Where the geometry is not accurately known, standard bond lengths and angles were used.

IIIa   Bond lengths and angles of II

IIIb–e   Bond lengths of II, C=C—C = 120°

V r_{12} = 1.337 Å.

     r_{18} = 1.501 Å.[55]

     r_{23} = 2.375 Å. (measured from Dreiding models)

VI r_{23} = 1.337 Å.   C=C—C = 120°

     r_{17} = 1.501 Å.   C—C—C = 109°28′

VII   Average measured Dreiding model distances were used. The coordinates were calculated from various groups of measured distances until consistency between calculated and measured values was achieved

IX   Bond lengths of II, C=C—C = 120°

Appendix II

Numerical Data.—Selected numerical data for the calculated spectra are given in Tables VII and VIII.[56] Molecular orbitals were obtained by diagonalizing ma-

(55) D. R. Lide, Jr., *Tetrahedron*, **17**, 125 (1962).

(56) These data for I have been published previously (ref. 1). For the other compounds treated in this paper the nuclear coordinates, atomic and molecular integrals, configuration energies, and configuration interaction elements are available from the authors.

trices of the form

$$
\begin{pmatrix}
0 & -\beta_{12} & -\beta_{13}\dots\dots\dots -\beta_{1N} \\
-\beta_{21} & 0 & -\beta_{23}\dots\dots\dots -\beta_{2N} \\
-\beta_{31} & -\beta_{32} & 0\dots\dots\dots\dots -\beta_{3N} \\
\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\
\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \\
-\beta_{N1} & -\beta_{N2} & -\beta_{N3}\dots\dots\dots 0
\end{pmatrix}
$$

where β is the corresponding number in $\mathbf{H}_{core}$. For butadiene (II), α was calculated from eq. 18 with the Coulomb penetration integrals $(q:pp)$ evaluated according to Parr and Crawford[57] and $(r:pp)$ neglected; eq. 19 was used for the other compounds. The spectroscopic value of 11.080 e.v.[58] was used for the one-center two-electron Coulomb repulsion integral γ_{11}, and −11.22 e.v. for the ionization potential W_c.

(57) R. G. Parr and B. L. Crawford, Jr., *J. Chem. Phys.*, **16**, 1049 (1948). These integrals are evaluated using hydrogenic orbitals. Slater orbitals would be more consistent since they are used for the other integrals calculated, but the differences are small. Later calculations of the N → V₁ energy for *cis*- and *trans*-II, neglecting penetration integrals, including $(q:pp)$ for Slater orbitals with $(r:pp)$ zero, and including both $(q:pp)$ and $(r:pp)$, gave results constant to within 3 mμ for both isomers.

(58) H. A. Skinner and H. O. Pritchard, *Trans. Faraday Soc.*, **49**, 1254 (1953).

The Addition of Acylcobalt Carbonyls to Acetylenes.
π-(2,4)-(Alkeno-4-lactonyl)cobalt Tricarbonyl Derivatives and Their Conversion to 2,4-Pentadieno-4-lactones

BY RICHARD F. HECK

Acylcobalt tetracarbonyls react with substituted acetylenes to form π-(2,4)-(alkeno-4-lactonyl)cobalt tricarbonyl derivatives. These complexes react with triphenylphosphine, with evolution of carbon monoxide, to form mono(triphenylphosphine) derivatives. The acetylcobalt tetracarbonyl–3-hexyne–triphenylphosphine complex was isolated and characterized. Reactions of the π-lactonyl complexes were investigated. The most significant finding was a new method of synthesizing 2,4-pentadieno-4-lactones by the reaction of π-lactonyl complexes with dicyclohexylethylamine.

Introduction

Alkyl- and acylcobalt carbonyls react readily with many compounds having unshared electron pairs. Phosphines[1,2] and phosphites[3] form acylcobalt tricarbonyl monophosphines or monophosphites. The alkyl- and acylcobalt carbonyls can react with olefins to form ketones[4] and with conjugated dienes to form 1-acylmethyl-π-allylcobalt tricarbonyls.[5] The present paper is concerned with the reaction of acetylenes with acylcobalt carbonyls.

Many reactions of acetylenes with transition metal carbonyls and their derivatives are known, but there ap-

pear to be only a few examples of the reaction of alkyl- (or acyl)-metal carbonyls with acetylenes. Coffield reported that methylmanganese pentacarbonyl reacted with acetylene at 150° under pressure to produce π-dihydropentalenylmanganese tricarbonyl.[6] The fate of the methyl group was not determined. Zeiss has investigated the reactions of various aryl- and alkylchromium compounds and other transition metal alkyls with acetylenes and found that aromatic trimers are formed, sometimes accompanied by products containing two acetylene units and an alkyl[7] or aryl group from the metal.[8] Diethylnickel and diphenylacetylene yielded tetraphenylcyclohexadiene as well as hexa-

(1) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **84**, 2499 (1962).

(2) R. F. Heck, *ibid.*, **85**, 651 (1963).

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

(4) R. F. Heck, *ibid.*, **85**, 3116 (1963).

(5) R. F. Heck, *ibid.*, **85**, 3381 (1963).

(6) T. H. Coffield, K. G. Ihrman and W. Burns, *ibid.*, **82**, 1251 (1960).

(7) M. Tsutsui and H. Zeiss, *ibid.*, **81**, 6090 (1959).

(8) W. Herwig, W. Metlesics, and H. Zeiss, *ibid.*, **81**, 6203 (1959).

phenylbenzene.[7] Trimethylchromium and diphenylacetylene gave tetraphenylcyclopentadiene and hexaphenylbenzene.[7] Triphenylchromium with diphenylacetylene gave 1,2,3,4-tetraphenylnaphthalene in addition to hexaphenylbenzene.[8] More recently Nakamura has investigated the reactions of several cyclopentadienyl(alkyl)iron and molybdenum carbonyls with acetylenes. The acetylenes were converted into both trimers and cyclopentadiene derivatives, where the fifth carbon atom of the cyclopentadiene ring arose from the original alkyl group.[9]

Numerous examples of the reaction of acetylenes with metal carbonyls and with cyclopentadienylmetal carbonyls not containing metal alkyl groups have been reported.[10] These reactions generally yield unsaturated cyclic carbonyl compounds, often with the ring π-complexed with the metal. Little is known about the mechanism of formation of these products.

The acylcobalt carbonyls react with acetylenes to produce unique complexes. The reactions are probably closely related to the other acetylene–metal alkyl reactions mentioned above.

Results

Solutions of acylcobalt tetracarbonyls reacted readily at 0° with acetylenes, producing orange to red solutions. The yields of particular products and their stabilities depended upon the particular acetylene used.

Acetylcobalt tetracarbonyl reacted with excess 3-hexyne at 0° in ether solution with the evolution of about 0.15 mole of carbon monoxide per mole of cobalt present. The infrared spectrum of the red-orange reaction mixture had a new carbonyl band at 5.70 μ in addition to several coordinated carbonyl bands at 4.85–5.00 μ. The 5.8 μ band of acetylcobalt tetracarbonyl completely disappeared. Chromatography of the reaction mixture gave 3-hexynedicobalt hexacarbonyl[11] and other fractions, with carbonyl bands at 5.7 μ, but other new bands were also present in the latter fractions indicating that decomposition was occurring on the chromatography column. Isolation of the unstable compound as the triphenylphosphine derivative proved more convenient than trying to isolate the compound itself. The addition of excess triphenylphosphine to the crude reaction mixture of 3-hexyne with acetylcobalt tetracarbonyl at 0° resulted in the evolution of 0.74 mmole of carbon monoxide per mmole of cobalt present. Under these conditions, the 3-hexynedicobalt hexacarbonyl does not react appreciably with triphenylphosphine.[12] From the solution, orange-red needles of the pure complex were isolated. Analyses, infrared spectra,[13] and the gas evolution data indicate that the complex is probably the π-allylcobalt carbonyl derivative II for which an appropriate name for which would be 2,3-diethyl-π-(2,4)-(penteno-4-lactonyl)cobalt dicarbonyl triphenylphosphine. Infrared spectra indicate the lactone derivative I is the major initial product and that 3-hexynedicobalt hexacarbonyl is the only other significant carbonyl product produced in the reaction.
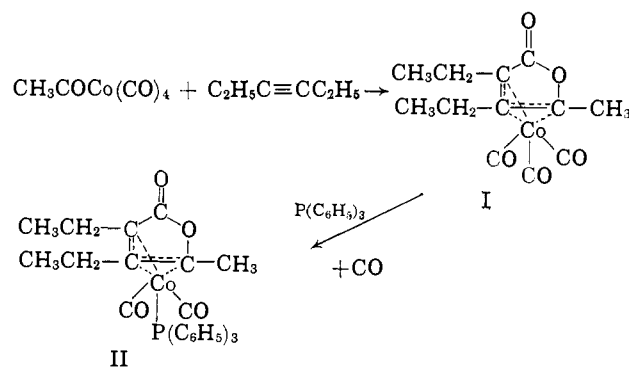
(9) A. Nakamura, Mem. Inst. Sci. Ind. Res. Osaka Univ., 19, 81 (1962); Chem. Abstr., 59, 8786 (1963).

(10) M. A. Bennett, Chem. Rev., 62, 611 (1962).

(11) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. H. Wotiz, R. Markby, and I. Wender, J. Am. Chem. Soc., 76, 1457 (1954); 78, 120 (1956).

(12) R. F. Heck, ibid., 85, 657 (1963).

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

The amount of gas evolved in the reaction of the acetylcobalt tetracarbonyl–3-hexyne products with triphenylphosphine suggests that 74% of the product is the lactonyl complex I and about 26% is the 3-hexynedicobalt hexacarbonyl complex.

The rate of gas evolution for the reaction of triphenylphosphine with I was measured as described previously.[2] The reaction was first order with respect to the cobalt complex and zero order with respect to the triphenylphosphine. The first-order rate constant at 0° was 6.22 ± 0.25 × 10^{-4} sec.$^{-1}$. This compares with a rate of 3.28 ± 0.14 × 10^{-4} sec.$^{-1}$ at 0° for the first-order reaction of π-allylcobalt tricarbonyl with triphenylphosphine.[14]

Infrared spectra and other data indicate that the same two types of products, π-lactonyl derivatives and acetylenedicobalt hexacarbonyls, are obtained in the reaction of other acetylenes with various acylcobalt tetracarbonyls, although relative yields vary and these two products may not always be the only ones formed. Linear addition products seem to be important products from acetylene itself and monosubstituted acetylenes. A number of reactions of the π-lactonyl complexes have been studied and the results of these experiments leave little doubt about the structure of the complexes.

Previous work has shown that carbon–cobalt bonds are readily hydrogenated[15,16] and the present complexes are no exception. For example, the acetylcobalt tetracarbonyl–acetylene reaction mixture, on hydrogenation at 3,000 p.s.i. of hydrogen in the presence of dicyclohexylethylamine (to absorb any cobalt hydrocarbonyl formed[16]) at 35°, yielded about 75% of the theoretical amount of γ-valerolactone based upon the cobalt present. It is possible in this example that the product arises, at least partly, from complexes other than the π-lactonyl derivative, since the 5.6 μ lactone carbonyl band is relatively weak in the acetylcobalt carbonyl–acetylene reaction mixture. Similarly, the 3-hexyne–acetylcobalt tetracarbonyl complex gave a cobalt-free product on hydrogenation which had infrared absorption at 5.68 μ, suggesting that a γ-butyrolactone derivative had been formed.

Iodine is well known to cleave carbon–cobalt bonds and, as expected, the π-lactonyl complexes reacted rapidly with the reagent. The 3-hexyne–benzoylcobalt tetracarbonyl complex, on treatment with excess iodine, led to gas evolution and to the formation of a new iodine-free compound which was isolated as color-

(14) R. F. Heck, ibid., 85, 655 (1963).

(15) D. S. Breslow and R. F. Heck, Chem. Ind. (London), 467 (1960).

(16) R. F. Heck and D. S. Breslow, "Actes du Deuxieme Congres International de Catalyse," Vol. I, Editions Technip, Paris, 1960, p. 671.
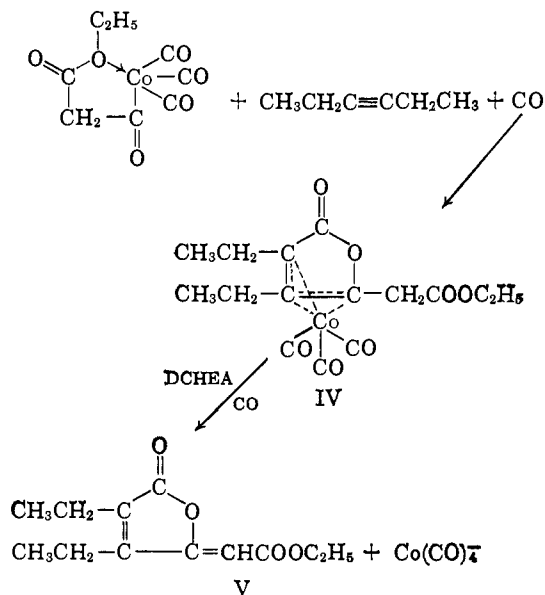
less crystals, m.p. 182.5–184°. The infrared spectrum of the product still had the lactone carbonyl band at 5.65 μ. Analyses and the n.m.r. spectrum indicated the product is probably an unsymmetrical dimer of the organic portion of the complex, probably III. This result is not difficult to explain since allyl halides are known to react with π-allylcobalt carbonyl to give

III
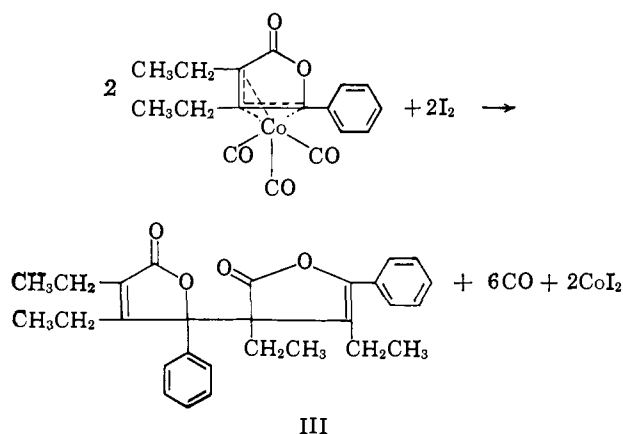
biallyl,[17] and an intermediate in this reaction should be a very reactive allylic iodide.

The π-lactonyl complexes generally react with sodium methoxide and absorb a mole of carbon monoxide, forming sodium cobalt carbonylate and elimination products, or possibly methoxy derivatives of the unsaturated lactones. None of these products has yet been isolated. Of more interest is the reaction of certain activated π-lactonyl complexes with hindered amines. It was observed previously that the hydrogen atom on a carbon atom between a π-allylcobalt carbon and an acyl group was quite acidic and easily removed by bases. The anion formed then underwent elimination of a cobalt carbonyl anion and an acylidene was formed.[18] A similar reaction was found with appropriately substituted π-lactonylcobalt carbonyls.

Carboethoxyacetylcobalt tricarbonyl[11] reacts at 0° with 3-hexyne in the presence of carbon monoxide, forming the expected lactone complex IV, as shown by

IV

V

(17) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 1097 (1961).
(18) R. F. Heck, *ibid.*, **85**, 3383 (1963).

the infrared spectrum of the reaction mixture and the amount of carbon monoxide absorbed. The addition of dicyclohexylethylamine to this solution results in the further absorption of carbon monoxide. The infrared spectrum of the reaction mixture after the gas absorption stopped clearly showed that cobalt carbonylate ion was formed, along with a carbonyl compound, with absorption at 5.59 μ and at 5.84 μ. From the reaction mixture a volatile, low melting compound was isolated which had a strong ultraviolet absorption band at 574 mμ (ε 28,500). The n.m.r. spectrum and carbon–hydrogen analyses confirmed that the compound was 2,3-diethyl-5-carboethoxy-2,4-pentadieno-4-lactone (V).
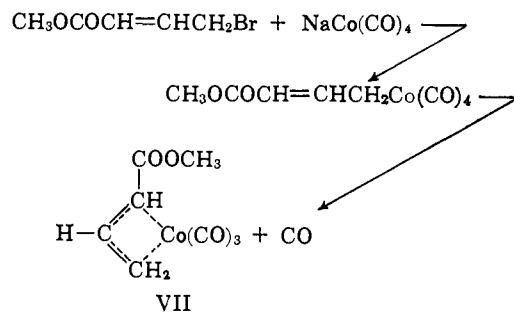
This reaction, of course, can be made catalytic if the acylcobalt tetracarbonyl is prepared from an alkyl or acyl halide and cobalt carbonylate ion in the presence of CO. Under the latter conditions, ethyl bromoacetate reacted with 3-hexyne to give a 51% yield of the lactone based upon the amount of carbon monoxide absorbed. The actual yield is probably higher, because a small amount of carbon monoxide is evolved from the side reaction, forming 3-hexynedicobalt hexacarbonyl.

Chloroacetonitrile reacts with 3-hexyne, cobalt carbonylate ion, carbon monoxide, and dicyclohexylethylamine in an analogous manner, giving a 62% yield of 2,3-diethyl-5-cyano-2,4-pentadieno-4-lactone based upon the quantity of carbon monoxide absorbed during the reaction. This product was isolated as a nearly colorless crystalline compound, m.p. 87–88°, λmax 278 mμ (ε 22,700). Using *t*-butylacetylene in place of 3-hexyne led to the formation of the analogous mono-*t*-butyl derivative in about 50% yield based upon the gas absorbed. The product melted at 92.8–94.2° and had λmax 281 mμ (ε 28,900). The position of the *t*-butyl group, 2 or 3, has not been determined.

Methyl 4-bromo-2-butenoate will react with cobalt carbonylate ion, carbon monoxide, dicyclohexylethylamine, and 3-hexyne to produce about a 30% yield of the interesting conjugated triene, 2,3-diethyl-7-carbomethoxy-2,4,6-heptatrieno-4-lactone (VI), m.p. 85.8–86.4°, λmax 318 mμ (ε 37,500). A side reaction in this

$$BrCH_2CH=CHCOOCH_3 + CH_3CH_2C\equiv CCH_2CH_3 + CO$$

VI
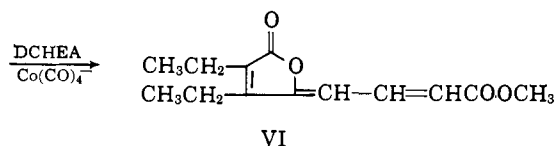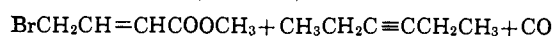
example, however, is the formation of 1-carbomethoxy-π-allylcobalt tricarbonyl (VII). Apparently, once the π-allyl complex is formed it does not re-form the σ-bonded allylcobalt complex.

$$CH_3OCOCH=CHCH_2Br + NaCo(CO)_4 \longrightarrow$$

$$CH_3OCOCH=CHCH_2Co(CO)_4 \longrightarrow$$

VII

The *p*-nitrophenyl group is also an effective activator for the 5-hydrogen atom in the π-lactonyl complexes.

p-Nitrobenzyl bromide reacts with cobalt carbonylate ion, carbon monoxide, dicyclohexylethylamine, and 3-hexyne to produce 2,3-diethyl-5-p-nitrophenyl-2,4-pentadieno-4-lactone, which was isolated in about 6% yield. The product is a yellow-brown crystalline solid, m.p. 135–136°, λ_{max} 347 (ϵ 31,800).

These examples show that the acetylene–acylcobalt tetracarbonyl reaction and the base-catalyzed elimination reaction of the acetylene–acylcobalt carbonyl complexes are general reactions. Probably hydrogen-activating substituents are not required for the latter reaction to occur, but, without activation, very strong bases are required and side reactions are a problem. A variety of acetylenes have been used in these reactions. Generally the disubstituted acetylenes give the highest yields of the lactone products; monosubstituted acetylenes and acetylene itself usually give less. The *monosubstituted acetylenes and acetylene itself*, as well as certain disubstituted acetylenes such as dimethylacetylene dicarboxylate, in this reaction, produce significant amounts of amorphous products which may be low molecular weight acetylene–carbon monoxide polymers. There are also indications that other complexes may be present in some of the reaction mixtures, but these products have not been investigated. Much remains to be done in this area. Nevertheless, enough is known so that some of these reactions can find practical use in the synthesis of various unsaturated organic compounds.
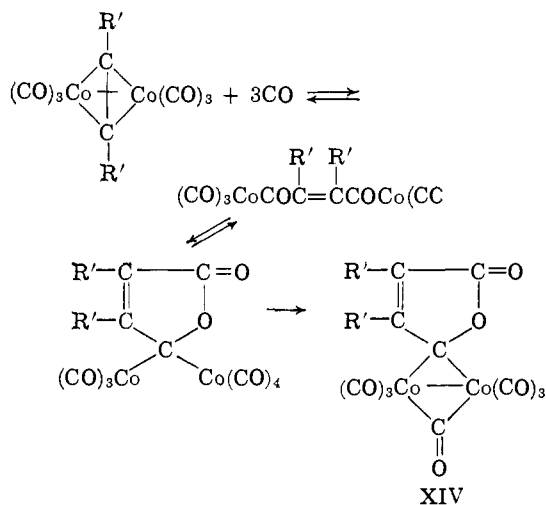
The mechanism of formation of the π-lactonylcobalt complexes is worth discussing, particularly in view of our previous work on the addition of phosphines,[1,2] olefins,[4] and conjugated dienes[5] to acylcobalt carbonyls. The acetylene reaction is probably an insertion reaction similar to the olefin and conjugated diene additions. The effect of carbon monoxide upon the acetylene addition reaction has not been determined, but in view of the previous work[2,15,16] it is reasonable to expect it will inhibit the reaction because the first step
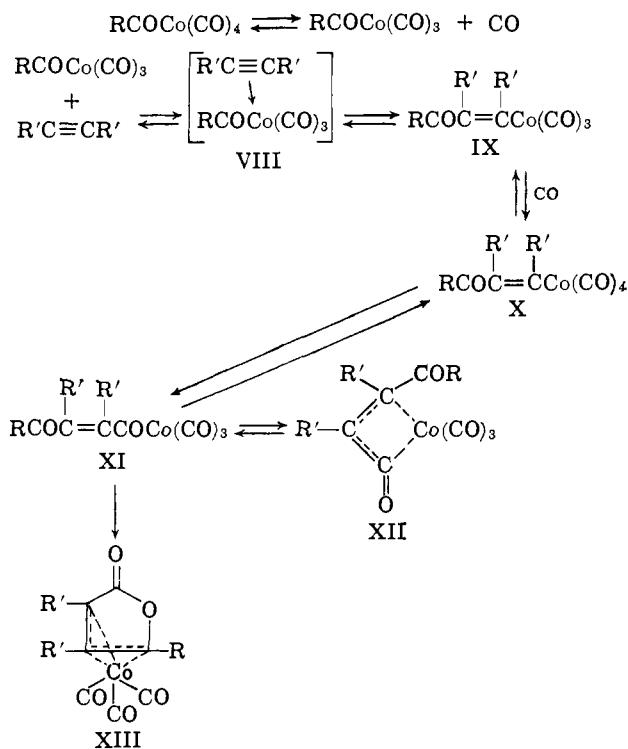
is probably the dissociation of the acylcobalt tetracarbonyl into an acyl tricarbonyl and carbon monoxide. This step could then be followed by the addition of the acetylene, presumably by coordination to the cobalt initially, forming VIII, and then by insertion between the acyl carbonyl and the cobalt atom to give an acyl-vinylcobalt tricarbonyl, IX. The latter complex could rapidly take up carbon monoxide, form the tetracarbonyl X, and then equilibrate with an acylacrylyl-cobalt tricarbonyl XI, which probably would exist mainly as the olefin π-complex XII. Addition of the acylcobalt group to the second acyl carbonyl, followed by coordination of the double bond, would give the observed π-lactonylcobalt product XIII. In reactions where monosubstituted acetylenes or acetylene itself are used, cyclization of the acylacrylylcobalt tricarbonyl may not be as favorable as the formation of linear compounds. The linear compound, of course, may also add more acetylene, eventually forming polymers.

Infrared spectra indicate that alkylcobalt tetracarbonyls react with acetylenes the same way as do the acyl compounds, even in the absence of carbon monoxide. Presumably a second acetylene molecule coordinates with the cobalt and makes possible the cyclization reaction. No attempt has been made to isolate the presumed acetylene π-complexes.

The formation of the π-lactonylcobalt complexes recalls the formation of the related dicobalt-lactone derivatives XIV, by the reaction of carbon monoxide with acetylenedicobalt hexacarbonyl complexes.[19,20]

The mechanism of formation of these binuclear lactone complexes is probably similar to the mechanism suggested above for the acylcobalt tetracarbonyl addition, where R is now a cobalt tetracarbonyl group and the acetylenedicobalt hexacarbonyl is analogous to the acylcobalt-π-acetylene tricarbonyl.

Experimental

The apparatus used for measuring gas volume changes during reactions, and the general techniques employed, have been described.[4]

2,3-Diethyl-π-(2,4)-(penteno-4-lactonyl)cobalt Tricarbonyl and Its Mono(triphenylphosphine) Derivative.—In a 100-ml. reaction flask, which had been filled with ether-saturated carbon monoxide

(19) H. W. Sternberg, J. G. Shukys, C. D. Donne, R. Markby, R. A. Friedel, and I. Wender, *J. Am. Chem. Soc.*, **81**, 2339 (1959).

(20) G. Albanesi and M. Tovaglieri, *Chim. Ind.* (Milan), **41**, 189 (1959).

at 0° and attached to a gas buret,[17] were placed 30 ml. of 0.07 M sodium cobalt carbonylate in ether solution[21] and 3.0 ml. of 1.2 M acetyl chloride in ether solution. After 1.5 hr. of stirring at 0°, the infrared spectrum of a sample of the reaction solution showed that acetylcobalt tetracarbonyl had been formed.[17] To this solution was added 2.0 ml. of 3-hexyne. The solution gradually changed color from yellow to orange, and gas was evolved. After 10 ml. of gas evolved in 2 hr., the evolution stopped. The infrared spectrum of the reaction mixture had carbonyl bands at 4.78 (w), 4.85 (s), 4.91 (m), 5.00 (vs), and 5.70 (m) μ. Evaporation of the solution under vacuum at 0° left an orange oil which was chromatographed on alumina. Pentane eluted a red complex with infrared bands at 4.81 (w), 4.90 (m), and 4.98 (s) μ. These bands and their intensities are identical with those of 3-hexynedicobalt hexacarbonyl.[11] Elution with ether–pentane gave several colored fractions, each containing 5.7 μ carbonyl bands. Since several new absorption bands appeared in these eluates, decomposition was apparently taking place on the alumina column.

The triphenylphosphine derivative of the π-lactone complex was prepared by adding 4.0 ml. of 1.0 M triphenylphosphine in ether solution at 0° to a solution of the complex in ether at 0° prepared from 30 ml. of 0.07 M sodium cobalt carbonylate as described above. The solution gradually became a darker red and gas was evolved. In 2.5 hr., 46 ml. or 1.56 mmoles of gas was evolved. The rate of gas evolution, measured as described previously,[2] was $6.22 \pm 0.25 \times 10^{-4}$ sec.$^{-1}$. Evaporation of the reaction mixture at 0° under vacuum, followed by extraction with tetrahydrofuran (4 ml.), and centrifuging, separated the inorganic salts. Addition of 5 ml. of pentane to the clear orange tetrahydrofuran extract caused the product to crystallize out as fine orange needles. After cooling to −80° the solid was separated by centrifuging and recrystallized three more times from tetrahydrofuran–pentane at −80°. The product, which was obtained in moderate yield, had no definite melting point, but it became dark at about 85° and gradually decomposed on further heating. The infrared spectrum of this compound in carbon tetrachloride solution had bands at 3.30 (w), 3.40 (w), 3.50 (w), 4.82 (w), 4.98 (s), 5.11 (s), 5.77 (m), 5.98 (w), 6.77 (m), 6.87 (w), 6.98 (m), 7.07 (m), 7.27 (w), 7.52 (w), 7.73 (w), 8.35 (m), 8.90 (w), 9.12 (m), 9.40 (w), 9.61 (w), 9.71 (w), 10.00 (w), 10.40 (w), 10.71 (w), and 11.10 (w) μ. There were additional bands in carbon disulfide solution at 13.46 (m), 13.88 (w), 14.20 (m), and 14.46 (s) μ.

Anal. Calcd. for $C_{29}H_{28}O_4PCo$: C, 65.66; H, 5.32. Found: C, 65.44, 65.46; H, 5.50, 5.53.

2,3-Diethyl-4-phenyl-π-(buteno-4-lactonyl)cobalt Tricarbonyl and Its Reaction with Iodine.—In a 500-ml., 3-necked flask filled with nitrogen, and equipped with a stirrer, a condenser, and an adaptor for a rubber stopule, was placed 200 ml. of 0.07 M sodium cobalt carbonylate in ether solution. The solution was stirred and cooled to 0°. Then 8 ml. of 3-hexyne and 3.06 g. of benzoyl bromide were added. After 2.5 hr. at 0°, the infrared spectrum indicated that the π-butenolactonyl complex had been formed. Carbonyl absorption bands were 4.84 (s), 4.90 (m), 4.99 (vs), and 5.67 (s) μ. To the stirred solution at 0° was added, a drop at a time, 120 ml. of 0.2 M KI_3 solution in water. When gas evolution stopped, aqueous sodium bisulfite was added to remove the excess iodine. The organic phase was separated and dried over magnesium sulfate. Evaporation of the solvent on the steam bath left a red, partially crystalline material, which was chromatographed on alumina. Pentane eluted a red compound which, from its infrared spectrum, appeared to be 3-hexynedicobalt hexacarbonyl. A 1:1 mixture of ether and pentane eluted a crystalline solid. Recrystallization from hot ethanol gave 1.1 g. of colorless crystalline product, m.p. 182.5–184°.

Anal. Calcd. for $C_{28}H_{30}O_4$: C, 78.10; H, 7.04. Found: C, 78.08, 77.94; H, 7.20, 7.12.

The n.m.r. spectrum at 60 Mc. in deuteriochloroform had two groups of phenyl protons at −71 and −53 c.p.s. with respect to an external benzene reference (total area 10), two unlike methylene groups at 185 and 245 c.p.s. (both multiplets with total area of 4), two equivalent methylene groups at 270 c.p.s. (both quartets of total area 4), and two groups of two equivalent methyl groups at 333 and 354 c.p.s. (both triplets with areas of 6.5).

The infrared spectrum of the compound in ether solution showed a very strong carbonyl band at 5.65 μ.

Hydrogenation of the Acetylene–Acetylcobalt Tetracarbonyl Complex.—In a reaction flask which had been filled with tetrahydrofuran-saturated acetylene at 25° and attached to a gas buret was placed 20 ml. of 0.1 M sodium cobalt carbonylate in tetrahydrofuran. The solution was stirred until it was saturated and 3.0 ml. of 1.0 M acetyl chloride in tetrahydrofuran was added. The solution turned red-brown and first evolved 22 ml. of gas and then absorbed gas. When the reaction was complete (about 5 hr.), a total of about 10 ml. of gas had been evolved and there was a moderate carbonyl band at 5.73 μ. The solution was then injected into a nitrogen-filled, 110-ml. hydrogenation vessel with 1.0 ml. of dicyclohexylethylamine,[22] and hydrogenated with rocking at 3000 p.s.i. of hydrogen and 35° for 22 hr. Analyses by vapor phase chromatography indicated the presence of 0.85% γ-valerolactone, which is about 75% of the theoretical amount, based upon the cobalt present.

2,3-Diethyl-5-carboethoxy-2,4-pentadieno-4-lactone. Stoichiometric Preparation.—In a 100-ml. reaction flask which had been filled with ether-saturated carbon monoxide at 0° and attached to a gas buret were placed 30 ml. of 0.07 M sodium cobalt carbonylate in ether solution, 2.0 ml. of 3-hexyne, and 3.0 ml. of 1.0 M ethyl bromoacetate in ether solution. After 3.5 hr. of stirring at 0°, 51 ml. of gas or 1.69 mmoles was absorbed and absorption stopped. The infrared spectrum of the reaction mixture had carbonyl bands at 4.82 (s), 4.98 (vs), 5.68 (m), and 5.76 (m) μ.

The addition of 2.0 ml. of dicyclohexylethylamine to the above reaction mixture caused further gas absorption to begin, with simultaneous darkening of the solution. After reacting 4 hr. at 0°, about 1.5 mmoles of gas had been absorbed and the reaction was almost complete. The infrared spectrum of the reaction mixture now had bands at 5.59 (m) and 5.84 (m) μ, with a weak band at 5.3 μ from cobalt carbonylate ion. Most of the cobalt carbonylate ion had separated from the solution as the dicyclohexylethylammonium salt. The lactone is best prepared for isolation by the catalytic method described below.

Catalytic Method.—The reaction vessel above was filled with carbon monoxide at 27° and in it were placed 30 ml. of 0.07 M sodium cobalt carbonylate in ether solution, 2.0 ml. of dicyclohexylethylamine, 2.0 ml. of 3-hexyne, and 2.5 ml. of 1.0 M ethyl bromoacetate in ether. The solution turned brown and, in 76 min., 1.5 mmoles of carbon monoxide was absorbed. Another 2.5 ml. of 1.0 M ethyl bromoacetate in ether was added and the reaction was continued overnight. A total of 2.54 mmoles of gas was absorbed. The reaction mixture was poured into water and the ether phase was washed with water, then with cold dilute hydrochloric acid, and finally with water again. After the solution was dried over magnesium sulfate, the solvent was evaporated, and the product was recrystallized three times from pentane at −80°, and finally distilled at about 150° and 1.0 mm. pressure. The pale yellow liquid obtained melted below room temperature. The ultraviolet spectrum in cyclohexane solution had λ_{max} 274 mμ (ϵ 28,500).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 63.21; H, 7.19. Found: C, 63.68; H. 7.41.

The infrared spectrum of the compound in carbon tetrachloride solution had bands at 3.31 (m), 3.35 (m), 3.41 (w), 5.58 (s), 5.76 (m), 5.85 (s), 6.02 (m), 6.41 (w), 6.49 (w), 6.58 (vw), 6.62 (vw), 6.83 (w), 7.30 (m), 7.50 (m), 7.83 (m), 8.03 (m), 8.60 (m), 8.98 (w), 9.10 (w), 9.60 (m), 9.75 (m), 10.40 (m), and 10.68 (w) μ.

The n.m.r. spectrum at 60 Mc. in carbon tetrachloride solution had bands at 71 c.p.s. with respect to an external benzene standard (single peak of area 0.8), 146 c.p.s. (four peaks of area 2.0), 243 and 252 c.p.s. (two overlapping quartets with total area 4.1), 320, 324, and 326 c.p.s. (three overlapping triplets with total area 9.1).

2,3-Diethyl-5-cyano-2,4-pentadieno-4-lactone.—In a reaction flask filled with carbon monoxide at 25° and connected to a gas buret were placed 30 ml. of 0.07 M sodium cobalt carbonylate in ether solution, 1.0 ml. of 3-hexyne, 1.0 ml. of dicyclohexylethylamine, and 2.7 ml. of 1.0 M chloroacetonitrile in ether solution. The reaction mixture turned dark red and, after reacting overnight, absorbed 140 ml. of gas (1.68 mmoles or 62% of theory). Two such reaction mixtures were combined and poured into water. The ether solution was washed with water, with cold dilute hydrochloric acid, and then with water again. After the solution was dried over magnesium sulfate, the solvent was

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

(22) S. Hünig and M. Kiessel, *Chem. Ber.*, **91**, 380 (1958).

evaporated on a steam bath. The product was recrystallized several times from methylene chloride–pentane and, finally, once from ethyl acetate–pentane. A colorless crystalline compound of m.p. 87–88.2° was obtained.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.57; H, 6.26. Found: C, 67.78; H, 6.26.

The ultraviolet spectrum of the compound in cyclohexane solution had λ_{max} 278 mμ (ϵ 22,700).

The infrared spectrum in carbon tetrachloride solution had bands at 3.23 (w), 3.35 (w), 3.45 (w), 4.48 (w) 5.56 (m), 6.06 (w), 6.83 (w), 6.98 (w), 7.25 (w), 7.52 (w), 8.12 (w), 8.90 (w), 9.31 (w), 9.80 (w), 10.40 (m), 10.70 (w), and 10.98 (w) μ. There was an additional band at 13.03 (w) μ in carbon disulfide solution.

The n.m.r. spectrum of this compound in deuteriochloroform solution at 60 Mc. had bands at 80 c.p.s. with respect to an external benzene standard (one peak of area 1.0), 238 and 244 c.p.s. (two overlapping quartets of total area 3.9), and at 319 and 321 c.p.s. (two overlapping triplets with total area 6.1).

2 or 3-t-Butyl-5-cyano-2,4-pentadieno-4-lactone.—In a 100-ml. reaction flask attached to a gas buret and filled with tetrahydrofuran-saturated carbon monoxide, at 30°, was placed 60 ml. of 0.1 M sodium cobalt carbonylate in tetrahydrofuran, 3.0 ml. of t-butylacetylene, 3.0 ml. of dicyclohexylethylamine, and 1.0 ml. of chloroacetonitrile. After reacting overnight, the reaction mixture had absorbed a total of 249 ml., or 7.8 mmoles, of carbon monoxide. The dark green solution was evaporated to a paste under vacuum and the product was extracted from the residue with ether. The extracts were washed with water, cold dilute sulfuric acid, water again, and finally with aqueous sodium bicarbonate. After the solution was dried with magnesium sulfate, the solvent was evaporated and the product was extracted from the remaining dark red oil with boiling hexane. Recrystallization with use of charcoal from hexane and a little benzene, to decolorize the solution, gave about 0.10 g. of nearly colorless plates, m.p. 92.8–94.2°.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26. Found: C, 67.98; H, 6.39.

The ultraviolet spectrum in cyclohexane solution had λ_{max} 281 mμ (ϵ 28,900).

The infrared spectrum in carbon tetrachloride solution had bands at 3.23 (w), 3.37 (w), 3.49 (w), 4.50 (w), 5.58 (m), 6.08 (m), 6.28 (w), 6.79 (w), 6.88 (w), 7.34 (w), 7.49 (w), 7.68 (w), 7.90 (w), 8.32 (w), 8.98 (w), 9.70 (w), 10.10 (w), 10.33 (m), 10.59 (w), and 11.34 (w) μ.

2,3-Diethyl-7-carbomethoxy-2,4,6-heptatrieno-4-lactone.—In a 100-ml. reaction flask, attached to a gas buret and filled with ether-saturated carbon monoxide at 0°, were placed 60 ml. of 0.07 M sodium cobalt carbonylate in ether solution, 4.0 ml. of 3-hexyne, 2.0 ml. of dicyclohexylethylamine, and 5.0 ml. of 1.0 M methyl 4-bromocrotonate[23] in ether solution. The solution

(23) W. J. Bailey and J. Bello, *J. Org. Chem.*, **20**, 529, 689 (1955).

turned red, evolved 18 ml. of gas in 18 min., absorbed 2 ml. in 43 min., and then the reaction stopped. The reaction mixture was poured into water and the ether phase was separated, washed with cold dilute hydrochloric acid, and finally with water. After the solution was dried over magnesium sulfate, the ether was evaporated on the steam bath, and the product was recrystallized several times from hot hexane to give 0.2 g. of shiny colorless needles, m.p. 85.8–86.4°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.09; H, 6.83. Found: C, 65.88; H, 6.85.

The ultraviolet spectrum in cyclohexane solution had λ_{max} 318 mμ (ϵ 37,500) with a shoulder at 330 mμ (ϵ 32,900). There was another band at 220 mμ (ϵ 8800).

The infrared spectrum in carbon tetrachloride solution had bands at 3.31 (m), 3.35 (w), 3.45 (w), 5.61 (vs), 5.78 (s), 6.08 (m), 6.17 (m), 6.81 (w), 6.96 (m), 7.20 (w), 7.46 (m), 7.66 (m), 7.90 (s), 8.18 (m), 8.36 (m), 8.71 (s), 9.08 (w), 9.41 (w), 9.57 (m), 9.71 (s), 10.08 (m), 10.34 (m), 10.60 (m), 11.10 (w), 11.37 (w), 11.60 (w), and 14.15 (w) μ.

The n.m.r. spectrum at 60 Mc. in deuteriochloroform solution had bands at −64 to −94 c.p.s. with respect to an external benzene standard (a quartet of area 1.0), 18 to 40 c.p.s. (quartet of area 2.0), 166 c.p.s. (singlet of area 3.1), 240 and 248 c.p.s. (two overlapping quartets of total area 3.9), and at 320 and 324 c.p.s. (two overlapping triplets of total area 6.0).

2,3-Diethyl-5-p-nitrophenyl-2,4-pentadieno-4-lactone.—In a carbon monoxide-filled 100-ml. flask which was attached to a gas buret, at 25°, were placed 40 ml. of 0.1 M sodium cobalt carbonylate in tetrahydrofuran solution, 3.0 ml. of 3-hexyne, 3.0 ml. of dicyclohexylethylamine, and 3.0 ml. of 1.0 M p-nitrobenzyl bromide in tetrahydrofuran solution. After an initial evolution of 12 ml. of gas, absorption began. After overnight reaction, 3.0 ml. more of 1.0 M p-nitrobenzyl bromide in tetrahydrofuran solution was added. After about 2 hr. more, the solution was evaporated to dryness under vacuum and the product was extracted from the residue with ether. The extracts were washed with cold dilute hydrochloric acid, with water, and with aqueous sodium bicarbonate. After the ether solution was dried with magnesium sulfate, the solvent was evaporated and the product was recrystallized several times from boiling hexane. There was obtained 0.10 g. of yellow-brown needles, m.p. 135.2–136.4°.

Anal. Calcd. for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53. Found: C, 65.81; H, 5.11.

The ultraviolet spectrum in cyclohexane solution had three absorption bands, 332 mμ (ϵ 27,000), 347 mμ (ϵ 31,800), and 366 mμ (ϵ 22,300).

The infrared spectrum in methylene chloride solution had bands at 3.25 (w), 3.35 (w), 3.47 (w), 5.68 (vs), 6.08 (m), 6.29 (m), 6.60 (m), 6.70 (w), 6.85 (w), 7.09 (w), 7.24 (w), 7.43 (vs), 7.69 (w), 7.98 (w), 8.07 (w), 8.33 (w), 8.41 (w) 8.98 (m), 9.44 (w), 9.73 (m), 10.40 (m), 10.59 (m), 11.40 (m), 11.51 (m), 11.94 (m), and 14.56 (w) μ.