

HYDROCARBONYLATION OF 2,2-DIMETHOXYPROPANE CATALYSED BY RHODIUM AND COBALT COMPLEXES

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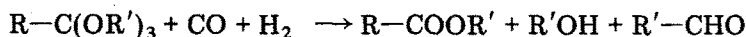
Summary

The hydrocarbonylation of 2,2-dimethoxypropane (DMP) with synthesis gas catalysed by rhodium and cobalt complexes has been studied. The major product is either diethyl ether or acetaldehyde dimethylacetal (ADMA), arising from the homologation of the methoxy groups of the ketal. The operating conditions and ligand environment of the metal have been optimized to reduce the secondary aldolization reactions.

Introduction

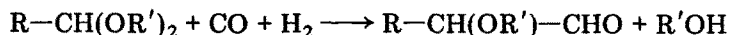
The reductive carbonylation of oxygenated compounds has been the subject of several recent reviews [1 - 3]. Among the oxygenated compounds considered, orthoesters and dialkylacetals exhibit opposite reactivity.

Indeed, the hydrocarbonylation of orthoesters leads to the homologation of the alkyl radical of one alkoxy group, according to:



with yields approaching 50 mol%.

By contrast, the reductive carbonylation of dialkylacetals leads to the homologation of the aldehyde portion of the acetal, according to:



with yields ranging from 30 to 65 mol% depending on the acetal involved.

Surprisingly, up to a very recent date there seems to have been no report in the literature concerning the reductive carbonylation of dialkylketals derived from ketones. Fleming and Bolker [4] have studied the cobalt carbonyl-catalysed hydrogenolysis of acetals and ketals at $T = 170^\circ\text{C}$, $P = 16\text{ MPa}$ and with $H_2/CO = 2/1$. They did not observe any hydrocarbonylation product.

In the course of a thesis prepared in this laboratory [6], we have evidenced the beneficial effect of the addition of 2,2-dimethoxypropane

(DMP) on the octacarbonyldicobalt-catalysed homologation of benzyl alcohol to 2-phenylethanol.

In the present study, we have focused our attention on the hydrocarbonylation of DMP itself [5]. A very recent patent reports also on this type of reaction [12].

Experimental

Materials

DMP (a commercial product) was dried over molecular sieves and distilled under inert atmosphere. The solvents were also dried over molecular sieves and deoxygenated according to known procedures.

The catalysts were either purchased from commercial sources ($\text{Co}_2(\text{CO})_8$, $\text{Rh}_6(\text{CO})_{16}$) or prepared according to literature synthetic procedures ($\text{RhCl}(\text{PPh}_3)_3$ [13], $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ [14], $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ [15] (acac = acetylacetonate), $(\text{CF}_3\text{C})\text{Co}_3(\text{CO})_9$ [16], $\text{PdCl}_2(\text{PMePh}_2)_2$ [17], $\text{PtCl}_2(\text{PPh}_3)_2$ [18]).

Apparatus and procedures

The hydrocarbonylation reaction is performed in an Autoclave Engineers Inc. Hastelloy C autoclave having a capacity of 300 ml, equipped with a Magnedrive-type stirrer. The stirring speed is set at 1500 r.p.m.

The starting materials, solvent and catalyst are introduced into the autoclave. This is then closed, purged three times with 2 MPa H_2 and pressurized first with CO, then with H_2 , in order to reach the H_2/CO ratio and the total pressure required (usually $\text{H}_2/\text{CO} = 1/1$ and $P = 12$ MPa at 25 °C). The autoclave is then heated to the required temperature.

When the reaction is complete, the autoclave is cooled and vented. The liquid reaction mixture is recovered and analyzed by gas chromatography (INTERSMAT Gas Chromatographs, Dexsil 300, Carbowax 20 M and Porapak Q columns) using benzene as an internal standard. When benzene is the solvent, it is also used as the internal standard.

Except for the heavy byproducts (*vide infra*), the products and other byproducts have been identified by GC-MS and GC-IR coupling and by comparison with authentic samples on the chromatographic columns. The heavy byproducts obtained as a residue after vacuum evaporation of the reaction mixture, are characterized by IR spectroscopy: 3450, ν (OH); 1715, ν (C=O); 1100 cm^{-1} , ν (C-O).

Expression of experimental results

The molar conversion of DMP is calculated on the basis of DMP consumed during the reaction.

The yield is defined as the ratio of the sum of the hydrocarbonylation products, expressed as molar equivalents, to the number of methoxy groups initially introduced. To establish this yield, the following products are taken

into account: acetaldehyde, acetaldehyde dimethylacetal (ADMA), ethanol, diethyl ether and butyraldehyde dimethylacetal, the last two being counted as two molar equivalents each.

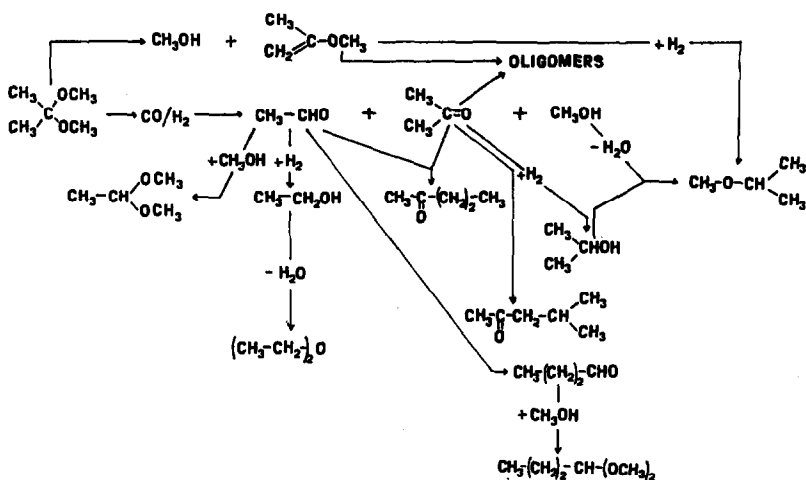
The yield of heavy byproducts, expressed as a weight percent of the reaction mixture, represents the sum of the products which are not detected by GC, and is determined by difference using the internal standard. In some experiments, particularly those using $\text{Co}_2(\text{CO})_8$ as catalyst, it has been verified that there is a good accordance between the values obtained by the internal standard procedure and by evaporation of a part of the reaction mixture.

Results

Origin of the products and byproducts

The main products observed during the hydrocarbonylation of DMP are acetaldehyde and its acetal ADMA, ethanol and diethyl ether. Besides these main products, we have also identified several byproducts, which together represent less than 10% of the total amount of products. These are butyraldehyde dimethylacetal, methyl propyl ketone, methyl isobutyl ketone and methyl isopropyl ether. Scheme 1 presents the reactions leading to products and byproducts, taking into account the possible thermal decomposition of DMP [7] and its dehydrating properties [8].

Concerning the heavy byproducts, the IR spectrum of the evaporation residue indicates that they consist mainly of a mixture of aldolization and crotonization products most likely derived from acetaldehyde and acetone.



Scheme 1.

Results obtained with different catalysts

Some transition metal complexes exhibit no activity at all in the hydrocarbonylation of DMP. These are, for example, $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{acac})_3$, $\text{HRu}_3(\text{CO})_{11}^-$ supported on magnesia, $\text{PdCl}_2(\text{PMePh}_2)_2$ with KOAc as a co-catalyst, $\text{PtCl}_2(\text{PPh}_3)_2 + \text{SnCl}_2$.

Among the complexes which have been tested, only the catalysts based on rhodium and cobalt exhibit some activity in the hydrocarbonylation reaction (Table 1).

TABLE 1

Effect of the nature of the catalyst

Run	Catalyst (mmol)		Tem- pera- ture ^a (°C)	Con- ver- sion (mol%)	Yield ^b (mol%)	Heavy by- products (wt.%)	Main products
H12	$\text{Rh}_6(\text{CO})_{16}$	(0.094)	172	93.4	13.05	11.5	Et_2O
H1	$\text{Rh}_6(\text{CO})_{16}/\text{Al}_2\text{O}_3$	(0.87)	172	96.3	9.5	30.2	Et_2O
H2	$\text{Rh}_6(\text{CO})_{16}/\text{Al}_2\text{O}_3$	(0.65)	136	43	10.8	12.3	Et_2O
H2ter	$\text{RhCl}(\text{PPh}_3)_3$	(0.54)	172	88.7	0.3	42.3	Et_2O
H3	$\text{RhH}(\text{CO})(\text{PPh}_3)_2$	(0.22)	172	100.0	6.1	36.4	ADMA
H14	$\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$	(1.16)	172	96.8	0	1.3	$\text{MeO}i\text{Pr}$, MeOH
H4	$(\text{CF}_3\text{C})\text{Co}_3(\text{CO})_9$	(0.39)	172	99.3	11.4	24.6	ADMA + EtOH
H24	$\text{Co}_2(\text{CO})_8$	(1.75)	183	99.2	15.6	15.3	ADMA

^aOther conditions: DMP = 0.4 mol, P ($\text{H}_2/\text{CO} = 1/1$) = 12 MPa at 25 °C, time = 6 h.

^bYield of hydrocarbonylation: see experimental part.

The rhodium-based catalyst, $\text{Rh}_6(\text{CO})_{16}$ leads to diethyl ether with moderate yields (13%). Supporting this cluster on alumina gives a catalyst exhibiting lower yields toward diethyl ether, whereas the heavy byproducts yield increases dramatically. This may be attributed to the acidic character of the support, which is able to catalyse aldolization reactions. The proportion of these secondary reactions decreases at lower temperatures, while the hydrocarbonylation yield is not much influenced.

The rhodium-phosphine complexes $\text{RhCl}(\text{PPh}_3)_3$ and $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ lead to high yields of heavy byproducts, the main hydrocarbonylation product being diethyl ether in the first case, ADMA in the second one. The complex $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ catalyses only the hydrogenolysis of DMP.

The most active catalyst in the hydrocarbonylation reaction of DMP is $\text{Co}_2(\text{CO})_8$, leading to ADMA as the main product. The cobalt cluster $(\text{CF}_3\text{C})\text{Co}_3(\text{CO})_9$ exhibits a different reactivity pattern, oriented mainly towards a mixture of ADMA and ethanol.

Influence of the reaction parameters with $\text{Co}_2(\text{CO})_8$ as catalyst

We have performed a series of experiments to optimize the selectivity of the hydrocarbonylation reaction towards ADMA and to reduce the condensation reactions leading to the heavy byproducts.

As clearly indicated in Table 2, the use of an apolar solvent like benzene does not change the selectivities at high temperatures compared to those obtained without solvent. But at lower temperatures, the yield of undesirable heavy oligomers is decreased. With dioxane as a solvent, such an effect is not observed. Therefore, a temperature decrease seems to have a favorable effect only in the case of benzene. However, even under those conditions, too long a reaction time is detrimental (run 29).

Table 3 describes the influence of ligands added to the octacarbonyl-dicobalt. The addition of tributylphosphine leads to an important decrease

TABLE 2

Effect of operating conditions with $\text{Co}_2(\text{CO})_8$

Run	Temperature ^a (°C)	Solvent	Conversion (mol%)	Yield (mol%)	Heavy byproducts (wt.%)	Remarks
H23	196	without	99.9	13.5	19.4	duration: 1h30
H24	183	without	99.2	15.6	15.3	duration: 0h30
H51	120	without	100.0	12.2	26.0	
H22	196	benzene	99.0	11.8	19.0	
H26	142	benzene	98.7	17.2	10.9	
H32	120	benzene	87.5	15.7	2.0	
H29	100	benzene	58.1	7.9	5.1	duration: 14h
H31	120	dioxane	96.4	9.5	25.3	

^aOther conditions: DMP = 0.4 mol (runs without solvent) or 0.2 mol (runs with solvent); solvent = 25 ml; P ($\text{H}_2/\text{CO} = 1/1$) = 12 MPa at 25 °C; $\text{Co}_2(\text{CO})_8 = 1.75$ mmol; duration 6 h (unless otherwise stated).

TABLE 3

Effect of ligands with $\text{Co}_2(\text{CO})_8$

Run	Ligand ^a	Molar ratio Ligand/cobalt	Solvent ^b	Temperature (°C)	Conversion (mol%)	Yield (mol%)	Heavy byproduct (wt.%)
H35	PBu ₃	1	C ₆ H ₆	130	13.9	0	9.4
H36	PBu ₃	1	without	170	52.2	3.7	32.7
H30	DMF	0.75	C ₆ H ₆	120	96.1	16.4	2.2
H44	py	0.5	C ₆ H ₆	120	90.5	14.4	11.6

^apy = pyridine; DMF = dimethyl formamide, PBu₃ = tributylphosphine.

^bOther conditions: DMP = 0.2 mol (H36: 0.4 mol), solvent = 25 ml, P ($\text{H}_2/\text{CO} = 1/1$) = 12 MPa at 25 °C, $\text{Co}_2(\text{CO})_8 = 1.75$ mmol, duration: 6 h.

in the catalytic activity. It is necessary to increase the reaction temperature from 130 °C to 170 °C to reach a conversion of roughly 50%, and then the amount of heavy byproducts becomes unacceptable. The presence of *N,N*-dimethylformamide as a ligand in benzene solution has a favorable effect, but addition of pyridine leads to a large increase in the proportion of heavy byproducts.

Finally, three more runs have been performed with a low H₂/CO ratio of 0.05/1, one without solvent, the other two with benzene as the solvent, with and without addition of pyridine, at 120 °C (other parameters as stated in Table 3). Under these conditions, DMP does not react.

Table 4 shows, as an example, the detailed repartition of the products obtained with optimized operating conditions.

TABLE 4

Example of an optimized repartition of products

Feed	DMP = 21.5 g Solvent: C ₆ H ₆ = 25 ml Co ₂ (CO) ₈ = 1.75 mmol DMF = 2.6 mmol	
Operating conditions	<i>P</i> (H ₂ /CO = 1/1) = 12 MPa at 25 °C <i>T</i> = 120 °C duration: 6 h	
Products	Light, unidentified	0.20 wt.%
	Me-CHO	0.27
	HCOOMe	0.11
	ADMA	20.68
	Me ₂ CO	41.64
	DMP	3.29
	MeOH	23.75
	Pr-CH(OMe) ₂	2.53
	Me-CO- <i>i</i> -Bu	5.33
	heavy byproducts	2.20

Discussion

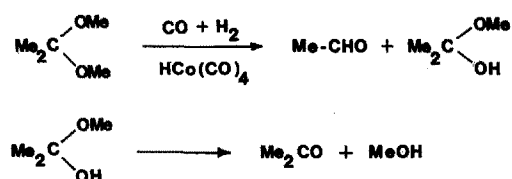
The main product of the hydrocarbonylation reaction of DMP is a derivative of acetaldehyde or of ethanol, depending on the nature of the catalytic complex. By analogy with our current understanding of the homologation reaction of methanol to ethanol, the compounds derived from ethanol should come from the hydrogenation of acetaldehyde, which is the primary reaction product.

The transformation of acetaldehyde either into acetal or into aldolization-crotonization products first depends on the acidic or basic properties of the reaction medium. In this reaction medium and under a pressure of synthesis gas, Co₂(CO)₈ is likely present as the dissociated acid form:

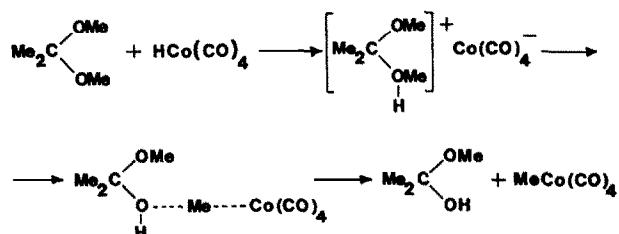
$\text{H}^+\text{Co}(\text{CO})_4^-$. This acidic character of the cobalt catalyst makes it able to promote transesterification and transacetalization reactions [9], and probably also aldolization reactions.

To reduce the secondary reactions, one can minimize the dissociation of $\text{HCo}(\text{CO})_4$ by adjusting the polarity of the medium. This is probably the role played by benzene. One can also reduce the acidity of $\text{HCo}(\text{CO})_4$ by introducing basic ligands [2, 10] into the coordination sphere of the metal. DMF seems in our case the most convenient. More basic ligands such as pyridine or phosphines induce aldolization of acetaldehyde to heavier by-products [11].

As far as the reaction scheme is concerned, one can regard the hydrocarbonylation reaction as occurring in two steps:



Assuming that the cobalt is present as a more or less dissociated form of $\text{HCo}(\text{CO})_4$, we propose for the first step a mechanism analogous to that suggested by Pino *et al.* in the case of orthoesters [1, 19]:



Once the methyl-cobalt bond is formed, insertion of CO and hydrogenolysis of the acylcobalt by H_2 or $\text{HCo}(\text{CO})_4$ can occur, following a classical scheme, leading to acetaldehyde.

In conclusion, it can be emphasized that under hydrocarbonylation conditions, a ketal seems to react more like an orthoester than like an acetal: it is the alkyl radical of the alkoxy group, and not the ketone radical, which is homologated.

Acknowledgements

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