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OPPI BRIEF

Efficient and Green Preparation of 2-Imidazolidinone using Sulfamic Acid as Acidic Catalyst

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Increasing global concern has led the governing bodies of many countries to establish and enforce laws to safeguard the environment and encourage the development of environmentally conscious processes (Principles 7-9 of the UN Global Compact).¹ Urea derivatives have extensive applications such as corrosion inhibitors, antioxidants in gasoline, and intermediates for pharmaceuticals and agrochemicals.^{2,3} Among urea derivatives, 2imidazolidinone is widely used as an intermediate for the synthesis of medicines, toiletries, cosmetic products,⁴ and as delignification solvent and chemotherapeutic agents.^{5,6} It is also the key intermediate in the synthesis of 1,3-dimethyl-2-imidazolidinone, which is one of the most widely used aprotic solvents in electrochemistry.⁷ It has been traditionally synthesized by the reaction of 1,2-ethylenediamine (EDA) with phosgene, triphosgene, or carbon dioxide. This reaction requires high pressure and leads to major toxicological and environmental problems when phosgene is used.⁸⁻¹⁰ In addition to the need to use expensive raw materials, many of the catalysts are expensive and harmful to human health. Accordingly, alternative routes involving EDA reaction with urea¹¹ and organic carbonates (such as dimethyl carbonate, diethyl carbonate, ethylene carbonate, and *bis(p*-carbomethoxylphenyl)carbonate) have been developed.^{3,6,12–14}

Dimethyl carbonate (DMC) is a safe, low-cost, green and eco-friendly alternative reagent^{1,15} to phosgene and other carbonylating agents. Recently, sulfamic acid (NH₂SO₃H) has been reported as a substitute for conventional acidic materials in catalytic and organic reactions because of its unique characteristics (non-toxicity, efficiency, and recyclability).^{16–18} We now report the use of NH₂SO₃H as a catalyst in the efficient synthesis of 2-imidazolidinone from EDA and DMC in 70% yield under optimal reaction conditions determined in this investigation.

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Our efforts toward the synthesis of 2-imidazolidinone (**5**) focused on the use of sulfamic acid because of its known reactivity.¹⁸ A series of experiments conducted to optimize the reaction conditions suggested that the reaction process proceeds as shown in *Scheme 1*.



Scheme 1

As a result of these experiments, it was established that the reaction is best conducted in two-stages of heating as illustrated in *Scheme 1*. It was found that an increase in the ratio of DMC to EDA from 1.2 to 2.0 equiv. had a negligible effect on the yield. Heating the reaction mixture for three hours at 50°C led to the maximum production of *N*carbomethoxyethylenediamine (**3**) as the major product, N,N'-*bis*-carbomethoxyethylene diamine (**4**) being formed in minor amounts; longer heating promoted increased formation of **4** which in a separate experiment, was shown to react with 2-imidazolidinone (**5**) to give *N*-methyl-2-imidazolidinone (**6**) and a small amount of **5** (thus not net increase in the yield), However, **4** was recovered, unreacted, when heated in the presence of the catalyst sulfamic acid only. The second stage of heating carried out at 160°C for 15 h (longer heating led to a decrease in yield and formation of unknown by-products), converted **3** to the final product **5** (plus a very small amount of **6**) and was accompanied by the gradual disappearance of **4** as a result of its reaction with the product to give *N*-methyl-2-imidazolidinone (**6**) as mentioned above (*Scheme 1*).

In conclusion, an efficient and green method for the synthesis of 2-imidazolidinone (5) from EDA and DMC using sulfamic acid as catalyst was developed. Mechanistic studies showed that 2-imidazolidinone was produced through two pathways. The proposed method appears suitable for industrial application and has the potential to be useful in the preparation of other urea derivatives.

Experimental Section

1,2-Ethylenediamine (>99%), sulfamic acid (>99%) were obtained from Sinopharm Chemical Reagent Co., P. R. China. Dimethyl carbonate (>98%) was purchased from Tianjin Guangfu Fine Chemical Research Institute, P. R. China. All other reagents and solvents are of analytical grade and were used without further purification unless indicated. The autoclave [100 ml, fitted with a thermocouple, a magnetic stirrer and a pressure gauge (the pressure range from 0 to 60 bar)] was manufactured by Zhenjiang Global Electrical

and Mechanical Parts Factory. Melting points were determined with a Tech X-6 micromelting-point apparatus manufactured in Beijing, P. R. China and are uncorrected. The ¹H and ¹³C NMR spectra were recorded in CDCl₃ solution on a Bruker 400 MHz spectrometer with TMS as the internal standard.

Preparation of 2-Imidazolidinone

A mixture of 1,2-ethylenediamine (3.0 g, 0.05 mol), dimethyl carbonate (5.4 g, 0.06 mol), sulfamic acid (1.0 g, 0.01 mol) and 4.5 ml of methanol in an autoclave (100 ml, fitted with a thermocouple to measure the temperature and a magnetic stirrer, at 20–60 bar)¹⁹ was heated to and kept at 50°C for 3 h (*CAUTION!*). The internal temperature was then raised to 160°C and maintained at that temperature for 15 h. After that time, heating was stopped and the system was allowed to cool to room temperature. The low boiling point substances were distilled off under vacuum (7.5 mm Hg). Then, acetone (15 ml) was added to the solid residue and the suspension was stirred for 10 minutes at room temperature. The suspension was filtered to remove insoluble material and the filtrate was distilled off under vacuum (7.5 mm Hg) to give 3.0 g (70%) 2-imidazolidinone as a white solid, mp. 130–132°C, lit.²⁰ mp. 130–131°C. ¹H NMR (400 MHz, CDCl₃): δ 3.53 (s, 4H, CH₂), 5.37 (s, 2H, NH); ¹³C NMR (100MHz, CDCl₃): δ 40.94, 165.35.

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