ e.u.}$ ) [22] and of 2-methyl-1,3-dioxolane ( $\Delta H_{25^\circ\text{C}}^\ddagger = 21.65 \text{ kcal mol}^{-1}$  and  $\Delta S_{20^\circ\text{C}}^\ddagger = +5.6 \text{ e.u.}$ ) [23].

The highly negative entropy of activation in the oxirane +  $\text{HCo}(\text{CO})_4$  reaction indicates very unfavorable stereochemical changes, which can be attributed to the structural changes around the cobalt in the ion pair formation and the  $S_N2$  type substitution. Substantial electronic rearrangements can also be expected in these steps. Electrons from the negatively charged hydride ligand in  $\text{HCo}(\text{CO})_4$  have to move to the carbonyl oxygens in the ion pair formation. In the substitution step these electrons have to move again to form the negatively charged alkyl-carbon in the new carbon-cobalt bond. Thus the mechanism of the oxirane +  $\text{HCo}(\text{CO})_4$  reaction is best described in terms of a preequilibrium tight ion-pair formation and a rate-determining nucleophilic substitution within the ion pair, which is not influenced by the external  $\text{Co}(\text{CO})_4^-$  concentration (Scheme 1).

The intermediate alkylcobalt tetracarbonyls could not be detected by infrared spectroscopy during the reaction or at the end. This is in accord with the general experience that under atmospheric pressure of CO the alkyl-acyl equilibrium is in most cases far on the side of the acyl complex [24].

## Experimental

All manipulations were carried out by Schlenk techniques [25]. Deoxygenated carbon monoxide was used. Ethyloxirane (Aldrich), methyloxirane (Fluka), n-butyloxirane (Fluka) and dry solvents were distilled under carbon monoxide. Stock solutions of  $\text{HCo}(\text{CO})_4$  in n-octane and n-pentane were prepared from  $\text{Co}_2(\text{CO})_8$ , DMF, and concentrated HCl [26], and the  $\text{HCo}(\text{CO})_4$  content was determined by titration of aliquots with 0.1 N aqueous NaOH with phenolphthalein indicator. Stock solutions of  $\text{NaCo}(\text{CO})_4$  in THF were prepared from  $\text{Co}_2(\text{CO})_8$  and NaOH [27], and were stored over sodium wire.

Infrared spectra were recorded by use of  $\text{CaF}_2$  cuvettes on a Specord IR 75 (Carl Zeiss, Jena) spectrometer, which was calibrated with benzene (1960) and polystyrene ( $1601 \text{ cm}^{-1}$ ).  $^1\text{H}$  NMR spectra were recorded on a Varian CFT-20 spectrometer ( $^1\text{H}$ : 80 MHz,  $^{13}\text{C}\{^1\text{H}\}$ : 20 MHz) Gas-chromatographic analyses were made on a Hewlett-Packard HP 5830A type instrument using a 25 m OV-1 capillary column,

Ar carrier gas and a flame ionization detector. Authentic samples of methyl 3-hydroxybutyrate (Aldrich) and methyl 3-hydroxy-2-methylpropionate (Aldrich) were used for identification and quantitation.

Kinetic studies were performed using thermostated reaction vessels with magnetic stirring and a gasometric apparatus fitted with a mercury-filled gas burette. The reaction was started by injecting the  $\text{HCo}(\text{CO})_4$  stock solution into the vigorously stirred solution of ethyloxirane. Initial rates of CO uptake were determined from readings of the gas burette during the first few minutes of the reaction. Usually 3–6 readings per minute were made and the initial rate was calculated from the tangent of these points. Reproducibility of the rates was between  $\pm 1$  and  $\pm 6\%$ .

*Preparation of (3-hydroxybutanoyl)cobalt tetracarbonyl,  $\text{MeCH}(\text{OH})\text{CH}_2\text{COC}(\text{CO})_4$*

To a solution of methyloxirane (2.5 g, 43 mmol) in n-hexane (7 mL) at  $0^\circ\text{C}$  were added dropwise 5 mL of a 0.4 M solution of  $\text{HCo}(\text{CO})_4$  in n-pentane under a CO atmosphere maintained at a total pressure of 860 mmHg. Ten minutes after the addition of the last drop of the  $\text{HCo}(\text{CO})_4$  solution a 0.1 mL sample was taken and diluted with n-hexane (0.2 mL) for IR spectroscopic analysis. The spectrum showed the bands of (3-hydroxybutyryl)cobalt tetracarbonyl (at 2104 (m), 2046 (s), 2027 (vs), 2006 (vs), and 1699 (w)  $\text{cm}^{-1}$ ), and the complete conversion of  $\text{HCo}(\text{CO})_4$  (lack of the band at 2114  $\text{cm}^{-1}$ ), and only traces of  $\text{Co}_2(\text{CO})_8$  (vw band at 2069  $\text{cm}^{-1}$ ). The reaction mixture was concentrated at  $-35^\circ\text{C}$  in vacuum to leave a yellow oil. For NMR spectroscopy this was dissolved in CO-saturated toluene- $d_8$ :  $^1\text{H}$  NMR (80 MHz, RT)  $\delta$  0.96 (d, 3H,  $\text{CH}_3$ ), 2.88 (s, 1H, OH), 3.02 (d,  $J = 4.4$  Hz, 1H,  $\text{CH}_2$ ), 3.10 (d,  $J = 7$  Hz, 1H,  $\text{CH}_2$ ), 3.97 (m, 1H, CH). After the spectrum had been recorded, the sample was diluted with n-hexane under CO. The IR spectrum of this solution was practically identical with that observed before concentration of the reaction mixture in vacuum.

*Preparation of (3-hydroxybutanoyl)cobalt tricarbonyl triphenylphosphine,  $\text{MeCH}(\text{OH})\text{CH}_2\text{COC}(\text{CO})_3\text{PPh}_3$*

To a stirred solution of 4.0 g (69 mmol) methyloxirane and 5 mL ether under 870 mmHg pressure of carbon monoxide at  $-15^\circ\text{C}$ , 5 mL of a cold ( $-78^\circ\text{C}$ ) 0.64 M stock solution of  $\text{HCo}(\text{CO})_4$  in n-pentane was slowly added from a syringe. The absorption of about 3.2 mmol carbon monoxide was complete in 1.5 h. To the light brown solution a solution of 0.89 g (3.4 mmol)  $\text{PPh}_3$  in 6 mL ether was added during 5 min, and this resulted in the release of ca. 3.4 mmol of gas. The resulting slurry was filtered on a P3 glass frit, the solid obtained washed twice with five mL portions of n-pentane, and dried in vacuum, to give yellow crystals (1.28 g, 81% yield). Anal.  $\text{C}_{25}\text{H}_{22}\text{O}_5\text{PCo}$  calc.: MW, 492.3; Co, 11.97; P, 6.29. Found: MW, 492 (osmometric in benzene); Co, 11.92; P, 6.22%.  $^1\text{H}$  NMR (80 MHz,  $\text{CDCl}_3$ , RT)  $\delta$  1.08 (d,  $J = 7$  Hz, 3H, Me), 2.9 (s, br, 1H, OH), 3.3 (m, 2H,  $\text{CH}_2$ ), 4.06 (m, 1H, CH).

*Preparation of (3-hydroxypentenoyl)cobalt tetracarbonyl,  $\text{EtCH}(\text{OH})\text{CH}_2\text{COC}(\text{CO})_4$*

A solution of ethyloxirane, 3 mL (35 mmol) in 5 mL n-pentane was cooled in a Schlenk tube to  $-30^\circ\text{C}$  and 5 mL of a 0.4 M  $\text{HCo}(\text{CO})_4$  solution in n-pentane was driven by a stream of CO from a flask kept at  $0^\circ\text{C}$  into the oxirane solution. After all of the  $\text{HCo}(\text{CO})_4$  solution had been transferred in this way, the pentane and the

excess of oxirane were evaporated off at  $-30^{\circ}\text{C}$  in vacuum, leaving the title compound as a yellow oil. IR (n-hexane)  $\nu(\text{CO})$  2107 (m), 2049 (s), 2028 (vs), 2009 (vs), 1696 (m)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , RT)  $\delta$  0.64 (t,  $J = 6$  Hz, 3H, Me), 0.94 (m, 2H,  $\text{MeCH}_2$ ), 1.91 (br s, 1H, OH), 2.79 (dd,  $J = 4.5$  Hz, 17 Hz, 1H,  $\text{CH}_a\text{H}_b\text{CO}$ ), 2.90 (dd,  $J = 7$  Hz, 17 Hz,  $\text{CH}_a\text{H}_b\text{CO}$ ), 3.51 (m, 1H, CH);  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , RT)  $\delta$  7.78 (Me), 26.6 ( $\text{MeCH}_2$ ), 67.9 ( $\text{CH}_2\text{CO}$ ), 69.5 (CH), 195.5 (4CO), 212.2 ( $\text{CoC}(\text{O})\text{CH}_2$ ).

*Formation of esters from the reaction mixture obtained from methyloxirane and  $\text{HCo}(\text{CO})_4$*

To a ca. 0.13 M acylcobalt tetracarbonyl solution (3 mL), prepared from methyloxirane and  $\text{HCo}(\text{CO})_4$  in n-pentane as described above, was added a solution of sodium methoxide (22 mg, 0.4 mmol) in methanol (2 mL) at room temperature. The reaction mixture was analyzed by GLC.

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