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THE BEHAVIOUR OF ALKYLCOBALT CARBONYLS UNDER "OXO" CONDITIONS

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Summary

Alkylcobalt carbonyls, synthesized under oxo conditions from alkyl halides and sodium tetracarbonylcobaltate, give the corresponding aldehydes on treatment with CO and H_2. The alkylcobalt carbonyls do not isomerize significantly under oxo conditions. Alkylcobalt carbonyls prepared from alkyl halides and sodium tetracarbonylcobaltate or from orthoformic esters dicobalt octacarbonyl, CO and hydrogen do not isomerize even in the presence of an excess of olefin.

Introduction

Alkylcobalt tetracarbonyls react with carbon monoxide to give the corresponding acyl derivatives which in turn are reduced with hydrogen to aldehydes [1,2]. Several investigations have been made of the stability of these compounds under various conditions. Triphenylphosphine substituted alkylcobalt carbonyls do not isomerize under carbon monoxide below 0°C [3] but unsubstituted alkylcobalt carbonyls isomerize when allowed to stand under nitrogen at 0°C or when heated at 100°C under carbon monoxide [4,5].

In the light of the role attributed to alkylcobalt carbonyls in the hydroformylation of olefins, and of the isomeric composition of the products [6,7], we have examined the behaviour of alkylcobalt carbonyls under "oxo" conditions [8]. We have considered both the straight to branched and the head to tail isomerization of straight-chain alkylcobalt carbonyls. The idea of studying the head to tail isomerization of straight-chain alkylcobalt carbonyls arose from preliminary results on the hydroformylation of [^{14}C]1-propene [9]; the butanal formed by hydroformylation of this olefin at 100°C and 200 atm CO and H_2 (1 : 1), with no olefin isomerization taking place [10], appears to arise from

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insertion of the formyl group on either of the terminal carbon atoms of the substrate. Alkylcobalt carbonyls are formed as intermediates in these reactions at temperatures of at least 80° C and pressures of carbon monoxide and hydrogen ranging from a few to several hundred atmospheres. In order to illuminate their role we have synthesized them under these conditions and observed their behaviour.

Results

The synthesis of alkylcobalt carbonyls involved introducing, at reaction temperature, a solution of the appropriate alkyl halide through an injector (operated with hydrogen) into an autoclave containing a solution of $NaCo(CO)_4$ in ethyl ether and carbon monoxide under the appropriate pressure. The pressure was kept constant throughout the whole reaction. Experiments were terminated when gas absorption ceased. The alkyl halides used were 1-iodopropane, 2-iodopropane and 1-iodopropane-3-d_3. Conditions chosen were 80° C, $p(H_2)$ 80 atm, $p(CO)$ 2 or 80 atm. Reaction mixtures were analysed for the presence of alkyl halides and aldehydes by GLC analysis. Recovery of the aldehydes, when necessary, was performed on the corresponding methyl esters by preparative GLC. Deuterium retention and distribution in the molecule were determined by NMR. The results are shown in Table 1.

At 80 atm carbon monoxide only one aldehyde is formed from both straight- or branched-chain alkyl halides. From 1-iodopropane-3-d_3, only butanal-4-d_3 is produced. The same aldehyde, containing all the deuterium on the methyl group, is obtained even when the reaction is performed in the presence of 1-pentene at high concentration, conditions analogous to those in which an alkylcobalt carbonyl is formed during an oxo reaction. At low carbon monoxide pressure, 14% of 2-methylpropanal is formed together with the straight-chain isomer from 1-iodopropane-3-d_3. As shown in Table 1, deuterium is distributed over the whole chain of the butanal formed.

We attempted to confirm these results by studying under similar conditions the carbonylation of tri-1-propoxy-3-d_3-methane and tri-1-propoxy-1-d_2-methane in the presence of $Co_2(CO)_8$ since the reaction of orthoformic esters with

TABLE 1

CARBONYLATION OF ALKYL IODIDES:

$NaCo(CO)_4$ 20 mmol; RI 18 mmol; diethyl ether 50 ml; $p(H_2)$ 80 atm; T 80°C; 3 h.

RI	$p(CO)$ (atm)	Aldehydes formed	Isomeric composition (%)
1-Iodopropane	80	Butanal	100
2-Iodopropane	80	2-Methylpropanal	100
1-Iodopropane-3-d_3	80	Butanal-4-d_3	100
1-Iodopropane-3-d_3	80 [a]	Butanal-4-d_3	100
1-Iodopropane-3-d_3	2	Butanal [b]	86
		and 2-methylpropanal [c]	14

[a] In the presence of an excess of 1-pentene. [b] Number of hydrogen atoms per carbon atom of the corresponding methyl ester: $\underset{0.4}{C}-\underset{1.8}{C}-\underset{1.8}{C}-COOCH_3$. [c] Deuterium content and distribution not determined.

TABLE 2

CARBONYLATION OF ORTHOFORMIC ESTERS

$Co_2(CO)_8$ 0.3 g, orthoformic ester 5 g, benzene 25 ml, $p(H_2)$ 80 atm, T 100°C, 5 h.

Orthoformic ester	p(CO) (atm)	Aldehydes formed	Isomeric composition (%)
Tri-1-propoxy-3-d_3-methane	80	Butanal-4-d_3	100
Tri-1-propoxy-3-d_3-methane	2	Butanal-4-d_3	99
		and 2-methylpropanal [a]	1
Tri-1-propoxy-1-d_2-methane	80	Butanal-2-d_2	100
Tri-1-propoxy-1-d_2-methane	2	Butanal-2-d_2	98.5
		and 2-methylpropanal [a]	1.5
Tri-1-propoxymethane [b]	80	Butanal	100

[a] Deuterium content and distribution not determined. [b] In the presence of an excess of 1-pentene.

carbon monoxide and hydrogen in the presence of $Co_2(CO)_8$ shows close analogies to the hydroformylation of olefins, and there is evidence that, after the formation of the alkylcobalt carbonyls these reactions are identical in course [11,12]. The results of these experiments are shown in Table 2.

Butanal-4-d_3 and butanal-2-d_2 were the only products obtained from tri-1-propoxy-3-d_3-methane and tri-1-propoxy-1-d_2-methane, respectively, at 100° C and 80 atm carbon monoxide. At low carbon monoxide pressures the straight-chain aldehyde formed from both substrates was accompanied by ~1% of the branched-chain isomer. In all cases deuterium was retained almost completely in the original position. In carbonylation of tri-1-propoxymethane in the presence of 1-pentene in high concentration at high CO pressure, n-butanal was the sole C_4 aldehyde formed. The analogy in behaviour under high CO pressures between alkylcobalt carbonyls formed from alkyl halides and those produced by carbonylation of orthoformic esters is therefore confirmed. At low CO pressure, however, the intermediates obtained from orthoformic esters show a higher stability. Either they are stabilized by the medium in which they are formed or the mechanism of their formation under these conditions does not give rise to labile intermediates.

Discussion

Alkylcobalt carbonyls do not isomerize under classical hydroformylation conditions ($p(CO) \geqslant 50$ atm, $p(H_2) \geqslant 50$ atm, $T \geqslant 80°C$) even in the presence of free olefin in solution, but are transformed into the corresponding acylcobalt carbonyls, which on hydrogenation give the expected aldehydes. The simultaneous formation of 2-methylpropanal and butanal and the complete retention of deuterium in the substrate, (though distributed through the chain) when the reaction is carried out at low carbon monoxide pressures is an indication that under these conditions the alkylcobalt carbonyl is at least partly transformed into an olefin—cobaltcarbonyl hydride complex. Hydroformylation of the olefin involved in this complex leads to all the 2-methylpropanal and part of the butanal, the remaining butanal arising from direct carbonylation of the original alkylcobalt carbonyl.

The retention of all the deuterium in the butanal in experiments at low CO pressures indicated that under these conditions alkylcobalt carbonyls do not decompose to free olefin and cobalt carbonyl hydride to any significant extent. Free cobalt carbonyl hydride if present in significant amount would, in fact, catalyze not only the isomerization of the olefin but also the exchange of deuterium with gaseous hydrogen present in the reaction vessel; cobalt carbonyl deuteride in hydrocarbon solution under CO and H_2 pressure does in fact exchange deuterium rapidly with hydrogen [13].

In the light of our results the formation of isomeric aldehydes by hydroformylation of olefins under classical "oxo" conditions or even the formation of a same aldehyde by insertion of a formyl group at either end of a straight-chain olefin cannot be attributed to isomerization of intermediate alkyl- or acyl-cobalt carbonyls. The explanation must be sought in the behaviour of the precursors of the alkylcobalt carbonyls.

Experimental

All boiling points are uncorrected. GLC analysis was performed on a Perkin—Elmer model F 30 instrument. Isomeric esters were separated with a Perkin—Elmer GLC F 21 preparative instrument. NMR spectra were recorded on a Varian T 60 spectrometer. Mass spectra were recorded on a Perkin—Elmer model 270 B mass spectrometer.

Materials

Octacarbonyldicobalt was prepared as described by Natta and Ercoli [14] and had m.p. 51.5° C. Sodiumtetracarbonylcobaltate was prepared according to Hieber [15]. Lithium aluminium deuteride was a Merck product (98% isotopic purity) and tetradeuteroacetic acid a Sorin product (99.6% isotopic purity).

Propan-1-ol-3-d_3 was prepared as follows: Tetradeuteroacetic acid (52.5 g) was reduced with $LiAlH_4$ (32 g) in diethyl ether (900 ml) at 0° C. After hydrolysis and distillation ethanol-2-d_3 (38 g) was recovered as an azeotropic mixture (95% alcohol). This alcohol by treatment with HBr/H_2SO_4 (140 ml HBr 48%, 86 ml H_2SO_4 96%) as described by Vogel [16], gave bromoethane-2-d_3 (73 g, b.p. 37—38° C). The NMR spectrum (int. TMS) of the product showed only a singlet at δ 3.4 ppm [17]. The Grignard reagent (Mg 16 g, diethyl ether 300 ml) from this bromide was carbonated in the usual manner to give propionic acid-3-d_3 (41 g, b.p. 80° C/72 mmHg, n_D^{25} 1.3844). This acid was reduced with $LiAlH_4$ (21 g, diethyl ether 500 ml) at 0° C. The reaction mixture was then added to ice and purified. The azeotropic mixture boiling at 81° C was then collected and treated with NaCl in excess. The upper layer was separated and distilled to give pure propan-1-ol-3-d_3 (23 g) b.p. 96—98° C, n_D^{25} 1.3825.

NMR (int. TMS): δ(ppm) 5.2 (s, 1 H, $\underline{OH}$), 3.5 (t, 2 H, $O\underline{CH_2}$), 1.5 (t, 2 H, $\underline{CH_2}CD_3$).

1-Iodopropane-3-d_3 was prepared as described by Vogel [18] for 1-iodopropane.

From propan-1-ol-3-d_3 (10 g), iodine (21 g) and red phosphorus (2 g), iodopropane-3-d_3 (25 g, b.p. 102—103° C) was obtained.

NMR (int. TMS, solvent CCl_4): δ(ppm) 3.1 (t, 2 H, $\underline{CH_2}I$), 1.8 (t, 2 H, $\underline{CH_2}CD_3$).

Tris-1-propoxy-3-d_3-methane was prepared as described by Roberts et al. [19] for undeuterated compounds.

From propan-1-ol-3-d_3 (12 g) and trimethoxymethane (5 g) tri-1-propoxy-3-d_3-methane (9 g, b.p. 110°C/41 mmHg, n_D^{25} 1.4042) was isolated by spinning band distillation.

NMR (int. TMS) δ(ppm) 4.9 (s, 1 H, $\underline{HC}$), 3.3 (t, 2 H, $O\underline{CH_2}$), 1.5 (t, 2 H, $\underline{CH_2}CD_3$).

Propan-1-ol-1-d_2 was prepared as follows: Propionic acid (35 g) was reduced with $LiAlD_4$ (20 g) in diethyl ether (800 ml) at 0°C. After hydrolysis of the reaction mixture and distillation an azeotropic mixture was collected (b.p. 87°C). Pure propan-1-ol-2-d_2 (23 g, b.p. 96—98°C, n_D^{25} 1.3829) was recovered as described for the preparation of propan-1-ol-3-d_3.

NMR (int. TMS) δ(ppm) 4.5 (s, 1 H, $\underline{OH}$), 1.5 (q, 2 H, $\underline{CH_2}CH_3$), 0.9 (t, 3 H, $CH_2\underline{CH_3}$).

Tri-1-propoxy-1-d_2-methane was prepared from propan-1-ol-1-d_2 (23 g) and trimethoxymethane (10 g). Tri-1-propoxy-1-d_2-methane (16 g, b.p. 79°C/11 mmHg, n_D^{20} 1.4067) was isolated by spinning band distillation.

NMR (int. TMS, solvent CCl_4): δ(ppm) 4.9 (s, 1 H, $\underline{HC}$), 1.5 (q, 2 H, $\underline{CH_2}CH_3$), 1.0 (t, 3 H, $CH_2\underline{CH_3}$).

Carbonylation of alkyl iodides

(a) 1-Iodopropane-3-d_3 at low p(CO). Sodiumtetracarbonylcobaltate (20 mmol) in diethyl ether (40 ml) was introduced into a 125 ml rocking autoclave, and carbon monoxide was then added to a pressure of 1.6 atm at 20°C. The autoclave was heated at 80°C for 30 minutes and a solution of 1-iodopropane-3-d_3 (18 mmol) in diethyl ether (10 ml) and hydrogen up to 82 atm were then introduced through an injection system. The gas pressure was kept constant during the reaction by supplying a carbon monoxide and hydrogen mixture (1 : 1) from a high pressure vessel.

After 3 h the pressure drop had ceased. The autoclave was then cooled to 0°C, the gas vented and the crude mixture analyzed by GLC. Butanal (86%), 2-methylpropanal (14%), and no starting material were present. The crude mixture was then treated with Ag_2O at 0°C and after the usual work up a mixture of the corresponding methyl esters was obtained. Pure deuterated butanoate was recovered by preparative GLC.

Its mass spectrum is in agreement with the formulation $C_5H_7D_3O_2$.
NMR (int. TMS, solvent C_6D_6, $Eu(DPM)_3$: δ(ppm) 5.4 (s, 3 H, $COO\underline{CH_3}$), 4.2 (t, 1.8 H, $\underline{CH_2}COOCH_3$), 3.0 (t, 1.8 H, $CH_3\underline{CH_2}$), 1.5 (m, 0.4 H, $\underline{CH_3}CH_2$).

(b) 1-iodopropane-3-d_3 in the presence of 1-pentene. The procedure was analogous to that described above, the olefin was introduced into the autoclave together with the alkyl iodide, diethyl ether and hydrogen. In addition to butanal the product also contained hexanal (81.7%), 2-methylpentanal (15.6%) and 2-ethylbutanal (2.7%). The mass and NMR spectra of the methyl butyrate agreed with the formulation $CD_3CH_2CH_2COOCH_3$.

Carbonylation of orthoformic esters

All the reagents except hydrogen were introduced into the autoclave at room temperature. Hydrogen was added at the reaction temperature (100°C). The experiments were carried out at constant pressure under the conditions indicated in Table 2. The product mixture was treated as described for alkyl iodides.

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