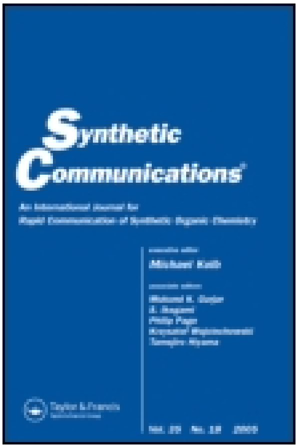

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Sulfamic Acid as a Cost-Effective and Recyclable Catalyst for Protection of Carbonyls to Acetals and Ketals Under Mild Conditions

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Sulfamic Acid as a Cost-Effective and Recyclable Catalyst for Protection of Carbonyls to Acetals and Ketals Under Mild Conditions

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ABSTRACT

An efficient H_2NSO_3H-catalyzed protection of various carbonyl compounds at room temperature was investigated. The features of mild

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conditions, cost-efficient catalyst, simple workup, and the recyclability of the catalyst were represented in this process.

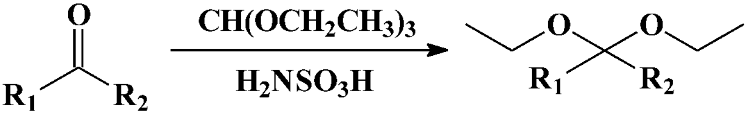
Key Words: Carbonyl compounds; Cost-efficient catalyst; Sulfamic acid.

INTRODUCTION

Protection of carbonyls and deprotection of acetals (or ketals) are two of the most important reactions in organic chemistry, and many methods have been developed for these reactions.[1] Although a lot of conventional catalysts, including acid catalysts,[1,2] have been reported for the protection of carbonyls into dimethyl acetals, the search for a new catalyst is still actively pursued.[3] Decaborane was proved to be an effective promoter for protection of carbonyls using orthoformate as protection reagent, however, its application in organic synthesis may be limited by the high toxicity of boron-containing compounds.[4] Some organic acids, such as *p*-toluenesulfonic acid, were also effective for this transformation, but the reaction rate and product yields are, in some instances, unsatisfactory.[5]

Sulfamic acid (NH_2SO_3H; SA) is a stable, nonvolatile, nonhygroscopic, odorless crystalline solid. Recently, it was shown that SA may prospectively be used as a substitute for conventional acidic catalytic materials. Last year, it was used as an efficient heterogeneous acid catalyst for ketal formation or acetalation[6] and Biginelli reaction.[7] Subsequently, we reported sulfamic acid catalyzed tetrahydropyranylation of hydroxy compounds,[8] esterification of cyclic olefins with aliphatic acids under solvent-free conditions,[9] transesterification of β-ketoesters in ionic liquids,[10] and Beckmann rearrangement of ketoxime.[11] Recently, sulfamic acid has been used as a promoter for intramolecular imino Diels–Alder reactions to produce tetrahydroquinolines.[12] In those homogeneous liquid reactions, SA is recyclable and is easy to handle as a catalyst owing to its immiscibility with common organic solvents. Unique catalytic features and the intrinsic zwitterionic property of SA are very different from the conventional acidic catalyst. This prompted us to explore further applications of NH_2SO_3H as an acidic catalyst in carbon–carbon and carbon–heteroatom forming reactions. Here, we wish to describe the protection of carbonyls to acetals using a catalytic amount of sulfamic acid (Scheme 1).

Various aldehydes and ketones were efficiently converted to the corresponding diethyl acetals in the presence of triethyl orthoformate using a catalytic amount of sulfamic acid at room temperature, and the results are shown in Table 1. Yields of these reactions are almost quantitative in most cases. Sulfamic acid (5 mol%) was used in all of the cases except for acetophenone (10 mol%). It was noteworthy that sulfamic acid is insoluble in the

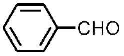
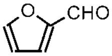
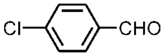
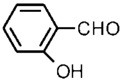
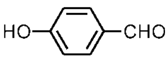
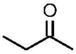
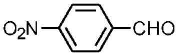
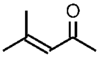
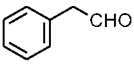
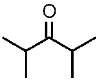
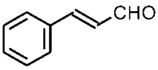
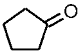
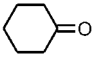
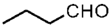
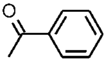
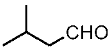
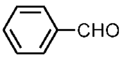


Scheme 1.

reaction mixture. Thus, it could be recycled by filtration after reaction and reused in the next run. In the reaction of benzaldehyde, sulfamic acid could be reused three times without detectable loss of activity.

In summary, sulfamic acid has proved to be an effective catalyst for protection of carbonyl compounds using triethyl orthoformate as the protection reagent. Mild conditions, cost-efficient catalyst, simple workup, and the recyclability of the catalyst are the features obtained in this method.

Table 1. Sulfamic acid catalyzed protection of carbonyls using triethyl orthoformate.

Entry	Substrates	Time (h)	Yield (%)	Entry	Substrates	Time (h)	Yield (%)
1		1.0	97	10		2.0	91
2		1.0	95	11		3.0	90
3		1.0	90	12		5.0	92
4		2.0	94	13		6.0	86
5		2.5	96	14		6.0	89
6		2.0	92	15		4.0	85
7		3.0	92	16		4.0	84
8		4.0	94	17		12.0	87
9		4.0	93	18[a]		1.0	96

[a] Catalyst was reused three times.

Another advantage of the use of sulfamic acid as a novel promoter for this transformation is its green property, because H_2NSO_3H is a degradable and metal-free species. This may be the most attractive for the development of clean organic transformation and green chemistry. Therefore, the present catalytic method is useful in organic synthesis.

EXPERIMENTAL

Typical Procedure

To a stirred mixture of carbonyl compounds (10 mmol) and triethyl orthoformate (15 mmol) in a reaction flask, H_2NSO_3H (1 mmol) was added. The mixture was stirred at room temperature (25°C), and the progress of the reaction was monitored by Hewlett-Packard 6890/5793 GC/MS. After completion of the reaction, the catalyst was recovered from the mixture by filtration, and was then evaporated to give an almost pure product. Further purification was achieved through a short column of silica gel (2 cm in length, 0.5 cm in diameter) with petroleum ether to obtain the pure product.

REFERENCES

1. Greene, T.W.; Wuts, P.G.M. *Protective Groups in Organic Synthesis*, 3rd Ed.; John Wiley & Sons: New York, 1991; 188.
2. (a) Perio, B.; Dozias, M.J.; Jacquault, P.; Hamelin, J. Solvent Free Protection of Carbonyl Group under Microwave Irradiation. Tetrahedron Lett. **1997**, *38*, 7867–7870; (b) Tateiwa, J.; Horiuchi, H.; Uemura, S. Ce3+-Exchanged Montmorillonite (Ce3+-Mont) as a Useful Substrate-Selective Acetalization Catalyst. J. Org. Chem. **1995**, *60*, 4039–4043; (c) Clerici, A.; Pastori, N.; Porta, O. Efficient Acetalisation of Aldehydes Catalyzed by Titanium Tetrachloride in a Basic Medium. Tetrahedron **1998**, *54*, 15679–15690; (d) Karimi, B.; Ashtiani, A.M. 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) as a Highly Efficient and Mild Catalyst for Diethyl Acetalization of Carbonyl Compounds. Chem. Lett. **1999**, 1199–1200.
3. Ishihara, K.; Karumi, Y.; Kubota, M.; Yamamoto, H. Scandium Trifluoromethanesulfonimide and Scandium Trifluoromethanesulfonate as Extremely Active Acetalization Catalysts. Synlett **1996**, 839–841.
4. Lee, S.H.; Lee, J.H.; Yoon, C.M. An Efficient Protection of Carbonyls and Deprotection of Acetals using Decaborane. Tetrahedron Lett. **2002**, *43*, 2699.

5. Bonacorso, H.G.; Martins, M.A.P.; Bittencourt, S.R.T.; Lourega, R.V.; Zanatta, N.; Flores, A.F.C. Trifluoroacetylation of Unsymmetrical Ketone Acetals. A Convenient Route to Obtain Alkyl Side Chain Trifluoromethylated Heterocycles. J. Fluorine Chem. **1999**, *99*, 177–182.
6. Jin, T.S.; Sun, G.; Li, Y.W.; Li, T.S. An Efficient and Convenient Procedure for the Preparation of 1,1-Diacetates from Aldehydes Catalyzed by H_2NSO_3H. Green Chem. **2002**, 255–256.
7. Li, J.T.; Han, J.F.; Yang, J.H.; Li, T.S. An Efficient Synthesis of 3,4-Dihydropyrimidin-2-ones Catalyzed by NH_2SO_3H under Ultrasound Irradiation. Ultrasonics Sonochem. **2003**, *10*, 119–122.
8. Wang, B.; Yang, L.M.; Suo, J.S. Solvent-Free Tetrahydropyranylation of Alcohols with Sulfamic Acid as Reusable Catalyst. Synth. Commun. **2003**, *33*, 3929–3932.
9. Wang, B.; Gu, Y.L.; Yang, L.M.; Suo, J.S. Sulfamic Acid as an Efficient and Recycling Catalyst for Addition of Aliphatic Acid to Cyclic Olefins. Catal. Lett. **2004**, *96* (1–2), 71–74.
10. Wang, B.; Yang, L.M.; Suo, J.S. Ionic Liquid-Regulated Sulfamic Acid: Chemoselective Catalyst for the Transesterification of β-Ketoesters. Tetrahedron Lett. **2003**, *44*, 5037–5039.
11. Wang, B.; Gu, Y.; Luo, C.; Yang, T.; Yang, L.; Suo, J. Sulfamic Acid as a Cost-Effective and Recyclable Catalyst for Liquid Beckmann Rearrangement; a Green Process to Produce Amides from Ketoximes Without Waste. Tetrahedron Lett. **2004**, *45*, 3369–3372.
12. Nagarajan, R.; Magesh, C.J.; Perumal, P.T. Inter- and Intramolecular Imino Diels–Alder Reactions Catalyzed by Sulfamic Acid: A Mild and Efficient Catalyst for a One-Pot Synthesis of Tetrahydroquinolines. Synthesis **2004**, 69–74.

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