



Regioselective hydroformylation of vinyl acetate catalyzed by rhodium complex of naphthyl-based monodentate bulky phosphine and phosphite ligands

Aasif A. Dabbawala, Hari C. Bajaj*, Ganga V.S. Rao, Sayed H.R. Abdi

Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Council of Scientific and Industrial Research, G. B. Marg, Bhavnagar 364002, Gujarat, India

ARTICLE INFO

Article history:

Received 1 June 2011

Received in revised form 19 January 2012

Accepted 21 January 2012

Available online 30 January 2012

Keywords:

Hydroformylation

Vinyl acetate

Monodentate bulky phosphite

High rate

Regioselective

ABSTRACT

The hydroformylation of vinyl acetate was carried out using rhodium complex of naphthyl-based monodentate bulky phosphine and phosphite ligands. All the naphthyl-based ligands favored the formation of desired branched aldehyde. High turnover frequency with excellent regioselectivity to branched aldehyde and high selectivity to aldehyde were observed with bulky phosphite ligands. The effect of partial pressure of CO and H₂, concentration of vinyl acetate, stirring rate and solvents on the hydroformylation of vinyl acetate catalyzed by Rh/bulky phosphite were examined precisely in order to improve the catalytic activity and selectivity. In contrast to conventional organic solvents, the significant influence on the activity and selectivity was observed in organic carbonates ('green' solvent) particularly in propylene carbonate (PC). The PC/catalyst system could be recycled without significant loss of activity and selectivity.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Catalytic hydroformylation is an elegant method to prepare wide range of aldehydes in a single step by the reaction of olefins, CO and H₂ with high selectivity [1,2]. It is mainly used for the preparation of bulk and specialties chemicals. The application of this process has also been extensively explored in pharmaceutical and fine chemical synthesis [1–6]. This powerful atom efficient process is very attractive however; simultaneous control of activity and selectivity (chemo- as well as regioselectivity) is one of the important issue and concern of hydroformylation. Rhodium complexes of modified phosphorous containing ligands display high activity and selectivity for the hydroformylation of olefins under mild reaction conditions. The steric and electronic properties of ligands play an imperative role in concern to activity and selectivity of hydroformylation catalysts. As a result, varieties of modified monodentate and bidentate phosphine/phosphite ligands have been synthesized by fine tuning their electronic and steric properties to address the issues of activity and selectivity [7–11].

Hydroformylation reaction has been mainly studied for terminal and internal olefins. The selective preparation of the linear aldehyde, the starting material for a variety of polymers, detergents, cosmetics and other widespread products by hydroformylation of terminal and internal alkenes have been reported

[12–14]. Recently, regioselective hydroformylation of functionalized alkenes such as alkyl acrylate, allyl cyanide, allyl alcohol, enamide and vinyl acetate [19] have also received attention. Hydroformylation of such substrates offers products having two functional groups widely used in organic syntheses [15–19]. Particularly, the hydroformylation of vinyl acetate provides gate way to valuable building blocks for the preparation of bifunctional intermediate which can be further converted into synthetically useful compounds such as 1,2- and 1,3-propanediol, lactic acid and ethyl lactate (Scheme 1).

Indeed, vinyl acetate, less reactive to syngas in comparison to terminal alkenes requires high pressure to achieve high turnover frequency [20], also suffers from a low selectivity and formation of by-products [21]. However, there are few reports wherein hydroformylation of vinyl acetate is carried out under mild conditions with good regioselectivity [22–24]. The hydroformylation reaction proceeds even at 2 atm pressure and 80 °C in the presence of diphosphines in the rhodium complex with large excess of triphenyl phosphine (PPh₃) and resulted in the vinyl acetate conversion from 38 to 60% with branched aldehyde regioselectivity from 53 to 82% [22]. Abatjoglou et al. reported vinyl acetate hydroformylation at low pressure and temperature (8.4 atm, 60 °C) with branched aldehyde regioselectivity from 77 to 86% depending on the phosphine and solvent used [23]. Trzeciak and Ziólkowski also demonstrated vinyl acetate hydroformylation at 1 atm and 40 °C by rhodium/triphenyl phosphite catalyst system [24]. In above cases, the regioselectivity was achieved but at the expense of the reaction rate. In consequent, over past decades, a great deal of efforts

* Corresponding author. Tel.: +91 278 2471793; fax: +91 278 2566970.

E-mail address: hcbajaj@csmcri.org (H.C. Bajaj).