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Letter

Amidocarbonylation of cyclohexene and 1-pentene with $Co_2(CO)_8$ modified with triarylstibines in very mild conditions

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In the memory of Prof. Jacobo Gómez-Lara.

Abstract

Interesting results, presenting the use of different stibine ligands in amidocarbonylation of cyclohexene and 1-pentene catalyzed by $Co_2(CO)_8$, not only enhance the activity of catalyst but also increases the selectivity in comparison to classical phosphinic ligands, have been reported. The stibine and phosphine ligands used were triphenylstibine (TPS), *o*- and *p*-tritolylstibine, (*o*-TTS, *p*-TTS) 2,4,6-trimesitylstibine (TMS), *p*-trifluorophenylstibine (*p*-TFPS), triphenylphosphine (TPP), *o*- and *p*-tritolylphosphine (*o*-TTP, *p*-TTP), respectively. All the reactions were carried out in a very mild syngas pressure (25 bar). © 2001 Published by Elsevier Science B.V.

Keywords: Amidocarbonylation; Cobalt; Stibines; Homogeneous catalysis; Aminoacids

1. Introduction

The olefin amidocarbonylation (Wakamatsu reaction) [1] constitutes a very convenient method to construct two functionalities in a single step, the reaction has been used to obtain racemic *N*-acyl aminoacids which have a very broad applications as sweeteners, surface active or chelating agents, detergents, etc. The study of cobalt catalyzed amidocarbonylation has reached several interesting progress [2–4] between 70 and 160°C with synthesis gas pressures of 150 and 200 bar [2–4] and in some cases with the presence of different type of ligands [5,6], however, the high operating syn gas and the problems of catalysts stability leads to a poor selectivity in the products as reported earlier [7]. In order to find an alternative catalyzed process herein, we wish to report the amidocarbonylation of olefins using a cobalt–stibine modified system. A good activity and selectivity was found using different type of stibinic ligands. We have previously reported that the use of these kinds of antimony compounds in the hydroformylation of 1-pentene increases extraordinarily the yield of aldehydes with an appreciable *n*/*iso* ratio [8].

2. Experimental

The THF (solvent) was purified, dried and deoxygenated prior to use, $Co_2(CO)_8$ was purchased from Strem Chemicals Co., cyclohexene, 1-pentene, the phosphinic ligands and triphenyl-

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Pathway (a)

$$\text{olefin} + H_2 + CO + H_2NCOCH_3 \xrightarrow[R_3Sb]{[Co]} \text{N-acyl aminoacid}$$

Pathway (b)

$$\text{olefin} + H_2 + CO \xrightarrow[R_3Sb]{[Co]} [\text{aldehyde}] \xrightarrow[H_2NCOCH_3]{[Co]} \text{N-acyl aminoacid}$$

Scheme 1.

stibine (TPS) were obtained from Aldrich. CO, H_2 were obtained from Matheson and Aga Gas Inc., respectively, and used without further purification. The ligands *o*- and *p*-tritolylstibine, (*o*-TTS, *p*-TTS) 2,4,6-trimesitylstibine (TMS), and *p*-trifluorophenylstibine (*p*-TFPS), were prepared according to a standard procedure [10–12].

The reaction products were analysed on a JEOL JMS-AX505HA GC–MS equipment with a 25 m × 0.25 mm glass column packed with 5% phenylsilicone and a Hewlett Packard 5890 analyzer with a 30 m × 0.53 mm glass column packed with methylsilicone.

The ^1H and ^{13}C NMR spectra were obtained in a JEOL 300 MHz spectrometer using TMS as internal reference in $CDCl_3$ as solvent at 25°C. The IR spectra were obtained by using a Nicolet FTIR Magna 750 spectrometer.

The isolation of the main products of the reaction (*N*-acyl aminoacids) was performed as follows:

1. cyclohexene derivative: the final solution was concentrated under vacuum and then treated with acetone to obtain the crystalline product of amidocarbonylation;
2. 1-pentene derivatives: the reactor solution was concentrated under vacuum and passed through a chromatographic column (silica gel 60–230 mesh) and eluted with hexene/ethyl acetate 40/60 in order to isolate the products.

2.1. General catalytic procedure

2.1.1. Pathway (a)

A solution of 3.46 mmol of the olefin, 5.20 mmol acetamide, 0.12 mmol of $Co_2(CO)_8$ and 0.12 mmol of R_3Sb in 10 ml of dry THF (in a Schlenk tube) was transferred to a stainless steel reactor (PARR) purged with N_2. After this, the reaction was taken until the desired pressure (28 bar, CO/H_2 3/1) and warmed in an oil bath at 120° for 20 h, at the end of this time, the reactor was cooled, the gases were liberated. The solution was worked up in order to yield the products of the reaction. The named solution was also analyzed by GC and GC–MS to quantify the remanent substrate and secondary products (aldehydes, alcohols).

2.1.2. Pathway (b)

A solution of 3.46 mmol of the olefin, 0.12 mmol of $Co_2(CO)_8$ and 0.12 mmol of R_3Sb in 10 ml of dry THF (in a Schlenk tube) was transferred to a stainless steel reactor (PARR) purged with N_2, taken until the desired pressure (28 bar, CO/H_2 3/1) and warmed in an oil bath at 120°C for 10 h, at the end of this time, the reactor was cooled and 5.20 mmol of acetamide were added, the reactor was recharged with 28 bar, CO/H_2 3/1 and warmed at 120°C for 10 h, at the end the solution was analyzed and worked up to give the reaction products.

Table 1
Selected experiments in cobalt–stibine catalyzed amidocarbonylation of cyclohexene pathway (a)[a]

Runs no.	*N*-acyl aminoacid isolated yield (mmol%)	Ligands
1	1.45	TMS
2	6.68	TPP
3	23.22	*p*-TTP
4	39.19	*o*-TTP
5	47.75	TPS
6	56.02	No ligand
7	57.18	*p*-TTS
8	77.50	*o*-TTS
9	77.79	*p*-TFPS

[a] $T = 120$°C; $t = 20$ h; $Co_2(CO)_8$/L (1/1) 0.12 mmol. Acetamide 5.20 mmol (1.5 eq), cyclohexene 3.46 mmol (1 eq); syn gas pressure CO/H_2 (3/1) (28 bar); THF (10 ml).

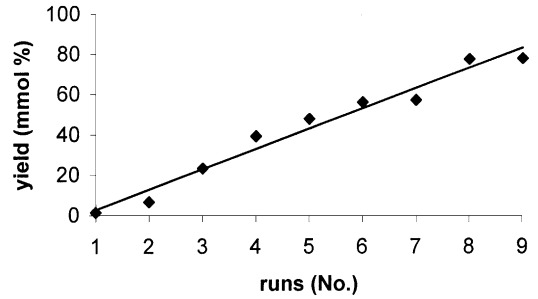

Fig. 1. *N*-acyl aminoacid pathway (a).

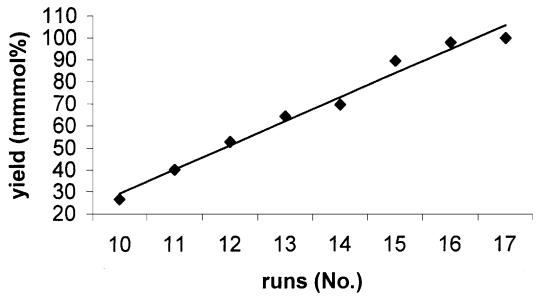

Fig. 2. *N*-acyl aminoacid pathway (b).

3. Results and discussion

This paper presents the early results obtained in the formation of *N*-acyl aminoacids via two different procedures: (a) the direct amidocarbonylation reaction, and (b) the hydroformylation-amidation reaction, both catalyzed by the $Co_2(CO)_8/R_3Sb$ system (Scheme 1) under very mild conditions of 25 bar of syn gas pressure and 120°C of temperature.

The results obtained when the reaction was studied using the pathway (a) are shown in the Table 1 and Fig. 1.

As we can see in these very mild conditions (25 bar of syn gas pressure), the reaction yields 60% of conversion in the absence of ligands while the addition of phosphinic ligands decreases the reaction rate because the formation of less active species which inhibits the aldehyde synthesis as previously reported [9]. However, when stibine ligands were used in the process, the reaction rate was increased and the total *N*-acyl aminoacid yield was almost 80% (in same conditions). In the present study, the ligands *o*-TTS and *p*-TFPS gave the best results, maybe the good π-acceptor character of these antimony species is responsible for the enhancement of exchange of ligands, giving the appropriate nucleophilic cobalt intermediates needed in the amidocarbonylation process.

When the reaction was carried out according to the conditions of pathway (b) the acetamide was added in the media after 10 h of reaction. The results are shown in Table 2 and Fig. 2.

As one can observe, these conditions the reaction is almost quantitative in *N*-acyl aminoacid. In this two steps formation of aminoacid also, the ligands *o*-TTS and *p*-TFPS gave the best results and it seems that the retardatary addition of the amide eliminates in

Table 2
Selected experiments in cobalt–stibine catalyzed amidocarbonylation of cyclohexene pathway (b)[a]

Runs no.	*N*-acyl aminoacid isolated (mmol%)	Ligands
10	26.71	TTP
11	40.06	*p*-TPP
12	52.83	TMS
13	64.15	TPS
14	69.52	No ligand
15	89.40	*p*-TTS
16	97.68	*o*-TTS
17	99.71	*p*-TFPS

[a] $T = 120$°C; $t = 20$ h; $Co_2(CO)_8$/L (1/1) 0.12 mmol. Acetamide 5.20 mmol (1.5 eq) (added after 10 h of reaction); cyclohexene 3.46 mmol (1 eq); syn gas pressure CO/H_2 (3/1) (28 bar); THF (10 ml).

Table 3
Selected experiments in cobalt–stibine catalyzes amidocarbonylation of 1-pentene pathway (b)[a]

Runs no.	*N*-acyl aminoacids		Isolated yield (mmol%)	Ligand
	n (%)	*iso* (%)		
18	51	49	43.17	No ligand
19	63	36	39.38	TMS
20	67	33	47.46	*p*-TFPS
21	67	33	60.34	*p*-TTS
22	67	33	60.82	*o*-TTS

[a] $T = 120$°C; $t = 20$ h; $Co_2(CO)_8$/L(1/1) 0.12 mmol. Acetamide 5.2 mmol (1.5 eq) (added after 10 h of reaction) 1-pentene 3.46 mmol (1 eq); syn gas pressure CO/H_2 (3/1) (28 bar); THF (10 ml). The *n*/*iso* ratio was determined by ^{1}H RMN using the signal at 6.38 ppm corresponding to the amide proton.

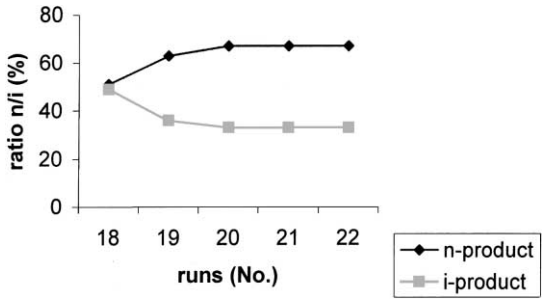

Fig. 3. Amidocarbonylation of 1-pentene.

this case, the possibility of competitive coordination to cobalt atom in the hydroformylation steps.

In order to have some information about the selectivity in amidocarbonylation with the catalytic system $[Co_2(CO)_8/R_3Sb]$ here studied, we carried up some experiments using 1-pentene as olefinic sustrate, reaction pathway (b) was selected and the results are show in Table 3 and Fig. 3.

It was found that the use of named stibinic ligands also improve marginaly the selectivity of the process here reported. Studies to explore the stibine effect into the cobalt species and the generalization of the reaction are in progress.

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