



Rhodium catalyzed selective hydroaminomethylation of biorenewable eugenol under aqueous biphasic condition

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ABSTRACT

This work reports a highly regioselective hydroaminomethylation of eugenol, anethole and estragole with piperidine in aqueous medium. This catalytic system was composed of rhodium complexes stabilized by trisulfonated triphenylphosphine (TPPTS) and of a native or chemically modified cyclodextrins. Various cyclodextrins such as α -cyclodextrins (α -CD), β -cyclodextrin (β -CD), γ -cyclodextrin (γ -CD), 2-hydroxy-propyl β -cyclodextrin (hp- β -CD) and RAndomly MEthylated β -cyclodextrin (RAME- β -CD) have been tested. The effect of different parameters such as syngas pressure, time, temperature, catalyst precursor/loading and the ratio of Metal/Ligand/Cyclodextrin were also investigated. The addition of cyclodextrins as a mass transfer agent remarkably increased the rate reaction and the selectivity of linear amines, specially in the case of RAME- β -CD. So, the Rh/TPPTS/RAME- β -CD as a catalyst exhibited high conversion (92%) and selectivity (79.2%) towards the linear amine as major product under mild conditions. Finally, the catalytic system was recycled up to five times without a significant loss in activity and selectivity.

1. Introduction

Amines are a class of valuable organic compounds for the pharmaceutical, agrochemical and fine chemical industries [1]. Hydroaminomethylation (HAM) reaction is a highly atom-economical, homogeneous industrial process for the synthesis of linear and branched amines from olefins, amines and syngas by the use of a single catalyst [2]. The HAM process is a triple sequential reaction involving hydroformylation of an alkene, condensation of the produced aldehyde with amine, and the hydrogenation of the resulting imine or enamine, which provides a highly efficient method to construct amines (Scheme 1) [3]. It has high attraction in industry as well as in academics, since it was discovered by Reppe in 1949 at BASF [4]. The several processes are available for the production of aliphatic amines consist of organic reactions like hydroamination, hydrocyanation of alkenes followed by reduction, nucleophilic substitution of alkyl halides, reductive amination of carbonyl compounds, etc. Despite these processes available, amine preparation often suffers from low generality, costly starting materials, side reactions and the necessity of protecting groups [5].

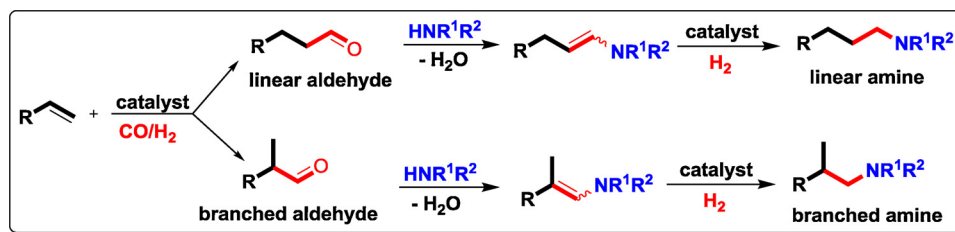
In general, the hydroaminomethylation reactions are carried out in a homogeneous catalytic system [6–9], which suffers from some shortcomings such as the difficulties of the catalyst recovery, catalyst

separation from products, selectivity of desired product, to control the hydrogenation and isomerisation, etc. [10]. Probable solutions to these troubles consist of making the homogeneous catalyst into heterogeneous by anchoring the metal on support or by using two-phase catalytic system [11]. Beller and co-workers [12] reported the hydroaminomethylation of C5 olefins in aqueous-organic biphasic catalysis in 1999. The catalytic system was composed of iridium and rhodium complexes stabilized by trisulfonated triphenylphosphine (TPPTS: P(m-C₆H₄SO₃Na)₃) or sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthylene (BINAS). Addition of iridium complex was required to increase the catalytic activity and amine selectivity. Indeed, the rhodium catalysts are not sufficiently active for the hydrogenation of the imine at high phosphorus to rhodium ratio.

In 2004, Li group [13] reported the hydroaminomethylation of long chain olefins with poor water solubility in an aqueous-organic biphasic system using the water-soluble rhodium complex RhCl(CO)(TPPTS)₂ as catalyst in the presence of the cationic surfactant cetyltrimethylammonium bromide. The use of sulfonated 2,2'-bis(diphenylphosphinomethyl)-1,1'-biphenyl ligand (BISBIS) instead of TPPTS ligand significantly improved the amine selectivity (80% vs. 46% for the BISBIS and TPPTS, respectively) and linear/branched amines selectivities (l:b ratio: 83 vs. 15 for the BISBIS and TPPTS, respectively) [14].

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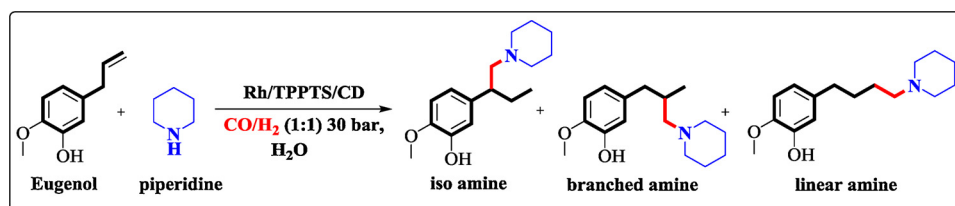


Scheme 1. The general hydroaminomethylation of olefins and amines.

Interestingly, A. Behr et al. have reported that the addition of inorganic and organic acids allowed the quantitative conversion of 1-octene with very high selectivity for the amines. For instance, the hydroaminomethylation of 1-octene with synthesis gas and di-*n*-butylamine gives rise to the desired amines in 96% yield in the presence of sulfuric acid [15].

Furthermore, Behr et al. [16] also achieved the hydroaminomethylation of 1-octene with morpholine in temperature-dependent solvent systems, in which reaction occurs in a single-phase at a higher temperature followed by splitting into two phases at a lower temperature. Wang and co-workers reported the biphasic hydroaminomethylation of long chain olefins in ionic liquids [17]. Although the catalyst could be easily separated by a simple phase separation, the catalyst recycling remained to be improved. Though the several practices have been explored for hydroaminomethylation of olefins in recent years [18], the synthesis of linear amines from internal and terminal natural olefins such as eugenol, anethole and estragole is always challenging. Such reactions are of industrially important because natural olefins such as eugenol, anethole and estragole are more cost-efficient and abundant in nature. These bio-renewable starting materials which are the derivatives of natural allyl benzenes were obtained from biomass, such as eugenol from cloves, anethole from basil and estragole from sweet basil etc. [19].

As a continuation of our research on the catalytic valorization of biomass to value-added products [20], we hereby report the aqueous biphasic hydroaminomethylation of eugenol into linear amines using Rh/TPPTS as catalytic system and cyclodextrins (CDs) as mass transfer promoters (Scheme 2). Chemically modified CDs are cyclic oligosaccharides composed of (α -1,4)-linked α -D-glucopyranose units which is obtained from the enzymatic conversion of starch [21]. These compounds allowed to achieve the catalytic functionalisation of numerous substrate in an aqueous organic two-phase system with high reaction rates, while avoiding the formation of an emulsion and the partition of the catalyst between the organic and aqueous phases. This outstanding result was attributed to the formation of inclusion complexes at the aqueous/organic interface [22]. The main objective of this work is to investigate the effect of the various cyclodextrins such as α -cyclodextrin (α -CD), β -cyclodextrin (β -CD), γ -cyclodextrin (γ -CD), hydroxyl propyl β -cyclodextrin (hp- β -CD) and RANdomly MEthylated β -cyclodextrin (RAME- β -CD) on the rate and selectivities of hydroaminomethylation of eugenol.



Scheme 2. Aqueous biphasic selective hydroaminomethylation of naturally occurring eugenol and piperidine using Rh/TPPTS/CD as greener and reusable catalytic system.

^[a]Reaction Conditions: eugenol (1 mmol), piperidine (1 mmol), Rhacac(CO)₂ (0.002 mmol), TPPTS (0.008 mmol), CD (0.02 mmol), CO/H₂ (30 bar), Distilled water (10 mL), 80 °C, 8 h. ^[b]Determined by GC and GC-MS.

2. Experimental

2.1. General methods and reagents

All the reaction experiments were carried out under the nitrogen atmosphere. Chemicals and reagents were procured from Sigma Aldrich, Alfa Aesar, Spectrochem Pvt. Ltd., India with a purity grade of 99% and higher which are used as received. Distilled deionized water was used as solvent in all experiments. A syngas containing mixture of hydrogen (49.9%) and carbon monoxide (49.9%) were purchased from Rakhangi Gas Service, Mumbai. All experiments were performed in a 100 mL autoclave. The reaction process was monitored by gas chromatography on Perkin Elmer Clarus 400 GC equipped with flame ionization detector with a capillary column (Elite-1, 30 m \times 0.32 mm \times 0.25 μ m). GC-MS-QP 2010 instrument (Rtx-17, 30 m \times 25 mm ID, film thickness 0.25 μ m df) (column flow 2 10 mL min⁻¹, 80–240 °C at 10°/min rise).

2.2. Typical experimental procedure for aqueous biphasic hydroaminomethylation of eugenol and recycling of the catalyst (Rh/TPPTS/CD)

In a 100 mL volume of high pressure reactor, eugenol (1 mmol), piperidine (1 mmol), [Rh(acac)(CO)₂] (0.0015 mmol), TPPTS (0.0075 mmol), RAME- β -CD (0.015 mmol) and deionised distilled water (10 mL) were added. Then reactor was closed, flushed three times with syngas and pressurized with 30 bar syngas pressure heated to 80 °C for 8 h. After the completion of the reaction, the reactor was cooled down to room temperature, remaining syngas was vented carefully and the reactor was opened. The organic layer containing product from aqueous layer was separated by a simple separation technique using separatory funnel. The reactor vessel was thoroughly washed with ethyl acetate (3 \times 5 mL) to remove traces of the product. Then reaction mixture and catalytic system was separated by separatory funnel. The organic layer containing product was passed through dry Na₂SO₄ to remove traces of water (moisture) if present and it is subjected to GC and GC-MS analysis. The recovery and recycling of the catalytic system were carried out under inert condition that is in nitrogen atmosphere. Aqueous solution containing metal, ligand and cyclodextrin was collected and used as it is for next recycle experiment. The Rh/TPPTS/CDs as biphasic catalytic system was easily recycled up to five consecutive cycles without losing its catalytic activity and selectivity.

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