Journal of Molecular Catalysis A: Chemical 411 (2016) 72–77

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Simple green dehydration in biphasic medium: Application to the synthesis of phenylacetaldehyde

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ARTICLE INFO

Article history:
Received 23 August 2015
Received in revised form
16 September 2015
Accepted 1 October 2015
Available online 14 November 2015

Keywords:
Phenylacetaldehyde
Iron chloride
Biphasic system
Microwave-assisted dehydration

ABSTRACT

A highly efficient, simple and versatile acid catalyst is proposed for the selective acid dehydration of 1-phenylethan-1,2-diol to phenylacetaldehyde in water-CPME biphasic media under microwave irradiation. A high stability and recyclability of the catalyst is also observed under the investigated conditions.

1. Introduction

Phenylacetaldehyde, a natural compound found in chocolate [1], buckwheat [2], has a narcissus-like smell. Synthetical phenylacetaldehyde is used in industry as upstream raw material and for downstream applications like preparation of fragrances [3] but also pharmaceuticals [4] and insecticides [5]. Among the different syntheses of phenylacetaldehyde, isomerization of styrene oxide both in liquid or in gas phase, Darzens glycidic ester condensation of benzaldehyde and dehydration of phenylethan-1,2-diol [6,7] were the most useful. The main drawbacks of these methodologies were the competitive aldol condensation or the polymerization of aldehyde products.

Due to the depletion of petroleum resources, organic reactions in water as green solvent were developed. Hydrothermal transformation using conventional heating or microwave activations permitted to realize the dehydration of polyols from biomass [8,9] and fossil resources [10–12]. Recently, our group published dehydration of glycerol to acrolein and the synthesis of quinoline in sub-critical water under conventional heating and microwave irradiation in batch [13,14] and in continuous flow [15]. In a previous work, we optimized a method for the dehydration of 1-phenylethan-1,2-diol **1** in sole water under microwave irradiation [16]. Best conditions were a temperature of 170 °C and a reaction time of 30 min. Among the different homogeneous and heterogeneous catalysts tested, mineral acids H_2SO_4 and HCl and metal chlorides $FeCl_3$ and $AlCl_3$ gave the highest phenylacetaldehyde **2** yields (55–63%). However, in water, phenylacetaldehyde formation was limited by the formation of the aldol condensation product **3**. In the present work, we report an efficient strategy for the selective formation of phenylacetaldehyde **2** under microwave irradiation by the addition of an extracting co-solvent, cyclopentyl methyl ether (CPME). Already exemplified for the synthesis of furans [17,18], this strategy uses the partition coefficient of aldehyde **2** between water and organic solvent. After dehydration of diol **1** to aldehyde **2** in water, the affinity of aldehyde **2** with organic solvent should permit to transfer aldehyde **2** to the organic phase while limiting the formation of compound **3** (Scheme 1).

2. Materials and methods

2.1. Materials

Substrates and products (1-phenylethan-1,2-diol, phenylacetaldehyde and styrene oxide) were purchased from Acros. Catalysts were purchased from Acros ($FeCl_3$, $AlCl_3$, and H_2SO_4

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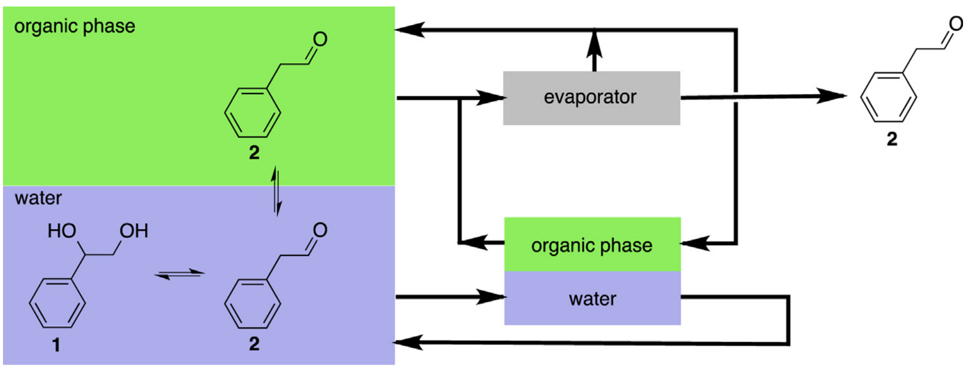
http://dx.doi.org/10.1016/j.molcata.2015.10.001



Scheme 1. Extraction of aldehyde 2 from water to the organic phase.

(96%)) and from Carlo Erba (hydrochloric acid (37%)). Solvents were purchased from Fisher Scientific (acetonitrile, tetrahydrofuran, toluene and ethyl acetate) and from Acros (cyclopentyl methyl ether and methyl-tetrahydrofuran). All materials were used without further purification. Distilled H_2O was used for preparation of all aqueous solutions.

2.2. General procedure for the synthesis of phenylacetaldehyde in water-CPME as biphasic media from 1-phenylethan-1,2-diol

In a typical experiment, a 10 mL glass vessel was charged with water (0.5 mL), CPME (1.4 mL), 1-phenylethan-1,2-diol (**1**, 100 mg, 0.725 mmol) and a catalyst (20 mol%). The vessel was sealed with a septum, placed in the microwave apparatus (AntonPaar Monowave 300) and heated to the desired temperature under magnetic stirring (600 rpm) for the desired time. Temperature in the vessel was measured by means of an IR sensor. At the end of the reaction, the vessel was cooled down to 40 °C using compressed air. Then, the reaction mixture was diluted in 100 mL of acetonitrile. An aliquot of the diluted solution was taken (ca. 1.5 mL) and filtered prior to analysis through a syringe filter (PTFE, 0.45 µm, VWR).

2.3. General procedure for the synthesis of phenylacetaldehyde in water-CPME as biphasic media from styrene oxide

In a typical experiment, a 10 mL glass vessel was charged with water (0.5 mL), CPME (1.4 mL), styrene oxide (**4**, 87 mg, 0.725 mmol) and a catalyst (20 mol%). The vessel was sealed with a septum, placed in the microwave apparatus (AntonPaar Monowave 300) and heated to the desired temperature under magnetic stirring (600 rpm) for the desired time. Temperature in the vessel was measured by means of an IR sensor. At the end of the reaction, the vessel was cooled down to 40 °C using compressed air. Then, the reaction mixture was diluted in 100 mL of acetonitrile. An aliquot of the diluted solution was taken (ca. 1.5 mL) and filtered prior to analysis through a syringe filter (PTFE, 0.45 µm, VWR).

2.4. Product analysis

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker UltraShield 400 MHz/54 mm Ultra long hold. Chemical shifts (d) are quoted in ppm and are referenced to TMS as an internal standard. Coupling constants (J) are quoted in Hz. All reactions were monitored by HPLC. The column used is a GRACE Prevail C18. The detector used is a SPD-M20A photo diode array detector (Shimadzu). The mobile phase is a mixture of water and MeOH (20:80). Reactant and product concentrations were determined using calibration curves that were obtained from references samples. The product yield (Y_i), the conversion (X), the selectivity (S_i) and the ratio **2**/(**2** + **3**) were calculated by the following equations:

$$\text{Product yield } Y_i = \frac{\text{Final amount of product i (mol)}}{\text{Initial amount of reactant (mol)}} \times 100$$

$$\text{Conversion } X = \frac{(\text{Initial reactant amount (mol)} - \text{Final reactant amount (mol)})}{\text{Initial amount of reactant (mol)}}$$

$$\text{Selectivity } S_i = \frac{\text{Yield of product i}}{\text{Conversion of reactant}} \times 100\%$$

$$\text{Ratio } 2/(2+3) = \frac{\text{Final amount of product 2 (mol)}}{\text{Final amounts of product 2} + \text{product 3 (mol)}} \times 100\%$$

3. Results and discussion

3.1. Effect of the nature of organic solvent

Cyclopentyl methyl ether (CPME), ethyl acetate, toluene, methyltetrahydrofuran (Me-THF) and tetrahydrofuran (THF) as organic solvents were tested in the presence of different selected acids ($AlCl_3$, $FeCl_3$, HCl or H_2SO_4) in water under microwave irradiation to investigate their effect on aldehyde **2** yield. The ratio between the organic solvent and water was 1:1, v/v (Table 1). It should be noted that, whatever the solvent used, reactions performed without acid catalyst afforded no conversion of the starting diol **1**. With ethyl acetate, a large amount of aldehyde **3** (9–25%) was detected. In our conditions, ethyl acetate was degraded during the process and only one phase was obtained at the end of reaction preventing the transfer of aldehyde **2** in the organic phase. With Me-THF and THF, yields of the target compound **2** were comprised between 47% and 86% yields and formation of enal **3** was observed whatever the acid. In contrast, toluene gave selectively the aldehyde **2** with good yield for the four acids. However substitution of toluene as fossil solvent was recommended. The ether CPME gave excellent yield (>86%) in presence of $FeCl_3$, HCl or H_2SO_4 and low amount of compound **3** (<2%). Even if CPME is industrially produced from fossil carbon, it is considered as green solvent and as an alternative to ethereal solvents [19,20]. For these reasons, a mixture of CPME and water for the dehydration of diol **1** to aldehyde **2** was chosen.

3.2. Effect of the ratio water/CPME on the phenylacetaldehyde yield

Variation of the ratio between water and CPME was realized to optimize the selectivity of aldehyde **2** and the selectivity between the aldehyde **2** and the enal **3** (Table 2). Five ratios were tested (water-CPME, 3:1; 2:1; 1:1; 1:2; 1:3, v/v) in presence of $AlCl_3$, $FeCl_3$,