Quite possibly the addition of the acyl group and the formation of the π-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-π-allylcobalt Tricarbonyls.—To 30 ml. of a saturated solution of sodium cobalt carbonyl in ether (~0.07 M)[10] 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 μ 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 tetracarbonyls 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°. After the solvent has been removed, the compounds may be purified by recrystallization from pentane at −80°, and the lower members may be distilled under high vacuum at 30 or 35°. 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 Tetracarbonyl 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., 13b, 192 (1958).

for 45 min. The infrared spectrum then showed complete reaction had occurred. The solution and excess reagents were then evaporated at 0° 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°.[5] 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-π-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) μ. There were additional bands in carbon disulfide at 13.40(s), 14.22(s), and 14.40(vs) μ.

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 methyl cobalt tetracarbonyl and cis-piperylene measured in deuterio-chloroform 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 tetracarbonyl 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.

The Preparation of 1-Acyl-1,3-butadiene Derivatives from Acylmethyl-π-allylcobalt Tricarbonyls

BY RICHARD F. HECK

1-Acylmethyl-π-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[1] and the carboxylation of epoxides are taking place.[2] More recently we have been investigating the reaction of conjugated dienes with alkyl- or acylcobalt tetracarbonyls.[3] The products of these reactions, 1-acyl-methyl-π-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-π-allylcobalt tricarbonyls are relatively stable organocobalt compounds. Investigation

(1) R. F. Heck and D. S. Breslow, J. Am. Chem. Soc., 83, 4023 (1961).
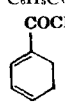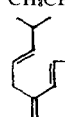(2) R. F. Heck, ibid., 85, 1460 (1963).
(3) R. F. Heck, ibid., 85, 3381 (1963)

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°, leads to the absorption of one mole of carbon monoxide per mole of complex present. The products of this reaction are cobalt tetracarbonyl anion, identified by its very strong characteristic infrared band at 5.3 μ, and a carbonyl compound with infrared absorption at about 6.0 μ. The ultraviolet spectra of the reaction mixtures have very strong absorption bands above about 260 mμ, depending upon the substituents present. The reaction mixtures usually give nicely crystalline, dark red 2,4-dinitrophenylhydrazone derivatives when added to acidic 2,4-dinitrophenylhydrazine in ethanol solution.[4] Analyses and the spectral data indicate these compounds are 1-acyl-1,3-butadiene derivatives.

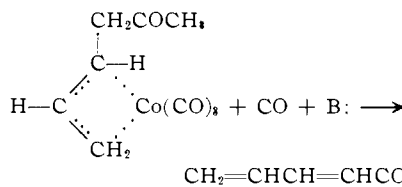The base probably first removes a proton from the methylene group α to the carbonyl and then a cobalt

(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.

TABLE I: PREPARATION AND PROPERTIES OF 1-ACYL-1,3-BUTADIENE DERIVATIVES

Acylmethyl-π-allylcobalt tricarbonyl prepared from — Diene	Alkyl or acyl halide	1-Acyl-1,3-butadiene obtained	Base used	Solvent	Temp., °C	% of theor. of CO absorbed (at atmos. press.)	λ_{max} of reacn. mixt. (methanol), mμ	ϵ assuming 100% yield	M.p. °C	2,4-Dinitrophenylhydrazone Formula	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found
Butadiene	Methyl iodide	$CH_3COCH=CHCH=CH_2$	DCHEA[a]	Ether	25	105	260	22,100	183.5–184.0	$C_{12}H_{12}O_4N_4$	52.17	52.23	4.38	4.72
trans-Piperylene	Methyl iodide	$CH_3COCH=CHCH=CHCH_3$	DCHEA	THF	40	74	272	26,400	197–198	$C_{13}H_{14}O_4N_4$	53.78	53.90	4.86	5.15
cis-Piperylene	Methyl iodide	$CH_3COC=CHCH-CH_2$ (CH_3)	NaOCH₃	Ether	25	57	266	16,500	188–189					
cis-Piperylene	Methyl iodide	$CH_3COC=CHCH=CH_2$ (CH_3)	DCHEA	Ether	40	...	...	....	193–194	$C_{13}H_{14}O_4N_4$	53.78	54.34	4.86	5.06
Isoprene	Methyl iodide	$CH_3COCH=CHC=CH_2$ (CH_3 CH_3)	DCHEA	Ether	25	82	266	16,700	190	$C_{13}H_{14}O_4N_4$	53.78	53.84	4.86	4.81
2,3-Dimethyl-1,3-butadiene	Methyl iodide	$CH_3COCH=C—C=CH_2$ (CH_3)	NaOCH₃	Ether	25	87	270	17,500	160–161	$C_{14}H_{16}O_4N_4$	55.25	55.00	5.30	5.30
Isoprene	Acrylyl chloride	$CH_2=CHCOCH=CHC=CH_2$	DCHEA	Ether	25	...	273	8,600	....[b]					
Butadiene	Chlorodimethyl ether	$CH_3OCH_2COCH=CHCH=CH_2$	DCHEA	THF	35	70	262	21,500	147	$C_{13}H_{14}O_5N_4$	50.98	50.65	4.61	4.71
Butadiene	Chlorodimethyl ether	$CH_3OCH_2COCH=CHCH=CH_2$	NaOCH₃	Ether	25	67	263	10,600						
Butadiene	Methyl chloroacetate	$CH_3OCOCH_2COCH=CHCH=CH_2$	DCHEA	Ether	45	...	305, 320	5,000, 7,150	146–147	$C_{14}H_{14}O_6N_4$	50.30	50.00	4.22	4.56
Butadiene	Benzoyl bromide	$C_6H_5COCH=CHCH=CH_2$	DCHEA	Ether	25	...	282	34,200	130–148[b]	$C_{17}H_{14}O_4N_4$	60.35	59.39	4.17	4.28
1,3-Cyclohexadiene	Methyl iodide	(cyclohexadienyl–$COCH_3$)	DCHEA	THF	25	88	260, 302	7,000, 9,150	189–190[b]	$C_{14}H_{14}O_4N_4$	55.62	54.79	4.67	4.95
Butadiene	Ethyl iodide	$CH_3CH_2COCH=CHCH=CH_2$	DCHEA	THF	25	89	262	21,400	152.0–153.5	$C_{13}H_{14}O_4N_4$	53.78	53.26	4.86	5.10
Myrcene	Methyl iodide	(myrcenyl–$COCH_3$)	DCHEA	THF	25	60	267	29,300	128.0–128.5	$C_{18}H_{22}O_4N_4$	60.32	60.51	6.19	6.51
Methyl sorbate	Methyl iodide	$CH_3OCOCH=CHCH=C$ ($COCH_3$, CH_3)	DCHEA	THF	25	42	268	25,700	218–219	$C_{16}H_{16}O_6N_4$	51.72	51.48	4.63	4.74
Isoprene	Pivalyl chloride	$(CH_3)_3CCOCH=CHC=CH_2$ (CH_3)	KO-t-Bu	Ether	25	10	266	10,400	.....					
4-Methyl-1,3-pentadiene	Methyl iodide	$CH_3C=CHCH=CHCOCH_3$	DCHEA	THF	40	53	279	23,300	171–172	$C_{14}H_{16}O_4N_4$	55.25	54.79	5.30	5.53
Cyclopentadiene	Methyl iodide	(cyclopentadienyl–$COCH_3$)	DCHEA	Ether	25	87	280	5,400	180–190 d.[b]					
trans-1-Methoxybutadiene	Methyl iodide	$CH_3OCH=CHCH=CHCOCH_3$	DCHEA	THF	25	...	297	35,800	.....					
trans-1-Methoxybutadiene	Chloromethyl ether	$CH_3OCH=CHCH=CHCOCH_2OCH_3$	DCHEA	THF	50	...	304	32,600	.....					
trans-1-Methoxybutadiene	Ethyl bromoacetate	$CH_3OCH=CHCH=CHCOCH_2COOC_2H_5$	DCHEA	THF	50	...	314	29,500	.....					
Isoprene	Cyclohexene oxide[c]	(2-hydroxycyclohexyl–$COCH=CH-C=CH_2$, CH_3, OH)	DCHEA	Ether	25	65	267	14,000	.....					

$$\text{H—C}\overset{\overset{\displaystyle CH_2COCH_3}{\underset{|}{C—H}}}{\underset{CH_2}{\diagup\diagdown}}Co(CO)_3 + CO + B: \longrightarrow$$

$$CH_2{=}CHCH{=}CHCOCH_3 + H{:}B^+ Co(CO)_4^-$$

tricarbonyl group is eliminated. The tricarbonyl anion would then absorb carbon monoxide forming the stable cobalt tetracarbonyl anion. In many of these reactions, the solutions become much darker in color initially when the base is added and the color gradually disappears as the reaction proceeds. Presumably the initial dark color is from the anion produced by removal of a proton from the acylmethyl-π-allylcobalt tricarbonyl.

Several different bases may be used in this reaction, but some do not give high yields because they react with the acyldienes as they are being formed. Alkali metal alkoxides, for example, react with acyldienes but they can be used at 0–25°, if only one equivalent per mole of cobalt complex is used. The most generally useful bases are hindered amines. We have used dicyclohexylethylamine[5] in most of our work. This base removes a proton from the cobalt compound but does not cause any side reactions with the acyldiene. Good yields of the acyldienes are usually obtained with this base. A list of the acyldienes prepared, ultraviolet spectra, and the melting points and analyses of the 2,4-dinitrophenylhydrazones of the acyldienes are given in Table I. Yields of the acyldienes obtained may be estimated to be about the same as the amount of carbon monoxide absorbed.

The structures of the acyldienes listed in Table I are based upon ultraviolet spectra, analysis of the 2,4-dinitrophenylhydrazones, and in some examples upon the structure of the organocobalt intermediate in the reaction as determined by n.m.r. spectra.

Only two of the products appear to have been reported in the literature, 1,3-hexadien-5-one[6] and 2,4-heptadien-6-one.[7] Unfortunately, the ultraviolet spectrum of 1,3-hexadien-5-one has not been published. 2,4-Heptadien-6-one is reported to have a λ_{max} of 270 mμ with ϵ 28,500.[7] Our reaction mixture from *trans*-piperylene, methylcobalt carbonyl, and dicyclohexylethylamine, which appears to have given 2,4-heptadien-6-one, had a λ_{max} of 272 mμ with ϵ 26,400, indicating that the yield may be higher than the carbon monoxide absorption would indicate (74%). The melting point of the 2,4-dinitrophenylhydrazone of authentic 2,4-heptadien-6-one, and the melting point of the same derivative of our product were the same and the mixture melting point was undepressed.

The structure of the *cis*-piperylene–methylcobalt tetracarbonyl product is based upon the structure of the intermediate acylmethyl-π-allylcobalt tricarbonyl as determined from its n.m.r. spectrum in the preceding paper.[3] The n.m.r. spectrum of the isolated acyldiene is also strong evidence that product is 4-methyl-1,3-hexadien-5-one.

Clearly *cis*- and *trans*-piperylene react with methylcobalt tetracarbonyl and a base to give two different acyldienes. Not only do the dinitrophenylhydrazones depress each others melting points but the intermediate 1-acylmethyl-π-allylcobalt dicarbonyl triphenylphosphine derivatives also are different. The *cis*-olefin gave a crystalline triphenylphosphine complex of m.p. 106.5–107.5°,[3] while it has not yet been possible to iso-

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

(6) A. S. Carter, U. S. Patent 2,263,378.

(7) S. Heilbron, E. R. H. Jones, and R. W. Richardson, *J. Chem. Soc.*; 287 (1949).

TABLE I

1-Acyl-1,3-butadiene	Diene	Halide	Base	Solvent	Temp, °C	Yield, %	B.p. of product, °C (mm.)	Formula	Analyses (C, H)	Ultraviolet spectrum λmax, mμ	ε
	1,3-Cyclohexadiene	Diethyl sulfate	DCHEA	THF	50	57	182–183		56.95, 56.70 / 5.09, 5.59	258, 295(sh)	42,500, 13,800
	Butadiene	"Crotyl bromide"[d]	DCHEA	Ether	25	60		$C_{10}H_8O_4N_4$		268	21,800
CH₃CH=CHCH₂COCH=CHCH₂·CH₃											

[a] DCHEA = dicyclohexylethylamine. [b] The 2,4-dinitrophenylhydrazone could not be purified. [c] 2-Hydroxycyclohexylcobalt carbonyl was prepared from cyclohexene oxide and cobalt hydrocarbonyl. [d] Equilibrium mixture of crotyl bromide and methylvinylcarbinyl bromide.

TABLE II: CATALYTIC PREPARATION OF 1-ACYL-1,3-BUTADIENES

1-Acyl-1,3-butadiene	Diene (mole)	Halide (mole)	Base used (mole)	Catalyst and solvent	CO pressure, p.s.i.	Temp, °C.	Time, hr.	B.p. of product °C. (mm.)	Yield, %	λmax, mμ	ε
CH₃COCH=CHCH=CH₂	22 ml. (0.25) butadiene	5.0 ml. (0.08) methyl iodide	20 ml. (0.09) DCHEA	20 ml. 0.2 M NaCo(CO)₄ in THF	50	50	6	52 (20)[b]	56,[c] (23)[d]	260	22,000
CH₃COCH=CHCH=CH₂	60 ml. (0.7) butadiene	25 g. (0.5) methyl chloride	140 ml. (0.59) DCHEA	300 ml. 0.12 M NaCo(CO)₄ in ethanol	120–130	85	24	52–54 (19)	35,[c] (10)[d]	258	32,500
CH₃COCH=CHC(CH₃)=CH₂	25 ml. (0.25) isoprene	5.0 ml. (0.08) methyl iodide	20 ml. (0.09) DCHEA	30 ml. 0.11 M NaCo(CO)₄ in THF	50	75	3.5	58–62 (15)	10[d]	266	19,900
CH₃COC(CH₃)=CHCH=CH₂	10 ml. (0.10) *cis*-piperylene	2.0 ml. (0.03) methyl iodide	10 ml. (0.04) DCHEA	20 ml. 0.2 M NaCo(CO)₄ in THF	50	70	20	62–65 (20)	~50[e] (15)[d]	266	21,000

[a] Based upon the alkyl halide used. [b] Reported boiling point 35–36° (5 mm.).[6] [c] Calculated from the ultraviolet spectrum of the reaction mixture. [d] Isolated yield. [e] Estimated from the infrared carbonyl absorption band.

late a crystalline compound from the corresponding reaction with the *trans*-olefin. Thus, the acetyl group has been added to the internal *cis* double bond of *cis*-piperylene. The *trans* isomer gives the product in which the acetyl group has been added to the terminal carbon of the diene system to give 2,4-heptadien-6-one. Thus, the acylcobalt group adds preferentially to a *cis* disubstituted olefin rather than to a terminal olefin, which, in turn, must be preferred over a disubstituted *trans*-olefin.

An authentic sample of 2-methyl-1,3-hexadien-5-one was prepared in about 10% yield by the base-catalyzed condensation of acetone with methacrolein, essentially by the same procedure as that used by Heilbron to prepare 2,4-heptadien-6-one.[7]

$$CH_3COCH_3 + OCH\overset{\overset{CH_3}{|}}{C}=CH_2 \longrightarrow CH_3COCH=CH\overset{\overset{CH_3}{|}}{C}=CH_2$$
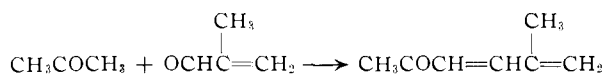
The ultraviolet spectrum and mixture melting points of the dinitrophenylhydrazones indicated this product was the same as the one obtained from isoprene and methylcobalt tetracarbonyl.

The structure of the *trans*-1-methoxybutadiene-methylcobalt tetracarbonyl–dicyclohexylethylamine product is based upon the structure which appeared most probable for the intermediate complex on the basis of the rate of reaction of the intermediate with triphenylphosphine as described in the preceding paper.[3]

The reaction of isoprene with the cyclohexene oxide–cobalt hydrocarbonyl product is included as an example in which the alkyl- or acylcobalt carbonyl used is not prepared by the alkylation of cobalt carbonyl anion. Actually, in this reaction, cobalt hydrocarbonyl was first treated with cyclohexene oxide in the presence of carbon monoxide at 0° to form *trans*-2-hydroxycyclohexylcarbonylcobalt tetracarbonyl.[2] This complex was then treated with isoprene and finally dicyclohexylethylamine was added. The 2-methyl-1,3-hexadiene type structure is assumed by analogy with the methylcobalt tetracarbonyl–isoprene reaction.

The reaction of the allylic mixture of crotyl bromide and methylvinylcarbinyl bromide with sodium cobalt carbonyl and carbon monoxide was previously found to yield, at least mainly, 3-pentenoylcobalt tetracarbonyl.[8] Therefore, the reaction of butadiene with crotylcobalt tetracarbonyl should, after reaction with dicyclohexylamine, give 1,3,7-nonatrien-5-one. Again the product was not isolated, but this structure appears most reasonable.

The usefulness of the acyldiene synthesis becomes more apparent when it is noted that the reaction can be made catalytic with respect to cobalt carbonyl anion. Since, when carried out in the presence of carbon monoxide, cobalt tetracarbonyl anion is a product as well as a reactant in many examples, the reaction will keep going with catalytic amounts of cobalt carbonyl anion present until one or the other of the reagents, alkyl, or acyl halide (or other alkylating agent), diene, carbon monoxide, or base is used up. Obviously for this reaction to proceed catalytically, the acyldiene product should not react again with the alkylcobalt tetracarbonyl. Attempted reaction of isolated 1,3-hexadien-5-one with methylcobalt tetracarbonyl under the usual reaction conditions indicated that the materials do not react. The electron-withdrawing effect of the acyl group probably makes the acyldiene a very poor ligand and the acyldiene, therefore, does not complete effectively with carbon monoxide or diene for the acylcobalt tricarbonyl. Three acyldienes have been prepared and isolated by use of the catalytic reaction.

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

Reaction conditions and the properties observed for the products are given in Table II. Several problems were responsible for the low yields of isolated products. The solutions employed were rather dilute because the amine–hydrogen halide salt produced in the reactions formed a thick slush of crystals which could not be stirred in more concentrated solutions. With such dilute solutions it was difficult to separate the rather volatile and moderately water-soluble acyldienes from the solvents and water solutions used in the isolation procedure. The reactions probably did not go to completion either. It is almost certain that higher yields could be obtained by varying the reaction conditions.

The 1,3-hexadien-5-one preparation from butadiene and methyl chloride was carried out on a large enough scale so that a pure sample of the product was obtained. Acceptable carbon and hydrogen analyses were obtained. The intensity of the ultraviolet absorption, a λ_{max} of 258 mμ with ϵ 32,500, suggests that the other two acyldienes isolated may not have been pure. Nevertheless, the n.m.r. spectrum of the 4-methyl-1,3-hexadien-5-one and of 1,3-hexadien-5-one itself agreed very well with the proposed structures. The 2-methyl-1,3-hexadien-5-one was obviously impure.

The infrared spectrum of 1,3-hexadien-5-one has a very strong band at 9.9 μ, indicating that the compound is probably the *trans* isomer. (There are no bands between 12.5 and 14.5 μ, the region where the *cis* isomer should absorb.) Presumably this synthesis leads to the most stable isomer in the other examples also.

The preparation of acyldienes from alkyl- or acylcobalt carbonyls, conjugated dienes, and a base is clearly a very general reaction. It is surely the best way now available for preparing many acyldienes. It can often be carried out in a single step from readily available starting compounds. Yields are usually good, although some difficulty has been experienced in isolating the products in high yields, and the products appear to be free from other similar compounds. The major difficulties with the synthesis are that the reaction must be carried out in the absence of air and the preparation requires relatively large volumes of solvent for the amount of acyldiene produced. The reaction should be of considerable use in the preparation of numerous types of highly unsaturated organic compounds.

Experimental

General Method for the Preparation of 1-Acyl-1,3-butadienes.—The preparation of ether solutions of 1-acylmethyl-π-allylcobalt tricarbonyls from alkyl- or acylcobalt carbonyls and conjugated dienes has been described in the preceding papers.[3] These solutions may be treated directly with base to form the acyldiene. Generally 1 ml. of dicyclohexylethylamine or 1.0 ml. of 1.0 M sodium methoxide in methanol was used per millimole of alkyl or acyl halide used. In examples in which yields of products were determined by carbon monoxide absorption, the 1-acyl-π-allylcobalt tricarbonyl solutions were evaporated to dryness under vacuum at 0° to remove unreacted halide and/or diene and fresh solvent added back so that only the yield of the stoichiometric reaction would be measured. Temperatures from 25 to 85° were used. Of course, a pressure vessel was necessary if the temperature was higher than the boiling point of the solvent present. The reaction can be carried out in ether or, just as well, in higher boiling solvents such as tetrahydrofuran or dioxane. If the 1-acylmethyl-π-allylcobalt tricarbonyl has been prepared in ether it is often convenient to evaporate the solvent under vacuum at 0° and add back a higher boiling solvent for the reaction with the base. The time required for the base reaction varies greatly with the structure of the intermediate cobalt complex. Generally, substitution at the 1- or 2-positions of the 1-acyl-π-allylcobalt complex greatly decreases the rate of reaction of the complex with base. As would be expected, the effect is much larger with dicyclohexylethylamine than with sodium methoxide.

1-Acyl-1,3-butadiene derivatives need not be prepared in two steps as described above. All the reagents may be combined

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

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

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.

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

BY RICHARD F. HECK

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-cyclo-

pentadienyl-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-

(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).