# Alkyl- and Acyl-cobalt Carbonyls Containing Olefinic Unsaturation. Allylcobalt Tricarbonyl and Related Compounds[1]

BY RICHARD F. HECK AND DAVID S. BRESLOW
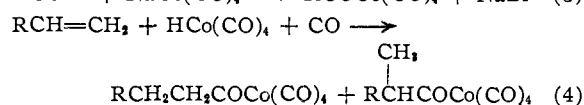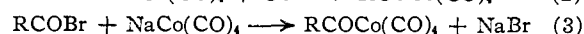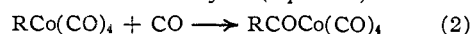
Allyl bromide reacts with NaCo(CO)₄ to form allylcobalt tricarbonyl. A symmetrical, non-classical structure (I) is suggested for this compound. Acrylyl chloride reacts with NaCo(CO)₄ to form acrylylcobalt tricarbonyl (IV), in which the double bond is coördinated with the cobalt. This complex is much less stable than I. 3-Butenoylcobalt tetracarbonyl (VII) has been prepared from NaCo(CO)₄, CO and allyl bromide and from NaCo(CO)₄ and 3-butenoyl chloride. The double bond in this material shows no tendency to coördinate with the cobalt but rather the compound decomposes by losing two moles of CO, forming allylcobalt tricarbonyl (I). The next higher homolog, 4-pentenoylcobalt tricarbonyl (X), prepared from 4-pentenoyl chloride and NaCo(CO)₄, again forms the cyclic coördinated olefin complex. On warming, X decomposes into 2-butenylcobalt tricarbonyl (XIII) which is formulated as the methyl analog of allylcobalt tricarbonyl (I). "Crotyl bromide," CO and NaCo(CO)₄ form the same complex as is obtained from HCo(CO)₄, CO and butadiene. The product is believed to be 3-pentenoylcobalt tetracarbonyl (XII). This material also decomposes into 2-butenylcobalt tricarbonyl. All of these cobalt compounds react with triphenylphosphine to give isolable crystalline complexes.

In connection with our investigation of the mechanism of the oxo reaction,[2] the preparation of a number of simple alkyl- and acyl-cobalt tetracarbonyls was carried out. The alkyl compounds were prepared by treating sodium cobalt tetracarbonyl with an alkylating agent[3] (eq. 1), while

$$RX + NaCo(CO)_4 \xrightarrow{Et_2O} RCo(CO)_4 + NaX \quad (1)$$
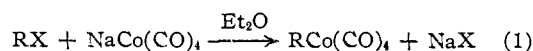
three methods were developed for the preparation of acylcobalt tetracarbonyls (eq. 2-4). All the

$$RCo(CO)_4 + CO \longrightarrow RCOCo(CO)_4 \quad (2)$$

$$RCOBr + NaCo(CO)_4 \longrightarrow RCOCo(CO)_4 + NaBr \quad (3)$$

$$RCH=CH_2 + HCo(CO)_4 + CO \longrightarrow$$
$$RCH_2CH_2COCo(CO)_4 + R\overset{|}{C}HCOCo(CO)_4 \quad (4)$$

cobalt compounds were found to be unstable, decomposing quite rapidly even at 0°, unlike the analogous manganese derivatives,[4] although they could be handled in solution. Allyl bromide, however, reacted differently with sodium cobalt carbonyl. Using excess carbonyl under nitrogen, one mole of CO was evolved per mole of bromide. Distillation yielded a low-melting, crystalline yellow solid which was stable indefinitely at room temperature. Treatment of the compound with iodine in methanol liberated three moles of CO per cobalt, indicating the compound was allylcobalt tricarbonyl.

$$CH_2=CHCH_2Br + NaCo(CO)_4 \xrightarrow[0°]{Et_2O}$$
$$C_3H_5Co(CO)_3 + CO + NaBr$$
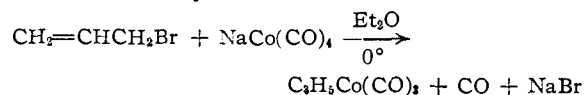
The compound was found to be diamagnetic by e.p.r. Since proton magnetic resonance showed three types of hydrogen in the ratio 2:2:1, structure I, an "open-faced sandwich" with the carbons and hydrogens in a plane, is considered most likely for allylcobalt tricarbonyl. In this structure the two methylene groups are equivalent, but the two

hydrogens on each methylene group are different, two being near the cobalt and two away. The
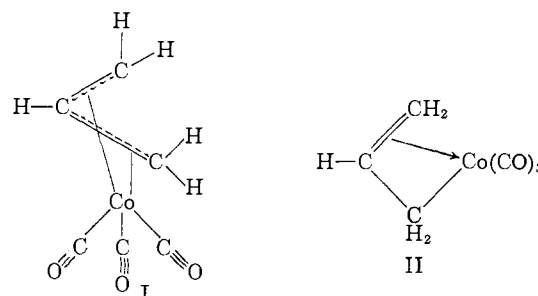
rapid equilibrium system found in allylmagnesium bromide[5] is ruled out, since this would require two different types of hydrogen in a 4:1 ratio. Although a simple π-bonded structure (II) should have four different kinds of hydrogen, the two vinyl hydrogens having different environments, this structure could not be ruled out unequivocally because of the rather poor resolution in the proton magnetic resonance spectrum. The proton magnetic resonance spectrum of allylcobalt tricarbonyl is very similar to that of the allylpalladium chloride dimer. The spectrum of the latter is very well resolved, however, and there is little doubt that it possesses the symmetrical structure.[6] It appears highly likely, therefore, that allylcobalt tricarbonyl is best represented by structure I.

Triphenylphosphine reacted with allylcobalt tricarbonyl to liberate one mole of CO and give allylcobalt dicarbonyl triphenylphosphine (III) as a crystalline complex. The fact that this is the only example we have found in which triphenylphosphine displaces CO from an alkylcobalt carbonyl without rearranging it into an acylcobalt compound[7] is further evidence for an unusual type of bonding.[8]

A different reaction occurred when excess allyl bromide was treated with sodium cobalt tetra-

(1) A preliminary account of a portion of this work appeared in J. Am. Chem. Soc., 82, 750 (1960).

(2) R. F. Heck and D. S. Breslow, Chemistry & Industry, 467 (1960); Second International Catalysis Congress, Paris, France, July 4-9, 1960.

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

(4) T. H. Coffield, J. Kozikowski and R. D. Closson, J. Org. Chem., 22, 598 (1957).

(5) J. E. Nordlander and J. D. Roberts, J Am. Chem. Soc., 81, 1769 (1959).

(6) H. C. Dehm and J. C. W. Chien, ibid., 82, 4429 (1960).

(7) R. F. Heck and D. S. Breslow, ibid., 82, 4438 (1960).

(8) It is interesting that triphenylphosphine displaces cycloöctatetraene from cycloöctatetraene-iron tricarbonyl[9] in spite of the fact that the thermal stability of the latter is considerably greater than that of allylcobalt tricarbonyl.

(9) T. A. Manuel and F. G. A. Stone, ibid., 82, 366 (1960).

carbonyl at 25°. Approximately one mole of CO per cobalt was liberated rapidly, followed by a slow evolution of additional CO; the solution turned green during the latter stage of the reaction. Analysis of the reaction mixture indicated the formation of one mole of 1,5-hexadiene per cobalt. Presumably allylcobalt tricarbonyl is first formed and this reacts with excess allyl bromide to form the diene. If the green color actually is due to the formation of cobalt bromide, an additional mole of allyl bromide is involved in the reaction; its fate has not been determined.
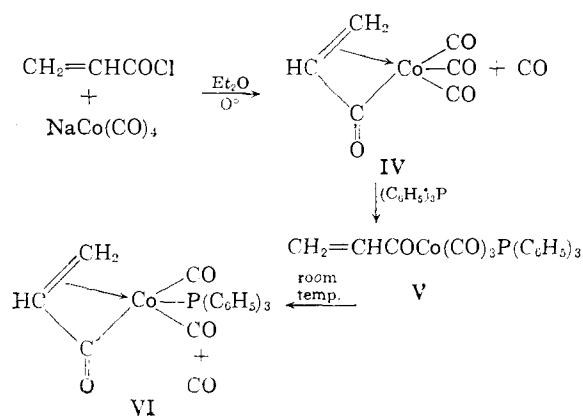
$$C_3H_5Co(CO)_3 + 2CH_2=CHCH_2Br \longrightarrow$$
$$(CH_2=CHCH_2)_2 + CoBr_2 + C_3H_5 (?)$$
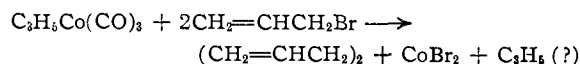
Evidence has been obtained that there is co-ordination of the double bond with cobalt in acrylylcobalt compounds also. The reaction of sodium cobalt tetracarbonyl with a slight excess of acrylyl chloride led to the evolution of about 0.9 mole of CO per cobalt. Whereas the carbonyl linkage in a simple acylcobalt compound absorbs at 5.8 μ, the complex in this case had a carbonyl peak at 5.4 μ, indicative of a highly strained system. Addition of iodine to the reaction liberated three moles of CO. Thus, although the complex was too unstable to be isolated pure, it appears reasonable to conclude that the double bond is coördinated with the metal atom in acrylylcobalt tricarbonyl (IV). This view was confirmed by the reaction of IV with triphenylphosphine. No gas was evolved, indicating that here, unlike allylcobalt tricarbonyl, triphenylphosphine displaced the double bond rather than CO. The infrared spectrum of the solution appeared to confirm this conclusion. Thus, the 5.4 μ peak in the spectrum of IV had disappeared, and a new carbonyl peak was observed at 6.0 μ; triphenylphosphine shifts the 5.8 μ peak in simple acylcobalt carbonyls to about 5.9 μ[7] and conjugation of the carbonyl with a double bond would be expected to lead to absorption at longer wave lengths. There was also a small peak at 6.11 μ, attributable to a vinyl group. Attempts to isolate acrylylcobalt tricarbonyl triphenylphosphine (V) led to a further change. The yellow, crystalline compound isolated analyzed as acrylylcobalt dicarbonyl triphenylphosphine (VI), indicating that the double bond had recoördinated with the cobalt, displacing CO in the process. The infrared spectrum was in accord with this
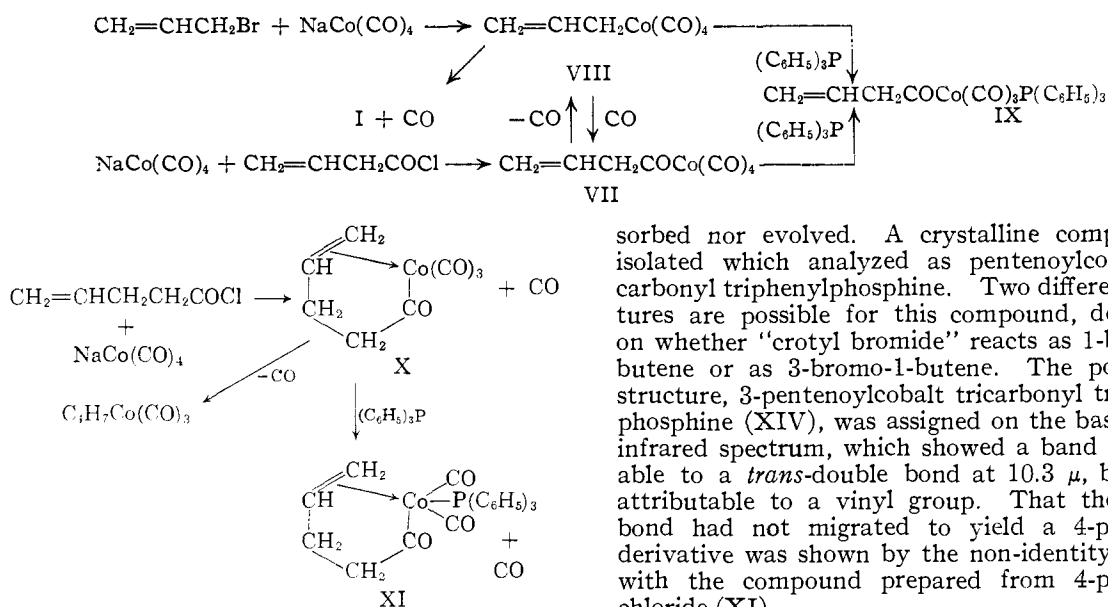
conclusion; the spectrum of VI was very similar to that of IV, the bands being shifted as usual about 0.1 μ to longer wave lengths because of the triphenylphosphine. It is unfortunate that these compounds were too unstable to be studied by proton magnetic resonance. Therefore, we know very little about the actual type of bonding in IV and VI.

The next higher homolog was prepared both with allyl bromide and CO and with 3-butenoyl chloride. When the reaction of allyl bromide with sodium cobalt tetracarbonyl was carried out at 0° in the presence of CO, about 0.5 mole of gas was absorbed. At this point the infrared spectrum of the solution showed a band at 5.8 μ, indicating the presence of an acylcobalt compound (VII), presumably formed from allylcobalt tetracarbonyl (VIII). On standing, gas was slowly evolved and the spectrum changed to that of allylcobalt tricarbonyl (I), which could be isolated by distillation. The same results were obtained with 3-butenoyl chloride and sodium cobalt tetracarbonyl. Initially the solution showed the 5.8 μ band, but about two moles of CO were evolved on standing and compound I was formed. In this case there was no tendency for coördination of the double bond with cobalt. When the allyl bromide–sodium cobalt carbonyl reaction was carried out in the presence of triphenylphosphine, no change in gas volume was observed, and a yellow, crystalline compound which proved to be 3-butenoylcobalt tricarbonyl triphenylphosphine (IX) was isolated; the same compound was formed from VII, prepared from the acid chloride and triphenylphosphine. The infrared spectrum of IX supported the open-chain structure, the spectrum having an acyl band at 6.0 μ and a vinyl band at 6.15 μ.

The importance of ring size on the structure of unsaturated alkyl- or acyl-cobalt carbonyls is shown by the reaction of sodium cobalt tetracarbonyl with 4-pentenoyl chloride. In this reaction, approximately one mole of CO was evolved per cobalt, indicating that in this instance the double bond is coördinated with the cobalt, forming 4-pentenoylcobalt tricarbonyl (X). A band at 5.9 μ in the infrared spectrum showed that an acylcobalt linkage was present, and treatment of the solution with iodine liberated the expected three moles of CO. Attempted isolation of the compound led to the formation of 2-butenylcobalt tricarbonyl by loss of two moles of CO (vide infra). Reaction of X with triphenylphosphine led to the evolution of one mole of CO and formation of 4-pentenoylcobalt dicarbonyl triphenylphosphine (XI), which was isolated as a stable, crystalline solid. Thus, in this instance also triphenylphosphine displaced CO rather than the double bond.

It is interesting that 2-allyl-4-pentenoyl chloride reacts with sodium cobalt tetracarbonyl, evolving only one mole of CO rather than two moles as might be expected. The similarity of the carbonyl spectrum of the product with 4-pentenoylcobalt tricarbonyl suggests the same type of complex is being formed. It is not known whether the second double bond fails to coördinate with the cobalt because it is more difficult to replace the second

$$CH_2=CHCH_2Br + NaCo(CO)_4 \longrightarrow CH_2=CHCH_2Co(CO)_4$$

VIII

$$I + CO \qquad -CO \uparrow \downarrow CO$$

$$(C_6H_5)_3P \downarrow$$

$$CH_2=CHCH_2COCo(CO)_3P(C_6H_5)_3$$
$$IX$$
$$(C_6H_5)_3P \uparrow$$

$$NaCo(CO)_4 + CH_2=CHCH_2COCl \longrightarrow CH_2=CHCH_2COCo(CO)_4$$
$$VII$$

$$CH_2=CHCH_2CH_2COCl \longrightarrow \underset{X}{\overset{CH_2}{\underset{CH_2}{\overset{CH}{\underset{CH_2}{\big|}}}}Co(CO)_3,CO} + CO$$

$$+$$

$$NaCo(CO)_4$$

$$C_7H_7Co(CO)_3 \xleftarrow{-CO}$$

$$\downarrow (C_6H_5)_3P$$

$$\underset{XI}{\overset{CH_2}{\underset{CH_2}{\overset{CH}{\underset{CH_2}{\big|}}}}Co-P(C_6H_5)_3, CO} + CO$$
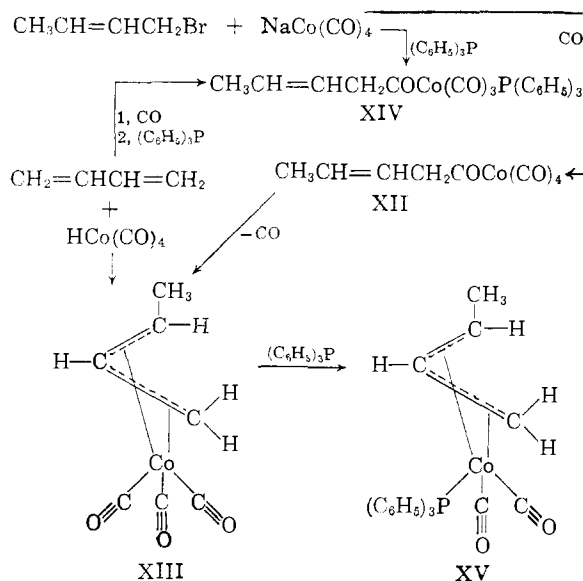
CO or whether the structure is not favorable for further coördination.

The reaction of "crotyl bromide" (the equilibrium mixture of 1-bromo-2-butene and 3-bromo-1-butene) with sodium cobalt tetracarbonyl is similar to the reaction of allyl bromide, and the products shed considerable light on the course of the butadiene–cobalt hydrocarbonyl reaction. Initially, cobalt hydrocarbonyl was thought to add to butadiene to yield $C_8H_7O_4Co$.[10] Subsequently it was shown that one mole of CO was lost during the reaction, the product being $C_7H_7O_3Co$.[11,12]

When "crotyl bromide" was added to excess sodium cobalt tetracarbonyl in the presence of CO at 0°, about 0.5 mole of CO was absorbed. The presence of a 5.8 μ band in the infrared spectrum indicated that an acylcobalt compound had been formed. On standing, this compound evolved CO slowly in an amount equivalent to that originally absorbed plus one mole per cobalt initially present. Thus, the reaction is essentially the same as that found with allyl bromide; presumably 3-pentenoylcobalt tetracarbonyl (XII) is first formed, and this loses CO to yield 2-butenylcobalt tricarbonyl (XIII). The infrared spectrum is identical with that of the compound prepared from butadiene and cobalt hydrocarbonyl. By analogy with allylcobalt tricarbonyl, it appears reasonable to assign a non-classical structure to XIII.[13] Further evidence for these structures was obtained by carrying out the reactions with triphenylphosphine. When "crotyl bromide" was treated with sodium cobalt tetracarbonyl in the presence of CO and triphenylphosphine, gas was neither ab-

(10) W. W. Prichard, U. S. Patent 2,600,571 (1952).

(11) H. B. Jonassen, R. I. Stearns, J. Kenttämaa, D. W. Moore and A. G. Whittaker, *J. Am. Chem. Soc.*, **80**, 2586 (1958).

(12) W. W. Prichard. U. S. Reissue 24,653 (1959).

(13) Although Jonassen and co-workers[14] originally proposed a simple π-bonded structure for XIII, they have recently reported[15] that proton magnetic resonance confirms the symmetrically bonded structure originally suggested by Heck and Breslow.[1]

(14) C. L. Aldridge, H. B. Jonassen and E. Pulkkinen, *Chemistry & Industry*, 374 (1960).

(15) D. W. Moore, H. B. Jonassen, T. B. Joyner and A. J. Bertrand, *ibid.*, 1304 (1960).

sorbed nor evolved. A crystalline complex was isolated which analyzed as pentenoylcobalt tricarbonyl triphenylphosphine. Two different structures are possible for this compound, depending on whether "crotyl bromide" reacts as 1-bromo-2-butene or as 3-bromo-1-butene. The postulated structure, 3-pentenoylcobalt tricarbonyl triphenylphosphine (XIV), was assigned on the basis of the infrared spectrum, which showed a band attributable to a *trans*-double bond at 10.3 μ, but none attributable to a vinyl group. That the double bond had not migrated to yield a 4-pentenoyl derivative was shown by the non-identity of XIV with the compound prepared from 4-pentenoyl chloride (XI).

The 3-pentenoyl compound XIV was formed also when cobalt hydrocarbonyl and CO were added to butadiene at 0° and the reaction mixture treated with triphenylphosphine. The infrared spectrum of the crystalline product isolated differed only slightly from that of the "crotyl bromide" product; the butadiene-derived material probably contained more *cis* isomer. Thus, if the structure assigned to XIV is correct, and the reasonable assumption is made that CO and the phosphine do not affect the course of the initial reaction and allylic rearrangements do not occur, it follows that cobalt hydrocarbonyl reacts with butadiene by 1,4-addition. At higher temperatures, or in the absence of CO, butadiene and cobalt hydrocarbonyl form the 2-butenylcobalt tricarbonyl complex observed by Jonassen[11] and Prichard.[12] When 2-butenylcobalt tricarbonyl (XIII), prepared from "crotyl bromide" and sodium cobalt tetracarbonyl, was treated with triphenylphosphine, CO was evolved and 2-butenylcobalt dicarbonyl triphenyl-

$$CH_3CH=CHCH_2Br + NaCo(CO)_4 \xrightarrow{\quad} \underset{\downarrow (C_6H_5)_3P}{\quad} CO$$

$$\longrightarrow CH_3CH=CHCH_2COCo(CO)_3P(C_6H_5)_3$$
$$XIV$$

$$\begin{array}{l} 1, CO \\ 2, (C_6H_5)_3P \end{array}$$

$$CH_2=CHCH=CH_2 \qquad CH_3CH=CHCH_2COCo(CO)_4$$
$$+ \qquad\qquad\qquad XII$$
$$HCo(CO)_4 \qquad \xrightarrow{-CO}$$

$$XIII \qquad\qquad\qquad XV$$

phosphine (XV) was isolated as a crystalline compound.

Although only a limited number of experiments was carried out, 2,3-dimethyl-1,3-butadiene appeared to react in the same manner as butadiene. Thus, treatment with cobalt hydrocarbonyl led to the absorption of CO. Gas was evolved upon addition of triphenylphosphine, and a compound was isolated which analyzed as the 3,4-dimethyl analog of XIV.

Acknowledgment.—The authors wish to acknowledge the assistance of Dr. James C. W. Chien in the n.m.r. determinations and of Mr. Anthony J. Testa with experimental work.

Experimental

All of the cobalt compounds described here are more or less air-sensitive, particularly in solution, and were protected as much as possible by working under an inert atmosphere. Hypodermic syringes were usually used for transferring solutions from one container to another. Samples were removed from or injected into bottles through Neoprene liners which were held in place by metal caps with two small holes in them.

Gas volume changes during reactions were determined in a standard thermostated microhydrogenation-type apparatus. The apparatus was flushed several times with the gas to be used in the apparatus before the reaction was begun. The gas used was always presaturated with the solvent at the temperature being used in the reaction. Air-stable solids could be placed in the reaction flask before flushing, or they could be added in solution as was done with air-sensitive material. These solutions were injected into the reaction flask through a side arm provided with a stopcock and closed by a rubber stopple on the end. Reaction mixtures were stirred magnetically.

Infrared spectra were taken on a Perkin–Elmer model 137 Infracord spectrophotometer with the exception of the allylcobalt tricarbonyl spectrum, which was measured on a Beckman model IR-4. The infrared cells were sealed with rubber stopples and flushed with nitrogen before air-sensitive samples were injected into the cells.

Allylcobalt Tricarbonyl (I).—Allyl bromide (0.5 ml., 5.8 mmoles) was added under nitrogen to 1.50 g. (0.77 mmole) of sodium cobalt tetracarbonyl[3] dissolved in 25 ml. of dimethyl ether at 0° in a capped bottle. After reacting at 0° overnight the solvent was distilled off at 0° and the residue extracted with three 2-ml. portions of n-pentane. The extracts were centrifuged to remove insolubles and then concentrated to about 2 ml. The solution was cooled to −100° to initiate crystallization and then kept at −80° until crystallization was complete. The compound was recrystallized twice more from n-pentane at −80° and dried by several distillations in high vacuum, m.p. −33 to −32°. The n.m.r. absorptions at 60 megacycles were at 286, 232 and 114 c.p.s. (2:2:1) referred to an external benzene reference. The infrared spectrum of this material had bands at 3.27(w), 3.33(w), 3.42(vw), 4.86(s), 5.00(vs), 6.72(w), 6.80(w), 7.21(w), 8.17(w), 8.34(w), 8.42(w), 8.88(w), 9.83(w), 10.55(w), 10.75(w) in CCl₄, and at 12.73(w) and 13.00(w) μ in CS₂.

Anal. Calcd. for $C_5H_5O_3Co$: CO, 45.6; Co, 32.0. Found: CO (by treatment with I_2 in methanol), 44.8; Co, 31.5, 31.1.

The above procedure is best for isolating allylcobalt tricarbonyl. However, the gas volume changes occurring during the reaction were best investigated in diethyl ether. For this purpose 50 ml. of 0.07 M sodium cobalt tetracarbonyl was placed in a gasometric apparatus at 0° under CO. To this stirred solution was added 0.2745 g. (2.27 mmoles) of allyl bromide. In 76 minutes 0.83 mmole of gas was absorbed. Then gas absorption stopped and evolution began. At this point the infrared spectrum of the solution showed a new carbonyl band at 5.9 μ which disappeared within 5 minutes at 25°. On standing at 0° the reaction mixture slowly evolved additional CO, 2.3 mmoles being evolved in addition to that absorbed initially. The infrared spectrum of the resulting solution was identical with that of the pure compound obtained in the above preparation.

1,5-Hexadiene from Allyl Bromide.—Allyl bromide (0.2 ml., 2.3 mmoles) was injected into 10 ml. of 0.07 M sodium cobalt tetracarbonyl in ether solution under nitrogen and the solution was shaken and left at room temperature overnight. Analysis of the green solution by mass spectroscopy showed it to contain 1.04 mole per cent. of 1,5-hexadiene in addition to 1.5 mole per cent. of unreacted allyl bromide; theory, 1.4 mole per cent. of 1,5-hexadiene.

Allylcobalt Dicarbonyl Triphenylphosphine (III).—To an ether solution of allylcobalt tricarbonyl prepared as above at 25° was added a slight excess of a 1 M solution of triphenylphosphine in ether. In a few minutes 1 mmole of CO was evolved per mmole of allylcobalt tricarbonyl. The triphenylphosphine complex was isolated in good yield by evaporating the solvent and recrystallizing the complex from a mixture of methylene chloride and n-pentane. Large yellow prisms were obtained, m.p. 132° dec. The infrared spectrum of this complex had bands at 3.28(w), 3.35(vw), 4.86(w), 5.01(s), 5.18(vs), 6.29(vw), 6.79(w), 7.00(m), 7.30(vw), 7.70(vw), 8.20(vw), 8.48(w), 8.96(w), 9.16(m), 9.37(vw), 9.72(w), 9.88(vw), 10.02(vw), 10.65–11.10(vw) in CCl₄, and at 11.83(vw), 13.42(m), 14.25(s) and 14.40(s) μ in CS₂.

Anal. Calcd. for $C_{23}H_{20}O_2PCo$: C, 66.03; H, 4.82. Found: C, 66.23, 66.36; H, 5.34, 5.23.

Acrylylcobalt Tricarbonyl (IV).—Acrylyl chloride (1.5 ml. of 1.1 M solution in ether) was added at 0° to 15 ml. of 0.07 M sodium cobalt tetracarbonyl in ether under CO. The resulting bright yellow solution evolved 0.97 mmole of CO in 30 minutes and the reaction stopped. The infrared spectrum of the solution showed absorption at 4.81(m), 4.95(vs), and 5.42(m) μ. Treatment with 25 ml. of 0.20 M iodine in methanol resulted in the evolution of 3.25 mmoles of CO. The complex could be isolated from the solution by distillation at low temperatures in high vacuum, but it was very unstable and could not be obtained in a pure state.

Acrylylcobalt Dicarbonyl Triphenylphosphine (VI).—Acrylylcobalt tricarbonyl was prepared from 30 ml. of 0.07 M sodium cobalt tetracarbonyl in ether and 3 ml. of 1.1 M acrylyl chloride in ether under CO as described above. When gas evolution stopped, a 1.0 M solution of triphenylphosphine in ether (3.5 ml.) was added. After 1 hour at 0° there was little if any change in the gas volume. The solution was centrifuged to remove insoluble salts and concentrated at 25–30°. The solution was filtered cold (−80°) and the yellow, crystalline solid was recrystallized from tetrahydrofuran–n-pentane. The product darkened at 100° and decomposed at about 106–107° without melting. The infrared spectrum of this material had bands at 3.29 (vw), 4.93(s), 5.06(vs), 5.56(m), 6.78(w), 7.00(m), 7.59(vw), 8.10(vw), 8.45(vw), 9.14(m), 9.75(w), 10.25(vw), 10.93(m) in CCl₄, and at 13.42(m), 14.20(m) and 14.41(s) μ in CS₂. The material was too insoluble for molecular weight determination in benzene and too unstable for n.m.r. determination.

Anal. Calcd. for $C_{23}H_{18}O_3PCo$: C, 63.90; H, 4.20. Found: C, 63.93; H, 4.34.

Acrylylcobalt carbonyl complexes with triphenylarsine, tri-p-anisylphosphine, tri-n-butylphosphine and trimethyl phosphite were also prepared, judging from the infrared spectra, but they could not be isolated in the crystalline state. Obviously they were quite unstable also.

3-Butenoylcobalt Tricarbonyl Triphenylphosphine (IX) from 3-Butenoyl Chloride.—To 15 ml. of 0.07 M sodium cobalt tetracarbonyl in ether at 0° was added 1.5 ml. of 1.0 M 3-butenoyl chloride in ether. After 10 minutes at 0°, 2.0 ml. of 1.0 M triphenylphosphine in ether was added. The carbonyl infrared spectrum of the solution after 1 hour at 0° was identical with the spectrum of the compound prepared below. If triphenylphosphine was not added, in several days about 2 moles of CO was evolved per mole of cobalt. Distillation of the solution in high vacuum led to the isolation of allylcobalt tricarbonyl.

3-Butenoylcobalt Tricarbonyl Triphenylphosphine (IX) from Allyl Bromide.—A mixture of 15 ml. of 0.07 M sodium cobalt tetracarbonyl in ether and 2.0 ml. of 1.0 M triphenylphosphine in ether was stirred at 0° and 1.0 ml. of allyl bromide (11.6 mmoles) was added. The solution turned yellow-red but gas was not evolved. After 30 minutes the solution was centrifuged to remove the inorganic salts. Evaporation left a yellow oil which crystallized on stirring with n-pentane. The compound was recrystallized three

times from ether–n-pentane. The yellow, microcrystalline compound melted at 82° with decomposition, with previous darkening at 75°. The infrared spectrum of this material had bands in CS_2 at 3.28(w), 4.90(m), 5.10(vs), 5.99(s), 6.15(w), 7.28(vw), 7.55(vw), 7.70(vw), 7.96(vw), 8.45(w), 9.14(m), 9.36(vw), 9.72(w), 10.01(w), 10.11(w), 10.40(w), 10.90(w), 11.43(w), 13.40(s), 14.13(s) and 14.42(s) μ. The compound decomposed rapidly in CCl_4, but two additional bands were observed in this solvent at 6.77(m) and 7.00(vs) μ.

Anal. Calcd. for $C_{25}H_{20}O_4PCo$: C, 63.30; H, 4.25 Found: C, 63.76, 64.00; H, 4.71, 4.63.

4-Pentenoylcobalt Tricarbonyl (X).—In the gasometric apparatus under CO at 0° was placed 25 ml. of 0.07 M sodium cobalt tetracarbonyl in ether. To the stirred solution was added 0.2540 g. (2.15 mmoles) of 4-pentenoyl chloride. After 280 minutes, 1.63 mmoles of CO had been evolved and evolution stopped. The infrared spectrum of the solution had bands at 4.81(s), 4.92(vs), 4.98(vs) and 5.87 (m) μ, indicating 4-pentenoylcobalt tricarbonyl was produced. Evaporation of the solvent and distillation of the yellow residue in high vacuum at 35° led to the isolation of a yellow oil with infrared bands at 4.85 and 5.03 μ, indicating that 2-butenylcobalt tricarbonyl (XIII) had been obtained. In another experiment 4-pentenoylcobalt tricarbonyl was prepared from 15 ml. of 0.07 M sodium cobalt tetracarbonyl in ether and 1.5 ml. of 0.9 M 4-pentenoyl chloride in ether. In 4 hours 0.94 mmole of CO was evolved. To this solution was added 10 ml. of 0.2 M KI–I_2 solution in water. In 20 minutes 3.26 mmoles of CO evolved.

4-Pentenoylcobalt Dicarbonyl Triphenylphosphine (XI).—4-Pentenoylcobalt tricarbonyl was prepared as above from 30 ml. of 0.07 M sodium cobalt tetracarbonyl in ether. In 2 hours 1.86 mmoles of CO were evolved. Now 3.5 ml. of 1.10 M triphenylphosphine in ether was added. In 30 minutes 1.77 mmoles of CO was evolved and the reaction stopped. The solution was evaporated to dryness at 0°. The light-colored residue was extracted three times with small portions of methylene chloride, the extracts were centrifuged to remove insoluble material, and were then evaporated to about 1 ml. Addition of n-pentane resulted in the crystallization of the complex. Several recrystallizations from tetrahydrofuran and n-pentane at −80° gave the pure complex, m.p. 106.5–107° with gas evolution. The infrared spectrum of this material had bands at 3.25(w), 3.40(vw), 4.91(m), 5.06 (s), 5.92(m), 6.73(w), 6.98(w), 9.12(w), 9.70(vw), 9.98(vw), 10.31(w), 11.50(w) in CCl_4, and at 12.40(vw), 13.42(m), 14.20(m) and 14.40(m) μ in CS_2.

Anal. Calcd. for $C_{25}H_{22}O_3PCo$: C, 65.21; H, 4.82. Found: C, 64.87, 64.99; H, 4.96, 4.91.

2-Allyl-4-pentenoyl Chloride Reaction with Sodium Cobalt Tetracarbonyl.—2-Allyl-4-pentenoic acid was prepared by the acetoacetic ester synthesis with allyl bromide; the acid chloride was prepared from the acid and thionyl chloride, b.p. 49.5–52° (3.0 mm.). In the gasometric apparatus filled with CO at 0° was placed 25 ml. of 0.07 M sodium cobalt tetracarbonyl. To this was added 2.0 g. (12.3 mmoles) of 2-allyl-4-pentenoyl chloride. The solution turned yellow and gas was slowly evolved, 1.45 mmoles of CO being collected after standing overnight at 0°. The infrared spectrum of the solution was very similar to that of 4-pentenoylcobalt tricarbonyl. After several hours at room temperature the infrared spectrum was unchanged. After several days at room temperature, however, the spectrum indicated an allyl-cobalt tricarbonyl-type complex was beginning to form.

2-Butenylcobalt Tricarbonyl (XIII).—To a stirred solution of 50 ml. of 0.07 M sodium cobalt tetracarbonyl in ether at 0° under CO was added 0.3167 g. (2.35 mmoles) of freshly distilled "crotyl bromide" (equilibrium mixture of 1-bromo-2-butene and 3-bromo-1-butene). The solution turned yellow and in 1 hour 1.25 mmoles of CO was absorbed; then gas evolution began. The infrared spectrum taken at this point showed a carbonyl band at 5.8 μ which disappeared on standing at room temperature for a short time. Gas evolution was slow at 0°, several days being required for evolution of the total amount (the amount initially absorbed plus 1 mmole per mmole of "crotyl bromide" added). At 25° the reaction was much more rapid. Distillation of the reaction mixture yielded an orange liquid. The infrared spectrum of the liquid was identical with that of the compound obtained in the reaction of cobalt hydrocarbonyl with butadiene.[14] The carbonyl groups absorbed at 4.85(s) and 5.03 (vs) μ.

3-Pentenoylcobalt Tricarbonyl Triphenylphosphine (XIV).—To a mixture of 30 ml. of 0.07 M sodium cobalt tetracarbonyl and 2.5 ml. of 1.0 M triphenylphosphine in ether at 0° under CO was added 3.0 ml. of 0.9 M "crotyl bromide" in ether. The solution turned yellow, but there was no gas volume change. After an hour at 0° the solvent was evaporated *in vacuo* at 0° and the complex was extracted with several portions of ether. The extracts were centrifuged to remove insoluble materials, evaporated to dryness, and the yellow, crystalline solid obtained was recrystallized three times from tetrahydrofuran–n-pentane at −80°. The product, obtained in good yield, had no definite melting point but darkened at about 80–96°. The infrared spectrum had bands at 3.26(w), 3.40(w), 3.50(w), 4.88(m), 5.06(vs), 5.96(s), 6.25(w), 6.76(m), 6.98(m), 7.65(w), 8.41(w), 9.11 (m), 9.33(w), 9.70(w), 9.99(w), 10.30(m) and 11.10(m) μ in CCl_4, and at 12.90(w), 13.40(s), 14.13(s), 14.11(vs), and 14.80(w) μ in CS_2.

Anal. Calcd. for $C_{26}H_{22}O_4PCo$: C, 63.94; H, 4.54. Found: C, 64.04; H, 4.83.

2-Butenylcobalt Dicarbonyl Triphenylphosphine (XV).—2-Butenylcobalt tricarbonyl was prepared from 30 ml. of 0.07 M sodium cobalt tetracarbonyl in ether and 3.0 ml. of 0.9 M "crotyl bromide" in ether at 25° as described above. To the solution at 25° was added 2.5 ml. of 1.0 M triphenylphosphine in ether. In 20 minutes gas evolution was complete and the solution was evaporated to dryness *in vacuo*. The complex was extracted with several portions of ether, centrifuged, the solvent evaporated, and the orange-red, crystalline complex was recrystallized three times from tetrahydrofuran–n-pentane at −80°, m.p. 91.5–94° with decomposition. The infrared spectrum of this compound had bands at 3.25(w), 3.38(m), 3.49(w), 4.87(w), 5.01(vs), 5.17(vs), 5.53(vw), 6.01(vw), 6.25(w), 6.76(m), 6.98(m), 7.29(w), 7.52(w), 7.67(w), 7.90(vw), 8.12(w), 8.42(w), 8.92(w), 9.12(m), 9.32(w), 9.70(m), 9.99(w), 10.15(vw), 10.30(vw), 10.92(w) and 11.40(vw) μ in CCl_4, and at 11.85 (w), 13.40(m), 14.22(m) and 14.39(s) μ in CS_2.

Anal. Calcd. for $C_{24}H_{22}O_2PCo$: C, 66.67; H, 5.13. Found: C, 66.69; H, 5.46.

Addition of Cobalt Hydrocarbonyl and CO to Butadiene.—Thirty ml. of butadiene was injected into a capped bottle containing 20 p.s.i. of CO at 0°. The solution was stirred at 0° and 5.0 ml. of 0.41 M cobalt hydrocarbonyl in n-pentane was added. After 1 hour at 0°, 2.5 ml. of 1.0 M triphenylphosphine in ether was added. After 30 minutes further stirring at 0° the solution was evaporated to dryness *in vacuo* and the complex was extracted from the orange residue with several portions of ether. The extracts were centrifuged to remove insoluble $[Co(CO)_3P(C_6H_5)_3]_2$ and then evaporated to a small volume. Addition of n-pentane and cooling caused crystallization of the yellow complex. Two further crystallizations from ether–n-pentane gave a moderate yield of yellow crystals of the complex. The infrared spectrum of this complex was practically identical with that of 3-pentenoylcobalt tricarbonyl triphenylphosphine (XIV) described above, the only differences being slightly stronger absorption at 13.85 μ and weaker absorption at 9.33 μ and 10.30 μ. The infrared spectrum of the mother liquors from the recrystallizations failed to show the presence of any 2-butenylcobalt dicarbonyl triphenylphosphine (XV). A Nujol mull of the ether-insoluble product showed only the bands of $[Co(CO)_3P(C_6H_5)_3]_2$, with no indication of any other complexes being present.

Anal. Calcd. for $C_{26}H_{22}O_4PCo$: C, 63.94; H, 4.54. Found: C, 64.55; H, 4.98.

Addition of Cobalt Hydrocarbonyl and CO to 2,3-Dimethyl-1,3-butadiene.—In the gasometric apparatus filled with CO at 0° were placed 30 ml. of 2,3-dimethyl-1,3-butadiene and 3.0 ml. of 0.42 M cobalt hydrocarbonyl in n-pentane. In 6 minutes 0.94 mmole (69% of theory) of CO was absorbed and the reaction stopped. At this point 2.0 ml. of 1.0 M triphenylphosphine in ether was added. In 1.5 hours 1.15 mmoles of CO was evolved. The solution was evaporated to dryness *in vacuo* at 0° and the complex was extracted with several portions of ether. Evaporation of the ether to a small volume, followed by the addition of n-pentane and cooling, led to the formation of yellow crystals of 3,4-dimethyl-3-pentenoylcobalt tricarbonyl triphenylphosphine. Another recrystallization from ether–n-pentane gave the pure complex, which decomposed at about 95° with

previous darkening at 65°. The infrared spectrum had bands at 3.28(w), 3.36(w), 3.42(w), 3.50(w), 4.88(m), 5.07 (vs), 5.98(s), 6.30(vw), 6.38(vw), 6.75(m), 6.98(m), 7.10 (vw), 7.28(w), 7.52(vw), 7.67(w), 7.82(w), 8.01(vw), 8.31 (w), 8.42(w), 8.65(w), 8.95(w), 9.11(m), 9.31(w), 9.71(w),

10.00(w), 10.30(vw), 10.77(w) and 11.40(w) μ in CCl$_4$, and at 13.10(m), 13.40(s), 14.15(s), 14.41(vs) and 14.95(m) μ in CS$_2$.

Anal. Calcd. for C$_{28}$H$_{26}$O$_4$PCo: C, 65.12; H, 5.08. Found: C, 65.41; H, 5.29.

Hydrolysis and Exchange in Esters of Phosphoric Acid[1a,b]

BY PAUL C. HAAKE[1c] AND F. H. WESTHEIMER

The acid-catalyzed hydrolysis of ethylene hydrogen phosphate in water enriched in ^{18}O is accompanied by exchange of heavy oxygen into the unreacted ester. The ratio of the rate of hydrolysis to the rate of exchange is about 5. This ratio, under somewhat different experimental conditions, is about 20 for dimethyl hydrogen phosphate and about 5 for methyl dihydrogen phosphate. Previous work has shown that ethylene hydrogen phosphate hydrolyzes about 10^7 as fast as does dimethyl hydrogen phosphate, and thermochemical studies have suggested that the large difference in rate is largely caused by strain in the cyclic ester. The results of the present work show that the exchange reaction, as well as the hydrolysis, has been strongly accelerated in ethylene hydrogen phosphate. Since strain is not relieved in the product of the exchange reaction (as it is in that of hydrolysis) these findings bear on the mechanism of the exchange reaction of phosphate esters. The argument is advanced that, provided that hydrolysis and exchange occur by parallel mechanisms, the activated complexes for the acid hydrolysis and exchange of these phosphates do not have the usual configuration for S_N2 displacement reactions. An activated complex with the geometry of a trigonal bipyramid or of a square pyramid, with reaction at a basal position in either case, is in accord with the experimental evidence. Additional chemistry of exchange and hydrolysis is presented and discussed.

The hydrolysis of five-membered cyclic esters of phosphoric acid is enormously more rapid than that of the corresponding open-chain analogs.[2] In particular, salts of ethylene phosphate[3,4] hydrolyze in alkali about 10^7 times as fast as do those of dimethyl phosphate, and ethylene hydrogen phosphate hydrolyzes in acid[5,6] about 10^7 times as fast as does dimethyl hydrogen phosphate. Salts of trimethylene phosphate, however, hydrolyze only slightly faster than those of dimethyl phosphate.[7,8]

The effect of structure on the lability of cyclic phosphates thus differs sharply from that for lactones,[9] where the six-membered lactone hydrolyzes most rapidly, and where the maximum rate factor (*ca.* 6,500) is much smaller than that for the phosphates. The proximate cause of the rapid hydrolysis of the five-membered cyclic phosphate esters has been shown to lie in strain in the ester itself; the heat of hydrolysis of methyl ethylene phosphate exceeds that for dimethyl hydroxyethyl phosphate by about 7–9 kcal./mole.[10]

In the present work, the position of cleavage of ethylene and dimethyl phosphates in both acid and base has been investigated using ^{18}O as tracer. The cyclic ester hydrolyzes (within experimental error) exclusively with P–O cleavage, whereas dimethyl phosphate (as anion or acid) hydrolyzes in large part with C–O cleavage. Therefore the rate of hydrolysis of ethylene phosphate anion or of ethylene hydrogen phosphate exceeds the corresponding rate for dimethyl phosphate at the P–O bond by a factor of 10^8 or more. Further investigations measured the exchange which accompanies hydrolysis (eq. 1), modeled on Bender's pioneering study of the hydrolysis of esters of carboxylic acids.[11]

$$\tag{1}$$
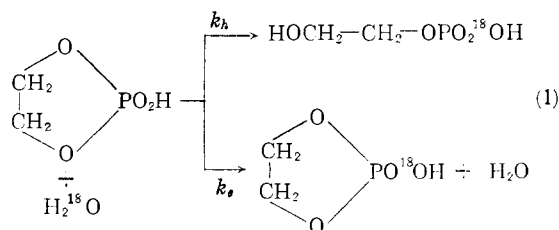
Oxygen exchange accompanies the hydrolysis of ethylene phosphate in acid solution, but not in base. The conclusion can reasonably be drawn that the exchange of ^{18}O into ethylene hydrogen phosphate has been strongly accelerated (as is hydrolysis) relative to the rate for an open-chain phosphate ester. On the basis of these facts, the geometry of the transition state for the acid hydrolysis and exchange of these phosphate esters may be partially delineated.

Experimental

Materials.—Barium ethylene phosphate, prepared by Cox,[4,6] was recrystallized from ethanol-water. The sample was bromide-free, and the structure previously assigned to

(1) (a) Presented at the Gordon Conference on Isotopes, New Hampton, New Hampshire, July 6, 1960. (b) Mono- and diesters are named specifically where possible (*e.g.*, dimethyl hydrogen phosphate, or dimethyl phosphate anion); where it is impossible to specify, the general name (*e.g.*, dimethyl phosphate) is used. (c) U. S. Rubber Fellow, 1957–1958; N. S. F. Fellow, 1958–1960.

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