Journal of Industrial and Engineering Chemistry 18 (2012) 174–177

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Efficient preparation of DHMF and HMFA from biomass-derived HMF via a Cannizzaro reaction in ionic liquids

Eun-Sil Kang [a], Da Won Chae [a], Baekjin Kim [b], Young Gyu Kim [a,*]

[a] Department of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Republic of Korea
[b] Green Chemistry & Manufacturing System Division, Green Process R&D Department & Polymer Materials Research, Korea Institute of Industrial Technology (KITECH), ChoeonAn 330-825, Republic of Korea

ARTICLE INFO

Article history:
Received 28 January 2011
Accepted 19 February 2011
Available online 7 November 2011

Keywords:
5-Hydroxymethylfurfural (HMF)
2,5-Dihydroxymethylfuran (DHMF)
5-Hydroxymethylfuranoic acid (HMFA)
Ionic liquid
Cannizzaro reaction

ABSTRACT

2,5-Dihydroxymethylfuran (DHMF) and 5-hydroxymethylfuranoic acid (HMFA) are the versatile intermediate chemicals of high industrial potential. An efficient preparation of both DHMF and HMFA is reported from biomass-derived HMF via a Cannizzaro reaction using ionic liquids as a reusable reaction solvent under the water-free conditions. The operationally simple and environment-friendly process produces both DHMF and HMFA from HMF consistently in good to high yields up to five runs with the recycled ionic liquid.

1. Introduction

The economics of biomass production has been improved over the years, and the growing concern about depletion of traditional energy resources is making biomass more attractive for a feedstock of energy and the chemical industry. 5-Hydroxymethylfurfural (HMF) is one of novel biomass-derived platform chemicals and has the potential as an alternative commodity chemical for fossil fuel-based platform chemicals such as terephthalic acid. Over one thousand papers related to HMF have been published until now, which is a proof for the importance of this compound, so-called “a sleeping giant” [1] and one of the “petrochemicals readily accessible from regrowing resources” [2].

HMF itself has two functional handles attached to a furan ring and can be converted into several value-added compounds that could be used in a wide variety of chemical manufacturing applications and industrial products (Fig. 1). For example, 2,5-dihydroxymethylfuran (DHMF), a reduction product of HMF, is used as a six-carbon monomer in a broad field of applications such as resins, polymers and artificial fibers [3,4]. It has also been used as an intermediate in the synthesis of drugs [5] and crown ethers [6]. An oxidation of the formyl group of HMF into a carboxylic acid results in 5-hydroxymethylfuranoic acid (HMFA) containing one hydroxyl group and the other carboxylic acid in the same molecule, which serves not only as a novel component in various polyesters [7] but also as a precursor of 2,5-furandicarboxylic acid (FDCA) with high potential applications in the polymer field. FDCA can replace terephthalic, isophthalic, and adipic acids that have been used to date in the manufacture of polyamides, polyesters, and polyurethanes [8,9].

Despite a plethora of synthetic and related efforts, interest in the chemical conversions of HMF remains undiminished. Several studies about the DHMF synthesis have been devoted to the catalytic reduction of HMF, for instance, the catalytic hydrogenation in the presence of nickel, copper, platinum, palladium or ruthenium catalysts [10]. Under noncatalytic conditions, the reductions with sodium borohydride have also been reported [6,11]. The papers about conversion of HMF to HMFA are mainly focused on the catalytic oxidation [12]. Using heterogeneous oxidation systems, good to excellent results were reported [13].

A Cannizzaro reaction is the base-induced disproportionation reaction of an aldehyde lacking a hydrogen atom at an α-position to the carbonyl group. One molecule of the aldehyde acts as a hydride-donor and the other as an acceptor, resulting in a carboxylic acid salt and an alcohol product, respectively. The Cannizzaro reaction is of limited use except when performed as an intramolecular reaction to yield a lactone. Because it yields an equimolar mixture of both a primary alcohol and a carboxylic acid salt as products, the maximum possible yield for each product is only 50%. However, the Cannizzaro reaction would be one of the most efficient routes for the simultaneous production of both DHMF and HMFA when it is applied to HMF. In particular, use of inexpensive and non-toxic

---

* Corresponding author.
E-mail address: ygkim@snu.ac.kr (Y.G. Kim).

1226-086X/$ – see front matter © 2011 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.
doi:10.1016/j.jiec.2011.11.020

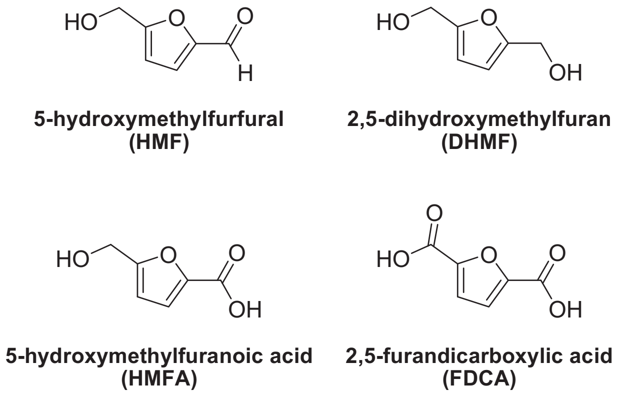


Fig. 1. Structures of HMF and its derivatives.

hydroxide ions in the Cannizzaro reaction is another advantage over the standard reduction or oxidation conditions employing expensive, reactive and/or toxic reagents.

Typical Cannizzaro reactions usually involve relatively harsh reaction conditions with an excess of alkali metal hydroxide in an aqueous solution at high temperature. Herein we report an efficient, mild, operationally simple, and eco-friendly Cannizzaro reaction of HMF in ionic liquids (ILs) (Scheme 1). Only a couple of reports on the Cannizzaro reaction of HMF have been known in the literature, both of which employed the same aqueous alkali solution [14]. Within the past few years, ILs have emerged as a new class of green solvents, reagents and Brønsted acids for chemical processes and have attracted considerable attention [15]. Although application of ILs in organic synthesis and catalysis is a very active area of chemistry [16], to the best of our knowledge, few papers report the use of ILs for Cannizzaro reactions.

2. Experimental

HMF was purchased from commercial suppliers and used as received. Unless otherwise noted, materials were obtained from commercial sources and were used without further purification. Analytical thin layer chromatography (TLC) was performed by using Merck 60 F_{254} glass plates precoated with a 0.25-mm thickness of silica gel. NMR spectra were measured on a JEOL JNM-LA300 instrument as solutions in acetone-d_6 with TMS as an internal standard (^1H at 300 MHz and ^{13}C at 75 MHz) and data were reported as follows in ppm (δ) from TMS: chemical shift (multiplicity, coupling constant in Hz, integration). Melting points were determined with an open capillary melting point apparatus and are uncorrected.

2.1. Preparation of ILs

1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIm]TFSI) and 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm]TFSI) were synthesized using a modified method of Watanabe et al. [17]. 1-Butyl-3-methylimidazolium tetrafluoroborate ([BMIm]BF_4) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm]PF_6) were prepared according to the literature procedures [18]. The two ammonium-based ILs, 1-methyl-1-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([PMPyrr]TFSI) and *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ($N_{122,201}$-TFSI), were synthesized using the methods reported in the literature [19].

2.2. A representative procedure

To a stirred solution of HMF (0.126 g, 1.00 mmol) in IL (1 ml) was added powdered NaOH (0.200 g, 5.00 mmol) at 0 °C. The resulting mixture was stirred vigorously at room temperature and the reaction was monitored by TLC. After completion of the reaction, dichloromethane (20 ml) was added to the dark green colored gummy mixture and the stirring was continued for another 15 min, resulting in the suspension mixture.

The IL remained in the dichloromethane layer was recycled as follows. The organic layer from the above suspension mixture was separated by filtration and the filtrate was passed through a neutral aluminum oxide pad to remove the precipitated salt and its yellowish color. The colorless solution was concentrated under reduced pressure to give the IL back in nearly the same amount.

2.3. DHMF (2,5-dihydroxymethylfuran)

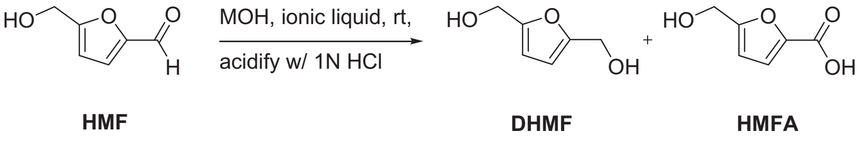
The filter cake left after the filtration of the dichloromethane layer was dissolved in water (2 ml) and then neutralized at 0 °C with an aqueous solution of 1 N HCl to pH 7–8. The resulting solution was extracted with ethyl acetate (3 × 50 ml). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification by recrystallization in ethyl acetate at 0 °C [20] or by column chromatography on silica gel with a EtOAc/hexane (from 2:1 to 4:1) mixture afforded DHMF as an off-white solid. ^1H NMR: δ 6.18 (s, 2H), 4.48 (d, J = 5.8, 4H), 4.18 (t, J = 5.8, 2H); ^{13}C NMR: δ 155.8, 108.22, 57.2; mp 76–78 °C (lit. mp 76–78 °C) [11(d)]; Anal. calcd. for $C_6H_8O_3$ (MW 128.13): C, 56.24; H, 6.29. Found: C, 56.17; H, 6.02.

2.4. HMFA (5-hydroxymethylfuranoic acid)

An aqueous solution of 1 N HCl was added to the aqueous layer, obtained after the extraction of DHMF from the above, until the pH of the aqueous solution reached less than 3. The acidified solution was extracted with ethyl acetate (3 × 50 ml). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification by recrystallization in a EtOAc/diethyl ether mixture or by column chromatography on silica gel with a dichloromethane/MeOH (from 1:0 to 20:1) mixture afforded HMFA as a pale-yellow solid. ^1H NMR: δ 7.16 (d, J = 3.4, 1H), 6.47 (d, J = 3.4, 1H), 4.59 (s, 2H); ^{13}C NMR: δ 160.9, 159.5, 144.9, 119.6, 109.6, 57.3; mp 165–166 °C (lit. mp 159–162 °C) [21]; Anal. calcd. for $C_6H_6O_4$ (MW 142.11): C, 50.71; H, 4.26. Found: C, 51.19; H, 4.73.

3. Results and discussion

For a preliminary study, the initial Cannizzaro reactions of HMF were studied using [BMIm]X (X = BF_4, PF_6 or TFSI, Fig. 2) ionic liquids as a reaction solvent (Table 1, entries 1–3). In those reactions, five equivalents of finely powdered NaOH were used to



Scheme 1. Cannizzaro reactions of HMF to DHMF and HMFA.