semicarbazone derivative of the ketone melted at 200–201° alone and when mixed with authentic material.

Monohydroboration of 1,2,6-Cyclononatriene.—Following the procedure described previously, 18.0 g. (0.15 mole) of 1,2,6-cyclononatriene[13] was allowed to react with diborane produced from 1.8 g. (0.045 mole) of sodium borohydride and 8.5 g. (0.060 mole) of boron trifluoride ether complex. The crude product, isolated in the usual way, was fractionated to give 4.5 g. of unreacted starting material, b.p. 62–63° (14 mm.,) and 8.0 g. of a mixture, b.p. 95–100° (14 mm.). The infrared spectrum possessed weak hydroxyl absorption and strong carbonyl absorption. Vapor–liquid chromatography showed only two components in the ratio 95/5 and on the basis of the infrared data this was interpreted as a ketone/alcohol ratio. A semicarbazone derivative was prepared in the usual way and purified by three crystallizations from 50% ethanol;· m.p. 170–171°.

Anal. Calcd. for $C_{10}H_{17}ON_3$: C, 61.50; H, 8.77; N, 21.52. Found: C, 61.47; H, 8.57; N, 21.39.

Regeneration[15] of the ketone from its semicarbazone afforded a pure sample, b.p. 96° (14 mm.), $n^{25}D$ 1.4931. A solution of 1.0 g. (7.2 mmoles) was ozonized at −30° with a *ca.* 4% ozone–oxygen mixture until the appearance of iodine in an adjoining potassium iodide trap. The mixture was then poured into a solution prepared by mixing 25 ml. of 10% sodium hydroxide with 25 ml. of 30% hydrogen peroxide. The flask was fitted with a reflux condenser and cautiously warmed until the onset of a vigorous reaction. When this subsided, the mixture was heated under reflux for 6 hours after which time it gave a negative test with sodium iodide. The usual work-up procedure by ether extraction afforded 0.85 g. of δ-ketoazelaic acid which melted at 110° after two recrystallizations from water (lit.[18] 110.5°). The semi-

(18) K. Sorm, *Collection Czech. Chem. Commun.*, **12**, 150 (1947).

carbazone derivative had m.p. 180–181° after crystallization from aqueous ethanol (lit.[18] 181°).

Monohydroboration of 2,3-Nonadiene.—2,3-Nonadiene was prepared from 2-octene[19] by the method used for the synthesis of all allenes required for this study.[11–13] Its preparation was uncomplicated and will therefore not be described here.[20] It had properties identical with those of a sample prepared by another method.[21]

Following the procedure described for 1,2-cyclononadiene, 12.4 g. (0.10 mole) of 2,3-nonadiene was allowed to react with 1.2 g. (0.030 mole) of sodium borohydride and 5.6 g. (0.040 mole) of boron trifluoride-ether complex. Fractional distillation of the processed reaction mixture afforded 2.5 g. (fraction 1), b.p. 49–52° (20 mm.), and 6.8 g. (fraction 2), b.p. 85–90° (20 mm.). Vapor–liquid chromatography of fraction 1 showed it to be 56% starting material and 44% of a single olefin. No effort was made to identify this substance. Fraction 2 was shown by vapor–liquid chromatography to be 85% of 3-nonanone accompanied by 15% of an alcohol. The semicarbazone derivative melted at 110–112° after two crystallizations from 50% ethanol (lit.[22] 111–112°).

(19) Phillips Petroleum Company.

(20) D. Devaprabhakara, Ph.D. Dissertation, The University of Texas, 1962.

(21) A. A. Petrov and V. A. Kormer, *Doklady Akad. Nauk SSSR*, **125**, 1041 (1959).

(22) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 1936 (1913).

[Contribution from the Research Center, Hercules Powder Co., Wilmington 99, Del.]

The Reaction of Epoxides with Cobalt Hydrocarbonyl and Cobalt Tetracarbonyl Anion

By Richard F. Heck

Cobalt hydrocarbonyl, carbon monoxide and epoxides react at 0° to give high yields of β-hydroxyacylcobalt tetracarbonyls. Complexes from ethylene oxide, propylene oxide and cyclohexene oxide have been isolated as their mono-(triphenylphosphine) derivatives. The cyclohexene oxide product was cleaved with iodine and methanol and shown to be the *trans* isomer. Isobutylene oxide gave mainly the isomer in which cobalt was attached to the primary carbon atom. Cobalt carbonyl anion in hydroxylic solvents will also react with epoxides at higher temperatures to give esters of β-hydroxyacids. Trimethylene oxide reacts readily with cobalt hydrocarbonyl and carbon monoxide to form 4-hydroxybutyrylcobalt tetracarbonyl which has been isolated as the triphenylphosphine derivative. The 4-hydroxybutyrylcobalt tetracarbonyl reacts with dicyclohexylethylamine to produce cobalt carbonyl anion and γ-butyrolactone. The mechanism of the cobalt hydrocarbonyl-epoxide reaction is discussed and explanations for the known reactions of epoxides with carbon monoxide are presented.
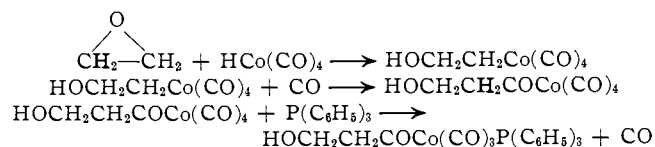
Introduction

The literature records several examples of the reaction of epoxides with carbon monoxide and water or alcohols using a cobalt salt or cobalt carbonyl as catalyst.[1–5] Generally, hydroxyacids, their derivatives or rearranged carbonyl products or both are formed. Employing the methods used in our study of the hydroformylation reaction,[6] it has been possible to isolate organocobalt complexes which appear to be intermediates in the epoxide carboxylation reaction. The structures of the intermediates provide considerable evidence about the mechanism of the reaction.

Results

Epoxides.—Ethylene oxide in ether solution reacts rapidly with cobalt hydrocarbonyl at 0°. Under one atmosphere of carbon monoxide, 0.96 mole of gas was absorbed in less than an hour and the absorption ceased. The infrared spectrum of the reaction mixture had a strong carbonyl band at 5.89 μ as well as co-

(1) M. Séon and J. Leleu, U. S. Patent 2,782,226 (1957).

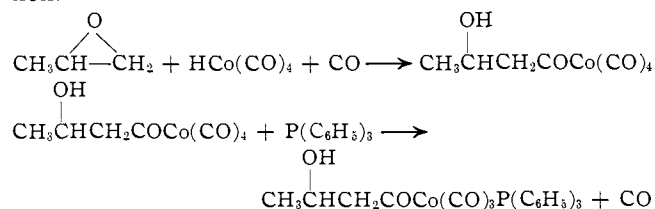(2) H. Nienburg and G. Elschnig, German Patent 1,066,572 (1959).

(3) J. L. Eisenmann, R. L. Yamartino and J. F. Howard, Jr., *J. Org. Chem.*, **26**, 2102 (1961).

(4) W. A. McRae and J. L. Eisenmann, U. S. Patent 3,024,275 (1962).

(5) J. L. Eisenmann, *J. Org. Chem.*, **27**, 2706 (1962).

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

ordinated carbonyl bands at 4.76 and 4.95 μ suggesting that 3-hydroxypropionylcobalt tetracarbonyl had been formed. This structure was confirmed by isolating the complex as the triphenylphosphine derivative. Addition of excess triphenylphosphine to the ethylene oxide–cobalt hydrocarbonyl reaction mixture led to the evolution of 0.97 mole of gas. Evaporation of the solvent and several recrystallizations from ether–pentane gave pale yellow crystals of 3-hydroxypropionylcobalt tricarbonyl triphenylphosphine, m.p. 95–100° dec.

$$\underset{\substack{\diagup \diagdown \\ CH_2{-}CH_2}}{\overset{O}{}} + HCo(CO)_4 \longrightarrow HOCH_2CH_2Co(CO)_4$$

$$HOCH_2CH_2Co(CO)_4 + CO \longrightarrow HOCH_2CH_2COCo(CO)_4$$

$$HOCH_2CH_2COCo(CO)_4 + P(C_6H_5)_3 \longrightarrow$$
$$HOCH_2CH_2COCo(CO)_3P(C_6H_5)_3 + CO$$

A similar reaction took place between propylene oxide, carbon monoxide and cobalt hydrocarbonyl. The complex was also isolated as the triphenylphosphine derivative, m.p. ~90° dec. Two isomeric products are possible in this reaction. At 130° Eisenmann[3] reports that propylene oxide in the carboxylation reaction yields· a product which is at least 95% the 3-hydroxybutyrate derivative. It is probable that at 0°

the same isomer was formed in the hydrocarbonyl reaction.

$$CH_3CH\text{—}CH_2 + HCo(CO)_4 + CO \longrightarrow CH_3\overset{OH}{CH}CH_2COCo(CO)_4$$

$$CH_3\overset{OH}{CH}CH_2COCo(CO)_4 + P(C_6H_5)_3 \longrightarrow$$
$$CH_3\overset{OH}{CH}CH_2COCo(CO)_3P(C_6H_5)_3 + CO$$

Isobutylene oxide reacts similarly, but the triphenylphosphine complex of the hydroxy(acyl)cobalt carbonyl is quite unstable and it could not be purified. Cleavage of the crude product with iodine in methanol[6] led to the formation of a mixture of esters. Analyses by vapor phase chromatography showed that the product was a mixture containing about 93% of methyl 3-hydroxy-3-methylbutyrate and 7% of methyl 3-hydroxy-2,2-dimethylpropionate.

$$CH_3\text{—}\overset{O}{C}\text{—}CH_2 + HCo(CO)_4 + CO \longrightarrow$$
$$\underset{CH_3}{}$$

$$CH_3\text{—}\overset{OH}{\underset{CH_3}{C}}\text{—}CH_2COCo(CO)_4 + HOCH_2\overset{CH_3}{\underset{CH_3}{C}}COCo(CO)_4$$

$$\downarrow I_2\text{-}CH_3OH \qquad\qquad \downarrow I_2\text{-}CH_3OH$$

$$CH_3\text{—}\overset{OH}{\underset{CH_3}{C}}\text{—}CH_2COOCH_3 \qquad HOCH_2\overset{CH_3}{\underset{CH_3}{C}}COOCH_3$$
$$\;\;\;\;\;\;93\% \qquad\qquad\qquad\qquad 7\%$$
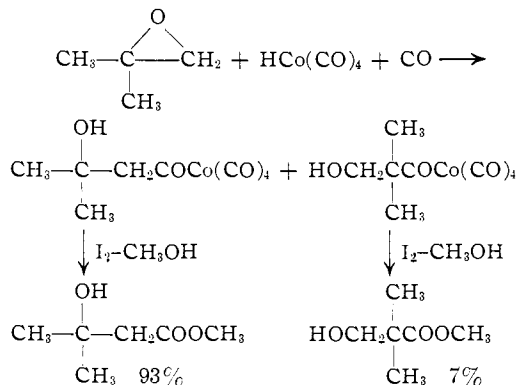
Styrene oxide also forms an unstable complex or complexes with cobalt hydrocarbonyl and carbon monoxide. The structure of the complex has not been determined. The triphenylphosphine derivative was too unstable to isolate.

Cobalt hydrocarbonyl and carbon monoxide add to cyclohexene oxide to form 2-hydroxycyclohexylcarbonylcobalt tetracarbonyl which has been isolated as the triphenylphosphine derivative. Cleavage of the crude triphenylphosphine complex with iodine and methanol led only to methyl *trans*-2-hydroxycyclohexanecarboxylate. There was no indication of any of the *cis* isomer being formed.

Epoxyacrolein reacts with cobalt hydrocarbonyl without carbon monoxide absorption. The major product is dicobalt octacarbonyl. Presumably a hydroxypropionaldehyde is the other product in view of the fact that acrolein itself reacts with cobalt hydrocarbonyl to undergo only reduction to propionaldehyde. Both reactions probably involve the formation of an α- or β-formyl-cobalt carbonyl intermediate which then reacts very rapidly with more cobalt hydrocarbonyl to produce only saturated or hydroxy aldehyde and dicobalt octacarbonyl.

$$2HCo(CO)_4 + CH_2\text{—}CHCHO \longrightarrow HOC_3H_4CHO + Co_2(CO)_8$$
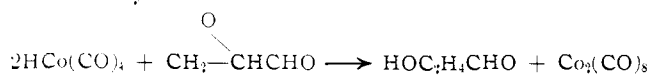
Cobalt carbonyl anion will react with epoxides in the presence of hydroxylic solvents such as water or alcohols to form hydroxyacids or esters. The anionic reaction, however, is much slower than the cobalt hydrocarbonyl addition. In non-hydroxylic solvents such as ether, a small amount of polymer is formed which precipitates and coats the catalyst and the reaction stops.

Ethylene oxide reacts with sodium cobalt carbonyl and carbon monoxide in methanol solution at 65° and 2000 p.s.i. pressure to give about a 55% yield of methyl
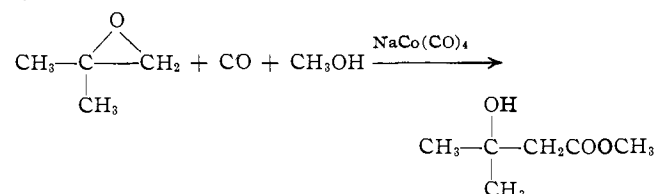
3-hydroxypropionate. The remainder of the product is acetaldehyde and a non-volatile oil. This reaction also will proceed nearly as well at only three or four atmospheres of carbon monoxide.
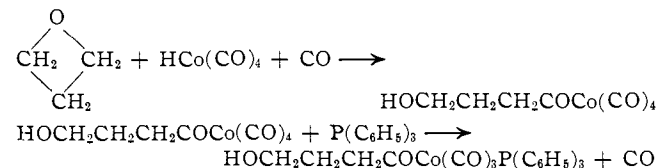
$$CH_2\text{—}CH_2 + CO + CH_3OH \xrightarrow{NaCo(CO)_4} HOCH_2CH_2COOCH_3$$
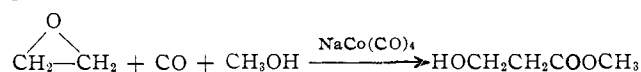
Similarly, propylene oxide gave about a 5-10% yield of methyl 3-hydroxybutyrate. Isobutylene oxide gave

$$CH_3\text{—}CH\text{—}CH_2 + CO + CH_3OH \xrightarrow{NaCo(CO)_4}$$
$$CH_3\overset{OH}{CH}CH_2COOCH_3$$
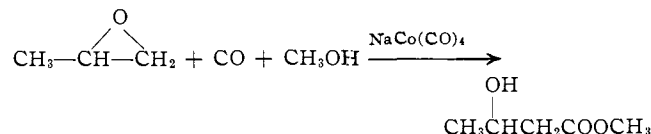
about a 30% yield of methyl 3-methyl-3-hydroxybutyrate.

$$CH_3\text{—}\overset{O}{\underset{CH_3}{C}}\text{—}CH_2 + CO + CH_3OH \xrightarrow{NaCo(CO)_4}$$
$$CH_3\text{—}\overset{OH}{\underset{CH_3}{C}}\text{—}CH_2COOCH_3$$

Trimethylene Oxide.—Trimethylene oxide reacts rapidly with cobalt hydrocarbonyl and carbon monoxide at 0°. The product, 4-hydroxybutyrylcobalt tetracarbonyl, yields a relatively stable triphenylphosphine derivative, m.p. 115–125° dec.

$$CH_2\overset{O}{\underset{CH_2}{}}CH_2 + HCo(CO)_4 + CO \longrightarrow$$
$$HOCH_2CH_2CH_2COCo(CO)_4$$

$$HOCH_2CH_2CH_2COCo(CO)_4 + P(C_6H_5)_3 \longrightarrow$$
$$HOCH_2CH_2CH_2COCo(CO)_3P(C_6H_5)_3 + CO$$

Support for the 4-hydroxybutyryl structure is found in the fact that the tetracarbonyl reacts readily at 0° with the strong, hindered base dicyclohexylethylamine to produce cobalt carbonyl anion and γ-butyrolactone (identified by its characteristic carbonyl band at 5.62 μ).

$$HOCH_2CH_2CH_2COCo(CO)_4 + (C_6H_{11})NC_2H_5 \longrightarrow$$
$$\underset{}{\overset{}{}} + (C_6H_{11})_2\overset{H+}{NC_2H_5}\;Co(CO)_4^-$$
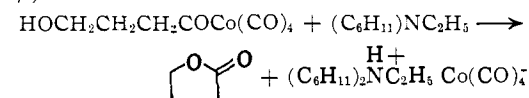
This same type of ring closure has been observed in another organocobalt carbonyl compound, 5-hydroxy-3-pentenoylcobalt tetracarbonyl. *cis*-4-Chloro-2-buten-1-ol reacts at 25° with dicyclohexylethylamine, carbon monoxide and sodium cobalt carbonyl to give about a 1:3 ratio of two products, 1-hydroxymethyl-π-allylcobalt tricarbonyl and the lactone of a 5-hydroxypentenoic acid.
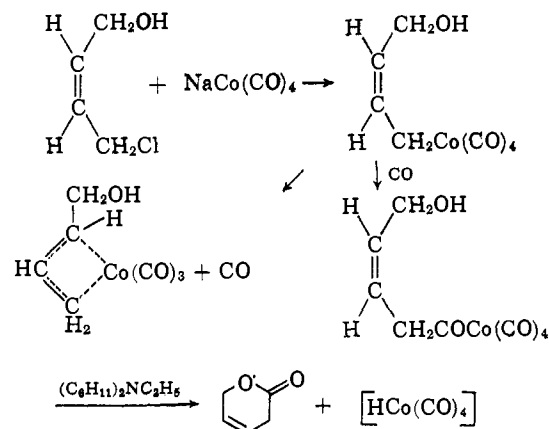
Discussion

There can be little doubt from the above results that the known carboxylations of epoxides and trimethylene oxides involve the formation of hydroxyacylcobalt carbonyls which then react with water or alcohols to give hydroxyacids or hydroxyesters and cobalt hydrocarbonyl, as is known to occur with simple acylcobalt tetracarbonyl.[7] Whether the reactions employing co-

$$HOCH_2CH_2COCo(CO)_4 + CH_3OH \longrightarrow$$
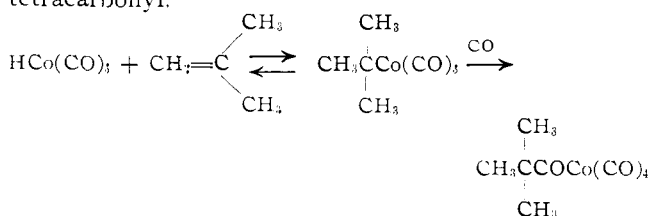$$HOCH_2CH_2COOCH_3 + HCo(CO)_4$$
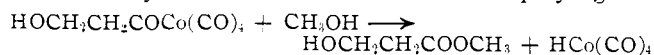
balt carbonyl or cobalt salts as catalysts are being catalyzed by hydrocarbonyl or cobalt carbonyl anion is not clear. Cobalt carbonyl is known to disproportionate reversibly in hydroxylic solvents into cobalt(II)-cobalt tetracarbonyl and carbon monoxide. Therefore,

$$Co_2(CO)_8 + 6ROH \longrightarrow Co(ROH)_6{}^{++}[Co(CO)_4]_2{}^- + 4CO$$
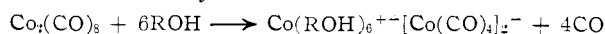
cobalt tetracarbonyl anion is undoubtedly present. Cobalt hydrocarbonyl is also present, because it is formed in the cleavage of the acylcobalt complex, and it is probably formed from cobalt octacarbonyl and water or an alcohol under the reaction conditions.
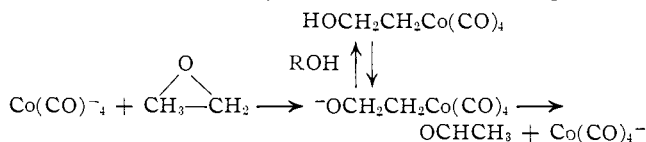
The fact that isobutylene oxide gave mostly, if not completely, the same isomeric product on treatment with either cobalt hydrocarbonyl or cobalt carbonyl anion suggests that the catalyst employed does not affect the direction of opening of the epoxide ring. It could be argued, however, that in this example the cobalt prefers the primary position for steric reasons and there might be more difference between the hydrocarbonyl and anion-catalyzed reactions where there is not as much difference between the two epoxide carbons. The major product formed from isobutylene oxide is the one expected from an anionic opening of the epoxide and, therefore, it is the hydrocarbonyl reaction which is unusual. Cobalt hydrocarbonyl is not very nucleophilic since it does not react with methyl iodide under the conditions of its reaction with epoxides. Thus, cobalt hydrocarbonyl does appear to be reacting as an acid. Further evidence on this reaction is found in the addition of cobalt hydrocarbonyl to cyclohexane oxide. The only product found (after methanol and iodine cleavage) was the *trans* isomer of methyl 2-hydroxycyclohexanecarboxylate. A concerted *cis* addition of cobalt hydrocarbonyl to the epoxide would have given the *cis* ester. The mechanism most consistent with all of the data is an ionic, acid opening of the epoxide which is more sensitive to steric effects than to electronic factors. This conclusion may at first appear to be inconsistent with our previous finding that isobutylene reacted with cobalt hydrocarbonyl to give exclusively addition of the cobalt to the tertiary position.[6] The inhibitory effect of carbon monoxide on that reaction, however, indicated that it was probably cobalt hydrotricarbonyl that was actually adding to the olefin and steric effects would be expected to be much less important with the tricarbonyl than with the tetracarbonyl.

$$HCo(CO)_3 + CH_2=C\overset{CH_3}{\underset{CH_3}{\big<}} \rightleftarrows CH_3\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}Co(CO)_3 \overset{CO}{\longrightarrow}$$

$$CH_3\overset{CH_3}{\underset{CH_3}{\overset{|}{C}}}COCo(CO)_4$$

The formation of carbonyl compounds by the rearrangement of epoxides has been observed by Eisenmann[5] and also in this work. In the present study

(7) R. F. Heck and D. S. Breslow, "Advances in the Chemistry of Co-ordination Compounds," The Macmillan Company, New York, N. Y., 1961, p. 281.

larger amounts of rearrangement occurred in the cobalt carbonyl anion reactions than in the cobalt hydrocarbonyl reaction. The anionic reactions were always carried out at higher temperatures, however, and it is not certain that there would be any difference under the same conditions. Nevertheless, a reasonable mechanism for the rearrangement would be the formation of the hydroxyalkylcobalt tetracarbonyl complex followed by loss of the cobalt carbonyl anion and then by a hydride shift. This reaction could be facilitated if the alcohol group were present as the anion, and it well could be that only the anion will rearrange. An-

$$HOCH_2CH_2Co(CO)_4$$
$$ROH \uparrow\downarrow$$
$$Co(CO)_4{}^- + CH_3-CH_2 \longrightarrow {}^-OCH_2CH_2Co(CO)_4 \longrightarrow$$
$$OCHCH_3 + Co(CO)_4{}^-$$

other possible mechanism is the elimination of cobalt hydrocarbonyl from the hydroxyalkylcobalt carbonyl to give the enol alcohol in the same way that alkylcobalt carbonyls can give olefins.[6]

The use of the cobalt hydrocarbonyl or cobalt carbonyl anion–epoxide and trimethylene oxide reactions as general preparative methods appears possible and indeed several similar reactions have already been reported and referred to above.[1-5] The present results again point out the unusual behavior of cobalt hydrocarbonyl because it does not give the products expected from a "normal acid."

Experimental

3-Hydroxypropionylcobalt Tricarbonyl Triphenylphosphine.— At 0°, in the previously described apparatus[8] filled with ether-saturated carbon monoxide, were placed 10 ml. of ether, 1.0 ml. of ethylene oxide and 10.0 ml. of 0.26 M cobalt hydrocarbonyl in pentane. In 53 minutes, 74 ml., or about 2.5 mmoles, of carbon monoxide was absorbed and the reaction ceased. The addition of 3.0 ml. of 1.0 M triphenylphosphine in ether caused the evolution of 76 ml., or about 2.5 mmoles, of gas in about 90 minutes, and the reaction stopped. The solvent was evaporated under vacuum and the product was separated from the insoluble material by extraction with ether under nitrogen. The extracts were centrifuged and concentrated under vacuum to about 5 ml. Addition of about 5 to 10 ml. of pentane and cooling to −80° gave a good yield of pale, yellow-brown crystals of 3-hydroxypropionylcobalt tricarbonyl triphenylphosphine. Two further recrystallizations from ether–pentane gave 0.30 g. of product melting at 95–100° dec. The infrared spectrum in carbon tetrachloride solution had bands at: 2.80(w), 3.25(w), 3.40(w), 3.48(w), 4.86(m), 5.06(vs), 6.03(s), 6.75(w), 6.98(m), 7.19(w), 7.65(w), 8.28(w), 8.40(w), 9.11(m), 9.42(m), 9.70(m), 9.98(w), 10.40(w), 11.21(w), 11.83(w) μ, and in carbon bisulfide there were additional bands at 13.39(m), 14.11(m), 14.40(s), and 14.80(w) μ.

Anal. Calcd. for $C_{24}H_{20}O_5PCo$: C, 60.26; H, 4.22. Found: C, 60.31; H, 4.42.

3-Hydroxybutyrylcobalt Tricarbonyl Triphenylphosphine.— At 0°, in the gasometric apparatus filled with carbon monoxide, were placed 15 ml. of propylene oxide and 2.0 ml. of 0.46 M cobalt hydrocarbonyl in pentane. In 10 minutes, 20 ml. of carbon monoxide was absorbed (~0.7 mmole) and the reaction stopped. The addition of 1.5 ml. of 1.0 M triphenylphosphine in ether resulted in the evolution of 18 ml. of gas in about an hour before the reaction stopped. Evaporation of the solvent and isolation of the product as described in the preceding example gave a good yield of yellow-brown crystals of product which decomposed at about 90–100°.

Anal. Calcd. for $C_{25}H_{22}O_5PCo$: C, 60.98; H, 4.50. Found: C, 60.55; H, 4.56.

The Reaction of Isobutylene Oxide with Cobalt Hydrocarbonyl and Carbon Monoxide.— At 0°, in the gasometric apparatus filled with ether-saturated carbon monoxide, were placed 20 ml. of ether, 1.0 ml. of isobutylene oxide and 2.5 ml. of 0.59 M cobalt hydrocarbonyl in pentane. In 70 minutes, 32 ml. or 1.1 mmoles of carbon monoxide was absorbed. In one experiment 3.0 ml. of 1.0 M triphenylphosphine in ether was added and 30 ml. of carbon monoxide was evolved. The infrared spectrum had bands at 4.88(w), 5.02(m), 5.09(s), and 6.00(m) μ indicating that the phosphine complex had been formed, but it decomposed on

(8) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).

attempted isolation. In another similar experiment, 15 ml. of 0.2 M iodine in methanol was added. After the gas evolution stopped (128 ml./was evolved), 5.0 ml. of 1.0 M sodium methoxide was added and the solution was analyzed by vapor phase chromatography. There were found 0.27% of methyl 3-hydroxy-3-methylbutyrate and 0.02% of methyl 3-hydroxy-2,2-dimethylpropionate in the reaction solution.

Reaction of Styrene Oxide with Cobalt Hydrocarbonyl and Carbon Monoxide.—This reaction was carried out as described in the preceding example, 0.5 ml. of styrene oxide being used in place of 1.0 ml. of isobutylene oxide. In less than an hour at 0°, after 56 ml. or 1.89 mmoles of carbon monoxide had been absorbed, the reaction stopped. The addition of 3.0 ml. of 1.0 M triphenylphosphine in ether led to the evolution of 60 ml., or 2.0 mmoles, of gas in about 2 hours. The infrared spectrum had bands at 4.88(w), 5.05(vs), and 6.00(m) μ, indicating that a phenylhydroxypropionylcobalt tricarbonyl triphenylphosphine complex had been formed.

Evaporation of the solvent at 0°, followed by extraction of the product with methylene chloride, centrifuging and evaporating gave a dark oil which crystallized when pentane was added. Attempts to recrystallize the compound at room temperature led to decomposition to the orange-brown cobalt tricarbonyl triphenylphosphine dimer.

2-Hydroxycyclohexylcarbonylcobalt Tricarbonyl Triphenylphosphine.—At 0°, in the gasometric apparatus filled with ether-saturated carbon monoxide were placed 20 ml. of ether, 1.0 ml. of cyclohexene oxide and 3.0 ml. of 0.59 M cobalt hydrocarbonyl in pentane. The solution turned brown, and in 30 minutes 43 ml. (1.45 mmoles) of carbon monoxide was absorbed. The addition of 2.0 ml. of 1.0 M triphenylphosphine in ether caused the evolution of 38 ml. of gas. Isolation of the complex as described for the 3-hydroxypropionylcobalt complex above, and several recrystallizations from tetrahydrofuran–pentane at −80°, gave very pale yellow crystals which had no definite melting point.

Anal. Calcd. for $C_{28}H_{26}O_5PCo$: C, 63.16; H, 4.92. Found: C, 63.45; H, 5.23.

Reaction of Cobalt Hydrocarbonyl with Epoxyacrolein.—At 0°, in the gasometric apparatus filled with ether-saturated carbon monoxide, were placed 15 ml. of ether, 1.0 ml. of freshly distilled epoxyacrolein and 2.6 ml. of 0.59 M cobalt hydrocarbonyl in pentane. The solution immediately turned red, but there was no gas volume change in 2.5 hours. The infrared spectrum had the characteristic bands at 4.85 μ and 5.4 μ indicating that cobalt octacarbonyl had been formed.

Carboxymethylation of Ethylene Oxide.—In a 500-ml., high-pressure vessel filled with carbon monoxide were placed 120 ml. of 0.13 M sodium cobalt carbonyl in methanol and 25 ml. of liquid ethylene oxide. The pressure was raised to 2000 p.s.i. with carbon monoxide and the solution was rocked and heated at 65° for 5 hours. The pressure was kept at 2000 p.s.i. by adding more carbon monoxide as it was needed. After the reactor cooled and was vented, the reaction mixture was distilled under vacuum. There was obtained 29.0 g. or 55% of colorless methyl 3-hydroxypropionate, b.p. 47–49° (4 mm.) (reported[9] b.p. 71° (13 mm.)). The alcohol solution which distilled first gave a very strong test with 2,4-dinitrophenylhydrazine reagent in alcoholic sulfuric acid. Vapor phase chromatography proved that the carbonyl compound present was acetaldehyde. After the distillation, a residue of 10.9 g. of viscous oil remained.

Carboxymethylation of Propylene Oxide.—In a pressure bottle filled with carbon monoxide were placed 10 ml. of 1.0 M sodium cobalt carbonyl and 10 ml. (8.3 g.) of propylene oxide. The solution was stirred magnetically, heated to 60°, and kept under 50 p.s.i. of carbon monoxide for 6 hours. Distillation of the reaction mixture gave 1.0 g. of methyl 3-hydroxybutyrate, b.p. 70° (22 mm.) (reported[3] b.p. 50–52° (2–3 mm.)) and equivalent weight 119.3 (calcd. 118). The n.m.r. spectrum at 60 Mc. had 4 bands in the area ratio of 3:2:3:2 at 330, 256, 182 and 155 c.p.s., respectively, with respect to an external benzene standard. The hydroxyl and tertiary hydrogen are probably together at 155 c.p.s. The data are consistent with the product being at least mainly methyl 3-hydroxybutyrate.

Carboxymethylation of Isobutylene Oxide.—In a pressure bottle were placed 1.6 g. of isobutylene oxide and 10 ml. of 1.0 M sodium cobalt carbonyl in methanol. The solution was

heated under 40 p.s.i. of carbon monoxide at 50° with stirring for 36 hours and distilled. There was obtained 0.7 g. of ester. No boiling point could be determined, but vapor phase chromatography indicated that it was practically pure methyl 3-methyl-3-hydroxybutyrate by comparison with pure known samples of this compound and the other possible isomer, methyl 3-hydroxy-2,2-dimethylpropionate.

4-Hydroxybutyrylcobalt Tricarbonyl Triphenylphosphine.—At 0°, in the gasometric apparatus filled with ether-saturated carbon monoxide, were placed 10 ml. of ether, 1.0 ml. of trimethylene oxide and 3.0 ml. of 0.59 M cobalt hydrocarbonyl in pentane. In about an hour 41 ml., or 1.4 mmoles, of carbon monoxide (78%) was absorbed and the reaction ceased. The addition of 2.5 ml. of 1.0 M triphenylphosphine in ether resulted in the evolution of 39 ml. of gas in 75 minutes (1.3 mmoles). The resulting solution was evaporated to dryness and the product was extracted from the residue with several small portions of ether. The insoluble material was removed by centrifuging and the solution was concentrated under vacuum to a few milliliters. The addition of pentane, followed by cooling, gave very pale yellow plates of the product. Three recrystallizations from ether–pentane gave material which decomposed at about 115–125°. The infrared spedtrum in carbon tetrachloride solution had bands at 3.70(w), 3.27(w), 3.45(w), 4.89(w), 5.04(vs), 5.09(vs), 5.98(m), 6.78(w), 6.99(w), 9.13(w) μ and there were additional bands in carbon bisulfide at 13.40(w), 14.16(w) and 14.40(m) μ.

Anal. Calcd. for $C_{25}H_{22}O_5PCo$: C, 60.98; H, 4.51. Found: C, 61.25; H, 4.79.

γ-Butyrolactone from 4-Hydroxybutyrylcobalt Tetracarbonyl.—4-Hydroxybutyrylcobalt tetracarbonyl was prepared as in the preceding example except 15 ml. of ether was used as solvent instead of 10 ml. After the gas absorption stopped, 1.0 ml. of dicyclohexylethylamine[10] was added at 0°. There was no gas volume change, but the infrared spectrum of the reaction mixture gradually changed. The acyl peak at 5.83 μ and the coördinated carbonyl bands at 4.73 and 4.95 μ decreased and the γ-butyrolactone band at 5.62 μ and the cobalt carbon anion band at 5.3 μ increased. The reaction was about 75% complete in 1 hour and completely over in about 3 hours at 0°.

Reaction of cis-4-Chloro-2-buten-1-ol with Sodium Cobalt Carbonyl, Carbon Monoxide and Dicyclohexylethylamine.—At 25°, in the gasometric apparatus filled with tetrahydrofuran-saturated carbon monoxide, were placed 20 ml. of 0.1 M sodium cobalt carbonyl in tetrahydrofuran, 1.0 ml. of dicyclohexylethylamine[10] and 4.5 ml. of 1.0 M cis-4-chloro-2-buten-1-ol[11] in tetrahydrofuran. Gas was slowly absorbed. About 10 ml. was absorbed in 15 hours at 25°. The infrared spectrum now had a strong new carbonyl band at 5.72 μ and coördinated carbonyl bands at 4.83(m) and 5.05(vs) μ. Addition of 3.0 ml. of 1.0 M triphenylphosphine in ether caused the evolution of about 1.0 mmole of gas, indicating about 25% of the product was the π-allyl derivative, 1-hydroxymethyl-π-allylcobalt tricarbonyl. The infrared spectrum still showed the 5.72 μ lactone band after the phosphine addition, but the coördinated carbonyl bands were shifted to 5.02(s) and 5.17(vs) μ, respectively, as expected. The lactone is probably from 5-hydroxy-3-pentenoic acid, but the infrared spectrum is not conclusive as to whether the double bond is conjugated with the lactone group or not.

Attempted Reaction of Cobalt Hydrocarbonyl with Methyl Iodide.—At 0°, in the gasometric apparatus filled with pentane-saturated carbon monoxide, were placed 10 ml. of 0.5 M cobalt hydrocarbonyl in pentane and 0.5 ml. of methyl iodide. No gas volume change occurred in an hour. Then 5.0 ml. of ether was added. Still there was not noticeable reaction in 30 minutes. Under these conditions sodium cobalt carbonyl would have reacted rapidly with methyl iodide and absorbed carbon monoxide, forming acetylcobalt tetracarbonyl. Likewise, cobalt hydrocarbonyl would have reacted rapidly with ethylene oxide under these conditions, absorbing carbon monoxide and forming 3-hydroxypropionylcobalt tetracarbonyl. Thus, methyl iodide cannot be reacting with cobalt hydrocarbonyl to give methylcobalt tetracarbonyl, and cobalt hydrocarbonyl must be much less nucleophilic than sodium cobalt carbonyl.

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