initially; a catalytic reaction will take place if sufficient amounts of the reagents are present.

2,4-Dinitrophenylhydrazones of the acyldienes are obtained merely by mixing the reaction mixtures with acidic 2,4-dinitrophenylhydrazine in aqueous alcohol.[4] The red to orange products are filtered off, washed with methanol, and recrystallized from chloroform–alcohol solution.

Catalytic Preparation of 1,3-Hexadien-5-one.—A 0.12 *M* solution of sodium cobalt carbonyl in absolute ethanol was prepared by evaporating 500 ml. of 0.07 *M* solution in ether[9] to dryness in the absence of air, at room temperature, and adding back 300 ml. of absolute ethanol. To this solution was added 140 ml. of dicyclohexylethylamine,[5] 25 g. of methyl chloride, and 60 ml. of butadiene. The cold solution was transferred by means of a double-ended hypodermic needle to a cooled, evacuated pressure vessel. The container was then pressured to 100 p.s.i. with carbon monoxide and heated to 85°. The solution was mixed by rocking at 85° under 120–130 p.s.i. of carbon monoxide for 24 hr. After cooling a small sample was removed for ultraviolet spectral analysis (35% yield calculated) and the rest was poured into water and steam distilled. The material distilling below 85° was discarded although the ultraviolet spectrum of this low boiling fraction showed it to contain an appreciable quantity of 1,3-hexadien-5-one. About 2 l. of distillate were collected above 85°. The oil phase was extracted with several portions of ether. After drying with anhydrous magnesium sulfate, the extracts were distilled. There was obtained 5.0 g. of 1,3-hexadien-5-one, b.p. 52–54° (19 mm.). The ultraviolet spectrum is reported in Table II.

Anal. Calcd. for C_6H_8O: C, 74.97; H, 8.39. Found: C, 74.68; H, 8.70.

The n.m.r. spectrum of the product at 60 Mc. had a sharp methyl proton band at 298 c.p.s. and a complex group of vinyl protons at −10 to 116 c.p.s. with respect to an external benzene standard. The area ratios of the two types of protons were 3.1 to 4.9, respectively (calculated 3 to 5). The infrared spectrum in carbon tetrachloride solution had bands at 3.20(w), 3.30(w), 3.33(w), 5.41(w), 5.99(vs), 6.17(s), 6.29(s), 7.07(m), 7.38(s), 7.68(m), 7.79(w), 7.95(vs), 8.38(m), 8.67(m), 9.92(vs), 10.22(w), 10.39(m), 10.79(s), 11.60(w), and 11.77 (w) μ.

4-Methyl-1,3-hexadien-5-one.—In a carbon monoxide-filled bottle, which had been capped with a self-sealing, rubber-lined cap containing two holes in it for hypodermic injections, were placed 20 ml. of 0.2 *M* sodium cobalt carbonyl in tetrahydrofuran, 10 ml. of *cis*-piperylene, and 10 ml. of dicyclohexylethylamine. The solution was heated to 70°, stirred magnetically, and 2.0 ml. of methyl iodide was injected. The carbon monoxide pressure was raised to 50 p.s.i. After about 20 hr. of reaction at 70° with 35–50 p.s.i. of carbon monoxide present, the solution was cooled and the slush of crystals and liquid obtained was steam distilled. The material distilling above 70° was collected and the product was extracted with several portions of pentane. The pentane solution was extracted with dilute hydrochloric acid and with water and dried with anhydrous magnesium sulfate. Distillation gave 1.5 g. of colorless liquid, b.p. 62–65° (20 mm.). The ultraviolet spectrum in methanol solution is given in Table II.

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 75.12; H, 9.26.

The n.m.r. spectrum at 60 Mc. had two sharp methyl bands at 287 and 316 c.p.s. and a series of vinyl protons at −8 to 102 c.p.s. with respect to an external benzene standard. The area ratios were 3.2:3.2:3.6, respectively (calculated 3:3:4). The infrared spectrum in carbon tetrachloride solution had bands at 2.35 μ (m), 5.40(w), 6.01(vs), 6.14(s), 6.30(m), 7.03(s), 7.32(vs), 7.50(m), 7.93(vs), 8.51(s), 9.15(m), 9.81(s), 10.10(vs), 10.32(m), 10.50(m), and 10.80(s) μ.

2-Methyl-1,3-hexadien-5-one from Acetone and Methacrolein.—A solution of 300 ml. of acetone and 50 ml. of methacrolein was neutralized to phenolphthalein at 0° by adding a dilute solution of potassium hydroxide. Then, 170 ml. of a 1% solution of potassium hydroxide in water was added and the solution was stirred at 0° for 2 hr. After 10 ml. of glacial acetic acid was added, the solution was diluted with 2 l. of water and the product was extracted with about a liter of ether in three portions. After being washed twice with water, the extracts were dried with anhydrous magnesium sulfate and vacuum distilled. About 10 g. of nearly colorless liquid, b.p. 60–75° (15 mm.), was obtained. There was a considerable amount of higher boiling material left in the distillation flask. The distillate was redistilled to give material of b.p. 62–65° (14.5 mm.). The compound had a very strong carbonyl band in the infrared region at 5.99 μ as expected. The ultraviolet spectrum had a λ_{max} of 264 mμ with ε 13,000 indicating that the compound was only about 50% or less pure. A 2,4-dinitrophenylhydrazone, prepared in the usual way[4] and recrystallized several times from chloroform–methanol solution, formed dark red needles, m.p. 193–194°. The mixture m.p. of this material with the corresponding product from isoprene and methylcobalt tetracarbonyl was 192–193°.

Anal. Calcd. for $C_{13}H_{14}O_4N$: C, 53.78; H, 4.86. Found: C, 53.70; H, 5.24.

Acknowledgment.—The author gratefully acknowledges helpful discussions with Drs. S. Winstein and D. S. Breslow. Nuclear magnetic resonance spectra were measured by Dr. J. C. W. Chien and Mr. C. R. Boss.

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

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO., WILMINGTON 9, DEL.]

Triphenylphosphine Derivatives of π-Cyclopentenonylcobalt Tricarbonyls and their Dehydrogenation to π-Cyclopentadienonecobalt Dicarbonyl Triphenylphosphine Cations

BY RICHARD F. HECK

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2,4-Hexadienoyl- and 2,4-pentadienoylcobalt carbonyls have been prepared by the reaction of 2,4-hexadienoyl and 2,4-pentadienoyl chloride with sodium cobalt carbonylate in ether solution at 0°. Both products exist as equilibrium mixtures of acylcobalt tetracarbonyls and π-olefin bonded, cyclic acylcobalt tricarbonyls under one atmosphere of carbon monoxide. Both products react with triphenylphosphine to give acylcobalt tricarbonyl triphenylphosphine derivatives. The latter complexes cyclize on heating to 2-methyl-π-(3,5)-cyclopentenonyl- and π-(2,4)-cyclopentenonylcobalt dicarbonyl triphenylphosphines, respectively. These compounds are dehydrogenated by triphenylmethyl tetrafluoroborate to π-cyclopentadienonecobalt dicarbonyl triphenylphosphine tetrafluoroborates. The 2-methyl derivative is stable; the unsubstituted compound is not. 4,6-Heptadienoylcobalt tricarbonyl triphenylphosphine has also been prepared. On heating it loses carbon monoxide, producing a derivative of π-allylcobalt dicarbonyl triphenylphosphine rather than cyclizing to form a π-cycloheptenonylcobalt complex.

Introduction

A considerable number of π-aromatic system–transition metal complexes are known. In many examples, however, only one or a few special compounds of a group can be prepared because of the method of synthesis. The π-cyclopentadienonecobalt complexes are in this group. Previously these complexes have been prepared by the reaction of acetylenes with certain cobalt carbonyl derivatives. Wender has found that 2-butyne reacts with cyclopentadienylcobalt dicarbonyl under the influence of light to give π-cyclopentadienyl-π-tetramethylcyclopentadienonecobalt.[1] Hübel has reported the reaction of acetylenes with mercuric cobalt tetracarbonylate to produce bis-π-cyclopentadienonecobalt dicarbonylmercury and he has reported the conversion of these compounds to the π-cyclopentadienonecobalt dicarbonyl halides by reaction with halogens.[2] These reactions, of course, are limited to the production of symmetrical π-cyclopenta-

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[1] R. Markby, H. W. Sternberg, and I. Wender, *Chem. Ind.* (London), 1381 (1959).

[2] U. Krüerke and W. Hübel, *Chem. Ber.*, **94**, 2829 (1961).

dienone complexes because the two acetylene groups employed in the reaction are the same. Possibly a mixture of acetylenes could be used to give unsymmetrical products, but it is doubtful that this method would be generally useful for preparing substituted π-cyclopentadienone complexes.

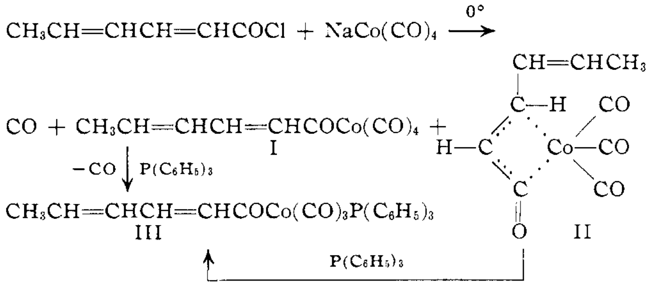
π-Cyclopentadienonemetal complexes have also been prepared by treating metal carbonyls with substituted cyclopentadienones,[3] but this reaction is limited by the difficulty of obtaining the substituted cyclopentadienones.

Another method for their preparation is reported in this paper. It promises to be more general, and similar reactions might lead to new π-aromatic–metal complexes which may not be obtainable by known methods.

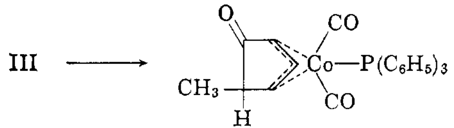
Results

Previous work has shown that conjugated dienes add readily to acylcobalt carbonyls to produce 1-acylmethyl-π-allylcobalt tricarbonyls.[4,5] This reaction has now been applied to compounds in which the diene system is in the acyl group of the acylcobalt carbonyl. On warming, these complexes may undergo cyclization to π-cycloalkenonylcobalt tricarbonyl derivatives.

trans,trans-2,4-Hexadienoyl chloride (sorbyl chloride) reacts with sodium cobalt carbonylate in ether solution at 0° under one atmosphere of carbon monoxide to evolve 0.2 mole of carbon monoxide. The infrared spectrum of the reaction mixture shows two acyl carbonyl absorptions, one at 5.5 μ and the other at 6.0 μ. An equilibrium mixture of sorbylcobalt tetracarbonyl (6.0 μ band), I, and 3-propenyl-π-acrylylcobalt tricarbonyl (5.5 μ band), II, is apparently formed. The situation is completely analogous to the linear and cyclic products formed when crotonyl chloride is treated with sodium cobalt carbonylate.[6] The mixture of products from the sorbyl chloride reaction reacts with excess triphenylphosphine at 0° to evolve 0.8 mole of carbon monoxide and form a single product, sorbylcobalt tricarbonyl triphenylphosphine (III), isolated as yellow crystals, m.p. 93.5–96.0° dec.



The sorbyl chloride–sodium cobalt carbonylate reaction mixture on warming to 25° undergoes further reaction, evolving carbon monoxide and producing a compound with a new carbonyl band at 5.8 μ. At the same time the 5.5 and 6.0 μ bands disappear. To isolate the new product from this reaction mixture proved difficult. However, heating sorbylcobalt tricarbonyl triphenylphosphine (III) to 75–80° for about an hour in ether solution caused similar changes in the infrared spectrum of this reaction mixture but at about 0.1 μ higher wave lengths. A new, crystalline, orange-red product which decomposed at 110° was readily isolated from the reaction mixture by chromatography The product was isolated in 33% yield in a single step from sorbyl chloride without isolating the intermediate sorbylcobalt tricarbonyl triphenylphosphine. The new complex had a moderately strong carbonyl band at 5.9 μ in addition to coordinated carbonyl bands at 4.9 and 5.1 μ. The two double bond adsorptions of the sorbylcobalt starting compound were no longer present. Elemental analyses indicate that the complex probably contains one sorbyl group, two carbon monoxides, and a triphenylphosphine group per cobalt atom. The n.m.r. spectrum in deuteriochloroform solution has five kinds of protons, in addition to the aromatic, triphenylphosphine protons, in a ratio of 1:1:1:1:3 with chemical shift values of 78, 157, 182, 220 (multiplet), and 310 (doublet) cycles per second with respect to an external benzene standard. (The aromatic protons are at −57 c.p.s.) The data indicate structure IV for this compound, 2-methyl-π-cyclopentenonylcobalt dicarbonyl triphenylphosphine. The methyl group is probably on the side of the cyclopentene ring away from the cobalt atom.

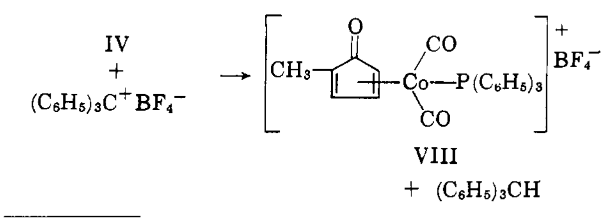


IV

trans-2,4-Pentadienoyl chloride reacts with sodium cobalt carbonylate in an analogous manner. The reaction evolves 0.36 mole of carbon monoxide at 0°. Addition of excess triphenylphosphine caused the evolution of 0.7 mole of carbon monoxide, forming 2,4-pentadienoylcobalt tricarbonyl triphenylphosphine as yellow crystals which decomposed at 80°. On heating to 80° for an hour in ether solution, the compound cyclized to π-cyclopentenonylcobalt dicarbonyl triphenylphosphine which was isolated in 22.5% yield, based upon the sodium cobalt carbonylate used, as orange-red crystals of m.p. 127–131° dec.

It is surprising that these cyclization reactions go as well as they do considering the fact that the starting dienoyl compounds are *trans* and the cyclic products must have been formed from either the *cis* isomers or from some intermediate where free rotation at the α- or β-carbon atoms was possible. One explanation for the isomerization is that the intermediate π-acrylyl-complex II, can equilibrate the *cis* and *trans* isomers by opening up to a σ-bonded ketene derivative.

The report of Dauben that triphenylmethyl tetrafluoroborate caused the dehydrogenation of π-cycloheptatrienemolybdenum tricarbonyl[7] suggested that it might be possible to dehydrogenate our π-cyclopentenonylcobalt compounds to π-cyclopentadienone complexes. Indeed this proved to be possible. 2-Methyl-π-cyclopentenonylcobalt dicarbonyl triphenylphosphine (IV) in methylene chloride solution at 0° reacts with triphenylmethyl tetrafluoroborate with noticeable darking of the solution. From the solution was isolated a good yield of a yellow-brown crystalline product which decomposed at 170–175°. The infrared spectrum of this compound had strong carbonyl bands at 4.71, 4.78, and 5.98 μ. The spectrum and carbon–hydrogen analyses indicate the compound is 2-methyl-π-cyclopentadienonecobalt dicarbonyl triphenylphosphine tetrafluoroborate (VIII).



VIII

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(3) E. Weiss and W. Hübel, *J. Inorg. Nucl. Chem.*, **2**, 42 (1959).

(4) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 3381 (1963).

(5) R. F. Heck, *ibid.*, **85**, 3383 (1963).

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

(7) H. J. Dauben, Jr., and L. R. Honnen, *ibid.*, **80**, 55 (1958).

π-Cyclopentenonylcobalt dicarbonyl triphenylphosphine also reacts with triphenylmethyl tetrafluoroborate, apparently to give the π-cyclopentadienonecobalt dicarbonyl triphenylphosphine cation, judging from the infrared spectrum of the reaction mixture. The compound, however, was unstable and it could not be purified.

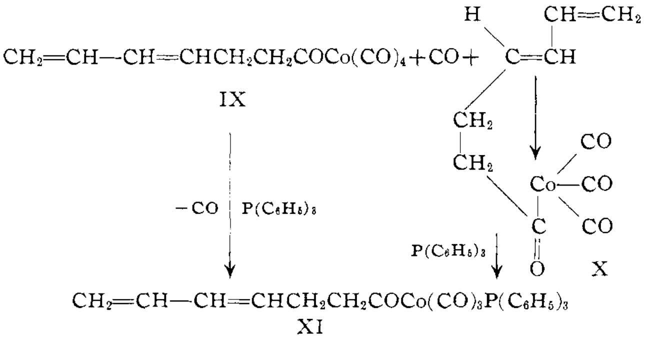
The cyclization of dienoylcobalt carbonyl complexes to cyclopentenonylcobalt compounds followed by reaction with bases, as described for other diene–acylcobalt carbonyl complexes,[5] should lead to the cyclopentadienones themselves. The cyclic complex from sorbylcobalt carbonyl reacted only very slowly with dicyclohexylethylamine. It did react rapidly with sodium methoxide to form cobalt carbonylate anion and probably 2-methylcyclopentadienone, but no attempt has been made to isolate the latter (or its dimer).

It is not only possible that this cyclization method could be useful to prepare cyclopentanone derivatives of other metal compounds but it may also be possible to use it to prepare compounds with larger rings π-bonded to the metal. One attempt was made to prepare a π-cycloheptenonylcobalt complex from 4,6-heptadienoylcobalt carbonyl. 4,6-Heptadienoic acid was prepared by the Wittig reaction of methyl β-formylpropionate[8] with allylidene triphenylphosphine followed by hydrolysis.

$$\mathrm{OCHCH_2CH_2COOCH_3 + CH_2{=}CHCH{=}P(C_6H_5)_3 \longrightarrow CH_2{=}CHCH{=}CHCH_2CH_2COOCH_3 + OP(C_6H_5)_3}$$

The acid chloride was prepared with thionyl chloride and then treated with sodium cobalt carbonylate. At 0° in ether solution, under one atmosphere of carbon monoxide, this reaction evolved 0.66 mole of carbon monoxide. The addition of excess triphenylphosphine led to the evolution of 0.34 mole of carbon monoxide and the formation of a single product, 2,4-heptadienoylcobalt tricarbonyl triphenylphosphine (XI) (yellow crystals, m.p. 80–85° dec.). Apparently the heptadienoylcobalt carbonyl exists as an equilibrium mixture of an open chain, tetracarbonyl form IX (34%) and a π-bonded cyclic form X (66%) as does the related 4-hexenoylcobalt carbonyl.[9] The 2,4-heptadienoyl cobalt tricarbonyl triphenylphosphine (XI) on being heated to 75° in ether solution undergoes a reaction, producing an orange solution. It has not yet been possible to isolate a crystalline compound from this reaction mixture, but it is clear from the infrared spectrum of the product that it is not the expected cyclic ketone because there are no significant bands in the 5.5–6.2 μ region. The presence of three coordinated carbonyl bands at 4.87, 5.02, and 5.16 μ suggests the product is a π-allylcobalt dicarbonyl triphenylphosphine derivative formed by loss of carbon monoxide and rearrangement. The product could either be 1-vinyl-3-methyl-π-allylcobalt dicarbonyl triphenylphosphine or possibly 1-allyl-π-allylcobalt dicarbonyl triphenylphosphine, or a mixture of these two, perhaps in more than one of their possible isomeric forms. This is the same kind of reaction which was observed previously when 4-pentenoylcobalt tetracarbonyl was heated and π-crotylcobalt tricarbonyl was formed.[10] In spite of the failure of this particular reaction, it is likely that other, appropriately substituted or longer chain derivatives will undergo the expected cyclization to π-cycloalkenonylmetal complexes.

$$\mathrm{CH_2{=}CHCH{=}CHCH_2CH_2COCl + NaCo(CO)_4 \longrightarrow}$$



IX

X

XI

Experimental

The equipment and techniques used in these experiments have been described previously.[10] The organocobalt complexes were handled under nitrogen as much as possible because they are all somewhat reactive toward oxygen.

Sorbylcobalt Tricarbonyl Triphenylphosphine.—In a magnetically stirred reaction flask attached to a thermostated gas buret[10] which was filled with ether-saturated carbon monoxide at 0° were placed 30 ml. of 0.07 *M* sodium cobalt carbonylate in ether solution[11] and 2.5 ml. of 1.0 *M* sorbyl chloride in ether solution. The solution turned yellow and, in 85 min., 14.0 ml. (0.47 mmole) of gas was evolved and the reaction stopped. The infrared spectrum of this reaction mixture had strong carbonyl bands at 5.50 and at 5.96 μ. The addition of 3.0 ml. of 1.0 *M* triphenylphosphine in ether solution led to the evolution of 49.5 ml. (1.67 mmoles) of carbon monoxide. Evaporation of the solvent at 0° under vacuum left a yellow residue. The product was taken up in tetrahydrofuran, centrifuged in the absence of air, and evaporated to about 3 ml. under vacuum. Pentane was added gradually. The amorphous green material which separated first was removed by centrifuging. Addition of more pentane, followed by cooling to −80°, gave yellow crystals. Two further crystallizations from tetrahydrofuran–pentane gave material which melted with decomposition at 93.5–96.0°.

Anal. Calcd. for $C_{27}H_{22}O_4PCo$: C, 64.81; H, 4.43. Found: C, 64.89; H, 4.71.

The infrared spectrum of this compound in carbon tetrachloride had bands at 3.27(w), 3.42(w), 4.88(m), 5.05(vs), 6.04(m), 6.14(m), 6.36(w), 6.75(w), 6.98(m), 7.30(w), 7.64(w), 7.80(w), 8.21(w), 8.41(w), 8.62(w), 9.03(w), 9.13(m), 9.32(w), 9.56(w), 9.70(w), 10.01(w), and 10.35(m) μ. There were additional bands in carbon disulfide solution at 13.45(m), 14.14(m), and 14.42(s) μ. The compound decomposed rather rapidly in both solvents and there is some doubt about the presence of the weaker absorption bands.

2-Methyl-π-cyclopentenonylcobalt Dicarbonyl Triphenylphosphine.—In a nitrogen-filled bottle at 0° were placed 60 ml. of 0.07 *M* sodium cobalt carbonylate in ether and 5.0 ml. of 1.0 *M* sorbyl chloride in ether. The bottle was shaken, let stand for an hour at 0°, and 5.0 ml. of 1.0 *M* triphenylphosphine in ether was added. The contents were mixed and let stand at 0° for 30 min. more. Then the capped bottle was heated in water at 80° for an hour. After the contents cooled, the solvent was removed under vacuum and the residue was dissolved in methylene chloride and poured onto an alumina chromatography column. After a yellow product was eluted with ether, the red major product was eluted with 1% methanol in ether. The red eluate was evaporated to dryness at room temperature under vacuum. The orange crystalline solid obtained was recrystallized from tetrahydrofuran–pentane at −80°. There was obtained 0.65 g. or 33%, based upon the sodium cobalt carbonylate used, of orange-red crystals of 2-methyl-π-cyclopentenonylcobalt dicarbonyl triphenylphosphine. Two more crystallizations from the same solvent mixture gave an analytical sample. The compound darkened on heating at about 110°, but it did not melt below 160°. The infrared spectrum of this compound in carbon tetrachloride solution had bands at 3.25(w), 3.40(w), 3.49(w), 4.93(s), 5.05(s), 5.92(m), 6.75(w), 6.97(m), 7.27(w), 7.86(w), 8.13(w), 8.61(w), 8.90(w), 9.11(m), 9.29(w), 9.48(w), 9.70(w), 9.99(w), 10.88(w), 11.40(w), 14.16(m), 14.37(m), and 14.80(w) μ.

Anal. Calcd. for $C_{26}H_{22}O_3PCo$: C, 66.11; H, 4.70. Found: C, 66.15; H, 4.88.

***trans*-2,4-Pentadienoylcobalt Tricarbonyl Triphenylphosphine.**—A reaction was carried out as described above for the preparation of sorbylcobalt tricarbonyl triphenylphosphine. The addition of 3.0 ml. of 1.0 *M* 2,4-pentadienoyl chloride [b.p. 57° (30 mm.)] in ether to 30 ml. of 0.07 *M* sodium cobalt carbonylate in ether at 0° resulted in the evolution of 19 ml. (0.64 mmole) of carbon monoxide in 50 min. and the reaction stopped. The infrared spectrum of the reaction mixture had carbonyl bands at

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[8] H. Adkins and G. Krsek, *J. Am. Chem. Soc.*, **71**, 3051 (1949).

[9] R. F. Heck, *ibid.*, **85**, 3116 (1963).

[10] R. F. Heck and D. S. Breslow, *ibid.*, **83**, 1097 (1961).

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

5.49 and at 5.98 μ. The addition of 3.5 ml. of 1.0 *M* triphenylphosphine in ether solution caused the evolution of 41 ml. or 1.39 mmoles more of carbon monoxide in 30 min. and the reaction stopped. The solvent was evaporated under vacuum and the product was taken up in tetrahydrofuran. Insoluble material was removed by centrifuging, and addition of pentane and cooling to −80° gave the phosphine complex as a yellow powder. Two more recrystallizations from tetrahydrofuran–pentane gave a pure sample. The compound darkened at 80° without melting. The compound in carbon tetrachloride solution had infrared bands at 3.23(w), 3.36(w), 4.86(m), 5.02(vs), 5.07(vs), 6.07(m), 6.20(w), 6.38(m), 6.45(m), 6.77(w), 7.00(w), 8.05(w), 8.95(w), 9.14(m), 9.96(m), 10.14(m), 10.61(w), and 10.88(w) μ. There were additional bands in carbon disulfide solution at 13.40(m), 13.61(m), 14.13(m), and 14.43(m) μ.

Anal. Calcd. for $C_{25}H_{20}O_3PCo$: C, 64.21; H, 4.15. Found: C, 64.12; H, 4.45.

π-Cyclopentenonylcobalt dicarbonyl triphenylphosphine was prepared by essentially the same method as that used above for the 2-methyl-π-cyclopentenonylcobalt dicarbonyl triphenylphosphine preparation. From 60 ml. of 0.07 *M* sodium cobalt carbonylate and 2.2 ml. of 2.0 *M* 2,4-pentadienoyl chloride, both in ether solution, there was obtained 0.50 g. (22.5% based upon the sodium cobalt carbonylate used) of pure π-cyclopentenonylcobalt dicarbonyl triphenylphosphine, orange-brown plates, m.p. 127–131° dec. The compound crystallizes from tetrahydrofuran–pentane solution with one molecule of tetrahydrofuran. The infrared spectrum in carbon tetrachloride solution had infrared absorption bands at 3.23(w), 3.36(w), 3.48(w), 4.95(s), 5.08(s), 5.92(m), 6.76(w), 6.98(m), 8.10(w), 8.58(w), 9.12(m), 9.31(w), 9.70(w), 9.99(w), 10.24(w), 10.66(w), and 10.91(w) μ. In carbon disulfide solution there were additional bands at 13.40(m), 14.20(w), and 14.40(m) μ.

Anal. Calcd. for $C_{25}H_{20}O_3PCo \cdot C_4H_8O$: C, 65.66; H, 5.32. Found: C, 65.83; H, 5.26.

2-Methyl-π-cyclopentadienonecobalt Dicarbonyl Triphenylphosphine Tetrafluoroborate.—A solution of 1.7 g. of triphenylmethyl tetrafluoroborate[7] in 10 ml. of methylene chloride at 0° was added to a solution of 2.4 g. of 2-methyl-π-cyclopentenonylcobalt dicarbonyl triphenylphosphine in 5 ml. of methylene chloride, also at 0°, under nitrogen. The solution immediately became a darker red. After 2 hr. at 0°, the solution was concentrated under vacuum to about 10 ml., and 5 ml. of ether was added. The crystals which separated were recrystallized twice more from methylene chloride–ether to give a good yield of a yellow-brown powder m.p. 170–175° dec. The infrared spectrum in Nujol had carbonyl bands at 4.71(m), 4.78(s), and 5.98(m) μ. In methylene chloride solution there were bands at 3.27(w), 3.35(w), 4.72(m), 4.81(m), 5.92(w), 6.05(w), 6.75(w), 6.98(m), 7.38(w), 9.11(m), 9.35(m), and 9.71(m) μ.

Anal. Calcd. for $C_{26}H_{21}PBF_4O_3Co$: C, 55.94; H, 3.79. Found: C, 56.23; H, 3.71.

π-Cyclopentenonylcobalt dicarbonyl triphenylphosphine reacted with triphenylmethyl tetrafluoroborate in exactly the same way as the 2-methyl derivative did, but the product decomposed on attempted purification.

Methyl 4,6-Heptadienoate.—In a 2-l. 3-necked flask equipped with a condenser with a drying tube attached, a stirrer, and a dropping funnel was placed 62 g. of allyltriphenylphosphonium bromide and about 1 l. of ether which had been distilled from lithium aluminum hydride. The reaction flask was flushed with nitrogen, and 58 ml. of 2.90 *M* *n*-butyllithium in pentane was added with stirring. The solution became dark red. After 1 hr., 18.6 g. of methyl β-formylpropionate[8] in 110 ml. of ether was added dropwise. After the addition the solution was refluxed for 2 hr. Water was added and the ether phase was separated, dried over anhydrous magnesium sulfate, and distilled. There was obtained 7.2 g. of ester, b.p. 60.5–61.5° (8 mm.).

4,6-Heptadienoic Acid.—The ester above (7.2 g.) was stirred 48 hr. with a solution of 4.0 g. of sodium hydroxide in 20 ml. of water and 20 ml. of methanol. The solution was then diluted with water, extracted three times with methylene chloride, and acidified with cold dilute hydrochloric acid. The product was extracted with several portions of methylene chloride and dried with magnesium sulfate. Distillation gave 5.8 g. of the acid, b.p. 77–80° (3 mm.). The infrared spectrum in carbon tetrachloride solution had bands at 3.30(s), 3.73(m), 5.53(m), 5.82(vs), 6.03(m), 6.22(w), 6.98(m), 7.08(m), 7.50(w), 7.77(m), 8.00(m), 8.23(m), 8.72(w), 9.92(s), 10.46(m), 11.00(s), and 11.83(w) μ.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.30; H, 8.07. Found: C, 66.64; H, 7.99.

The acid chloride was obtained by dissolving 5.7 g. of the acid in 30 ml. of dry ether, adding 13.5 g. dicyclohexylethylamine, cooling to 0°, and adding 4.0 ml. of thionyl chloride during 30 min. After the mixture was let stand at 25° for an hour more, the salts were removed by centrifuging and the solution was distilled. There was obtained 3.75 g. of the acid chloride, b.p. 46.5–48° (5.5 mm.). The ultraviolet spectrum taken in methanol solution (methyl ester formed), had a λ_{max} of 224 mμ with ε 24,000.

4,6-Heptadienoylcobalt Tricarbonyl Triphenylphosphine.—In a carbon monoxide-filled, magnetically stirred reaction flask at 0° attached to a thermostated gas buret[10] were placed 30 ml. of 0.07 *M* sodium cobalt carbonylate in ether and 3.0 ml. of 1.0 *M* 4,6-heptadienoyl chloride in ether. The solution turned red, and in 3 hr., 41 ml. (1.38 mmoles) of carbon monoxide was evolved and the reaction stopped. To this solution at 0° was added 3.0 ml. of 1.0 *M* triphenylphosphine in ether. When the reaction was complete, 21 ml. or 0.71 mmole more of carbon monoxide had been evolved. The solution was evaporated to dryness under vacuum and the product was recrystallized three times from ether–pentane solution. There was obtained a good yield of yellow prisms which melted at 89–90° dec.

Anal. Calcd. for $C_{28}H_{24}O_4PCo$: C, 65.38; H, 4.70. Found: C, 65.56; H, 4.97.

An ether solution of the above complex in a capped tube was heated in boiling water for about an hour. The infrared spectrum now showed carbonyl bands only at 4.85(w), 5.02(s), and 5.13(s) μ. There were no significant bands in the 5.5–6.2 μ region. Only yellow-orange oils could be isolated from the reaction mixture.

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gem-Dihalides from α-Haloamides. II. Rearrangement of N-Bromo-α-haloamides Utilizing Bromide-82 Tracer[1]

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Two N-bromo-α-haloamides were allowed to react in the presence of sodium hydroxide and bromide ion to form *gem*-dihalides. Potassium bromide-82 was utilized internally and externally in separate experiments to establish (1) the degree of retention of bromine in the *gem*-dihalide product and (2) the extent to which external bromide ion was incorporated in the *gem*-dihalide. With N-bromo-α-chloroisobutyramide under cold, 0°, conditions, retention was 100.0 ± 1.0% and incorporation was 0.2 ± 0.2%. With N-bromo-α-bromoisovalerylamide, under hot distillation conditions, retention was 99.4 ± 1.0% and incorporation was 0.6 ± 0.3%. The *gem*-dihalides were stable under the experimental conditions and no isotopic exchange with bromide-82 was detected. The results indicate the reaction is almost exclusively intramolecular in character and offer additional support for a stereospecific four-center mechanism.

In the first paper of this series,[2] the limited literature relating to the conversion of the α-haloamides to *gem*-dihalides under conditions similar to those employed in the Hofmann rearrangement reaction was reviewed.

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[2] C. L. Stevens, T. K. Mukherjee, and V. J. Traynelis, *J. Am. Chem. Soc.*, **78**, 2264 (1956). This reference is considered paper I of this series.