



Pt-based chiral organotin modified heterogeneous catalysts for the enantioselective hydrogenation of 3,4-hexanedione

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ABSTRACT

In this paper we have studied the liquid-phase enantioselective hydrogenation of 3,4-hexanedione using Pt-based catalysts, modified with chiral organotin compounds derived from the (–)-menthyl group: (–)-Pt-MenSnBu₃ and (–)-Men₃Sn-Sn-(–)-Men₃. The organotin chiral modifiers were carefully synthesized and characterized in order to obtain optically pure compounds.

The catalysts were prepared through a controlled surface reaction between the supported transition metal and the organometallic compound, using techniques derived from Surface Organometallic Chemistry on Metals (SOMC/M). The organobimetallic catalytic systems were found to be active and enantioselective in the hydrogenation of 3,4-hexanedione, yielding an enantiomeric excess of 25–27% for 4-hydroxy-3-hexanone.

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1. Introduction

Most of the work reported in the literature on the heterogeneous enantioselective hydrogenation of carbonyl compounds employs catalysts based on Pt modified with alkaloids from the cinchona family [1]. As is well known, these catalysts are particularly effective in the hydrogenation of α -ketoesters, allowing one to obtain the corresponding α -hydroxy esters with enantiomeric excesses of up to 98% [2]. To a lesser extent, these systems have been employed in the hydrogenation of α -diketones, such as 2,3-butanedione, 2,3-hexanedione, 3,4-hexanedione, 1,2-cyclohexanedione and 1-phenyl-1,2-propanodione, reaching enantiomeric excesses generally much lower than those obtained for α -ketoesters [3–7].

The hydrogenation of α -diketones presents an interesting challenge, both in terms of regio- and enantioselectivity due to the fact that these compounds have two carbonyl groups that may be hydrogenated. Due to the presence of two conjugated keto groups, the reaction proceeds in two consecutive steps: in the first place, one C=O group is hydrogenated and in a later stage the other one is [4]. The products of the hydrogenation of these vicinal

ketones, optically active hydroxyketones and diols, are widely used in the synthesis of pharmaceutical products. An interesting example is the hydrogenation of 1-phenyl-1,2-propanodione, whose hydrogenation product (R)-1-hydroxy-1-phenyl-2-propanone is an intermediate product in obtaining ephedrine derivatives.[8]

Fig. 1 outlines the reaction products of a relatively simple α -diketone, 3,4-hexanedione. As can be seen, in a first stage two α -hydroxyketones are formed, (S)- and (R)-4-hydroxy-3-hexanone, and in a second step (S,S)- and (R,R)-3,4-hexanediol and meso-hexanediol appear. According to bibliographic reports for the hydrogenation of 3,4-hexanedione using Pt/cinchonidine catalysts, 4-hydroxy-3-hexanone is mainly formed, the highest enantiomeric excesses reported being of ca. 20% [3,9].

The addition of tin compounds in general, and organotin compounds in particular, have proven to have a great influence on the behavior of platinum catalysts. Thus, the addition of tin to a Pt/Al₂O₃ reforming catalyst results in a higher catalytic activity toward the aromatization of hydrocarbons [10,11], and also the use of tin in Pt-based systems leads to a large increase in the overall rate in the hydrogenation of α,β -unsaturated aldehydes together with a high selectivity toward the formation of the corresponding unsaturated alcohols [12,13].

To fully understand the reason for the benefit of adding tin to platinum catalysts, it should also be noted how tin is added. Among the techniques of controlled preparation of catalysts are those derived from the Surface Organometallic Chemistry on Metals (SOMC/M), which consists of the reaction of organometallic com-

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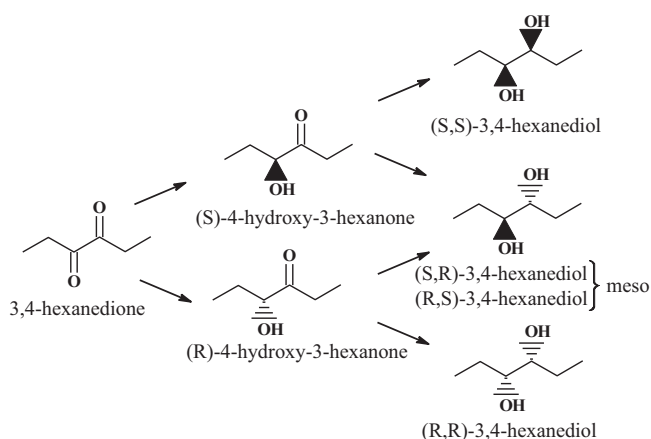


Fig. 1. Reaction pathway for 3,4-hexanedione hydrogenation.

pounds of elements from the representative groups, transition metals, lanthanides and actinides with the surface of supported metals [14]. By applying this technique, it is not only possible to prepare well-defined catalysts that may be alloys of a given composition but also catalysts in which organometallic fragments are likely adsorbed (coordinated) at some particular crystallographic positions of the metallic particles. These materials exhibit interesting and unusual selectivities in many catalytic reactions [15,16].

Special mention should be made of organobimetallic catalytic phases where one or more of the organic fragments have chiral characteristics. In this case, by using SOMC/M techniques, heterogeneous chiral catalysts of very good quality in terms of chemo- and enantioselectivity, as well as good stability and reuse capability, have been obtained [17,18].

The present paper reports on the controlled route for the preparation of chiral organobimetallic catalysts via SOMC/M techniques, as well as an interesting application in a reaction requiring high activity as well as chemo- and enantioselectivity, as is the liquid phase hydrogenation of 3,4-hexanedione. The selected chiral organotin compounds contain (–)-menthyl groups in their composition, and must be carefully synthesized and characterized in order to assume a high optical purity.

2. Experimental

2.1. Synthesis and characterization of (–)-menthyl derived organotin compounds

2.1.1. (–)-Menthyltributyltin (1*R*,2*S*,5*R*)-(–)-MenSnBu₃

To a solution of (–)-menthylmagnesium chloride in THF (5.3 mmol, 3.3 mL of a 1.59 M solution), a solution of *n*-tributyltin chloride (1.5 g, 4.6 mmol, 1.24 mL) and triphenylphosphine (1.26 g, 4.8 mmol) in dry THF (6 mL) was added from a pressure-equalizing funnel, with stirring and under a nitrogen atmosphere. The mixture was kept under stirring at room temperature for 20 h. Then, it was decomposed with the addition, dropwise, of a solution of HCl 10%. The organic phase was extracted with dichloromethane (10 mL), washed twice with distilled water and dried with MgSO₄.

The solvent was distilled under reduced pressure. To the residue obtained hexane (3 mL) and dichloromethane (2 mL) were added to precipitate the triphenylphosphine, which was removed by filtration. The product was purified by chromatography on a silica gel 60 column, eluting with hexane (1.72 g, 4.0 mmol, 87%), $[\alpha]_D^{20} = -30.5^\circ$ (1.5, benzene).

2.1.2. Hexa-(–)-menthyliditin (–)-Men₃Sn-SnMen₃

The reaction was carried out in a three-necked round-bottomed flask, fitted with a reflux condenser, magnetic stirrer and pressure equalizing ampoule, under N₂ atmosphere. To a solution of 10.3 g (0.040 mol) of SnCl₄ in 48 mL of dry benzene, in an ice bath, 150 mL of 1.58 M solution (0.240 mol) of (–)-menthylmagnesium chloride in dry THF was added dropwise. Upon completion of the addition, the reaction mixture was heated under reflux for 60 h and then it was allowed to cool to room temperature under stirring. A 10% HCl solution (25 mL) and distilled water (25 mL) were added. After addition of ethyl ether (200 mL), the organic phase was separated and dried on anhydrous MgSO₄. The solvent was distilled under reduced pressure and the product was recrystallized from ethanol, yielding 12.9 g (0.012 mol, 59.8%) of hexa (–)-menthyliditin, mp: 230 °C (dec.), $[\alpha]_D^{20} = -214^\circ$ (0.99 dry benzene).

The compounds obtained were characterized by ¹H NMR, ¹³C and ¹¹⁹Sn in a Bruker ARX 300 instrument.

2.2. Preparation and characterization of the catalysts

The monometallic catalyst was prepared by ion exchange, using SiO₂ (Evonik (previously Degussa) Aerosil 200, 180 m² g⁻¹) as support, which had been previously treated with an ammonia solution. The functionalized solid was put in contact with an aqueous solution of [Pt(NH₃)₄]Cl₂ of the appropriate concentration to obtain a catalyst with a Pt content of 1 wt.%. After 24 h exchange at room temperature, the solid was filtered off, washed and dried at 105 °C and subsequently reduced in H₂ flow at 500 °C.

The chiral organotin catalysts were prepared using techniques derived from the Surface Organometallic Chemistry on Metals (SOMC/M). After the reduction step, 0.25 g of monometallic catalyst was put in contact with either (–)-MenSnBu₃ or (–)-Men₃Sn-Sn-(–)-Men₃ dissolved in *n*-decane. The reaction was carried out for 4 h in H₂ atmosphere at 120 °C. Upon completion of the reaction, the catalyst was washed repeatedly with *n*-heptane in Ar atmosphere. These catalysts, which have a molar ratio Sn/Pt of 0.8, are designated Pt-Men₆Sn₂ and Pt-MenSnBu₃, and correspond to solids containing organic groups anchored to their surfaces.

The composition of the catalysts was determined by atomic absorption spectroscopy (AAS) using a Varian Spectra AA55 instrument, after digestion in an acid solution and dilution. Temperature Programmed Reduction (TPR) tests were performed in a Quantachrome apparatus equipped with a thermal conductivity detector. Each sample, previously calcined at 500 °C for 4 h, was heated from room temperature to 800 °C at a heating rate of 10 °C min⁻¹ in a reducing gas stream (25 cm³ min⁻¹, 5% H₂ in N₂). Hydrogen and CO chemisorption measurements were performed in pulse dynamic equipment with catharometric detection, considering a stoichiometry of adsorption H/Pt_s and CO/Pt_s. The determination of metallic particle size distribution was carried out by transmission electron microscopy (TEM) in a JEOL 100Cx microscope, having a resolution of 6 Å and an accelerating voltage of ca. 100 kV. The samples were ground and ultrasonically dispersed in distilled water. To estimate the mean particle size, the particles were considered spherical and the second moment of the distribution was employed. The expression used for the calculation was:

$$d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2}$$

where n_i is the number of particles with d_i size. Over 200 particles were measured.

The Sn/Pt atomic ratio of the organobimetallic catalysts was measured spectrophotometrically, at 530 nm, by forming a complex between Sn and phenylfluorone in a GBC Cintra 20

spectrophotometer, following the procedure of reference [19]. For the preparation of standard solutions metallic Sn (0.4930 g) was used, which was dissolved in concentrated HCl (50 mL) and allowed to stand for 24 h, heating without boiling. From this solution, the necessary dilutions were made using 1:9 HCl as a diluent. Tests performed for different concentrations of tin allowed us to determine that the optimal working range is 0.02–0.12 ppm Sn.

2.3. Hydrogenation of 3,4-hexanedione

Hydrogenation of 3,4-hexanedione was carried out in autoclave-type reactor at 1 MPa H₂ pressure, with temperature ranging from 40 to 80 °C, using 0.25 g of catalyst and 2-propanol as solvent. The catalysts obtained were transferred to the autoclave reactor in Ar atmosphere. In each test, 0.4 mL of 3,4-hexanedione and 60 mL of 2-propanol (0.06 M) were used. It was verified that the stirring speed and the catalyst particle size used ensured that diffusional limitations were negligible.

The course of the reaction was followed by taking a series of micro-samples, which were analyzed in a Varian CP-3800 gas chromatograph equipped with a capillary column CP wax 52 CB (30 m, 0.53 mm i.d.) and a FID detector. The reaction products were identified using a GC/MS Shimadzu QP5050 with a capillary column Supelco SPB™-5 (30 m, 0.25 mm i.d.). The enantiomeric excess (ee) was calculated according to the following equation: $ee\% = 100(S - R)/(S + R)$, from the data obtained by gas chromatography on a capillary column BETA DEX™ 120 (30 m, 0.25 mm i.d.).

3. Results and discussion

3.1. Synthesis and characterization of (–)-menthyl derived organotin compounds

A key step in the preparation of the enantioselective heterogeneous catalysts used in this work is the synthesis of the organotin compounds employed as chiral precursors. Due to the configurational instability of the most common intermediates employed in the synthesis of chiral organotin compounds, triorganotin halides, many techniques aiming to stabilize the configuration of these compounds have been developed [20–25].

In order to control the configuration of the metal, Schumann et al. anchored a (–)-menthyl ligand to a tin atom (see Fig. 2) [26,27]. In 1994 Podestá and Radivoy obtained the hexa-(–)-menthyliditin from which other derivatives of (–)-menthyl could be synthesized [28]. The studies of these authors confirmed that, in the binding of (–)-menthyl ligand to a tin atom by reacting (–)-menthylmagnesium chloride and tin tetrachloride, the configuration could be retained.

Chiral organotin compounds containing the chiral carbon atom directly bonded to the Sn atom exert a greater asymmetric induction than those with the chiral center in a more remote position [28]. Taking this fact into account, it was proposed to synthesize (–)-menthyltin derivatives for use in the preparation of chiral heterogeneous catalysts.

The (–)-menthyl radical, which will be called in abbreviated form (–)-Men or just Men, has three chiral centers of configuration (1R,2S,5R) (Fig. 2). In this figure it can also be seen that for the two organometallic compounds synthesized in this work, (–)-menthyltributyltin and hexa-(–)-menthyliditin, the carbon atom of the (–)-menthyl group designated as 1 is the one that is bound to the Sn atom. It is expected that the enantioselectivity of the resulting catalysts will not only be given by this chiral center directly attached to Sn, but also by a steric effect caused by the (–)-menthyl group as a whole. Fig. 2 shows the spatial structure of these compounds.

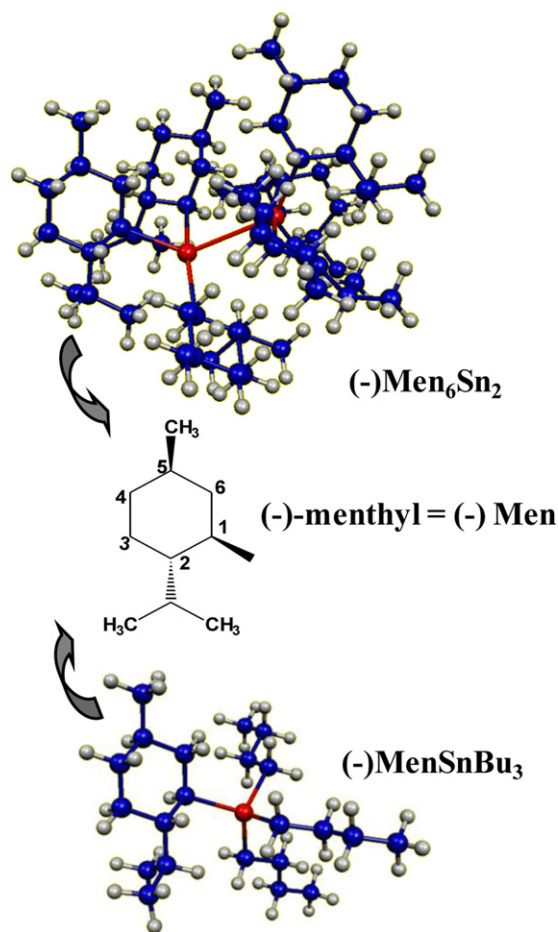


Fig. 2. Structure of (–)-menthyltin derivatives (●) H; (●) C; (●) Sn.

The preparation of compounds derived from (–)-menthyl tin involves several steps where, as already mentioned, the main problem is the retention of the configuration of the chiral inductor group until the end of the synthesis. The C1 carbon atom of the (–)-menthyl group has a marked tendency to epimerization, i.e. to change its configuration, which can lead to obtaining a mixture of product of little use as chiral modifier. One of the strategies used to prevent the epimerization of this carbon atom is the addition of a Lewis base such as triphenylphosphine during the synthesis [29].

Generally speaking, the synthesis of (–)-menthyl derived organotin compounds involves the reaction between a triorganotin halide and a Grignard reagent containing the (–)-menthyl group. According to what is reported in the literature, the epimerization could be related to the Lewis acidity of the triorganotin precursor. The first step in the above-mentioned general reaction would involve the transfer of an electron from the Grignard reagent to the Lewis acidic Sn atom of the triorganotin compound. As a result of this electron transfer, a radical cation of planar geometry is formed losing its original stereochemistry. The addition of a Lewis base results in an interaction between it and the triorganotin halide, with the formation of an adduct. The adduct has different electronic properties from the triorganotin halide, inhibiting the electron transfer from the Grignard reagent and the subsequent inversion of configuration of the C1 atom of the (–)-menthyl group.

The synthesis of (–)-MenSnBu₃ is represented by the following equation:

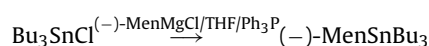


Table 1
¹³C and ¹¹⁹Sn NMR characteristics of synthesized compounds.^a

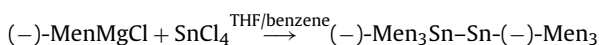
δC_n [$^nJ(^{13}C, ^{119}Sn)$]	MenSnBu ₃ ^b	Men ₆ Sn ₂
C ₁ (¹ J)	32.57 (409.1)	39.62 (196.4)
C ₂ (² J)	47.24 (14.6)	46.30 (19.0)
C ₃ (³ J)	27.11 (56.0)	27.63 (46.3)
C ₄ (⁴ J)	36.04 (NO)	35.70 (NO)
C ₅ (³ J)	35.76 (58.2)	36.54 (63.7)
C ₆ (² J)	41.79 (16.9)	45.50 (NO)
C ₇	23.02	22.42
C ₈ (³ J)	34.0 (17.6)	34.43 (11.8)
C ₉	22.49	22.10
C ₁₀	16.17	17.32
¹¹⁹ Sn	-23.8	18.0

^a In CDCl₃; chemical shifts, δ , in ppm with respect to TMS (¹³C spectra) and Me₄Sn (¹¹⁹Sn spectra); coupling constants, $^nJ(Sn, C)$, in Hz (in parenthesis); NO, not observed.

^b Other signals: 9.05 (295.9), 14.08; 28.04 (54.1), 29.82 (19.2).

In the absence of triphenylphosphine, a mixture of (1R,2S,5R)-MenSnBu₃ and (1S,2S,5R)-MenSnBu₃ epimers in a 3:1 ratio is obtained.

The hexa-(–)-menthyliditin was obtained by direct alkylation of tin tetrachloride, SnCl₄, with (–)-menthylmagnesium chloride (–)-MenMgCl. The following equation outlines the reaction involved in this synthesis:



During the course of this reaction, besides hexa-(–)-menthyliditin, tri-(–)-menthyltin chloride (–)-Men₃SnCl and di-(–)-menthyltin dichloride (–)-Men₂SnCl₂ are also obtained. Studies on the variation of experimental parameters in the yield of this reaction allowed optimizing the conditions leading to a greater proportion of the desired product [30]. Tables 1 and 2 list the results of ¹H, ¹³C and ¹¹⁹Sn NMR characterization of both compounds synthesized in this work. The results there presented indicate that optically pure compounds were obtained, without epimerization of the C1 atom.

3.2. Catalysts preparation and characterization

The Pt/SiO₂ monometallic catalyst (1 wt.% Pt measured by atomic absorption) was prepared by ionic exchange, a method that allows catalysts having a high dispersion to be obtained (H/Pt = 0.65 and 0.55, measured by H₂ and CO chemisorption, respectively).

The results of Transmission Electron Microscopy (TEM) measurements indicate that the particle size distribution of the monometallic Pt/SiO₂ catalyst is very narrow, with a mean particle diameter around 2.5 nm. The metal dispersion is calculated from the Pt particle size distribution obtained from TEM measurements by the following equation, assuming spherical particles [31]:

$$D = \frac{6M_{Pt} \sum n_i d_i^2}{\sigma \rho_{Pt} \sum n_i d_i^3}$$

where M_{Pt} and ρ_{Pt} are the molar mass and density of Pt, respectively; n_i is the fraction of particles with a diameter d_i , and σ is the area occupied by 1 mol of Pt at the surface ($3.75 \times 10^4 \text{ m}^2 \text{ mol}^{-1}$). The value of the dispersion calculated using the above-mentioned

Table 2
¹H NMR characteristics of synthesized compounds.^a

Compound	δ , ppm (multiplicity, n° H, coupling constants nJ in Hz), CDCl ₃
MenSnBu ₃	0.54–0.93 (m, 24H); 0.94–1.89 (m, 22H)
Men ₆ Sn ₂	0.73 (d, 18H); 0.79 (d, 18H); 0.84 (d, 18H); 1.07–2.17 (m, 60H)

^a In CDCl₃; chemical shifts, δ , in ppm with respect to TMS.

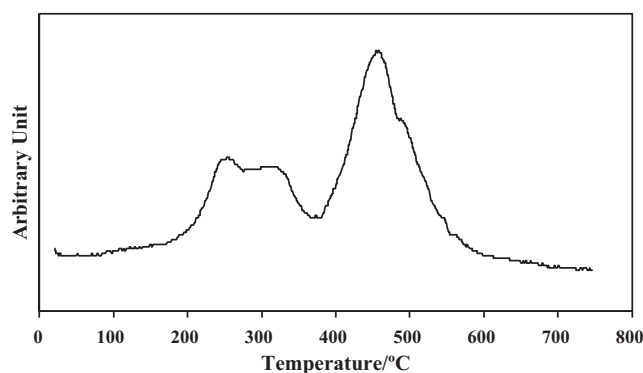
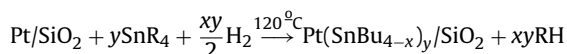


Fig. 3. Temperature Programmed Reduction of Pt/SiO₂.

expression for the Pt/SiO₂ catalyst is 0.58. It can be seen that the dispersion value obtained from TEM measurements is quite similar from the one obtained by H₂ and CO chemisorption. The high dispersion of the metallic phase is a consequence of the strong interaction between the metal precursor and the support generated during the impregnation step and that is maintained even after the reduction in H₂ for obtaining the supported metal particles. This characteristic of high dispersion of the monometallic system is essential to ensure an adequate preparation of the organobimetallic catalysts through SOMC/M techniques.

Temperature Programmed Reduction (TPR) results obtained for the Pt/SiO₂ system showed the presence of two peaks: one at about 250 °C and the other at 500 °C (Fig. 3). According to the literature, the low temperature peak can be assigned to the presence of Pt(IV) species, generated during the calcination pretreatment. The high temperature peak may be assigned to species of the type Pt-(O-Si≡)_y^{n-y} ($n = +2$ or $+4$), formed through the interaction of the metallic precursor and the support [32]. The peaks obtained were broad and presented shoulders, which could be due to the different environment of the ions on the support surface. From this profile, a reduction temperature of 500 °C was chosen, in order to obtain a completely reduced Pt/SiO₂ catalyst.

Tin-modified catalysts were obtained by a controlled surface reaction between the previously reduced monometallic catalyst and the organotin compound dissolved in n-decane. At the temperature of 120 °C, which was selected for the preparation, the reaction that takes place may be schematized by the following equation:



In this equation, R indicates the organic fragments bonded to the tin atom in the organotin precursor. After the reaction, the product is an organobimetallic system with some organic groups anchored to the surface. These organic fragments represent either butyl or (–)-menthyl groups bonded to the tin. The amount of tin fixed, measured spectrophotometrically, is indicated by the “y” value ($y = \text{Sn}/\text{Pt} = 0.8$). Organobimetallic catalyst are designated Pt-Men₆Sn₂ and Pt-MenSnBu₃. Unfortunately, so far it has not been possible to determine the number and characteristics of organic groups anchored to the surface. However, the results presented in this paper and others previously published show that these systems induce enantioselectivity in the hydrogenation of certain prochiral carbonyl compounds, strongly suggesting that at least some (–)-menthyl groups remain anchored to the surface [17,18]. Furthermore, in the case of modifier MenSnBu₃, theoretical calculations carried out in our research group work show that the difference in binding energy Sn–C (where C is the carbon atom belonging to each substituent, which is attached to Sn) for butyl (–)-menthyl is very small, the retention of menthyl groups on the catalyst surface being highly probable [33].

Table 3
Selectivity at 90% of conversion for Pt-Sn₂Men₆ catalyst.

T (°C)	ri ^a	S _I % ^b	S _{II} % ^b	S _{III} % ^b	ee _I % ^c	ee _{II} % ^c
40	110	80	7	13	27	4
60	280	75	8	17	20	5
80	670	78	7	15	15	–

^a Initial reaction rate (ri) ($\mu\text{mol s}^{-1} \text{gPt}_s^{-1}$). Estimated between conversion 0 and 10%.

^b I = (S)- + (R)-4-hydroxy-3-hexanone; II = (S,S)- + (R,R)-3,4-hexanediol; III = meso-hexanediol.

^c ee% = 100(S – R)/(S + R).

3.3. Hydrogenation of 3,4-hexanedione

The influence of temperature on catalytic activity was investigated between 40 and 80 °C, 1 MPa H₂ pressure and an initial 3,4-hexanedione concentration of 0.06 M, employing the Pt-Sn₂Men₆ catalyst. As can be observed in Table 3, the initial reaction rate increased from 110 to 670 $\mu\text{mol s}^{-1} \text{gPt}_s^{-1}$ when the temperature was raised from 40 to 80 °C. After 180 min reaction, over 90% conversion was achieved at the three temperatures. Concerning selectivity, for all the studied temperatures, 4-hydroxy-3-hexanone was obtained as the major product with a selectivity of ca. 80%.

Table 3 also lists the enantiomeric excess (ee%) achieved at the three temperatures tested. The values shown in the table indicate a decrease in the enantiomeric excess for the first hydrogenation step from 27% to 15% when the reaction was carried out at 40 °C and 80 °C, respectively. In an enantioselective hydrogenation reaction, one of the enantiomers is to be produced predominantly over the other. However, due to the similarity of the spatial arrangement of the contributing intermediate activation complexes, the activation energy that leads to the formation of either one enantiomer or the other will not be very different and, therefore, it is expected that a reduction in the reaction temperature would promote the differentiation between them and, accordingly, a higher ee% would be obtained. The achievement of higher ee% values with decreasing reaction temperature is a fact that has been observed by several authors in asymmetric heterogeneous catalysis [34,35].

Fig. 4 shows the variation in the molar composition of the reaction mixture as a function of time obtained when studying the hydrogenation of 3,4-hexanedione, at 40 °C, with the three catalysts prepared: Pt (Fig. 4a), Pt-MenSnBu₃ (Fig. 4b) and Pt-Sn₂Men₆ (Fig. 4c). As can be seen, for the three systems, after an induction period, the hydrogenation takes place in two stages. In a first step, up to about 150 min reaction, the hydrogenation of one of the C=O groups of the 3,4-hexanedione molecule occurs, yielding solely 4-hydroxy-3-hexanone. At a later stage, by hydrogenation of the hydroxyketone, the corresponding diols are obtained. As shown in the figure, all the catalytic systems allow an almost complete conversion of 3,4-hexanedione at about 250 min. However, for the second reaction step there is some difference in the behavior of the catalysts. Systems modified with organotin compounds (Fig. 4b and c) seem to be somewhat more active than the monometallic catalyst (Fig. 4a), in particular the Pt-Sn₂Men₆ catalyst. The analysis of Fig. 4 shows that when using the systems Pt-Men₆Sn₂ and Pt-MenSnBu₃ the hydrogenation of 4-hydroxy-3-hexanone occurs faster. This is particularly clear in Fig. 3c that shows a sharp decline in the composition of the hydroxyketone as a function of time, and a significant increase in the amount of hexanediols obtained at the end of the experiment (53% meso-hexanediol and 25% (S,S)- and (R,R)-3,4-hexanediol).

To explain these facts it is necessary to take into account the changes in the characteristic of the hydrogenation active sites that may be caused by the addition of an organotin compound to the catalytic system. Catalytic systems based on Pt modified with SnBu₄,

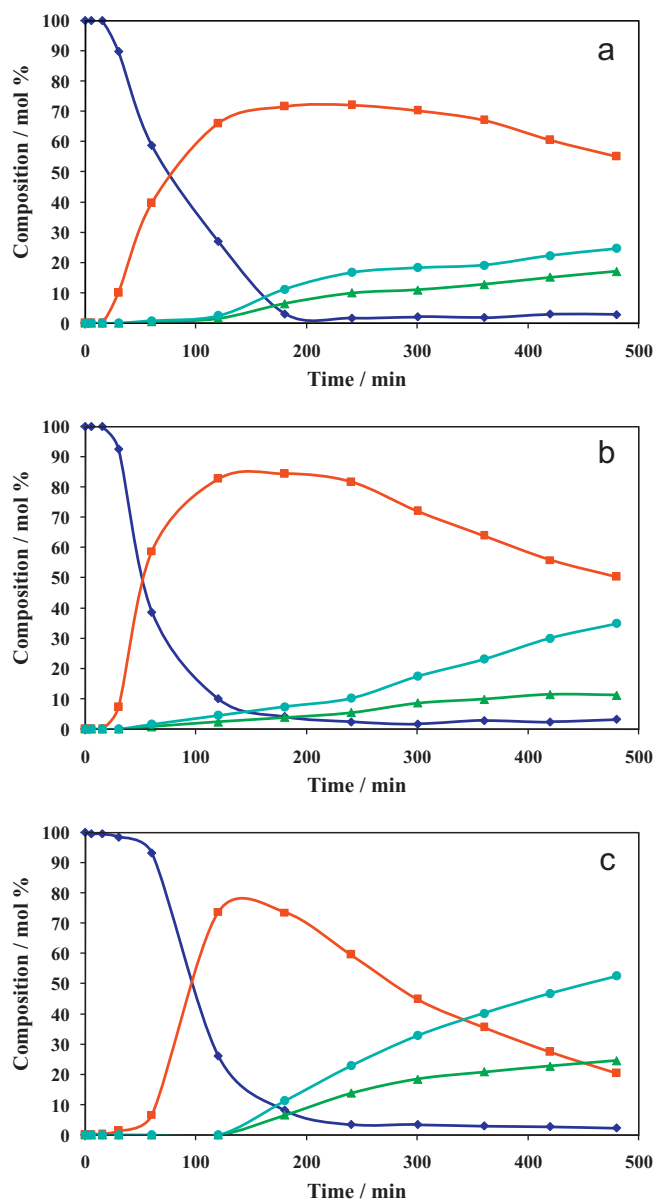


Fig. 4. Concentration profiles (mol%) along the reaction on Pt (a); Pt-MenSnBu₃ (b) and Pt-Men₆Sn₂. (♦) 3,4-hexanedione, (■) 4-hydroxy-3-hexanone, (▲) 3,4-hexanediol, (●) meso-3,4-hexanediol.

analogous to those presented here, have been characterized by our research group using EXAFS, XANES and XPS techniques [36]. These studies revealed that in the organobimetallic systems there is a convergence of geometric and electronic effects due to the presence of Sn. It has also been found that Sn is present on the surface of the catalyst both in ionic state (Sn(II,IV)) and as a metal (Sn(0)). The presence of ionic tin, having electrophilic properties, increases the polarization of the C=O group of the hydroxyketone thereby facilitating the attack of the chemisorbed hydrogen and favoring the second stage of hydrogenation. For the catalytic systems studied here, these facts allow us to explain why 3,4-hexanediol is obtained from 4-hydroxy-3-hexanone. On the other hand, the presence of (–)-menthyl groups attached to tin could contribute to the effect observed by some kind of geometrical interaction.

Table 4 lists the selectivity to the reaction products at two levels of conversion of 3,4-hexanedione. As can be seen, there is an increase in the selectivity to diols, at the expense of the hydroxyketone, as the reaction evolves. It is worth mentioning that for

Table 4
Selectivity to products at 40 °C, measured at two different levels of conversion.

Conversion %		Catalyst		
		Pt	Pt-MenSnBu ₃	Pt-Sn ₂ Men ₆
S _I % ^a	X = 70	94	96	>99
	X = 98	71	84	62
S _{II} % ^a	X = 70	2	1	<1
	X = 98	12	6	14
S _{III} % ^a	X = 70	4	3	<1
	X = 98	17	10	24
ee _I % ^b	X = 70	–	23	25
	X = 90	–	25	27
ee _{II} % ^b	X = 70	–	4	–
	X = 90	–	3	4

^a I = (S)- + (R)-4-hydroxy-3-hexanone; II = (S,S)- + (R,R)-3,4-hexanediol; III = meso-hexanediol

^b ee% = 100(S – R)/(S + R).

none of the catalytic systems used in this work, we have detected the formation of hemiketals between the solvent (2-propanol) and 3,4-hexanedione or 4-hydroxy-3-hexanone. According to what has been reported in the literature, these by-products have been observed in the hydrogenation of 2,3-butanedione in the presence of ethanol as solvent [4].

Systems modified with organotin chiral inductors proved to be enantioselective, especially in the first stage of hydrogenation reaching, for both systems, enantiomeric excess values of approximately 25% for 4-hydroxy-3-hexanone. However, these chiral catalysts showed a low enantiodifferentiating capacity to the corresponding diols. In Table 4 are reported the enantiomeric excesses obtained at two levels of conversion, which remain approximately constant. In addition, no significant variation in these values throughout the experiment has been detected. From the results presented in this work, it can be concluded that the structure of the chiral modifier seems to have no influence on the enantiodifferentiating ability of the systems. It is noteworthy that the enantiomeric excess obtained for 4-hydroxy-3-hexanone is comparable to that reported in the literature when classic Pt/cinchonidine systems are employed as catalysts [4,9]. The organotin chiral catalysts proposed in this paper have the additional advantage of being able to be reused, maintaining their activity, and chemo- and enantioselectivity in several successive cycles of hydrogenation, as has been shown previously for the enantioselective hydrogenation of other prochiral carbonyl compounds [17].

4. Conclusions

The main conclusions of this study are summarized below:

- It has been possible to obtain (–)-menthyl derivatives of organotin compounds with retention of the configuration of the chirality-inducing group.
- It has been possible to prepare organobimetallic heterogeneous catalysts by a surface controlled reaction, between the chiral organotin compound and the monometallic Pt/SiO₂ catalyst.
- The chiral heterogeneous systems obtained have been active in the liquid phase hydrogenation of 3,4-hexanedione.
- An increase in the ee% obtained with a decrease in the reaction temperature has been observed.
- The systems Pt-Men₆Sn₂ and Pt-MenSnBu₃ proved to be enantioselective reaching an ee% for 4-hydroxy-3-hexanone of

approximately 25%. This value remained constant throughout the reaction.

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