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THE PREPARATION OF ACYLTETRACARBONYLCOBALT COMPOUNDS FROM KETENES AND HYDRIDOTETRACARBONYLCOBALT

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Summary

Ketenes ($R^1R^2C{=}C{=}O$, R^1, $R^2 = H$ or alkyl) react rapidly at −79°C with hydridotetracarbonylcobalt in a 1/1 molar ratio to form quantitatively the corresponding acyltetracarbonylcobalts, which can be isolated in good to excellent yields. Electron-withdrawing substituents in the ketene lower the reactivity towards $HCo(CO)_4$.

Introduction

Acylcarbonylcobalts are the key intermediates in several cobalt-catalyzed carbonylations and related reactions, such as: hydroformylation [1] and hydrocarboxylation [2] of olefins; carbonylation of alkyl halides [3] conjugated dienes [4] and acetylenes [5]; ketone formation from olefins, CO and H_2 [6]; homologation of alcohols [7]; reduction of carbon monoxide [8], synthesis of glycol from CO and H_2 [9] and double carbonylation of benzyl halides [10]. Little is known, however, of their chemical properties owing to the difficulty of their preparation [11].

Acyltetracarbonylcobalts have been prepared previously in low yields by a reaction sequence starting from alkenes [12] or epoxides [13] and $HCo(CO)_4$ or by the reaction of acyl halides [14], sulfonates [15], sulfates [15], or carboxylic anhydrides [16] with $Na[Co(CO)_4]$.

Recently we found that n-butyryltetracarbonylcobalt and isobutyryltetracarbonylcobalt (which are the precursors of n-butyraldehyde and isobutyraldehyde, respectively, in the industrially important hydroformylation of propylene) can be prepared conveniently from $HCo(CO)_4$ and the corresponding ketenes [17]. As an extension of this work we now describe in detail the preparation of acyltetracarbonylcobalts using various ketenes.

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Results and discussion

The results listed in Table 1 show that ketene and ketenes with at least one alkyl substituent can be converted into the corresponding acyltetracarbonylcobalts by $HCo(CO)_4$ in a pentane diethyl ether mixture.

$$R^1R^2C{=}C{=}O + HCo(CO)_4 \rightarrow R^1R^2CHCOCo(CO)_4 \qquad (1)$$

The conversion is rapid and quantitative at −79°C in the case of ketene, methyl ketene, ethyl ketene, and dimethyl ketene using a 1/1 molar ratio of reactants. Evaporation of the solvent below −30°C in vacuum left the acyltetracarbonylcobalt complexes as yellow oils in good to excellent yields. According to cobalt analyses, infrared and NMR spectra of the isolated acyl complexes, purities of more than 95% were achieved. These complexes proved to be moderately stable under carbon monoxide even at room temperature, especially in hydrocarbon solution. For example 0.1–0.4 *M* solutions were stored under carbon monoxide at 25°C in the dark for a week without change.

Deviation from the 1/1 molar ratio or use of higher temperatures results in the formation of side products such as ketene dimers, aldehydes, and octacarbonyldicobalt. The last two products arise from a subsequent reaction between the acyl complex and $HCo(CO)_4$.

$$R^1R^2CHCOCo(CO)_4 + HCo(CO)_4 \rightarrow R^1R^2CHCHO + Co_2(CO)_8 \qquad (2)$$

The reaction in eq. 2 can be supressed by high pressures of carbon monoxide [18] which do not affect the time needed for the reaction shown in eq. 1. This suggests that the reaction between the ketene and $HCo(CO)_4$ proceeds by proton transfer and combination of the resulting ions.

Electron-withdrawing substituents greatly lower the reactivity of ketenes towards $HCo(CO)_4$. No reaction could be observed at −79°C for R^1,R^2 = Ph or halogen, or

TABLE 1

REACTIONS OF KETENES[a] ($R^1R^2C{=}C{=}O$) WITH HYDRIDOTETRACARBONYLCOBALT[b] IN 1/1 MOLAR RATIO TO GIVE THE CORRESPONDING ACYLTETRACARBONYLCOBALT ($R^1R^2CHCOCo(CO)_4$) COMPLEXES

R^1	R^2	Temperature (°C)	Reaction time	Conversion[c] of ketene (%)	Conversion[c] of $HCo(CO)_4$ (%)	Yield of $R^1R^2CHCOCo(CO)_4$ (%)
H	H	−79	1 min	100	100	62[d]
CH_3	H	−79	1 min	100	100	70[d]
C_2H_5	H	−79	5 min	100	100	95[d]
CH_3	CH_3	−79	5 min	100	100	90[d]
Ph	CH_3	+10	4 days[e]	81	100	33[c,f]
Ph	Ph	+10	6 days[e]	45	95	0[c,g]

[a] Added as 0.05–0.75 *M* solution in diethyl ether. [b] Added as 0.8 *M* solution in n-pentane. [c] Based on the infrared spectrum of the reaction mixture. [d] Isolated yield (after evaporating the solvent below −30°C in vacuum). [e] Under 120 bar carbon monoxide pressure. [f] The reaction mixture also contained 13% ethylbenzene, 18% styrene and 18% α-phenylpropionaldehyde based on the amount of ketene taken. [g] The reaction mixture contained 18% diphenylmethane and 27% diphenylacetaldehyde based on the amount of ketene taken.

in the case of carbon suboxide. Raising the temperature led to conversion of methyl phenyl ketene and diphenyl ketene into mixtures of products. From methyl phenyl ketene not only (α-phenylpropionyl)tetracarbonylcobalt and α-phenylpropionaldehyde but also ethylbenzene and styrene were formed. The formation of these products is in accord with formation of (α-phenylpropionyl)tetracarbonylcobalt from styrene and $HCo(CO)_4$ to regenerate a radical pair intermediate [19]. Similarly the formation of diphenylmethane in the reaction of diphenyl ketene and $HCo(CO)_4$ can be explained as shown in Scheme 1.

$Ph_2C{=}C{=}O + HCo(CO)_4 \rightarrow Ph_2CHCOCo(CO)_4$

$Ph_2CHCOCo(CO)_4 \rightleftharpoons Ph_2CHCo(CO)_4 + CO$

$Ph_2CHCo(CO)_4 \rightarrow \overline{Ph_2\dot{C}H\dot{C}o(CO)_4} \rightarrow Ph_2\dot{C}H + \dot{C}o(CO)_4$

$Ph_2\dot{C}H + HCo(CO)_4 \rightarrow Ph_2CH_2 + \dot{C}o(CO)_4$

$2\dot{C}o(CO)_4 \rightarrow Co_2(CO)_8$

SCHEME 1

Experimental

All operations involving carbonylcobalts and ketenes were performed under carbon monoxide using standard Schlenk techniques [20]. Pentane and diethyl ether were freshly distilled from sodium/benzophenone ketyl prior to use. Solutions of hydridotetracarbonylcobalt in pentane (0.8 M) were prepared from octacarbonyldicobalt, DMF, and concentrated HCl [21]. Solutions of ketene, methyl ketene, ethyl ketene, dimethyl ketene and carbon suboxide in diethyl ether (0.05–0.75 M) were prepared by published procedures [22] by debromination of α-bromoacyl bromides with activated zinc shavings [23] and distillation into a cold trap (-79°C). Published procedures were also used for the preparation of diphenyl ketene [24], methyl phenyl ketene [25], and dichloroketene [26]. IR spectra were recorded on a Carl Zeiss Jena IR 75 spectrophotometer using a 0.1 mm CaF_2 cuvette. Analysis of the volatile compounds was performed on a Hewlett–Packard Model 5830A gas chromatograph using cumene as internal standard. NMR spectra were recorded on a Tesla BS 487/c 80 MHz Spectrometer (^1H) and on a Varian CFT-20 Spectrometer (^{13}CO), with TMS as internal standard.

n-Butyryltetracarbonylcobalt. A cold (-79°C) solution of $HCo(CO)_4$ (3.4 mmol) in pentane (4.4 ml) was added with stirring to a solution of ethyl ketene (3.5 mmol) in diethyl ether (60 ml) at -79°C. Infrared analysis after 5 min. showed that all $HCo(CO)_4$ had reacted and the only cobalt complex in the reaction product was n-butyryltetracarbonylcobalt. Removal of the solvent at -30°C in vacuum left a yellow oil (0.55 ml, 0.78 g, 94.8% yield), which, at -79°C gave yellow needles, with a melting point of -60°C. Anal. Found. Co, 24.68. $C_7H_7CoO_5$ calcd.: Co, 24.37%. IR (n-heptane): $\nu(cm^{-1})$ (ϵ_M (cm^2 $mmol^{-1}$): 2105 (ϵ_M) 1420), 2046 (ϵ_M 3010), 2024 (ϵ_M 4150), 2004 (ϵ_M 4950), 1969 (ϵ_M 131), 1717 (ϵ_M 418). ^1H NMR (C_6D_6): δ 0.65 (3H, t, J 7.2 Hz), 1.32 (2H, sextet, J 7.1 Hz), 2.74 (2H, t, J 6.7 Hz) ppm. ^{13}C NMR (C_6D_6): δ 13.2 s CH_3, 19.8 s $CH_3\mathit{C}H_2$, 66.6 s $\mathit{C}H_2CO$, 197.6 br $(CO)_4$, 226.1 s $CH_2\mathit{C}O$, ppm.

Using the above procedure the following complexes were additionally obtained:

(a) Isobutyryltetracarbonylcobalt. (1.75 g, 2.39 ml, 90% yield) from $HCo(CO)_4$ (11 mmol) in pentane (14 ml) and dimethyl ketene (11.7 mmol) in diethyl ether (39 ml). Anal. Found. Co, 24.82. $C_7H_7CoO_5$ calcd.: 24.37%. IR (n-heptane): ν 2104 (ϵ_M 1490), 2046 (ϵ_M 2920), 2023 (ϵ_M 4190), 2003 (ϵ_M 4900), 1968 (ϵ_M 135), 1737 (ϵ_M 500), 1669 ϵ_M 370) cm^{-1}. ^1H NMR (C_6D_6): δ 0.93 (6H, d, J 6.5 Hz), 3.03 (1H, septet, J 6.5 Hz) ppm. ^{13}C NMR (C_6D_6): δ 18.9 s CH_3, 62.3 s CH, 197.6 br $(CO)_4$, 231.6 s CH*C*O, ppm.

(b) Propionyltetracarbonylcobalt. (0.42 g, 70% yield) from $HCo(CO)_4$ (2.63 mmol) in pentane (3.3 ml) and methyl ketene (2.70 mmol) in diethyl ether (55 ml). IR (n-heptane): 2105s, 2046s, 2024vs, 2003vs, 1742m, 1700m cm^{-1}. ^1H NMR (C_6D_6): δ 0.68 (3H, t, J 6.7 Hz), 2.60 (2H, q, J 7.0 Hz) ppm.

(c) Acetyltetracarbonylcobalt. (0.24 g, 62% yield) from $HCo(CO)_4$ (1.80 mmol) in pentane (2.3 ml) and ketene (1.89 mmol) in diethyl ether (10 ml). IR (n-heptane): 2107s, 2048s, 2026vs, 2007vs, 1720m cm^{-1}. ^1H NMR (C_6D_6): δ 2.15 s ppm.

Reaction of methyl phenyl ketene with $HCo(CO)_4$. A solution of $HCo(CO)_4$ (2.0 mmol) in pentane (2.5 ml), and a solution of methyl phenyl ketene (2.0 mmol) in diethyl ether (5.5 ml), and 30 μl of cumene were placed under CO in a 20 ml stainless-steel rocking autoclave which was pressurized to 120 bar with CO. After 4 days' agitation at 10°C the autoclave was cooled to -79°C and the pressure released. Crystals of $Co_2(CO)_8$ (448 mg, 1.31 mmol, 65% yield) were filtered off from the cold reaction mixture. The infrared spectrum of the solution in the ν(C–O) region showed the presence of (α-phenylpropionyl)tetracarbonylcobalt [19] and α-phenylpropionaldehyde (0.368 mmol, 18% yield using ϵ_M 240 at 1741 cm^{-1} for the calculation). Gas chromatography of the solution (25 m 0.15 μ OV-1 glass capillary column 50–250°C, 10°C/min, Ar, FID) after quenching with methanol (50 μl/ml) showed the presence of ethylbenzene (0.26 mmol), styrene (0.36 mmol), α-phenylpropionaldehyde (0.37 mmol) and methyl α-phenylpropionate (0.37 mmol). From the $HCo(CO)_4$ and methyl phenyl ketene balance the yield of (α-phenylpripionyl)tetracarbonylcobalt was calculated to be 33%.

Reaction of diphenyl ketene with $HCo(CO)_4$. The same procedure as described above for methyl phenyl ketene but using diphenyl ketene and 6 days' agitation gave $Co_2(CO)_8$ (325 mg, 95% yield) and a solution which was shown to contain diphenylacetaldehyde (0.54 mmol, 27% yield by GC and IR analyses), diphenylmethane (0.36 mmol, 18% yield by GC analysis), and unreacted diphenyl ketene (1.1 mmol by GC analysis).

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