

## ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO., WILMINGTON 99, DEL.]

## The Addition of Acyl- and Alkylcobalt Carbonyls to Conjugated Dienes

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RECEIVED APRIL 24, 1963

Alkyl- and acylcobalt tetracarbyls have been found to react readily with a wide variety of conjugated dienes to produce 1-acylmethyl- $\pi$ -allylcobalt tricarbonyls. These compounds react with triphenylphosphine, with the evolution of carbon monoxide, to form easily isolable mono-(triphenylphosphine) derivatives.

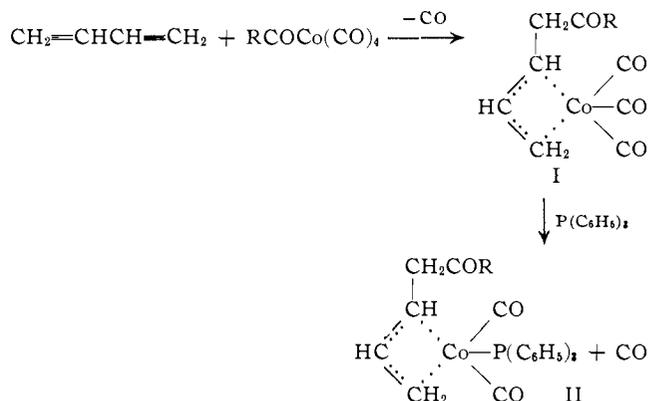
## Introduction

Acylcobalt carbonyls are very reactive compounds. Previously we found that the acylcobalt group would react with hydrogen,<sup>1</sup> sodium alkoxides,<sup>2</sup> and sometimes with olefin groups.<sup>3</sup> As a continuation of the study of the reactions of acylcobalt carbonyls, the reaction with conjugated dienes is now reported.

## Results

Acylcobalt tetracarbyls in ether solution at 25° react readily with excess conjugated dienes, with the evolution of about a mole of carbon monoxide, to form new yellow to red complexes. The reaction ordinarily requires a few hours for completion at 25°. The infrared spectra of the new complexes have bands at about 4.85 (s), 5.00 (vs), and at 5.8 (m)  $\mu$ . Decomposition with iodine of the typical complex from butadiene and acetylcobalt tetracarbyl leads to the evolution of about 3 moles of carbon monoxide per mole of cobalt present, indicating that there are probably three coordinated carbon monoxide groups per molecule present. The complexes can be isolated as such but they are generally low melting, very soluble in organic solvents, and are readily oxidized by air. It is much more convenient to isolate the complexes as their mono-(triphenylphosphine) derivatives. These are easily obtained by adding triphenylphosphine to solutions of the complexes, whereupon a mole of carbon monoxide is evolved and the monophosphine derivatives are produced. Even with a large excess of the phosphine only monoderivatives are formed. These derivatives are higher melting, less soluble, and less air sensitive than the carbonyl compounds from which they are prepared. Elemental analyses show that the triphenylphosphine derivatives are complexes containing one triphenylphosphine group, one acyl group, one diene molecule, and two carbon monoxides per cobalt atom. The infrared spectra of the monophosphine derivatives have three carbonyl bands as before, but the two coordinated carbonyl bands are shifted from about 4.85 and 5.00  $\mu$  to 5.00 and 5.15  $\mu$ , respectively, while the other carbonyl band is hardly affected. Clearly the latter carbonyl group is not directly attached to cobalt or it would have been affected by the triphenylphosphine substitution.<sup>4</sup> The data are consistent with the products being 1-acylmethyl derivatives of  $\pi$ -allylcobalt tricarbonyl (I) or dicarbonyl triphenylphosphine (II).

Indeed these compounds are very similar to  $\pi$ -allyl- and  $\pi$ -crotylcobalt tricarbonyls and their phosphine derivatives described previously.<sup>5</sup> As expected, the same compounds can also be prepared from alkyl-



cobalt tetracarbyls and conjugated dienes. The complexes can be prepared in a single, very simple reaction and in good yield merely by mixing the diene with sodium cobalt tetracarbyl in ether solution and adding an alkyl halide. The rate of reaction, of course, depends upon the reactivity of the halide. Methyl iodide reacts in a few minutes while some other halides require many hours. Of course, acid halides can be used in the same reaction. Generally the acid chloride reaction is slower than the reactions with methyl or ethyl iodide. Presumably both the alkyl- and the acylcobalt tetracarbyls must form the reactive acylcobalt tricarbonyls by isomerization and dissociation, respectively, before they can react with a diene. Thus, on this basis, the rate of dissociation of the acylcobalt tetracarbyl must be much slower than the rate of isomerization of the alkylcobalt tetracarbyls. As an example of the difference between the alkyl and acyl halide reactions, acetylcobalt tetracarbyl requires about 24 hr. to react completely with 2,3-dimethylbutadiene while under the same conditions, but under nitrogen instead of carbon monoxide, methylcobalt tetracarbyl reacts completely in less than 30 min. Yields are comparable by both methods. The alkyl halide reactions are easily followed by observing the disappearance of the cobalt carbonyl anion band at 5.3  $\mu$ ; the acyl halide reaction, by the amount of carbon monoxide evolved.

The alkyl- or acylcobalt tetracarbyl-diene reaction is a very general one. In Table I are listed the reactions of methylcobalt tetracarbyl with eight different conjugated dienes. Also, which alkyl- or acylcobalt tetracarbyl is used makes little difference (most of the evidence for this statement will appear in the following paper).

The 1-substituted  $\pi$ -allylcobalt tricarbonyl complexes may exist in two isomeric forms, *endo* and *exo*, depending upon whether the 1-substituent is close to or away from the cobalt atom.<sup>6,7</sup> The n.m.r. spectra of one of the complexes, the methylcobalt tetracarbyl-

(1) R. F. Heck and D. S. Breslow, "Actes du Deuxieme Congres International de Catalyse," Paris, 1960, Vol. 1, Editions Technip, p. 671; *Chem. Ind. (London)*, 467 (1960).

(2) R. F. Heck and D. S. Breslow, "Advances in the Chemistry of the Coordination Compounds," The MacMillan Co., New York, N. Y., 1961, p. 281.

(3) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 3116 (1963).

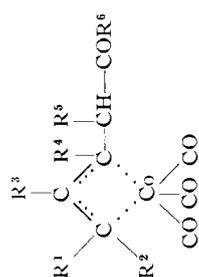
(4) R. F. Heck and D. S. Breslow, *ibid.*, **84**, 2499 (1962).

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

(6) D. W. Moore, H. B. Jonassen, and T. B. Joyner, *Chem. Ind. (London)*, 1304 (1960).

(7) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muettterties, and B. W. Hawk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

TABLE I  
THE REACTION OF METHYLCOBALT TETRACARBONYLS WITH CONJUGATED DIENES



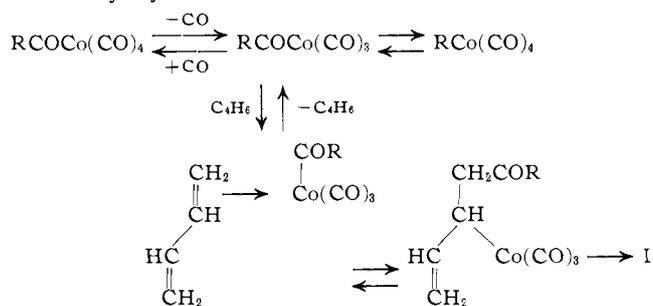
Conjugated diene	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>	R <sup>6</sup>	M. p., °C.	Triphenylphosphine derivative		Formula	Carbon, %		Hydrogen, %	
								Calcd.	Found		Calcd.	Found		
Butadiene	H	H	H	H	H	CH <sub>3</sub>	87-91 dec.	65.83	65.48	C <sub>26</sub> H <sub>24</sub> O <sub>3</sub> P <sub>3</sub> Co	65.83	5.10	5.28	
Isoprene	H	H	CH <sub>3</sub>	H	H	CH <sub>3</sub> <sup>a</sup>	107.5-108.5 dec.	66.40	66.51	C <sub>27</sub> H <sub>26</sub> O <sub>3</sub> P <sub>3</sub> Co	66.40	5.37	5.45	
2,3-Dimethylbutadiene	H	H	CH <sub>3</sub>	CH <sub>3</sub>	H	CH <sub>3</sub>	101-103 dec.	66.93	67.22	C <sub>28</sub> H <sub>28</sub> O <sub>3</sub> P <sub>3</sub> Co	66.93	5.62	6.04	
<i>cis</i> -Piperylene	H	H	H	H	CH <sub>3</sub>	CH <sub>3</sub> <sup>a</sup>	106.5-107.5 dec.	66.40	66.51	C <sub>27</sub> H <sub>26</sub> O <sub>3</sub> P <sub>3</sub> Co	66.40	5.37	5.55	
4-Methyl-1,3-pentadiene	CH <sub>3</sub>	CH <sub>3</sub>	H	H	H	CH <sub>3</sub>	120 dec.	66.93	66.92	C <sub>28</sub> H <sub>28</sub> O <sub>3</sub> P <sub>3</sub> Co	66.93	5.62	5.84	
Cyclopentadiene	R <sup>1</sup> = R <sup>4</sup> = -(CH <sub>2</sub> ) <sub>2</sub> -	H	H	R <sup>1</sup> = R <sup>4</sup> = -(CH <sub>2</sub> ) <sub>2</sub> -	H	CH <sub>3</sub>	None	66.67	67.06	C <sub>27</sub> H <sub>24</sub> O <sub>3</sub> P <sub>3</sub> Co	66.67	4.97	5.25	
<i>trans</i> -1-Methoxybutadiene	CH <sub>3</sub> O	H	H	H	H	CH <sub>3</sub>	108.5-110.5 dec.	64.29	64.77	C <sub>27</sub> H <sub>26</sub> O <sub>3</sub> P <sub>3</sub> Co	64.29	5.20	5.54	
Methyl sorbate	CH <sub>3</sub> OCO	H	H	H	CH <sub>3</sub>	CH <sub>3</sub> <sup>b</sup>	85 dec.	63.74	63.75	C <sub>23</sub> H <sub>20</sub> O <sub>3</sub> P <sub>3</sub> Co	63.74	5.17	5.48	
Isoprene <sup>c</sup>	H	H	CH <sub>3</sub>	H	H	CH <sub>3</sub> CH <sub>2</sub> <sup>d</sup>	93-95 dec.	66.93	67.02	C <sub>28</sub> H <sub>28</sub> O <sub>3</sub> P <sub>3</sub> Co	66.93	5.62	6.06	

<sup>a</sup> Structure determined in *J. Am. Chem. Soc.*, **85**, 3383 (1963). <sup>b</sup> Structure not proved. <sup>c</sup> Reacted with ethylcobalt tetracarbonyl. <sup>d</sup> Structure assumed to be similar to the methylcobalt tetracarbonyl product.

*cis*-piperylene complex, was obtained and indications are that the acylmethyl group is in the *exo* position. Presumably this isomer is the most stable in the other cases also. Isomers are also possible when unsymmetrical dienes are used in the reaction. Some of these isomers have been identified, although it is not certain that the isomer identified is the only one formed. The structure of the methylcobalt tetracarbonyl-isoprene product was established unambiguously by a degradation reaction which is the subject of the following paper. The *cis*-piperylene-methylcobalt tetracarbonyl complex was identified by the n.m.r. spectrum of its triphenylphosphine derivative. The structure given for the 4-methyl-1,3-pentadiene-methylcobalt tetracarbonyl complex is only a guess based upon the assumption that the acyl group will be added to the less substituted position of the diene. The structure of the *trans*-1-methoxybutadiene-methylcobalt tetracarbonyl complex is based upon the fact that the first-order rate of reaction of this complex with triphenylphosphine at 25° in ether solution ( $2.24 \pm 0.15 \times 10^{-4}$  sec.<sup>-1</sup>) is about one-thirty-fifth as fast as the rate of reaction of the corresponding complex without the methoxyl group, 1-acetylmethyl- $\pi$ -allylcobalt tricarbonyl (about  $8.0 \times 10^{-3}$  sec.<sup>-1</sup> at 25°, calculated from the rate at 0°,  $2.24 \pm 0.11 \times 10^{-4}$  sec.<sup>-1</sup>, assuming an activation energy the same as observed for  $\pi$ -allylcobalt tricarbonyl, 22.75 kcal.<sup>8</sup>). To produce such a large effect, the methoxyl group must be attached directly to the  $\pi$ -allyl ring rather than to the side chain. The structure of the methyl sorbate-methylcobalt tetracarbonyl complex was arrived at by assuming the acyl group was added to the end of the conjugated chain. The ethylcobalt tetracarbonyl-isoprene complex is assumed to have the same structure as the corresponding methylcobalt tetracarbonyl complex. Admittedly there is little or no evidence to support some of the proposed structures and some of the products are probably mixtures. Further work needs to be done to determine which factors influence the direction of addition of the acylcobalt carbonyls.

1-Acylmethyl- $\pi$ -allylcobalt tricarbonyls might be expected as products of the reaction of cobalt hydrocarbonyl with 1-acyl-1,3-dienes, but these products are not obtained. The major reaction is probably reduction of the double bonds since cobalt octacarbonyl is rapidly formed in the reaction mixture. This is not surprising since it is known that  $\alpha,\beta$ -unsaturated ketones and aldehydes are reduced by cobalt hydrocarbonyl.<sup>9</sup>

The mechanism of the addition of the acylcobalt carbonyl to the diene is of considerable interest. The most reasonable mechanism would seem to be coordination of one double bond of the diene with an acylcobalt tricarbonyl followed by insertion of the double bond between the acyl group and the cobalt atom. Finally, the remaining double bond could coordinate and form the  $\pi$ -allyl system.



(8) R. F. Heck, *J. Am. Chem. Soc.*, **85**, 655 (1963).

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

Quite possibly the addition of the acyl group and the formation of the  $\pi$ -allyl system occur simultaneously. This reaction is very probably another example of the insertion of a group into a carbon-metal bond.

### Experimental

**General Method for the Preparation of 1-Acylmethyl- $\pi$ -allylcobalt Tricarbonyls.**—To 30 ml. of a saturated solution of sodium cobalt carbonyl in ether ( $\sim 0.07 M$ )<sup>10</sup> in a nitrogen-filled bottle at room temperature were added 3 or 4 ml. of the diene and about 1 or 2 ml. of methyl or ethyl iodide (or other halide). After about 30 to 60 min. the infrared spectrum of the solution is taken. The absence of the  $5.3 \mu$  cobalt carbonyl anion band indicates the reaction is complete. If acyl chlorides are used in place of the alkyl iodides, a considerably longer reaction time is required because the acylcobalt tetracarboxyls react much more slowly with dienes than the alkylcobalt carbonyls do. It is also advisable not to use a large excess of the acid chloride since it is difficult to remove later on. After the formation of the complex is complete, the solutions are centrifuged to remove the sodium halide formed and evaporated under vacuum at  $0^\circ$ . After the solvent has been removed, the compounds may be purified by recrystallization from pentane at  $-80^\circ$ , and the lower members may be distilled under high vacuum at  $30$  or  $35^\circ$ . More conveniently, the complexes may be redissolved in ether or some other suitable solvent and treated with excess triphenylphosphine to form the less soluble, higher melting, mono-(triphenylphosphine) derivatives. The course of the triphenylphosphine reaction is easily followed by measuring the gas evolved. When gas evolution is complete, the reaction is over and the complex is isolated by evaporation of the solvent at room temperature and recrystallization of the product, under nitrogen, from tetrahydrofuran or methylene chloride and pentane. The dry compounds can be handled in the air for short periods, but they slowly oxidize.

**Analysis of the Butadiene-Methylcobalt Tetracarboxyl Complex.**—In a nitrogen-filled bottle, capped with a self-sealing, rubber lined, metal cap, with 2 holes in it for hypodermic injections, were placed 45 ml. of  $0.07 M$  sodium cobalt carbonyl in ether solution, 6.0 ml. of liquid butadiene, and 3.0 ml. of methyl iodide. The solution was shaken and left at room temperature

(10) W. Hieber, O. Vohler, and G. Braun, *Z. Naturforsch.*, **19b**, 192 (1958).

for 45 min. The infrared spectrum then showed complete reaction had occurred. The solution and excess reagents were then evaporated at  $0^\circ$  and 3-mm. pressure. Then 45 ml. of ether was added and 15 ml. of the resulting solution was placed in a carbon monoxide-filled gasometric apparatus at  $0^\circ$ .<sup>5</sup> The addition of 15 ml. of  $0.2 M$  potassium triiodide in water with magnetic stirring resulted in the evolution of 99 ml. of gas or 3.05 mmoles in about 45 min. and evolution ceased, corresponding to three coordinated carbonyl groups per molecule.

**Infrared spectra** were measured on Perkin-Elmer Model 137 Infracord. 1-Acetylmethyl- $\pi$ -allylcobalt dicarbonyl triphenylphosphine in carbon tetrachloride solution has infrared bands at 3.27(m), 4.84(m), 5.02(vs), 5.18(vs), 5.82(m), 6.78(m), 6.98(m), 7.40(m), 7.78(w), 7.92(w), 8.22(w), 8.67(m), 9.13(m), 9.32(w), 9.71(w), 10.00(w), 10.28(w), and 10.88(w)  $\mu$ . There were additional bands in carbon disulfide at 13.40(s), 14.22(s), and 14.40(vs)  $\mu$ .

**Nuclear Magnetic Resonance Spectra.**—The compounds investigated were not sufficiently soluble to obtain good n.m.r. spectra. However, it was possible to measure some areas and chemical shift values and be fairly certain of some of the structures.

The triphenylphosphine derivative of the complex from methylcobalt tetracarboxyl and *cis*-piperylene measured in deuteriochloroform solution at 60 Mc. had bands at 345, 320, 290, 274, 180, 108, and  $-25$  c.p.s. with relation to an external benzene standard. The 320 and the 345 c.p.s. bands are about three times larger than any one of the others and are probably from the acetyl methyl group and the side-chain methyl group, respectively. The absence of a large peak near 295 c.p.s. argues against the second possible isomer, with a methylene group next to the acyl group. The absence of a band at about 209 c.p.s. and the presence of one at 180 c.p.s. indicate the compound is probably the *exo* isomer.

The triphenylphosphine derivative of the complex from methylcobalt tetracarboxyl and 2,3-dimethylbutadiene had bands at 234, 296, 339, and 414 c.p.s. with reference to an external benzene standard. The acyl methyl and probably the 2-methyl group are at 339 c.p.s. and the 1-methyl appears to be at 414 c.p.s. This relatively high value for the latter methyl group probably means it is in the *endo* position, close to the cobalt atom.

**Acknowledgment.**—The n.m.r. spectra were measured by J. C. W. Chien and C. R. Boss.

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO., WILMINGTON 99, DEL.]

## The Preparation of 1-Acyl-1,3-butadiene Derivatives from Acylmethyl- $\pi$ -allylcobalt Tricarbonyls

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RECEIVED APRIL 24, 1963

1-Acylmethyl- $\pi$ -allylcobalt tricarbonyl derivatives, prepared from alkyl- or acylcobalt carbonyls and conjugated dienes, react with bases to form 1-acyl-1,3-butadiene derivatives. The reaction appears quite general, and yields are good. Under the proper conditions with cobalt carbonyl anion as catalyst, it is possible to obtain acyldiene directly from alkyl or acyl halides, a conjugated diene, carbon monoxide, and a base.

### Introduction

The use of transition metals as catalysts for the synthesis of organic compounds has long been known, but it is only relatively recently that the mechanisms of these reactions have been investigated. Our interest in organocobalt chemistry has led to experiments which suggested how the hydroformylation reaction<sup>1</sup> and the carboxylation of epoxides are taking place.<sup>2</sup> More recently we have been investigating the reaction of conjugated dienes with alkyl- or acylcobalt tetracarboxyls.<sup>3</sup> The products of these reactions, 1-acylmethyl- $\pi$ -allylcobalt tricarbonyls, are now readily available compounds. In this paper is reported a reaction of these compounds which promises to be of general use for the synthesis of 1-acyl-1,3-butadiene derivatives.

### Results

The 1-acylmethyl- $\pi$ -allylcobalt tricarbonyls are relatively stable organocobalt compounds. Investigation

of the chemistry of these compounds showed that they react readily with bases. In the presence of one atmosphere of carbon monoxide, the reaction with base, at  $25-50^\circ$ , leads to the absorption of one mole of carbon monoxide per mole of complex present. The products of this reaction are cobalt tetracarboxyl anion, identified by its very strong characteristic infrared band at  $5.3 \mu$ , and a carbonyl compound with infrared absorption at about  $6.0 \mu$ . The ultraviolet spectra of the reaction mixtures have very strong absorption bands above about  $260 m\mu$ , depending upon the substituents present. The reaction mixtures usually give nicely crystalline, dark red 2,4-dinitrophenylhydrazine derivatives when added to acidic 2,4-dinitrophenylhydrazine in ethanol solution.<sup>4</sup> Analyses and the spectral data indicate these compounds are 1-acyl-1,3-butadiene derivatives.

The base probably first removes a proton from the methylene group  $\alpha$  to the carbonyl and then a cobalt

(1) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **83**, 4023 (1961).

(2) R. F. Heck, *ibid.*, **85**, 1460 (1963).

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

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