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°).

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

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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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TABLE I

THE REACTION OF COBALT HYDROCARBONYL WITH α,β-UNSATURATED ALDEHYDES AND KETONES AT 25° AND 1 ATMOSPHERE OF CARBON MONOXIDE

Substrate[a]	Substrate[b] HCo(CO)$_4$	k_1, l./mole min.	Gas evolved, moles/mole of Co	Product Compound	Yield,[c] %
CH$_2$=CHCOCH$_3$	5	>1.5[d]	<0.1	CH$_3$CH$_2$COCH$_3$	36
CH$_2$=CHCOCH$_3$	0.8	...	..	CH$_3$CH$_2$COCH$_3$	70
C$_6$H$_5$CH=CHCHO	5	0.26	0.17	C$_6$H$_5$CH$_2$CH$_2$CHO	97
C$_6$H$_5$CH=CHCOCH$_3$	5	0.22	<0.1	C$_6$H$_5$CH$_2$CH$_2$COCH$_3$	57
C$_6$H$_5$CH=CHCOCH$_3$	1	...	..	C$_6$H$_5$CH$_2$CH$_2$COCH$_3$	56
CH$_3$CH=C(CH$_3$)CHO	5	0.033	0.25	CH$_3$CH$_2$CH(CH$_3$)CHO	15
(CH$_3$)$_2$C=CHCOCH$_3$	5	0.032	<0.1	(CH$_3$)$_2$CHCH$_2$COCH$_3$	16
(CH$_3$)$_2$C=CHCOCH$_3$	1	...	..	(CH$_3$)$_2$CHCH$_2$COCH$_3$	24
CH$_3$CH=CHCHO	5	0.014	0.6	CH$_3$CH$_2$CH$_2$CHO	80
CH$_2$=CHCHO	5	0.012	0.6	CH$_3$CH$_2$CHO	93

[a] Normally, 25 mmoles of substrate and variable quantities of HCo(CO)$_4$. [b] Mole ratio. [c] Based on starting HCo(CO)$_4$ and the stoichiometry: 2HCo(CO)$_4$ + substrate → product. [d] This is approximately the same rate at which terminal olefins are hydroformylated under similar conditions.

to cobalt ratio of 5, and the respective rate constants were 0.34 and 0.5 l./mole/min. Both hydroformylation and reduction of the double bond occurred with both substrates. With the vinyl ether, the yield of reduced product was 10% and of hydroformylation product was 33%. With the allyl compound the yields corresponded to 29% reduction and 71% hydroformylation. Under comparable conditions olefins give practically no reduced product, and hence the relatively large quantity of reduced product formed with the unsaturated ethers is probably due to ether–oxygen participation in the intermediate complex, and such coordination inhibits CO insertion.

Discussion

The observed results can be rationalized by the reaction scheme

$$\text{complex I} \xrightarrow[-\text{CO}]{k_3} \text{complex II} \xrightarrow[\text{HCo(CO)}_4 + \text{CO}]{k_4} \text{products} \quad (2)$$
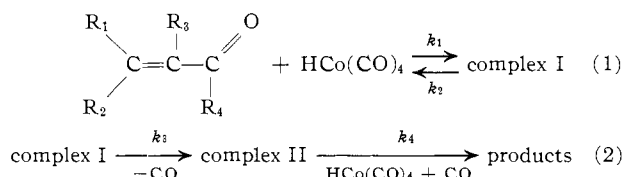
Cobalt hydrocarbonyl acts as an electron acceptor in most of its known reactions. For instance, in the hydroformylation reaction the mechanisms which have been proposed involve nucleophilic attack of the olefin on the cobalt. In the present system, complex I may likewise involve partial displacement of one of the CO's by the carbon pπ-electrons of the α,β-unsaturated carbonyl system, as
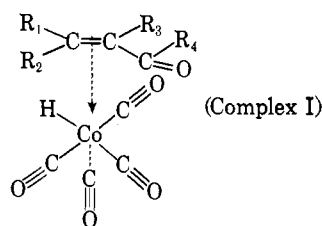
(Complex I)

The increased electron density around cobalt should increase the hydridic character of the hydrogen on cobalt. Transfer of hydrogen to the β-carbon would result in the formation of the new complex II, which
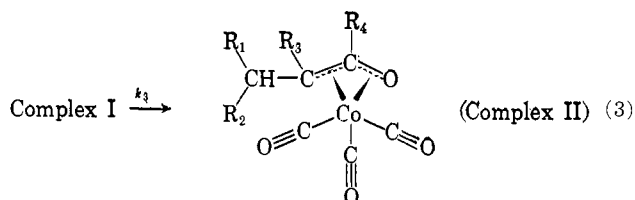
might be considered a π-oxapropenyl (or pseudo-π-allyl) complex. The driving force for the formation of complex II is the presumed stability of the π-oxapropenyl structure analogous to a π-allyl complex.

π-Allyl complexes of manganese,[5,6] iron,[7-9] cobalt,[10-14] and nickel[15] carbonyls have been prepared and have unusual stability. The π-1-methallyl- and π-1,3-dimethylallylcobalt tricarbonyls have been prepared by the reaction of cobalt hydrocarbonyl with butadiene and 1,3-pentadiene, respectively. Since the bonding in these complexes involves considerable electron drain from the allylic group, electron-releasing substituent in this group should increase the stability in the absence of strong steric interactions. The electron-release properties of alkyl substituents would thus explain the observed differences in rates and yields in the reduction of the variety α,β-unsaturated carbonyl compounds studied. A comparison of the butenone and 2-butenal reactions which follows is illustrative.

The π-oxapropenyl complex formed by 2-butenal has only an ethyl substituent (eq. 3, R$_1$ = CH$_3$, R$_2$ = R$_3$ = R$_4$ = H) on the oxapropenyl group. The complex from butenone with two methyl substituents (R$_1$ = R$_2$ = R$_3$ = H, R$_4$ = CH$_3$) would be expected therefore to be more stable than the corresponding complex from 2-butenal. Such increased stability would be expected to have two effects: (1) increased driving force to form the complex and thereby consume hydrocarbonyl and (2) decreased rate of the cleavage reaction (eq. 2) thereby reducing the yield of product. The increased rate of reaction under an inert atmosphere is also consistent with this reaction sequence. In the absence of a carbon monoxide atmosphere the competition for nucleophilic ligand sites on the cobalt favors the rates of formation of both complexes I and II.

The cleavage of complex II by hydrocarbonyl would probably proceed by proton addition to the oxygen atom giving the enol form of the carbonyl product, and dicobalt heptacarbonyl. The heptacarbonyl would

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then absorb carbon monoxide from the solution to account for the observed octacarbonyl.

Experimental

Reduction of 2-Butenal.—A 0.30 M hexane solution of HCo(CO)$_4$ was prepared by disproportionation of Co$_2$(CO)$_8$ with N,N-dimethylformamide followed by acidification with HCl.[2] The resultant solution was washed with water and dried with anhydrous Na$_2$SO$_4$. A 20-ml. portion of the dry solution (6.0 mmoles of HCo(CO)$_4$) was injected into a 50-ml. round-bottom flask connected to a gas buret. The flask had a serum stoppered side arm and a magnetic stirring bar, and the whole system was under one atmosphere of carbon monoxide. The solution was stirred rapidly and 2.5 ml. (30 mmoles) of 2-butenal was injected. The disappearance of HCo(CO)$_4$ was followed by titration of 0.5-ml. samples withdrawn periodically.[4] When all the HCo(CO)$_4$ had been consumed, 12 ml. of a 0.5 M ether solution of triphenylphosphine was injected to convert all the cobalt to insoluble complexes. The resultant slurry was centrifuged and the supernatant solution was analyzed by vapor phase chromatography after standardization with the pure compounds expected as products. The analysis showed a yield of 2.4 mmoles of butanal and only a trace, if any, of butanol.

All of the reactions reported above were run in a similar manner.

Some benzene was used as a solvent in the two reactions involving aromatic compounds (Table I).

Reaction of Allyl Ethyl Ether.—A 0.31 M octane solution of HCo(CO)$_4$ was prepared as described above and dried with anhydrous Na$_2$SO$_4$. A 27-ml. portion of the dry solution (8.4 mmoles of HCo(CO)$_4$) was injected into a 50-ml. round-bottom flask connected to a gas buret. The flask had a serum stoppered side arm and a magnetic stirring bar, and the whole system was under one atmosphere of carbon monoxide. The solution was stirred rapidly and 4.6 ml. (42 mmoles) of allyl ethyl ether was injected. After 6 min. all the hydrocarbonyl had been consumed and 0.6 mmole of gas had been absorbed. The cobalt compounds were removed as solids by adding 8.4 mmoles of triphenylphosphine and centrifuging. The supernatant solution was analyzed by vapor phase chromatography after standardization with pure ethyl propyl ether. This analysis showed a yield of 1.2 mmoles of ethyl propyl ether. Titration of the solution for aldehydes[16] indicated a yield of 2.5 mmoles of hydroformylation product.

The butyl vinyl ether reaction was performed in an analogous manner.

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Structural Studies by Nuclear Magnetic Resonance. II. Aldehyde 2,4-Dinitrophenylhydrazones

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The reaction of aliphatic aldehydes with 2,4-dinitrophenylhydrazine leads to *syn*-2,4-dinitrophenylhydrazones (DNP's). Prolonged standing of DNP solutions or the addition of acid effects *syn–anti* equilibrations; in all cases the *syn* isomer is thermodynamically favored over the *anti*. Several reported forms of acetaldehyde DNP which differ in melting point are all the *syn* isomer. Solvents capable of hydrogen bonding with N–H of the DNP increase the *syn–anti* ratio. Two N–H proton resonances appear in pyridine, dimethyl sulfoxide, and dimethylformamide solutions. The proton chemical shift and coupling constant data obtained on several aldehyde DNP's are discussed.

We have previously reported n.m.r. studies on the problem of structural isomerism in 2,4-dinitrophenylhydrazones (DNP's) and semicarbazones of various ketones.[2] α-Hydrogens *cis*[3] to the anisotropic group resonate at higher magnetic fields (shielded) than the corresponding *trans*-hydrogens; β- and γ-hydrogens *cis* to the anisotropic group resonate at lower magnetic fields (deshielded) than the corresponding *trans*-hydrogens. From the findings we determined the proportions of *syn* and *anti* isomers of these compounds in solution.

Extension of such studies to aldehyde DNP's appeared attractive for several reasons: (1) In aliphatic ketone DNP's the presence of only one set of aromatic proton resonances suggested that the various alkyl groups exert similar anisotropy effects on these aromatic protons. In this respect, comparison of alkyl groups with hydrogen seemed worthwhile. (2) Examination of molecular models indicated that the erstwhile aldehydic hydrogen *cis* to the aromatic ring should be deshielded relative to such a hydrogen occupying the *trans* position. (3) In solutions of acetaldehyde oxime the *anti* isomer is thermodynamically favored over the *syn*.[4] We anticipated reversal of the thermodynamic

stability of the corresponding isomers of acetaldehyde DNP because of the large size of the 2,4-dinitrophenyl group. (4) Previous investigators have reported several forms of acetaldehyde DNP.[5,6] Ingold and co-workers[6] isolated two forms melting at 146° and 162°; Bryant[5] isolated three forms, m.p.'s 168.5°, 156–157°, and 149°. The latter investigator suggested that the 168.5° and 157° forms represented the stable and unstable isomers, respectively, and that the 149° form was a mixture of the two. Van Duin[7] isolated two isomers, m.p.'s 167–168°, and 93–94°, to which he assigned *syn* and *anti* structures, respectively. On the basis of previous findings[2] we expected to be able to assign structures (*syn–anti*) to the various forms from n.m.r. studies.

The present study includes comments on the above points as well as discussions of new results, in particular those concerning long-range spin–spin couplings.

Results and Discussion

The proton n.m.r. spectra of several aldehyde DNP's (as dilute solutions in chloroform, methylene chloride, methylene bromide, acetone, dimethyl sulfoxide, dimethylformamide, pyridine, dioxane, tetramethylurea, and nitrobenzene) were examined at 60 Mc. For convenience we have adopted the numbering system shown in I.

syn–anti **Isomerism.**—Table I summarizes the pertinent data on the isomeric compositions of several

(1) Mellon Institute, Pittsburgh, Pa.

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(3) To make unequivocal the terminology used in this paper, note the following: The isomeric *forms* of the DNP of RCHO are denoted as (i) *syn* (in which H and the dinitroanilino group are on the same side of the C–N double bond) and (ii) *anti* (in which the groups are on opposite sides). The erstwhile aldehydic hydrogen in the *syn*-form is referred to as a *cis*-hydrogen (*i.e.*, *cis* to the dinitroanilino group), whereas the corresponding hydrogen of the *anti* isomer is referred to as a *trans*-hydrogen, etc.

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