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Sulfamic Acid: A Very Useful Catalyst

Compiled by Bo Wang

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Introduction

Sulfamic Acid ($\text{NH}_2\text{SO}_3\text{H}$, SA) is a dry, nonvolatile, non-hygroscopic, odorless, uncorrodible crystalline solid with outstanding physical stability. It has been determined that SA is comprised not of the aminosulfonic acid form, but rather of $^+\text{H}_3\text{N}-\text{SO}_3^-$ zwitterionic units by both X-ray and neutron diffraction techniques.¹ It dissolves moderately in water, and can be highly ionized to form strongly acidic solutions. Sulfamic acid is immiscible with commonly used non-polar organic solvents, such as toluene and THF. It is commercially available and is inexpensive. Recently, SA emerged as a promising solid-acid catalyst for acid-catalyzed reactions, such as functional group protections

and deprotections,^{2–4} and the synthesis of isoamyl acetate⁵ and polymeric ethers.⁶ Moreover, some important organic transformations, including Beckmann rearrangement,⁷ inter- and intramolecular imino Diels–Alder reactions,⁸ and Pechmann⁹ and Biginelli condensations,^{10,11} have also been performed successfully in the presence of sulfamic acid.

SA should be especially useful for applications in which a highly ionized nonvolatile acid is desired, or where precipitation of insoluble salts must be avoided.¹² It is widely used as a calibrating reagent in titrations,¹³ a cleaning agent in industry, and an enzyme inhibitor in biochemistry.¹⁴

Abstracts

(A) SA can be used as an alternative to conventional acid catalysts in the Pechmann condensation of phenols with β -ketoester, leading to the formation of substituted coumarins. The method is simple, cost-effective, solvent-free and gives good yields in a short reaction time.⁹

(B) An efficient SA-catalyzed solvent-free tetrahydropyranylation of various alcohols was investigated. The features of mild conditions, cost-efficient catalyst, simple work-up and the recyclability of the catalyst were displayed in this work.¹⁵

(C) SA has been used as an effective catalyst for addition esterification of cyclic olefins to aliphatic acids, and good results were obtained. The catalyst could be recycled simply by filtration, and reused directly in the next run with satisfactory results.¹⁶

(D) In the acetolysis reaction of THF to produce 1,4-diacetoxybutane, SA has proved to be an efficient catalyst and green alternative to various metal-containing acidic materials. This method is also applicable to the acetolysis of other cyclic ethers, such as methyl-substituted THF and tetrahydropyran.¹⁷

(E) Beckmann rearrangements of ketoximes can be performed with a SA/dried acetonitrile system and an efficient product isolation procedure. The use of a basic neutralizing agent has been avoided. Both the solvents and the catalyst were recovered and reused. Thus it is a green process for the preparation of amides from ketoximes.¹⁸

(F) 1-Propyl-3-methylimidazolium chloride ([C₃MIm]Cl) ionic liquid-regulated SA has been employed to chemoselectively catalyze the transesterification of β -ketoesters. [C₃MIm]Cl not only acted as a solvent to dissolve the NH₂SO₃H, but also made it a chemoselective catalyst.¹⁹

(G) The condensation of aldehydes, β -ketoesters and urea catalyzed by NH₂SO₃H in ethanol resulted in the production of dihydropyrimidinones in high yields under ultrasound irradiation.^{10,11}

(H) The use of SA as a catalyst in the inter- and intramolecular inverse-electron-demand Diels–Alder reactions of iminodienes was described. A one-pot synthesis of tetrahydroquinolines was achieved by the three-component coupling of benzaldehyde and anilines with electron-rich dienophiles, such as 2,3-dihydrofuran, dihydropyran and cyclopentadiene, in the presence of SA as catalyst. The intramolecular cycloaddition of imines, derived from *O*-prenylsalicylaldehyde with anilines catalyzed by SA proceeds smoothly and yielded the diastereomeric tetrahydrochromanoquinolines in good yields.⁸

(I) SA has been used as an efficient and recyclable catalyst for acetalization and ketalization of carbonyl compounds.^{20,21} The use of this stable, inexpensive, green catalyst, convenient reaction operation and high product selectivity are features of this reaction. SA can be reused up to five times in the reaction between benzaldehyde and neopentyl glycol, without noticeable loss of activity.

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