Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 45 (2004) 6599–6602

Tetrahedron Letters

Sulfamic acid as a cost-effective catalyst instead of metal-containing acids for acetolysis of cyclic ethers

Bo Wang, Yanlong Gu, Weizhong Gong, Yuru Kang, Liming Yang* and Jishuan Suo

State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

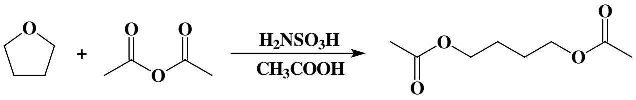
Received 23 May 2004; revised 2 July 2004; accepted 7 July 2004

Abstract—Sulfamic acid has been used as an efficient catalyst and green alternative for metal-containing acidic materials to promote the acetolysis reaction of THF to produce 1,4-diacetoxybutane. This method is also applicable to the acetolysis of other cyclic ethers, such as methyl substituted THF and tetrahydropyran and 1,4-dioxane, which is less reactive.

1. Introduction

Reactions, which cleave cyclic ethers to diacetoxyalkane is an effective method of obtaining difunctional synthetic intermediates and are important for the removal of ethereal protecting groups.[1] Previous reports described the acylative cleavage of cyclic ethers to diacetoxyalkane using reagent systems such as heteropolyacid,[2] and $Yb(OTf)_3$.[3] These methods always use metal-containing acids as promoters, therefore, they are not green and should be replaced by a suitable one because these elements are deleterious for human health, and consequently, a tedious post treatment is needed concerning environmental problems.

Sulfamic acid (NH_2SO_3H, SA) is a dry, nonvolatile, nonhygroscopic, odorless and white crystalline solid with an outstanding physical property and stability. The crystals can be kept in the laboratory for many years without change. It is commercially available and is a very cheap chemical. Recently, it was shown that SA has the prospect to be used as a substitute for conventional acidic catalytic materials. It has been used as an efficient heterogeneous acid catalyst for ketal formation or acetalation[4] and deprotection of acetals.[5] Subsequently, we reported sulfamic acid catalyzed tetrahydropyranylation of hydroxy compounds,[6] esterification of cyclic olefins with aliphatic acids under solvent-free conditions,[7] Beckmann rearrangement of ketoxide[8] in dried CH_3CN and transesterification of β-ketoesters in ionic liquid.[9] We report herein, for the first time, sulfamic acid catalyzed acetolysis of cyclic ethers to produce corresponding diacetoxyalkane. This method is characterized by the reaction of THF with a mixture of acetic acid and acetic anhydride as nucleophiles (Scheme 1). This method is also applicable to the acetolysis of other cyclic ethers, such as methyl substituted THF and tetrahydropyran (THP). Normally inert 1,4-dioxane was also effectively converted through this method to yield a single product, ethylene glycol diacetate.



Scheme 1.

2. Results and discussion

Initially, THF has been used as a substrate to test the feasibility of sulfamic acid as catalyst for the acetolysis reaction. Figure 1 illustrates the change in THF conversion with reaction time in the acetolysis with a mixture of acetic acid (AcOH) and acetic anhydride (AcOAc) at various volume ratios. In the equal volume AcOH/AcOAc mixture, the reaction proceeded selectively to

---

Keywords: Sulfamic acid; Acetolysis; Cyclic ether; Acid catalysis; Tetrahydrofuran.

* Corresponding author. Tel.: +86-931-8277635; fax: +86-931-8277088; e-mail: limy@ns.lzb.ac.cn

0040-4039/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2004.07.024

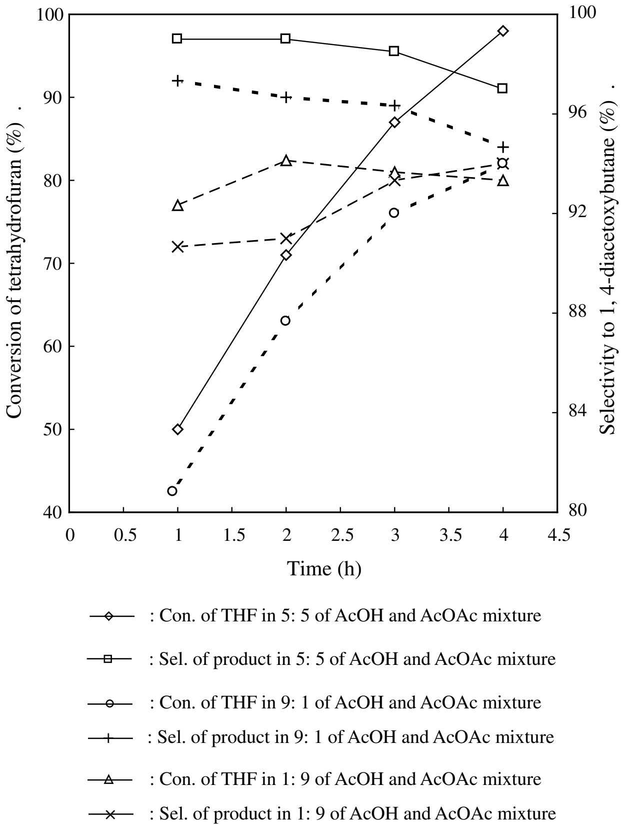


Figure 1. Acetolysis reaction of THF in different ratios of AcOH and AcOAc mixture. Reaction conditions: THF, 0.5mL; sulfamic acid, 0.06g, temperature, 60°C.

yield the product, 1,4-diacetoxybutane, with a complete THF conversion after 4h. When the volume ratio of AcOH/AcOAc was changed to 1:9 or 9:1, the acetolysis of THF did not substantially occur at 60°C and some polymeric products were also detected in reaction mixtures. It appears that a 50% v/v content of AcOH in the reaction system is the suitable choice for sulfamic acid catalyzed acetolysis reaction of THF. It should be pointed that the ability to run this THF acetolysis reaction over H_2NSO_3H represents a substantial improvement over previous methods, wherein a metal-containing catalyst, which is toxic and deleterious for human health and environmental protection, was required to effect reaction.

Figure 2 gives THF conversion versus time profile under different amounts of sulfamic acid. When the catalyst quantity was increased, maximum THF conversion was reached sooner: for a 2-fold rise in catalyst amount, the reaction time can be halved. Because 20% of catalyst amount seems to be thriftless, and the reaction time has to be prolonged to 8h when using 5% of sulfamic acid, 10% of catalyst was used in later experiments.

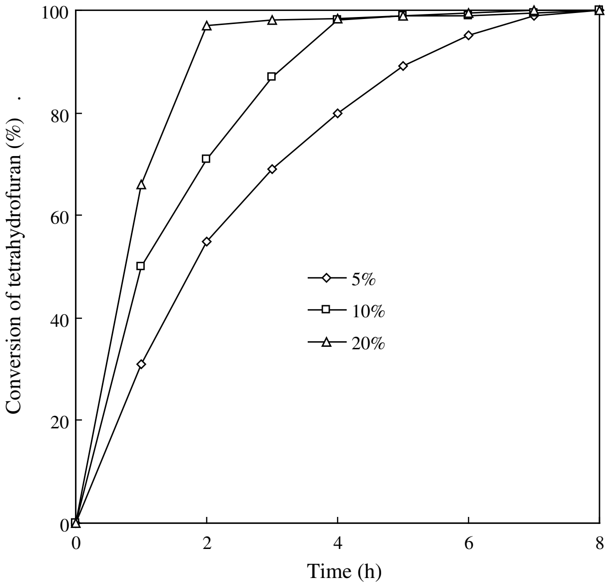


Figure 2. Effect of catalyst amount on the acetolysis reaction of THF. Reaction conditions: THF, 0.5mL; AcOH, 5mL; AcOAc, 5mL; temperature, 60°C.

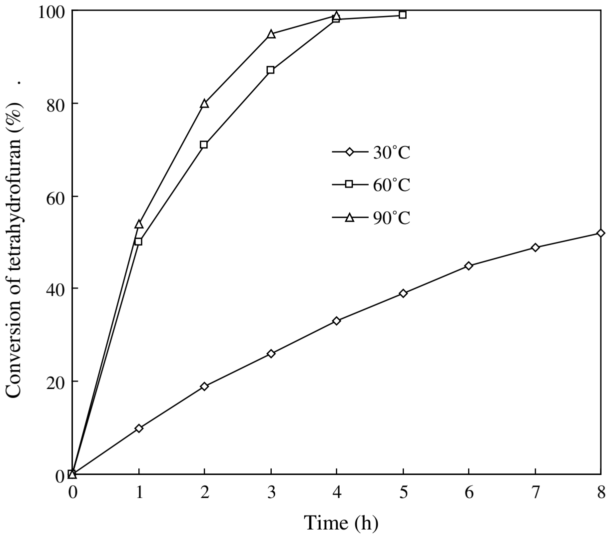
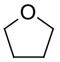
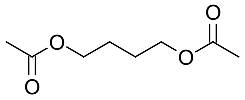
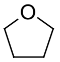
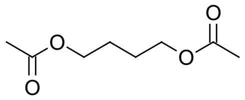
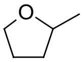
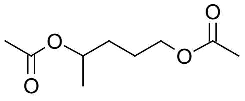
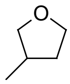
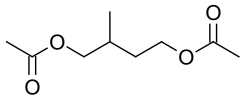
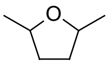
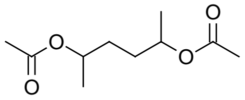
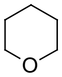
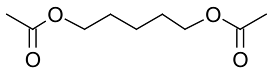
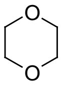
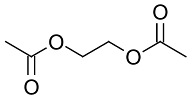
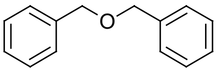
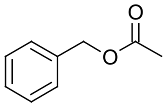


Figure 3. Effect of temperature on the reaction of acetolysis of THF. Reaction conditions: THF, 0.5mL; AcOH, 5mL, AcOAc, 5mL; sulfamic acid, 0.06g.

We next investigate the effect of reaction temperature on the conversion of THF in the above acetolysis reaction and the results are shown in Figure 3. THF could be smoothly consumed at 30°C, but the reaction rate seems to be sluggish and the THF conversion was only 52% after 8h. The reaction rate could markedly be increased when the reaction temperature was elevated to 60°C, and THF could be completely converted within 4h. Although further increase in temperature was of benefit for the improvement of reaction rate, its magnitude is very limited, and as a result, 60°C seems to be suitable for this acetolysis reaction using sulfamic acid as catalyst. This temperature condition is comparable with the heteropolyacid catalytic system reported previously.[1,3]

Having these results in hand, other cyclic ethers have been subjected to the optimized conditions, and the results are summarized in Table 1. All the examined tetrahydrofuran derivatives are readily reacted in equal

Table 1. Sulfamic acid catalyzed acetolysis of ethers[a]

Entry	Ethers	Products	Yield (%)
1			97
2[b]			0
3			95
4			96
5			91
6			89
7			86
8			96

[a] Reaction conditions: sulfamic acid, 0.06 g, cyclic ether, 6.1 mmol; AcOH, 5 mL; AcOAc, 5 mL; reaction temperature, 60 °C ; reaction time, 4 h.

[b] Reacted at 90 °C for 8 h in the absence of sulfamic acid.

volume of AcOH/AcOAc mixture in the presence of 10% sulfamic acid to give corresponding 1,4-diacetoxybutanes with good to excellent yields. In the absence of sulfamic acid, THF did not react with AcOAc even after prolonged reaction time and under elevated temperature (entry 2). It indicated that an acidic catalyst is necessary for this type of reaction. When using a six membered cyclic ether, tetrahydropyran, as substrate, analogous acetolysis reaction was also successful under the above-mentioned optimized conditions and a nearly 90% of 1,5-diacetoxypentane yield was obtained. It was worth noting that normally inert 1,4-dioxane was also effectively converted through this method to yield a single product, ethylene glycol diacetate. The reactivity of an acyclic ether, benzyl ether, was also examined in our system, and the expected benzyl acetate could be obtained in a yield of 96% (entry 8). This implies that the reaction of 1,4-dioxane might involve two reaction sequences: one is the first acetylation–acetoxylation of 1,4-dioxane to produce the acyclic fragment, and the second acetylation–acetoxylation might proceed with the resulting acyclic ether to give the desired ethylene glycol diacetate.

3. Conclusions

Sulfamic acid has proved to be an efficient catalyst and green alternative for metal-containing acidic materials, which are toxic and deleterious for human health and environmental protection, to promote the acetolysis reaction of THF to produce 1,4-diacetoxybutane. This method is also applicable to the acetolysis of other cyclic ethers, such as methyl substituted THF and tetrahydropyran. Normally inert 1,4-dioxane was also effectively converted through this method to yield a single product, ethylene glycol diacetate. Enhanced reaction rates, improved yields and low cost of catalyst are the features obtained in this catalytic system. Another advantage of the use of sulfamic acid as a novel promoter for this transformation is that the experimental procedure is quite simple and convenient, and the reaction conditions are amenable to scale-up.

4. Experimental

In a typical experiment, sulfamic acid (0.06 g) was dissolved into AcOH (5 mL) and AcOAc (5 mL) mixture in a 25 mL round bottom flask equipped with a distillation condenser. Then THF (0.5 mL) was introduced. The content was stirred vigorously at 60 °C. After the desired reaction time, the reaction mixture was cooled to room temperature, and then was analyzed by GC (HP 1790 GC equipped with a FID detector) and GC/MS (HP 6890/5973). The concentration of reactant and product was directly given by the system of GC chemstation according to the area of each chromatograph peak. The pure acetolysis products could be obtained by distillation under reduced pressure (1,4-diacetoxybutane: 97–99 °C/8 mmHg).

References and notes

1. Izumi, Y.; Matsuo, K.; Urabe, K. *J. Mol. Catal.* **1983**, *18*, 299.
2. Izumi, Y.; Iida, K.; Usami, K.; Nagata, T. *Appl. Catal. A: General* **2003**, *256*, 199.
3. Miles, W. H.; Ruddy, D. A.; Tinorgah, S.; Geisler, R. L. *Synth. Commun.* **2004**, *34*, 1842.
4. (a) Jin, T. S.; Sun, G.; Li, Y. W.; Li, T. S. *Green Chem.* **2002**, 255; (b) Li, Y. Q. *Chin. J. Int. Chem.* **2003**, *5*(5), 40.
5. Jin, T. S.; Sun, G.; Li, Y. W.; Li, T. S. *J. Chem. Res. Synop.* **2003**, *1*, 30.
6. Wang, B.; Yang, L. M.; Suo, J. S. *Synth. Commun.* **2003**, *33*, 3929.
7. Wang, B.; Gu, Y. L.; Yang, L. M.; Suo, J. S. *Catal. Lett.* **2004**, *96*(1–2), 71.
8. Wang, B.; Gu, Y. L.; Luo, C.; Yang, T.; Yang, L. M.; Suo, J. S. *Tetrahedron Lett.* **2004**, *45*, 3369.
9. Wang, B.; Yang, L. M.; Suo, J. S. *Tetrahedron Lett.* **2003**, *44*, 5037.