which drives the y-axis of the Variplotter. For most experiments (where the reactions were carried only to 50% completion), the sensitivity for the pen was set at 5 v./in., so that 50% completion would produce full scale deflection.

Figure 6 shows the circuit diagram. The mechanical arm of the multiplier was driven by $m/100$, which taps off the fraction m of both q_1 and q_2, and so generates the products mq_1 and mq_2. The outputs labeled Hg, Mono, Di, and Tri produce m, $-q_1$, $-q_2$, and $-q_3$, respectively.

Attenuators 1 to 8 were set with the indicated coefficients, using the experimental values of α, β, and r. The circuit is provided with three extra amplifiers which generate the quantity $1 - m - q_1 - q_2 - q_3$ at the output marked Z. Stoichiometry requires that this quantity be zero, so that digital readout of Z provided a check on the correctness of the analog program. A further check on internal consistency was provided by allowing the machine simulation to run until m had decreased to 0.1 v., corresponding to 99.9% of reaction. Digital readout of q_1, q_2, and q_3 allowed the computation of α and β; these values were found to correspond within 1% to those originally introduced into the program. It would have been possible to determine α and β by adjusting the appropriate attenuators until the ratios of products, determined by v.p.c., could be reproduced. However, the analytic method is preferred, as more direct; the analog method would require the successive adjustment of six potentiometers, and might be subject to electronic error.

Time Generation in Analog Simulation.—Integrating a constant voltage generates time to drive the x-axis of the Variplotter. The voltage was chosen as 100 κ volts. The value of κ was then found by adjusting the attenuator (number 9 on the diagram) until the experimental data (in dimensionless variables) were reproduced by the computer. Only this one variable was adjusted; the rather complex shapes were thus fitted with a single rate constant. The relationship between the first-order rate constant and κ may be understood by considering the case where $\alpha = \beta = 0$. Let Θ be the machine time, in seconds, and let the
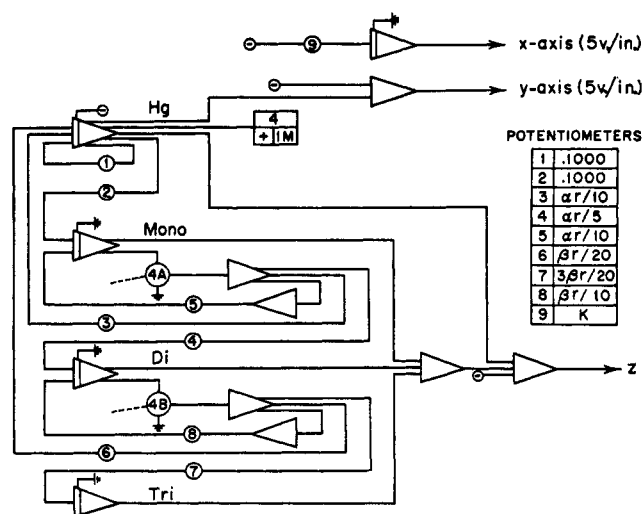

Fig. 6.—The circuit diagram for the PACE analog computer. Open triangles are summing amplifiers, barred triangles are integrators, the rectangle represents the servomultiplier, and open circles are attenuators. The numbers within the symbols are for identification purposes only.

horizontal scale on the graph paper be n min. (reaction time)/inch. Assume that the potentiometer has been adjusted so that the machine traces a curve through the experimental points. After Θ seconds, the recorder arm has traveled

$$(100\kappa \text{ v.}) \ (\Theta \text{ sec.})/(5 \text{ v. per in.}) \ = \ 20 \ \kappa\Theta \text{ in.}$$

On the y-axis, the pen plots $(1 - e^{-\Theta/10})$, the solution to the simplified differential equation, with the motion reduced by a factor of $1/10$ due to the retardation factor deliberately introduced on each integrating amplifier. The equation with $\alpha = \beta = 0$ would be $(1 - e^{-ktr})$ vs. t_r. Therefore we may identify $\Theta/10$ with kt_r. But t_r must be t_r/n inches along the horizontal axis, or $x = t_r/n$. From the above, we also have $x = 20\kappa\Theta$, and we may solve to obtain $k = 0.005/n\kappa$.


Carboxyalkylation Reactions Catalyzed by Cobalt Carbonylate Ion

BY R. F. HECK AND D. S. BRESLOW

Acylcobalt carbonyls react with alcohols to produce esters and cobalt hydrocarbonyl. The reaction is more rapid in the presence of sodium alkoxides, sodium cobalt carbonylate being produced in addition to the ester. A catalytic carboxylation of alkyl halides, sulfates, or sulfonates has been demonstrated using cobalt carbonylate ion as catalyst in the presence of a base, an alcohol (or water), and carbon monoxide. If unhindered amines are used as the base, amides are obtained. This reaction takes place under mild conditions with reactive halides, and yields are reasonable. If the reaction is carried out at 50° or below, isomerization is not observed and only the expected carboxylated derivatives are found. Thus, the reaction should be of preparative value.

Introduction

The carboxylation of olefins with carbon monoxide in the presence of water or alcohols, catalyzed by nickel or cobalt carbonyls, has been known for several years.[1] Mixtures of isomeric acids or esters are produced. More

$$RCH{=}CH_2 + CO + R'OH \longrightarrow$$

$$RCH_2CH_2COOR' + \overset{\overset{\textstyle COOR'}{\textstyle |}}{RCHCH_3}$$
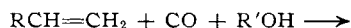
recently, Chiusoli has reported a carboxylation of allylic halides with carbon monoxide and water or alcohols under unusually mild conditions using a nickel carbonyl catalyst. The products are mixtures of 2- and 3-butenoic acids or esters.[2]

$$CH_2{=}CHCH_2X + CO + ROH \xrightarrow{Ni(CO)_4}$$
$$CH_2{=}CHCH_2COOR + CH_3CH{=}CHCOOR + HX$$
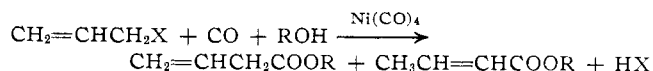
The close similarity between the hydroformylation and carboxylation reactions with a cobalt catalyst, differing only in the use of hydrogen in the former and

(1) W. Reppe and H. Kroper, *Ann.*, **582**, 38 (1953); J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publishing Corp., New York, N. Y., 1949; R. Ercoli, U. S. Patent 2,911,422 (1959); R. Ercoli, G. Signorini, and E. Santambrogio, *Chim. ind.* (Milan), **42**, 587 (1960).

(2) G. P. Chiusoli, *ibid.*, **41**, 503 (1959); *Gazz. chim. ital.*, **89**, 1332 (1959).
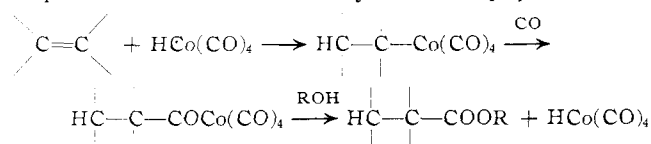
Table I

Carboxymethylation of Various Halides, Sulfates, and Sulfonates with Methanol and Carbon Monoxide at Atmospheric Pressure

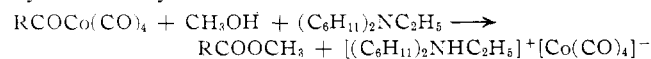| Alkylating agent	Concn., M	Base[a]	Concn. of NaCo(CO)$_4$, M	Temp., °C.	Time, hr.	Product	Yield, %
Methyl iodide	0.2	Sodium methoxide[b]	0.1	0	20	Methyl acetate	80[c]
Methyl p-toluenesulfonate	.3	DCHEA[d]	.1	50	16.5	Methyl acetate	33[c]
Diethyl sulfate	.5	DCHEA[d]	.1	50	25	Methyl propionate	20[c]
Amyl iodide	.3	DCHEA[d]	.1	50	21	Ethyl hexanoate[e]	33[c]
1-Chlorooctane	1.5	DCHEA[d]	.1	100[f]	25	Methyl nonanoate	28[g,h]
						Methyl 2-methyloctanoate	6[g,h]
1-Iodooctane	0.5	DCHEA[d]	0.1	50	20	Methyl nonanoate	56[g]
2-Iodooctane	.4	Sodium methoxide	.1	25	16	Methyl 2-methyloctanoate	41[g]
2-Iodooctane	.5	DCHEA[d]	.1	50	20	Methyl 2-methyloctanoate	9[g,i]
Allyl bromide	.1[j]	Sodium methoxide[j]	0.1-0.02	35	20	Methyl butenoate	33[c]
Benzyl bromide	.8	DCHEA[d]	0.1	50	1.1	Methyl phenylacetate	25[c,k]
α,α'-Dichloro-p-xylene	.36	DCHEA[d]	.07	50	2	Dimethyl p-phenylenediacetate	32[l]
α-Chloromethylnaphthalene	.7	DCHEA[d]	.07	50	20	Methyl α-naphthylacetate	71[m]
Methyl chloroacetate	.7	DCHEA[d]	.7	50	3	Dimethyl malonate	20[c,n]
Methyl α-bromopropionate	.5	DCHEA[d]	.5	25	25	Dimethyl methylmalonate	18[g]

[a] Base was in excess of the amount of halide used. [b] Added as a 1.0 M solution in methanol after acetylcobalt carbonyl had been formed. [c] Yield based upon the carbon monoxide absorption. Where necessary, a correction was made for the base-catalyzed reaction of carbon monoxide with methanol to form methyl formate. [d] Dicyclohexylethylamine. [e] Ethanol was used as solvent. [f] Under about 1000 p.s.i. of carbon monoxide. [g] Yield based on analysis by vapor phase chromatography. [h] 63.5% of 1-chlorooctane was unreacted. [i] 55% of 2-iodooctane was unreacted. [j] Sodium methoxide as a 1.0 M solution in methanol and allyl bromide were added during 6 hr. in 1-ml. portions as they reacted. [k] A 20% yield of N-benzylphenylacetamide, m.p. 119.5–121° and mixture m.p. with authentic material 121–123°, was obtained from the reaction mixture upon treatment with benzylamine. [l] Yield of p-phenylenediacetic acid, m.p. 238–245°, isolated by basic hydrolysis of the reaction mixture. [m] Yield of α-naphthylacetic acid, m.p. 128.5–130°, isolated by basic hydrolysis of the reaction mixture. [n] About a 20% yield of ester was isolated by distillation of the reaction mixtures; equiv. wt. found, 68.6; calcd. for dimethyl malonate, 66.1.

a hydroxylic solvent in the latter, has led to the conclusion that the mechanism previously suggested for the hydroformylation reaction[3] can be modified to give a reasonable explanation for the carboxylation reaction. Cobalt hydrocarbonyl is probably the true catalyst. It can be formed in the absence of hydrogen by a reaction between the solvent and cobalt carbonyl.[4] The hydrocarbonyl adds to the olefin to form a mixture of isomeric alkylcobalt tetracarbonyls. These then add carbon monoxide to form acylcobalt tetracarbonyls.[3] Hydrolysis or alcoholysis, finally, could give acid or ester and regenerate cobalt hydrocarbonyl. The final step of the reaction is the subject of this paper.

$$C=C \;+\; HCo(CO)_4 \longrightarrow HC-C-Co(CO)_4 \xrightarrow{CO}$$

$$HC-C-COCo(CO)_4 \xrightarrow{ROH} HC-C-COOR \;+\; HCo(CO)_4$$

Results

Acylcobalt tetracarbonyls begin to react rapidly with methanol at about 50°, giving esters and cobalt hydrocarbonyl. The hydrocarbonyl, however, decomposes rapidly under these conditions (or reacts with the acylcobalt carbonyl[3]). If the reaction is carried out in the presence of a strongly basic hindered amine, such as dicyclohexylethylamine,[5] the cobalt hydrocarbonyl is converted into a stable salt. Alternatively, sodium alkoxide yields ester and sodium cobalt carbonylate. The reaction proceeds very rapidly even at 0° with sodium methoxide. Acids, on the other hand, appear to have no effect upon the rate of alcoholysis of acylcobalt tetracarbonyls.

$$RCOCo(CO)_4 + CH_3OH + (C_6H_{11})_2NC_2H_5 \longrightarrow$$
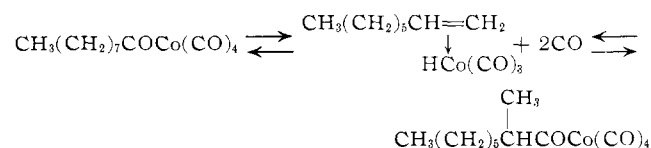$$RCOOCH_3 + [(C_6H_{11})_2NHC_2H_5]^+[Co(CO)_4]^-$$

If the acylcobalt tetracarbonyls are prepared by the reaction of alkyl halides, sulfates, or sulfonates with cobalt carbonylate ion and carbon monoxide,[3] in alcohol solution in the presence of a base, a catalytic car-

(3) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).
(4) W. Hieber and H. Schulten, *Z. anorg. allgem. Chem.*, **232**, 17 (1937).
(5) S. Hünig and M. Kiessel, *Chem. Ber.*, **91**, 380 (1958).

boxyalkylation reaction will take place. Some reactions which were carried out to prepare methyl esters are listed in Table I. Generally, yields were 10–80%,

$$RX + CO + R'OH + B \xrightarrow{Co(CO)_4^-} RCOOR' + HB^+X^-$$
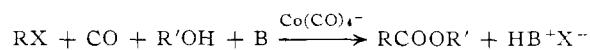
depending upon the alkylating agent. Several of the reactions were incomplete, and no attempt was made to optimize yields. Side reactions must also be important in some examples, such as elimination to form olefin and reaction of the alkylating agent with the alcohol to give ether.

If the reactions are carried out at 50° or below, only the expected ester is obtained. In three reactions where the isomeric compositions of products were determined, the 1-iodooctane, 2-iodooctane, and methyl α-bromopropionate carboxymethylations, only one isomeric product was formed, the one in which the halogen had been directly replaced by the carbomethoxyl group. Thus, at low temperatures the mixture of isomers formed by olefin carboxylation is avoided. At 100°, however, 1-chlorooctane gave about a 5:1 mixture of methyl nonanoate and methyl 2-methyloctanoate. Isomerization probably results from the previously postulated[3] dissociation of acylcobalt tetracarbonyl to an olefin–cobalt hydrotricarbonyl complex followed by readdition.

$$CH_3(CH_2)_7COCo(CO)_4 \rightleftarrows \begin{array}{c} CH_3(CH_2)_5CH=CH_2 \\ \downarrow \\ HCo(CO)_3 \end{array} + 2CO \rightleftarrows$$

$$CH_3(CH_2)_5\overset{\overset{\textstyle CH_3}{|}}{C}HCOCo(CO)_4$$

It is also conceivable that the isomeric ester arose from a reaction of octene, formed by dehydrohalogenation, with dicyclohexylethylammonium cobalt carbonylate at 100°. Although a control experiment showed that a mixture of esters ($\sim$1:1) was obtained from 1-octene and the dicyclohexylethylammonium cobalt carbonylate in methanol at 100°, the yield was much too low to account for all of the isomerization observed in the 1-chlorooctane reaction.

When the cyclic π-acrylylcobalt tricarbonyl[6] is treated with methanol and dicyclohexylethylamine or sodium methoxide under carbon monoxide, a mole of gas is absorbed and cobalt carbonylate ion and probably methyl acrylate are formed.   Similarly, π-4-pentenoyl-
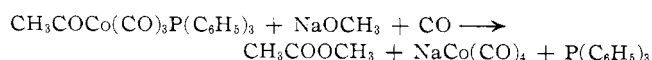

$$\text{NaCo(CO)}_4 + \text{CH}_2\text{=CHCOOCH}_3$$
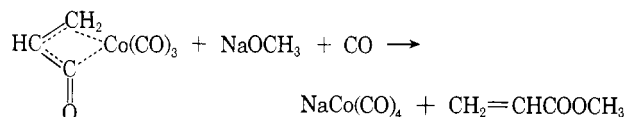
cobalt tricarbonyl[6] reacts with sodium methoxide under carbon monoxide, absorbing a mole of gas and forming sodium cobalt carbonylate and ester.   π-Allyl-

$$\text{NaCo(CO)}_4 + \text{CH}_2\text{=CHCH}_2\text{CH}_2\text{COOCH}_3$$
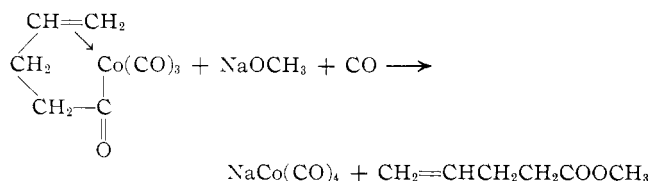
cobalt tricarbonyl[6] reacts with sodium methoxide, but an ester is not obtained. A mole of carbon monoxide is absorbed, forming sodium cobalt carbonylate and allyl methyl ether.

$$\text{NaCo(CO)}_4 + \text{CH}_2\text{=CHCH}_2\text{OCH}_3$$
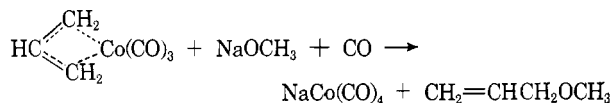
The triphenylphosphine derivatives of acylcobalt carbonyls[7] also react rapidly with sodium methoxide, giving ester and sodium cobalt tricarbonyltriphenylphosphine. In the presence of carbon monoxide, the sodium cobalt tricarbonyltriphenylphosphine forms free triphenylphosphine and sodium cobalt carbonylate. Thus, when acetylcobalt tricarbonyltriphenylphosphine is treated with sodium methoxide under carbon monoxide at 25°, a mole of gas is absorbed. The trialkyl phosphite derivatives of acylcobalt carbonyls react similarly with sodium methoxide.[8]

$$\text{CH}_3\text{COCo(CO)}_3\text{P(C}_6\text{H}_5)_3 + \text{NaOCH}_3 + \text{CO} \longrightarrow$$
$$\text{CH}_3\text{COOCH}_3 + \text{NaCo(CO)}_4 + \text{P(C}_6\text{H}_5)_3$$

Nucleophilic amines react with acylcobalt tetracarbonyls to produce amides and the corresponding ammonium salt of cobalt hydrocarbonyl. Thus, benzyl chloride reacted with carbon monoxide and aniline in tetrahydrofuran solution at 35° with a sodium cobalt carbonylate catalyst to give a 47% yield of phenylacetanilide.
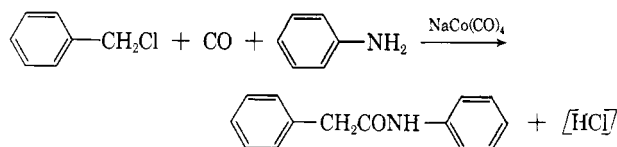
The carboxylation reaction is probably quite a general reaction among the transition metals. Disodium iron tetracarbonylate reacted with 2-iodooctane at 25° under carbon monoxide to give a 43% yield of methyl 2-methyloctanoate; none of the isomeric methyl nonanoate was detected. Since the completion of our work, Filbey has reported that acylmanganese pentacarbonyls also react with alkoxides to give esters and manganese pentacarbonyl anion.[9] Acyl-

rhenium pentacarbonyls[10] should react similarly. The mechanism of the nickel carbonyl-catalyzed carboxylation is probably similar to the cobalt carbonyl reaction with a different initial reaction.[10a]

Experimental

Sodium cobalt carbonylate was prepared from dicobalt octacarbonyl and sodium amalgam in ether solution as described by Hieber.[11] Solutions of the salt in other solvents were prepared by evaporating the ether solution under vacuum and adding the appropriate amount of the new solvent, carrying out all operations in the absence of air.

Disodium Iron Carbonylate.—A mixture of 30 g. of 1% sodium amalgam, 100 ml. of purified anhydrous tetrahydrofuran, and 0.7 ml. of iron pentacarbonyl was shaken in a capped bottle under nitrogen at room temperature for two days. The clear yellow solution was about 0.05 M in $\text{Na}_2\text{Fe(CO)}_4$. The solution is very sensitive to oxygen and must be handled in an inert atmosphere.

Carboxyalkylation Reactions.—Reactions at atmospheric pressure were carried out in a thermostated gasometric apparatus as described previously.[6] Solutions of sodium cobalt carbonylate or sodium iron carbonylate in methanol or ethanol were injected into the reaction vessel of the apparatus which had previously been flushed several times with solvent-saturated carbon monoxide at the reaction temperature. The appropriate base was then added, usually in about 10–50% excess over the amount of alkylating agent being used. The internal and atmospheric pressures were equalized and the reagent to be carboxylated was added. Gas absorption began immediately. The reactions usually became quite slow toward the end. When the gas absorption stopped, infrared spectra were taken to confirm the presence of cobalt carbonylate anion (very strong absorption at 5.3 μ) and ester carbonyl groups (absorption at 5.7–5.8 μ). When sodium methoxide was used as the base, control experiments were run in order to correct for the usually minor amount of carbon monoxide absorbed by the base-catalyzed reaction of methanol with carbon monoxide to form methyl formate. In several reactions where checks were made, the amount of gas absorbed corresponded closely to the amount of ester found by other means.

The carboxymethylation of 1-chlorooctane at 100° was carried out with rocking under 1000 p.s.i. of carbon monoxide in a stainless steel pressure vessel.

Gas chromatography was used for the analyses of some of the reaction mixtures. A 6-ft. column of Carbowax 1000 on Chromosorb W, programmed from 55 to 225° at 9° per minute, was used.

The Reaction of Dicyclohexylethylammonium Cobalt Carbonylate with 1-Octene.—To 17 ml. of 0.23 M cobalt hydrocarbonyl in pentane solution[12] at −80° was added 1.0 ml. of dicyclohexylethylamine. After mixing, the mixture was warmed to room temperature and the insoluble salt which separated as a dark oil was separated from the solution. The oil was dissolved in 13 ml. of methanol and added to 13 ml. of dicyclohexylethylamine and 10 ml. of 1-octene (two-phase mixture) in a 110-ml. pressure vessel flushed with carbon monoxide beforehand. The container was pressured to 1000 p.s.i. with carbon monoxide and heated at 100° for 25 hr. After cooling, the solution was analyzed by vapor phase chromatography. Only 0.01% of methyl 2-methyloctanoate and slightly less methyl nonanoate were found. In the corresponding carboxymethylation of 1-chlorooctane under similar conditions, about 1.52% of methyl 2-methyloctanoate and 6.97% methyl nonanoate were present.

Carboxymethylation of 2-Iodooctane with Disodium Iron Carbonylate.—In the gasometric apparatus, filled with methanol-saturated carbon monoxide at 25°, were placed 10 ml. of 0.125 M disodium iron tetracarbonyl in methanol (obtained by evaporating 25 ml. of a 0.05 M solution in tetrahydrofuran to dryness under vacuum and adding back 10 ml. of methanol) and 6.0 ml. of 1.08 M sodium methoxide in methanol. When equilibrium was reached with the gas phase, 1.0 ml. (6.2 mmoles) of 2-iodooctane was added. After reacting for about 20 hr., 108.4 ml. (2.8 mmoles) of carbon monoxide was absorbed. Analyses of the reaction mixture by gas chromatography indicated a 43% yield of methyl 2-methyloctanoate had been obtained. No methyl nonanoate was detected.

The Reaction of Acrylylcobalt Tricarbonyl with Sodium Methoxide.—Acrylylcobalt tricarbonyl was prepared as described previously[6] at 0° from 15 ml. of 0.07 M sodium cobalt carbonylate and 1.0 ml. of 1.2 M acrylyl chloride in ether. In 30 min. 27 ml. (0.9 mmole) of gas was evolved and the reaction stopped. Then, to the yellow solution, 2.0 ml. of 1.08 M sodium methoxide in methanol was added. The solution immediately turned dark red and in 30 min. the reaction stopped after 31.5 ml. (1.06

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

(7) R. F. Heck and D. S. Breslow, *ibid.*, **84**, 2499 (1962).

(8) R. F. Heck, *ibid.*, **85**, 1220 (1963).

(9) A. H. Filbey, J. C. Wollensak, and K. A. Keblys, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept. 11–16, 1960, p. 54P.

(10) W. Hieber, G. Braun, and W. Beck, *Chem. Ber.*, **93**, 901 (1960).

(10a) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 2013 (1663).

(11) W. Hieber, O. Vohler, and G. Braun. *Z. Naturforsch.*, **13b**, 192 (1958).

(12) H. W. Sternberg, I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **75**, 2717 (1953).

mmoles) of gas was absorbed. The reaction mixture now was pale yellow. The infrared spectrum showed a very strong cobalt carbonylate anion band at 5.3 μ and an ester carbonyl band at 5.7 μ.

The Reaction of 4-Pentenoylcobalt Tricarbonyl with Sodium Methoxide.—4-Pentenoylcobalt tricarbonyl was prepared at 0° from 15 ml. of 0.07 M sodium cobalt carbonylate in ether and 1.5 ml. of 1.0 M 4-pentenoyl chloride in ether as described previously.[6] In 3 hr. 28 ml. (0.92 mmole) of gas was evolved. The addition of 4.0 ml. of 1.08 M sodium methoxide in methanol at 0° resulted in the absorption of 33.4 ml. (1.1 mmoles) of carbon monoxide in 100 min. The infrared spectrum showed a very strong cobalt carbonyl anion band at 5.3 μ and an ester carbonyl at 5.7 μ.

The Reaction of Sodium Methoxide with π-Allylcobalt Tricarbonyl.—To a stirred solution of 10 ml. of methanol and 10 ml. of 1.08 M sodium methoxide in methanol in the gasometric apparatus at 25°, under carbon monoxide, was added 2.0 ml. of a freshly prepared 0.50 M solution of π-allylcobalt tricarbonyl[6] in methanol. A slow absorption of gas began and in 17 hr. the reaction had just about stopped after absorbing 52 ml. of gas. In a control experiment it was estimated that under these conditions about 22 ml. of carbon monoxide would be absorbed in the base-catalyzed reaction of carbon monoxide with methanol to form methyl formate. Thus, about 30 ml. or 1.0 mmole of carbon monoxide was absorbed by the π-allylcobalt tricarbonyl. The infrared spectrum showed only a strong cobalt carbonylate anion band at 5.3 μ. The mass spectrum of the reaction mixture revealed the presence of methyl allyl ether as the major if not the only product.

The Reaction of Acetylcobalt Tricarbonyltriphenylphosphine with Sodium Methoxide.—In the gasometric apparatus at 0° was placed 0.48 g. (1.07 mmoles) of acetylcobalt tricarbonyltriphenylphosphine. The apparatus was flushed with methanol-saturated carbon monoxide at 0° and 17 ml. of methanol was added. After the liquid and gas phases were equilibrated, 2.0 ml. of 1.01 M sodium methoxide in methanol was added. Little or no reaction occurred at 0° and so the reaction mixture was warmed to 25°. After 3.5 hr. at 25°, gas absorption stopped. After cooling back to 0°, it was found that 24.4 ml. (1.04 mmoles) of carbon monoxide had been absorbed. The infrared spectrum of the reaction mixture showed a strong cobalt carbonylate anion band at 5.3 μ and an ester carbonyl at 5.7 μ.

Formation of Phenylacetanilide from Benzyl Chloride.—In the gasometric apparatus, which had been flushed and filled with tetrahydrofuran-saturated carbon monoxide at 35°, were placed 10 ml. of 0.1 M sodium cobalt carbonylate in tetrahydrofuran solution and 1.0 ml. of freshly distilled aniline. After equilibrium with the gas phase was reached, 2.0 ml. of 1.0 M benzyl chloride in tetrahydrofuran was added. Gas was slowly absorbed. After reacting for about 20 hr., the green solution was poured onto ice and hydrochloric acid in a good hood (cobalt hydrocarbonyl was evolved). The brownish solid which separated was filtered off, washed several times with water, and air dried. Recrystallization from aqueous methanol gave 0.198 g. (0.94 mmole) of phenylacetanilide, m.p. 115–116° (reported[13] m.p. 117°).

(13) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 223.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

The Reaction of Cobalt Hydrocarbonyl with α,β-Unsaturated Aldehydes and Ketones

BY RICHARD W. GOETZ AND MILTON ORCHIN

α,β-Unsaturated aldehydes and ketones are reduced to saturated aldehydes and ketones by cobalt hydrocarbonyl at 25° and atmospheric pressure. The results can be rationalized by a mechanism involving a π-oxapropenyl tricarbonyl intermediate complex analogous to the well characterized π-allyl complexes. Unsaturated ethers are both reduced and hydroformylated.

Introduction

Heating dicobalt octacarbonyl at 110° under 1:1 hydrogen–carbon monoxide at about 200 atmospheres (oxo conditions) results in its rapid conversion to cobalt hydrocarbonyl.[1] If olefins are present in the reaction mixture, these react to produce aldehydes (hydroformylation or oxo reaction). Olefins are also rapidly converted to aldehydes at 25° by treatment with a stoichiometric quantity of cobalt hydrocarbonyl under either one atmosphere of carbon monoxide[2] or under an inert atmosphere.[3] Accordingly there is little doubt that in the oxo reaction, the cobalt transfers both hydrogen and carbon monoxide to the olefinic substrate via cobalt hydrocarbonyl, HCo(CO)₄. Our understanding of the catalytic hydroformylation reaction is thus unusual in that the active catalyst is known and can be separately prepared and studied.

When an α,β-unsaturated aldehyde or ketone is treated with a cobalt catalyst under oxo conditions, the olefinic linkage is reduced rather than hydroformylated. Previous work in this Laboratory[4] showed that pure cobalt hydrocarbonyl in hexane solution reacts with saturated aldehydes at room temperature to give the corresponding alcohol at a rate very much slower than the reaction with olefins under the same conditions. It is thus of considerable interest to study the reaction of cobalt hydrocarbonyl with molecules containing both

the olefinic and the aldehydic functions, in the conjugated relationship. The present work describes and interprets the reaction of α,β-unsaturated aldehydes and ketones with cobalt hydrocarbonyl at 25° under one atmosphere pressure.

Results

The results of the reactions between a series of α,β-unsaturated aldehydes and ketones with HCo(CO)₄ are summarized in Table I.

In the 5:1 mole ratio reactions the disappearance of hydrocarbonyl was followed by titration. The standard semilog plot of the data gave straight or very nearly straight lines. The pseudo-first-order rate constants listed in Table I were calculated from these plots.

Dicobalt octacarbonyl was isolated from each of the reactions by cooling the reaction mixture to −60°. The yield of the octacarbonyl was determined in the butenone reaction and was found to be identical with the yield of butanone. The yields of the reduction products were determined by vapor phase chromatography.

When 4-methyl-3-penten-2-one was treated in 5:1 mole ratio with hydrocarbonyl under argon, the rate constant was 0.12 l./mole min., and the yield of 4-methyl-2-pentanone was 12.5%, whereas comparable figures for the reaction under carbon monoxide were 0.032 l./mole min. and 16%, respectively. The yield of propanal from propenal under nitrogen was 75% compared to 93% under carbon monoxide.

Butyl vinyl ether, C₄H₉OCH=CH₂, and allyl ethyl ether, C₂H₅OCH₂CH=CH₂, were also treated with cobalt hydrocarbonyl under carbon monoxide at a substrate

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