



Heterogeneous selective hydrogenation of *trans*-4-phenyl-3-butene-2-one to allylic alcohol over modified Ir/SiO₂ catalyst

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ABSTRACT

The heterogeneous selective hydrogenation of *trans*-4-phenyl-3-butene-2-one to allylic alcohol, catalyzed by Ir/SiO₂ stabilized with phosphines and modified by cinchona alkaloids, was described herein. Under the optimized conditions, the chemoselectivity to α,β -unsaturated alcohol was more than 99% with enantioselectivity up to 46%.

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1. Introduction

The quest for economic and green methods to prepare enantiomerically pure α,β -unsaturated alcohols continues as a result of the important role these intermediates serve in drug design [1,2]. Generally, they are obtained by the enantioselective reduction of C=O in α,β -unsaturated carbonyl compounds. These hydrogenation reactions have been remarkably developed in homogeneous catalytic reactions since the groundbreaking discovery disclosed by Noyori and co-workers [3,4]. However, the recuperation of homogeneous catalysts is still a problem. Moreover, the selective hydrogenation of the C=O group of an unsaturated ketone to chiral allylic alcohol on heterogeneous catalysts remains a formidable scientific challenge [5,6]. The heterogeneous chemoselective reduction of unsaturated ketones to allylic alcohols has been studied occasionally on metal Au [7–12], Ir [13], Ru [14], Pt [15,16], Pd [16,17] or Ni [18,19]. The enantioselective reduction of unsaturated ketones to chiral allylic alcohols is much more difficult, only a few such reactions have been described. Enone testosterone and cholestenone undergo reduction to the corresponding allylic alcohols with almost completely chemoselectivity and high diastereoselectivity (d.r. >97:3) over Ir/H- β [13].

Ketoisophorone can be reduced with high chemoselectivity and 14% ee over cinchona-modified Pt/alumina [16]. In above limited cases, the chemoselective and enantioselective reactions have only been demonstrated for specific substituted substrates. We focus on the selective hydrogenation of ketones, an important organic transformation, since the resulting alcohols are versatile precursors to many natural products and drug molecules. We succeed in heterogeneous enantioselective hydrogenation of aromatic ketones [20–22], with enantioselectivity up to 98%. More than 99% allylic alcohol selectivity was obtained in the chemoselective hydrogenation of *trans*-4-phenyl-3-butene-2-one employing 1,2-diphenylethylene-1,2-diamine- and PPh₃-modified Ru/ γ -Al₂O₃ as catalyst [14]. As part of our ongoing research, we herein firstly report the heterogeneous enantioselective hydrogenation of *trans*-4-phenyl-3-butene-2-one, catalyzed by phosphines stabilized Ir/SiO₂ modified by cinchona alkaloids, with chemoselectivity to unsaturated alcohol more than 99% and enantioselectivity up to 46%.

2. Experimental

2.1. Materials

The *trans*-4-phenyl-3-butene-2-one (Acros), cinchona alkaloids (Acros), triphenylphosphine (PPh₃) (Aldrich), and H₂IrCl₆·6H₂O (Institute of Kunming Noble Metals, China)

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