duction periods and the elimination of such induction periods by addition of IO_3^-.

The conclusion that only approximately one-half of the $Co(NH_3)_5I^{++}$ disappears by direct reaction with H_2O_2 and that the balance reacts with HOI or some other intermediate oxidation state of iodine may explain the variation of R with (Cl^-) shown in Fig. 2. If a single intermediate reacts with Cl^-, then R must be linear in (Cl^-); but if intermediates of different reactivity and leading only to the same products are present, the form of the variation of R with (Cl^-) will be qualitatively at least like that shown in Fig. 2.

The absence of Co(II) in all the reactions described contrasts with the formation of Co(II) in the reactions of $Co(NH_3)_5I^{++}$ [2] and $Co(NH_3)_5C_2O_4^+$ [16] with "one-electron" oxidizing agents, but conforms to the results obtained in the reaction of $Co(NH_3)_5C_2O_4^+$ with "two-electron" oxidizing agents.[16] The absence of Co-(II) further shows that I and OH are not formed in the O_3, H_2O_2, and $S_2O_8^{-2}$ systems since these radicals have

(16) P. Saffir and H. Taube, J. Am. Chem. Soc., **82**, 13 (1960).

been shown to react rapidly with $Co(NH_3)_5I^{++}$ to yield Co(II).[2]

The most novel aspect of the present investigation is the extraordinary efficiency for the transfer of halide ions to the coordination sphere of Co(III), in particular for the reactions of $Co(NH_3)_5I^{++}$ and $Co(NH_3)_5Br^{++}$ with Cl_2. These reactions do not appear to have a precedent in the organic systems where apparently the nonfree-radical chlorination of organic iodides proceeds by a nucleophilic displacement of a complex $> ClCl_2$ by Cl_2.[17]

(17) R. M. Keefer and L. J. Andrews, *ibid.*, **75**, 543 (1953); **76**, 253 (1954); E. J. Corey and W. J. Wechter, *ibid.*, **76**, 6040 (1954); F. M. Beringer and H. S. Schultz, *ibid.*, **77**, 5533 (1955).

Alkyl- and Acylcobalt Carbonyls Containing Olefinic Unsaturation. II. Cyclization of 5-Hexenoylcobalt Tetracarbonyl and Nonterminal Olefin Complexes

BY R. F. HECK

Alkenoylcobalt tetracarbonyls, $RCH=CH(CH_2)_nCOCo(CO)_4$, decompose thermally into a variety of products depending upon the value of n and upon the *trans*-substituent R. When $n = 0$ or 2 and R = H or CH_3, relatively stable cyclic π-alkenoylcobalt tricarbonyls are formed. When $n = 1$ and R = H or CH_3, decomposition leads mainly to π-allylcobalt tricarbonyl derivatives. If $n = 3$ and R = H or CH_3, mixtures of saturated and unsaturated cyclic ketones are formed along with cobalt hydrocarbonyl or octacarbonyl. Unsaturated alkoxyacylcobalt tetracarbonyls behave similarly. Mechanisms are proposed to explain these and two related reactions from the literature.

Introduction

The interactions of transition metal compounds with olefins are of considerable interest because these interactions are responsible for many catalytic reactions such as hydroformylation, catalytic hydrogenation, and the Ziegler olefin polymerization. In this and the previous paper of this series,[1] the reactions of olefins with acylcobalt tetracarbonyls have been investigated by determining structures and thermal decomposition products of a series of alkenoylcobalt tetracarbonyl complexes. These complexes undergo various reactions depending upon the structure of the unsaturated acyl group.

Experimental

5-Hexenoyl Chloride.—3-Butenyl *p*-toluenesulfonate was prepared at $-20°$ by adding 90 g. of *p*-toluenesulfonyl chloride slowly to a solution of 28 g. of 3-butene-1-ol in 200 ml. of pyridine. After the addition, the solution was kept at 0° for 30 min. and then diluted with ice and cold water. The product was extracted with several portions of ether. The extracts were then washed with water, cold dilute hydrochloric acid, and finally with aqueous sodium bicarbonate. After being dried, the solvent was evaporated at room temperature under vacuum and the product was recrystallized twice from ether–pentane at $-80°$. The entire product, m.p. 7.5–9.5° and $n^{20}D$ 1.5150, was then rinsed with a little dry methanol into a solution of 53 g. of dimethyl malonate in 400 ml. of dry methanol in which 9.7 g. of sodium had been previously dissolved. The reaction mixture was refluxed for about 4 hr. About half of the methanol was removed by distillation. Water was added to the residue and the product was extracted with ether and distilled, b.p. 76–87° (5.5 mm.). There was thus obtained 13.5 g. of dimethyl 3-butenylmalonate. About 10 g. of higher boiling material, b.p. 160–180° (5.5 mm.), was also obtained; it was probably the dibutenyl derivative. The monobutenyl ester was hydrolyzed by adding it to a solution of 30 g. of

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

potassium hydroxide in 30 ml. of water and 30 ml. of methanol. After 1 hr. at room temperature, the solution was acidified with cold, concentrated hydrochloric acid, diluted with water, and extracted several times with ether. Evaporation of the ether and recrystallization from benzene gave 8.2 g. of 3-butenylmalonic acid, m.p. 90–91°. *Anal.* Calcd. for $C_7H_{10}O_4$: C, 53.14; H, 6.37. Found: C, 53.18; H, 6.66.

5-Hexenoic acid was obtained by distilling the malonic acid at 130° at 20 mm. Redistillation gave 5.4 g. of pure acid, b.p. 108.5–109° (21 mm.).

The 5-hexenoyl chloride was prepared by refluxing the 5-hexenoic acid with 10 ml. of thionyl chloride for 1 hr. and distilling. There was obtained 4.85 g. of colorless liquid, b.p. 53–54° (21.5 mm.).

5-Hexenoylcobalt Tricarbonyl Triphenylphosphine.—In a gasometric apparatus[1] at 0°, which had been filled and flushed with ether–saturated carbon monoxide, were placed 30 ml. of of 0.07 M sodium cobalt carbonyl in ether solution and 3.0 ml. of 1.0 M 5-hexenoyl chloride in ether. After 2 hr. at 0° there was no change in the gas volume but the infrared spectrum of the solution showed that all of the sodium cobalt carbonyl had reacted. (The characteristic 5.3 μ band of cobalt carbonyl anion had disappeared.) The addition of 3.5 ml. of 1.0 M triphenylphosphine in ether resulted in the evolution of 1.54 mmoles of carbon monoxide. Evaporation of the solution below room temperature and several recrystallizations of the product from ether–pentane at $-80°$ gave yellow-brown prisms of the phosphine complex, m.p. 90.5–93° dec. *Anal.* Calcd. for $C_{27}H_{24}O_4PCo$: C, 64.54; H, 4.82. Found: C, 64.70; H, 4.96. The infrared spectrum of the complex had bands in carbon tetrachloride at 3.23 (w), 3.40 (w), 4.88 (s), 5.08 (vs), 5.96 (vs), 6.78 (m), 6.99 (s), 7.15 (w), 7.69 (w), 8.43 (w), 9.12 (s), 9.33 (w), 9.52 (w), 9.72 (m), 10.00 (m), 10.08 (m), 10.90 (m), 11.34 (w) and in carbon disulfide at 13.40 (m), 14.14 (m), and 14.42 (s) μ.

Cyclization of 5-Hexenoylcobalt Tetracarbonyl.—5-Hexenoylcobalt tetracarbonyl was prepared at 0° as described in the preceding experiment except that 1.0 ml. of dicyclohexylethylamine was added. The reaction mixture was then warmed to 25°. About 34 ml. of gas was evolved over a period of several hours. The infrared spectrum of the solution showed the bands of cobalt carbonyl and a new carbonyl band at 5.73 μ. The bands of the

starting compound had disappeared. The reaction mixture was then added to 10 ml. of 2,4-dinitrophenylphenylhydrazine sulfate in ethanol solution[2] and the orange product which separated was removed by centrifuging and recrystallized several times from chloroform–ethanol. A red crystalline compound, m.p. 213–215°, was isolated. The melting point was undepressed when the compound was mixed with authentic 2-methyl-2-cyclopentenone 2,4-dinitrophenylhydrazone (m.p. 220–221.5°). *Anal.* Calcd. for $C_{12}H_{12}O_4N_4$: C, 52.17; H, 4.38. Found: C, 52.09; H, 4.56. From the mother liquors, an orange compound was isolated melting at about 164°. *Anal.* Calcd. for $C_{12}H_{14}O_4N_4$: C, 51.79; H, 5.07. Found: C, 52.16; H, 5.11. This product was not pure, but it appears to be the derivative of a saturated, cyclic, six-carbon ketone.

Analyses by vapor phase chromatography indicated about a 54% yield 'of 2-methylcyclopentanone was produced along with 16% 2-methylcyclopentenone and 8% cyclohexenone. No cyclohexanone or 2-methylenecyclopentanone was observed.

The reaction takes the same course with or without dicyclohexylethylamine present.

6-Heptenoyl Chloride.—5-Hexen-1-ol was prepared by the hydroboration of biallyl as described by Brown and Zweifel.[3] Treatment of 8.0 g. of this alcohol with 10 ml. of thionyl chloride at reflux for 1 hr. gave 6.3 g. of 5-hexenyl chloride, b.p. 129–130°. The chloride was then heated to 100–130° for 1 hr. with a solution of 6.5 g. of potassium cyanide in 50 ml. of dimethylformamide. After cooling, the reaction mixture was diluted with water and the product extracted with ether and distilled. The crude nitrile obtained, 6.7 g., b.p. 45–80° (30 mm.), was refluxed for 3 hr. with 5.0 g. of sodium hydroxide in 40 ml. of methanol and 10 ml. of water. About half of the solvent was distilled off and the residue was diluted with water and extracted with ether. The aqueous solution, on acidification, gave the free acid. The product was extracted with ether and distilled, b.p. 120° (30 mm.). There was obtained 1.2 g. The acid chloride was prepared by refluxing the acid with 5 ml. of thionyl chloride for 30 min. Vacuum distillation gave about 1.0 g. of the acid chloride, b.p. 68–70° (20 mm.). The infrared spectrum of the product had a double bond absorption at 6.1 μ and a carbonyl absorption at 5.5 μ as expected.

6-Heptenoylcobalt tricarbonyl triphenylphosphine was prepared exactly as described for the 5-hexenoyl compound above. The triphenylphosphine caused the evolution of 1.96 mmoles of CO. The product, after several recrystallizations from ether–pentane, formed large yellow-brown needles, m.p. 34°. *Anal.* Calcd. for $C_{28}H_{26}O_4PCo$: C, 65.12; H, 5.08. Found: C, 65.44; H, 5.60.

Decomposition of 6-Heptenoylcobalt Tetracarbonyl.—A solution of 6-heptenoylcobalt tetracarbonyl in ether was prepared as described for 5-hexenoylcobalt tetracarbonyl. On standing at 25°, the solution slowly evolved gas. After several days, the infrared spectrum showed cobalt carbonyl was being formed along with new carbonyl compounds with bands at 5.77 and 5.88 μ and probably a π-allylcobalt tricarbonyl derivative [(bands at 4.82 (s) and 5.00 (vs) μ]. To complete the reaction, the mixture was heated to 80° for 30 min. in a capped, nitrogen-filled bottle. Gas chromatography indicated the presence of about a 10–15% yield of 2-methylcyclohexanone. No cycloheptanone or 2-ethylcyclopentanone was detected in the reaction mixture.

10-Undecenoylcobalt Tetracarbonyl.—10-Undecenoylcobalt tetracarbonyl was readily obtained from the acid chloride and sodium cobalt carbonyl in ether at 0°. The compound remained practically unchanged in ether solution at 25° during 24 hr. with very little gas being evolved.

trans-**4-Hexenoyl chloride**, b.p. 55° (23 mm.), was prepared by the reaction of the acid[4] with thionyl chloride.

trans-**4-Hexenoylcobalt Tricarbonyl Triphenylphosphine.**—In a gasometric apparatus[1] filled with ether-saturated CO were placed 60 ml. of 0.07 M sodium cobalt carbonyl and 5.0 ml. of 1.0 M *trans*-4-hexenoyl chloride in ether. The solution turned red-brown and evolved gas. In 100 min. 2.06 mmoles of gas was evolved and the reaction stopped. Addition of 6.0 ml. of 1.0 M triphenylphosphine in ether resulted in the evolution of 2.23 mmoles of carbon monoxide in 2 hr. and the reaction stopped. Evaporation and recrystallization from tetrahydrofuran–pentane gave shiny tan plates, m.p. 98–99° dec. *Anal.* Calcd. for $C_{27}H_{24}O_4Co$: C, 64.54; H, 4.82. Found: C, 64.56; H, 4.97. The infrared spectrum of the compound had bands in carbon tetrachloride at 3.29 (w), 3.41 (w), 4.90 (m), 5.10 (vs), 5.98 (s), 6.78 (w), 7.00 (m), 7.18 (w), 7.53 (w), 7.70 (w), 8.45 (w), 9.15 (m), 9.35 (w), 9.72 (w), 10.00 (w), 10.34 (w), 10.89 (w), 11.48 (w) and in carbon disulfide at 13.40 (s), 14.15 (s), and 14.45 (vs) μ.

Decomposition of *trans*-4-Hexenoylcobalt Tetracarbonyl.—At 25° in a gasometric apparatus[1] which had been flushed with ether-

saturated CO were placed 30 ml. of 0.07 M sodium cobalt carbonyl in ether, 1.0 ml. of dicyclohexylethylamine, and 3.0 ml. of 1.0 M 4-hexenoyl chloride in ether. In 4 hr., about 2.0 mmoles of gas was evolved and the reaction stopped. (Gas evolution measurements are not reliable in our apparatus when the solvent has a high vapor pressure.) The infrared spectrum of the solution showed only two strong carbonyl bands, at 4.85 (s) and 5.04 (vs) μ, indicating a π-allylcobalt tricarbonyl complex was present. A weak band which occurred at 5.94 μ could have been from a small amount of cyclic unsaturated ketone. Addition of 3.5 ml. of 1.0 M triphenylphosphine in ether resulted in the evolution of about 1 mmole of gas and the formation of a new compound which was isolated by evaporating the solvent and recrystallizing it from ether–pentane solution. The orange-red crystalline product, m.p. 111–114° dec., had analyses close to the expected values for ethyl- or dimethyl-π-allylcobalt dicarbonyl triphenylphosphine. *Anal.* Calcd. for $C_{25}H_{24}O_2PCo$: C, 67.27; H, 5.42. Found: C, 67.76; H, 5.76.

trans-**5-Heptenoyl Chloride.**—4-Hexenoic acid,[4] 32.2 g., was reduced with 11 g. of lithium aluminum hydride in 600 ml. of ether. There was obtained 25.8 g. of 4-hexen-1-ol, b.p. 81.5–82.5° (36 mm.). The alcohol was converted into the p-toluenesulfonate by treating it with 55 g. of p-toluenesulfonyl chloride in about 200 ml. of pyridine at −40°. After standing 1 hr. at 0°, the sulfonate was isolated by adding ice and water and extracting with ether. The extracts were washed with cold dilute hydrochloric acid, then with water and dried. The solvent was evaporated under vacuum and the crude toluenesulfonate was refluxed for 4 hr. with 35 g. of potassium cyanide and 250 ml. of dry methanol with stirring. Most of the alcohol was distilled off and water was added to the residue. The nitrile was extracted with several portions of ether. The ether was evaporated and the crude nitrile was refluxed for 5 hr. with 30 g. of potassium hydroxide in 75 ml. of water and 75 ml. of alcohol. Then ice and water were added. A small amount of oil was removed by extraction with methylene chloride. Acidification of the aqueous solution with concentrated hydrochloric acid liberated the 5-heptenoic acid. The product was extracted with several portions of methylene chloride. The extracts were washed with water, dried, and distilled. There was obtained 11.2 g. of the acid, b.p. 121–122° (19 mm.). *Anal.* Calcd. for $C_7H_{12}O_2$: C, 65.58; H, 9.44. Found: C, 65.38; H, 9.54.

The acid chloride, b.p. 65–66° (17 mm.), was obtained by treating the acid with excess thionyl chloride in the usual way.

5-Heptenoylcobalt Tetracarbonyl and its Decomposition.—5-Heptenoylcobalt tetracarbonyl was prepared by the usual method from 30 ml. of 0.07 M sodium cobalt carbonyl and 2.5 ml. of 1.0 M 5-heptenoyl chloride in ether at 0°. After 2 hr. there was no gas evolution but the infrared spectrum showed the typical bands of an acylcobalt tetracarbonyl. At 25°, gas evolution began. In 24 hr., 144 ml. of gas was evolved. The infrared spectrum showed the presence of ketones, 5.72 μ band, and probably a π-allylcobalt tricarbonyl derivative. Vapor phase chromatography of the reaction mixture indicated the presence of 2-methylcyclohexanone and other unknown compounds.

In another similar experiment carried out at 25° in the presence of 1.0 ml. of dicyclohexylethylamine, similar results were obtained. Cobalt carbonyl anion was formed instead of the octacarbonyl, however, and the major product was clearly a π-allylcobalt complex (infrared bands at 4.83 (m) and 5.01 (vs) μ). The reaction mixture was added to 10 ml. of 2,4-dinitrophenylhydrazine reagent.[2] After standing several hours, the red derivative was separated and recrystallized several times from chloroform-methanol to give shiny red crystals of m.p. 190–192° which gave the correct analysis for a cyclic, 7-carbon, unsaturated ketone derivative. *Anal.* Calcd. for $C_{13}H_{14}O_4N_4$: C, 53.80; H, 4.86. Found: C, 53.81; H, 4.85.

In a third experiment similar to the preceding one, an attempt was made to isolate the triphenylphosphine derivative of the π-allylcobalt carbonyl derivative, but the orange oil obtained could not be crystallized. About 40–45% of one mole of CO evolved in the triphenylphosphine reaction.

The Addition of Cobalt Hydrocarbonyl to Divinyl Ether.—At 0° in a gasometric apparatus[1] which had been flushed with ether-saturated CO were placed 30 ml. of divinyl ether and 4.0 ml. of 0.41 M cobalt hydrocarbonyl in pentane. In 1 hr., about 5.2 ml. of gas was absorbed and the reaction was complete. The addition of 2.0 ml. of 1.0 M triphenylphosphine in ether caused the evolution of 19 ml. of gas in 3 hr. The volatile material was removed under vacuum and the product was recrystallized several times from ether–pentane or tetrahydrofuran–pentane solution. Yellow crystals of m.p. 103° dec. were obtained. *Anal.* Calcd. for $C_{25}H_{22}O_4PCo$: C, 63.04; H, 4.67. Found: C, 62.94; H, 4.78. The complex had infrared bands in carbon tetrachloride solution at 3.25 (w), 4.92 (m), 5.07 (s), 5.98 (m), 6.76 (w), 6.99 (w), 7.91 (w), 8.55 (w), 9.13 (w), 9.70 (w), 10.43 (w), 11.73 (w) and in carbon disulfide at 13.40 (m), 14.20 (m), and 14.38 (m) μ.

(2) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(3) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 5832 (1959)

(4) E. N. Eccott and R. P. Linstead, *J. Chem. Soc.*, 2163 (1929).

Allyloxyacetyl Chloride.—Allyloxyacetic acid,[5] b.p. 85–86° (4 mm.), was treated with excess thionyl chloride at reflux temperature for 1 hr. and distilled to give the acid chloride, b.p. 140–145°.

Allyloxyacetylcobalt Tetracarbonyl and its Decomposition.—At 0°, allyloxyacetyl chloride reacts with sodium cobalt carbonyl in ether solution without gas evolution, producing allyloxyacetylcobalt tetracarbonyl, judging by the infrared spectrum of the reaction mixture. Addition of excess triphenylphosphine resulted in the evolution of 76% of one mole of CO. The phosphine derivative, however, could not be crystallized.

At 25°, in the presence of dicyclohexylethylamine, allyloxyacetylcobalt tetracarbonyl decomposed spontaneously, evolving CO. After 24 hr., the reaction was over. The infrared spectrum had a ketone band at 5.82 μ. The cobalt apparently was converted mainly into the ether-insoluble dicyclohexylethylammonium cobalt tetracarbonyl. The ultraviolet spectrum of the reaction mixture in methanol solution had λ_{max} 265 mμ with ϵ 6100.

Results and Discussion

The unsaturated acylcobalt tetracarbonyls decompose thermally in dilute ether solution into several isolable, or at least detectable, products: π-allylcobalt tricarbonyl derivatives, cyclic, coordinated π-alkenoylcobalt tricarbonyls, and cyclic saturated and unsaturated ketones. Further heating of the second product mentioned usually leads to one or more of the other products also. In addition, decomposition to dienes by the usual decomposition route of saturated acylcobalt tetracarbonyls[6] must also take place here, but these products were not investigated. A summary of the products obtained from the various alkenoylcobalt tetracarbonyls studied in this and in the previous paper is given in Table I.

The results can be explained as shown in the equations
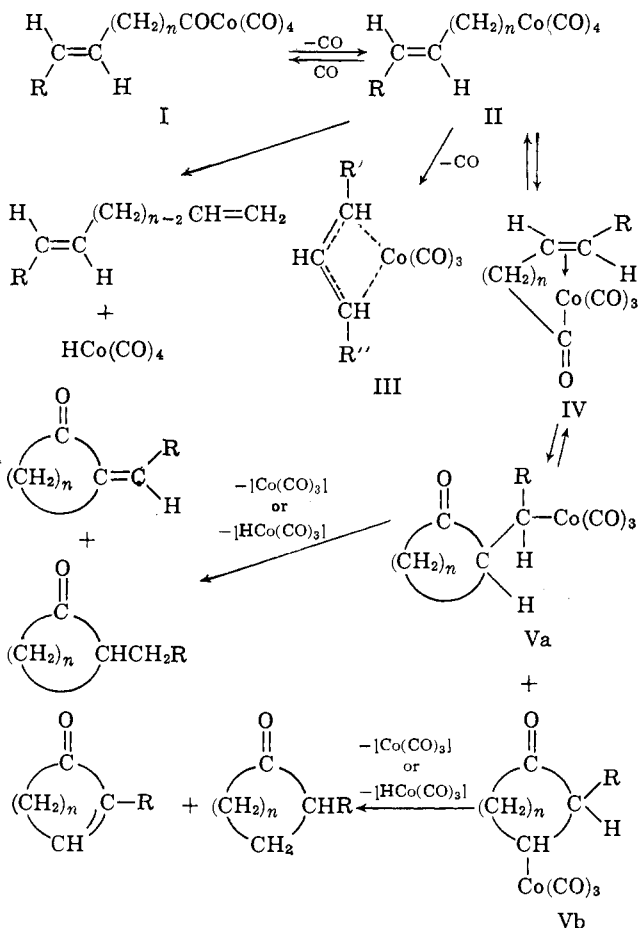
(5) Q. F. Soper, C. W. Whitehead, O. K. Behrens, J. J. Corse, and R. G. Jones, J. Am. Chem. Soc., **70**, 2849 (1948).

(6) R. F. Heck and D. S. Breslow, ibid., **83**, 4023 (1961).

TABLE I

DECOMPOSITION PRODUCTS OF VARIOUS ALKENOYLCOBALT TETRACARBONYLS

R	n	Reacn. temp. (ether soln.), °C.	π-Allyl-cobalt tricarbonyl deriv.	π-Alkenoyl-cobalt tricarbonyl	Cyclic ketones
H	0[a]	0	...	~100	..
H	1[a]	0	~100	...	..
H	2[a]	0	...	~100	..
H	2[a]	25	~100	...	..
H	3	25	...	...	75
H	4	25	Major	...	>10
CH₃	0[b]	0	...	44[c]	..
CH₃	1[a]	0	~100	...	..
CH₃	2	0	...	48[c]	..
CH₃	2	25	Major	...	Some?
CH₃	3	25	~40	...	60[d]

[a] Ref. 1. [b] R. F. Heck, J. Am. Chem. Soc., **85**, 651 (1963). [c] In equilibrium with alkenoylcobalt tetracarbonyl under one atmosphere of carbon monoxide. [d] Value obtained by difference, not determined directly.

Loss of carbon monoxide from the alkenoylcobalt tetracarbonyl I leads to an alkenylcobalt tetracarbonyl, II, which then can undergo any of three further reactions. The usual mode of decomposition of alkylcobalt tetracarbonyls is to form olefin and cobalt hydrocarbonyl.[6] This reaction must be happening in the alkenoylcobalt carbonyl decompositions also, but to a minor extent when n is less than 4.

The second reaction that II may undergo is the formation of π-allylcobalt tricarbonyl derivatives III. In compounds where $n = 1$ a direct cyclization would lead to the π-allyl derivative, while if n is larger than 1 rearrangement must occur first. Such rearrangements are well known in cobalt carbonyl reactions.[6] Presumably only the cobalt carbonyl group moves down the chain to form the π-allyl complex but proof is lacking.

The third reaction of II leads to the reversible formation of a cyclic, π-alkenoylcobalt tricarbonyl, IV. Complex IV may be stable enough to be observed or even to be isolated as a triphenylphosphine complex as when $R = H$ and $n = 0^1$ or 2^1 or it may react further, soon after it is formed, to produce mixtures of saturated and unsaturated cyclic ketones as happens when $R = H$ and $n = 3$ or 4 or when $R = CH_3$ and $n = 3$. Presumably the latter reaction proceeds by way of cyclic alkylcobalt tricarbonyl compounds Va and b. The intermediates Va and b might have been expected to absorb carbon monoxide and form comparatively stable acylcobalt tetracarbonyl complexes. The γ-keto-alkylcobalt carbonyl complexes rapidly lose cobalt carbonyl and do not form acyl derivatives, however. This is shown by the fact that the alkylcobalt tetracarbonyls formed by the addition of cobalt hydrocarbonyl to acrolein,[7] crotonaldehyde,[7] or to glycidaldehyde,[8] which should lead to at least some of the γ-keto isomers, do not form stable acyl compounds but instead rapidly form reduction products and cobalt carbonyl, exclusively.

Complex IV is apparently important only when $n = 0, 2, 3$ and to a lesser extent when $n = 4$. A trans-methyl substituent on the double bond has a significant effect upon the relative stability of IV compared with II or I. Thus, under the same conditions (0° under one atmosphere of carbon monoxide in dilute ether solution), complexes with $R = H$ and $n = 0$ or 2 exist essentially entirely as IV, whereas if $R = CH_3$ with

(7) R. W. Goetz and M. Orchin, J. Org. Chem., **27**, 3698 (1962).

(8) R. F. Heck, J. Am. Chem. Soc., **85**, 1460 (1963).

$n = 0$ or 2 the compounds exist as equilibrium mixtures of IV and I containing roughly equal amounts of each. Triphenylphosphine reacts differently with the *trans*-methyl complexes (R = CH$_3$, $n = 0$ and 2), giving open chain alkenoylcobalt tricarbonyl triphenylphosphine derivatives, whereas the corresponding compounds without the methyl group (R = H and $n = 0$ and 2) give cyclic π-alkenylcobalt dicarbonyl triphenylphosphine complexes.[1]

The formation of cyclic ketones from alkenoylcobalt carbonyls is of considerable theoretical interest because it appears to be a clear example of the addition of a carbon–transition metal group across a double bond. The cyclic ketone formation proceeds best when $n = 3$ or 4 and five- and six-membered rings are formed. Thus, 5-hexenoylcobalt tetracarbonyl (R = H and $n = 2$) decomposes in ether solution at 25° over a period of several hours to give a 75% yield of cyclic ketones. Vapor phase chromatography indicated the mixture contained 2-methylcyclopentanone (54%), 2-methyl-2-cyclopentenone (16%), and cyclohexenone (8%). No cyclohexanone or 2-methylenecyclopentanone was detected. Presumably the 2-methylenecyclopentanone initially formed was isomerized under the reaction conditions to 2-methyl-2-cyclopentenone. The remaining 25% of the product was not identified, but if the amount of hydrogen is to be the same in the products as in the starting compound, it is likely that the missing material is derived from unsaturated ketones. Since cobalt octacarbonyl was formed in this reaction even in the presence of the strong but very hindered base, dicyclohexylethylamine, which forms a stable salt with cobalt hydrocarbonyl, the hydrocarbonyl (or hydrotricarbonyl) probably was not an intermediate in the reaction. Similarly, 6-heptenoyl-cobalt tetracarbonyl (R = H, $n = 3$) decomposes at 25° but more slowly, giving a mixture of ketones and a π-allylcobalt tricarbonyl complex, probably 1-propyl-π-allylcobalt tricarbonyl. Vapor phase chromatography indicated that 10–15% of the product was 2-methylcyclohexanone. There was little or no cycloheptanone or 2-ethylcyclopentanone present. Unsaturated ketones were probably also present but they were not identified. The *trans*-methyl group in *trans*-5-heptenoylcobalt tetracarbonyl has a significant effect upon the cyclization reaction: less than about 60% of the product was cyclic ketones (2-methylcyclohexanone was identified by gas chromatography), and the remainder of the product was a π-allylcobalt tricarbonyl complex, probably 1-methyl-3-ethyl-π-allylcobalt tricarbonyl. When carried out in the presence of dicyclohexylethylamine, the *trans*-5-heptenoylcobalt tetracarbonyl reaction gives cobalt carbonyl anion as one of the products, suggesting that a cobalt hydrocarbonyl may be an initial product in this reaction. It is not clear why this reaction gave cobalt carbonyl anion in the presence of the amine while the 5-hexenoylcobalt tetracarbonyl gave cobalt octacarbonyl under similar conditions.

When $n = 0$ and R = H or CH$_3$ in formula IV, pyrolysis leads to polymer formation. If $n = 2$, structure IV is relatively stable but pyrolysis leads mainly if not completely to π-allylcobalt tricarbonyls rather than to cyclic ketones. Presumably there is a steric problem when $n = 2$ such that the π-complex IV can easily form but the olefin group cannot readily attain a position where it can react with the acylcobalt group. If n is greater than 4, the compounds exist mainly as the alkenoylcobalt tetracarbonyls I. They are more stable than when n is smaller and they probably decompose mainly to olefins (dienes) and cobalt hydrocarbonyl. π-Undecenoylcobalt tetracarbonyl

in ether solution, for example, remained essentially unchanged for 24 hr. at 25° under one atmosphere of carbon monoxide.

The coordination and cyclization of unsaturated acylcobalt tetracarbonyls is not limited to all carbon chains. Two unsaturated alkoxyacylcobalt carbonyl derivatives have been investigated and they behave similarly.

Cobalt hydrocarbonyl reacts with a large excess of divinyl ether at 0° under CO, producing an acylcobalt carbonyl derivative and probably a considerable amount of the usual oxo-type products judging from the amount of carbon monoxide absorbed during the reaction. Addition of triphenylphosphine resulted in gas evolution and the formation of a yellow crystalline derivative, m.p. 108° dec. The analyses and the infrared spectrum of the complex indicated it was probably a cyclic, coordinated π-vinyloxyacylcobalt derivative, most probably the cyclic, coordinated π-2-vinyloxy-propionylcobalt dicarbonyl triphenylphosphine, although the 3-vinyloxy isomer is also a possibility.

CH$_2$=CHOCH=CH$_2$
+ $\xrightarrow{}$ $\xrightarrow{P(C_6H_5)_3}$
HCo(CO)$_4$
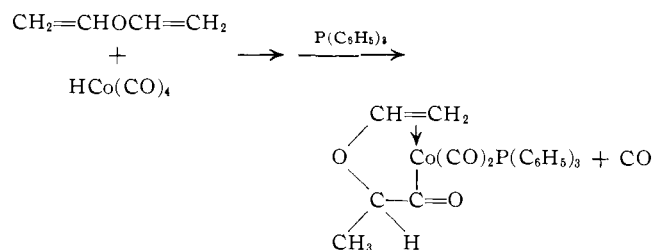
Allyloxyacetylcobalt tetracarbonyl was the second alkoxyacyl compound prepared. The complex was prepared from allyloxyacetyl chloride and sodium cobalt carbonyl in ether at 0°. The tetracarbonyl, in the presence of dicyclohexylethylamine, slowly evolved gas, forming cobalt carbonyl anion and a new carbonyl complex with absorption at 5.82 μ. The ultraviolet spectrum of the reaction mixture in methanol solution had λ_{max} 265 mμ with ϵ 6100. The spectral properties suggest that the product is 2-methyl-3-hydroxyfuran, or, more probably, its tautomeric keto form, since Eugster[9] showed that 2,5-dimethyl-3-hydroxyfuran absorbed at 260 mμ with ϵ 12,200. If the reaction product has the same absorption intensity as the above compound, then the yield of cyclic product was about 50%. No attempt was made to isolate the product.

$$CH_2=CHCH_2OCH_2COCo(CO)_4 \rightarrow \text{[ring]} + [HCo(CO)_4]$$
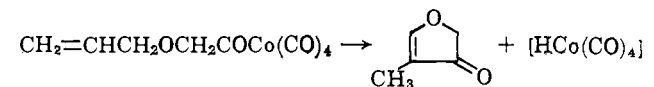
While this work was in progress, a patent appeared which is very closely related to the cyclization reaction. Klemchuk has reported that nonconjugated dienes react with carbon monoxide, water, and cobalt octacarbonyl in acetone solution at 100–200° and at 1000–5000 p.s.i. to give mixtures of saturated and unsaturated cyclic ketones.[10] Biallyl, for example, gave a 35% yield of 2,5-dimethylcyclopentanone and 6% 2,4-dimethylcyclopenten-3-one. There seems little doubt but that this reaction involves the addition of cobalt hydrocarbonyl (from cobalt carbonyl and water)[11] and CO to the diene to produce a mixture of unsaturated acylcobalt carbonyls[6] followed by cyclization as observed in this work.

Perhaps the most important result of this investigation is the conclusion that the acylcobalt group can be added across a carbon–carbon double bond. This

(9) C. H. Eugster, R. E. Rosenkranz, K. Allner, and A. Hofmann, *Angew. Chem.*, **73**, 737 (1961).

(10) P. P. Klemchuk, U. S. Patent 2,995,607 (August 8, 1961).

(11) W. Hieber and H. Schulten, *Z. anorg. allgem. Chem.*, **232**, 17 (1937).

kind of reaction is most probably involved in other organometallic reactions also, such as the formation of diethyl ketone from ethylene and CO with a cobalt catalyst and a hydrogen donor at 350° as reported by Staib, Guyer, and Slotterbeck.[12]

[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH 13, PA.]

Phosphorus- and Arsenic-Bridged Complexes of Metal Carbonyls. I. Cyclopentadienyliron Complexes[1]

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The reactions of $[C_5H_5Fe(CO)_2]_2$ with tetrasubstituted biphosphines and biarsines, R_4M_2 ($M = P$, As; $R = CH_3$, C_6H_5) and of $Na[C_5H_5Fe(CO)_2]$ with R_2MCl have been found to give $[C_5H_5Fe(MR_2)(CO)]_2$ and $[(C_5H_5)_2-Fe_2H(PR_2)(CO)_2]$. The infrared and nuclear magnetic resonance spectra of the compounds have been used to show that they contain bridging MR_2 groups. $[C_5H_5Fe(MR_2)(CO)]_2$ has been isolated in both cis and trans isomeric forms.

In recent years there has been considerable interest in the reactions of organosulfur compounds with metal carbonyls and, as a result, a number of sulfur-bridged, usually binuclear complexes (for example I[2a] and II[2b]), have been prepared containing most of the elements of the first transition series. Comparatively little attention, however, has been given to the study of related complexes containing phosphorus or arsenic as the

I   II
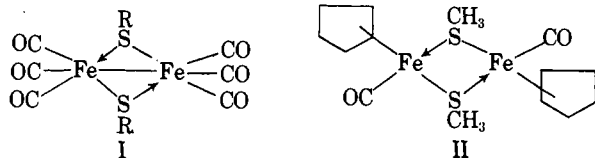
bridging atom, although, in general, tertiary phosphine complexes of the metal carbonyls are more stable than those of the substituted sulfides. This neglect may be due to the fact that only recently have good synthetic methods been developed for some of the key methylphosphine intermediates, although the corresponding arsine compounds have been known for some time.

Recent studies have shown the four-membered Pd_2P_2 ring in some complexes of Pd(II) to be a stable molecular unit.[3] Unfortunately, the method of preparation (reaction of secondary phosphines with palladium halides, in the presence of a base) does not appear to be one which can be readily applied to a wide range of transition elements. In a search for alternative synthetic methods, we are investigating the reactions of (a) metal carbonyls and their cyclopentadienyl derivatives with tetrasubstituted biphosphines and biarsines (R_4M_2; $M = P$, As; $R = CH_3$, C_6H_5) and (b) reactions of the alkali metal salts of suitable metal carbonyl compounds with chlorophosphines and -arsines (R_2MCl). It was anticipated that in reactions of type a the M–M bond of the ligand would be cleaved to give R_2M radicals, which can act as three-electron bridging groups in linking two metal atoms. In much the same way, I and II are obtained by reaction between R_2S_2 and iron pentacarbonyl and $[C_5H_5Fe(CO)_2]_2$, respectively. In b, elimination of sodium chloride, followed by ring closure with loss of carbon monoxide, could also lead to bridged complexes.

In reactions of type a, we have found that, in general, the ease of cleavage of the R_2M–MR_2 or RS–SR ligands increases (P < As < S) in the order of decreasing strength of the M–M or S–S bond. The tetrasubstituted biphosphines are thus the most difficult to cleave, although cleavage appears to occur more readily when the metal carbonyl compound contains a metal–metal bond (as in $[C_5H_5Fe(CO)_2]_2$ or $Co_2(CO)_8$) and when $P_2(C_6H_5)_4$ rather than $P_2(CH_3)_4$ is used. The latter effect may be due to the greater electronegativity of the phenyl group.

Experimental

Analyses and Apparatus.—Microanalyses and molecular weight determinations were by Schwarzkopf Laboratories, Woodside, N. Y.; Huffmann Microanalytical Laboratories, Wheatridge, Colo.; and Dr. A. Bernhardt, Max-Planck Institut für Kohlenforschung, Mülheim, Germany. Melting points were determined in evacuated capillaries and are uncorrected.

Infrared spectra were measured on a Beckman IR 9 spectrophotometer and the nuclear magnetic resonance spectra on Varian Associates A-60 and HR-60 spectrometers. Unless otherwise stated, the n.m.r. spectra were determined using saturated carbon disulfide solutions and tetramethylsilane as an internal standard. All the compounds described in this paper gave sharp n.m.r. spectra and are thus presumed to be diamagnetic. Resonances due to cyclopentadienyl protons were observed in the range $\tau = 5.6$–6.2, methyl protons in the range $\tau = 8.0$–8.8, and phenyl protons $\tau = 2.5$–2.9.

Starting Materials and Experimental Conditions.—All reactions and the handling of phosphines and arsines were carried out under nitrogen. The pure crystalline complexes were usually stable to air, but solutions decomposed more or less rapidly on exposure to air. Chromatographic separations were carried out on Merck acid-washed alumina.

Dimethylchlorophosphine was prepared by a modification of Parshall's method,[4] in which diphenylchlorophosphine was substituted for phenyldichlorophosphine in the reaction with tetramethylbiphosphine disulfide. The yields were in the range 51–67%. In some preparations, the distillate (b.p. 70–115°) from the reaction mixture separated into two layers. After removal of the lower layer, the upper layer was almost pure $(CH_3)_2PCl$, b.p. 74–74.5°. Tetramethylbiphosphine[5] and tetraphenylbiphosphine[6] were synthesized by published methods, $(C_6H_5)_4P_2$ being prepared as needed from $(C_6H_5)_2PH$ and $(C_6H_5)_2PCl$ in toluene or n-heptane solution. Dimethylchloroarsine[7] and tetramethylbiarsine[8] were also prepared by well-established methods.

Cyclopentadienyliron dicarbonyl dimer was prepared from iron pentacarbonyl.[9] Sodium cyclopentadienyliron dicarbonyl[10] was

(1) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., March 31–April 5, 1963.

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