



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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