

## Sulfamic Acid as a Cost-effective Catalyst for Acetolysis of Cyclic Ethers

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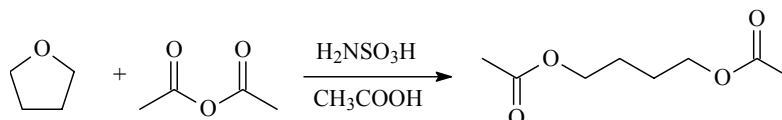
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**Abstract:** Sulfamic acid has been used as an efficient catalyst and green alternative for conventional acidic materials to promote the acetolysis reaction of THF to produce 1,4-diacetoxybutane. This method is also applicable in the acetolysis of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

**Keywords:** Sulfamic acid, acetolysis, cyclic ether, acid catalysis, ionic liquid.

The reaction, which cleavages cyclic ethers to diacetoxyalkane, is an effective method for obtaining difunctional synthetic intermediates and important for the removal of ethereal protecting groups<sup>1</sup>. Although, the acylative cleavage of cyclic ethers is catalyzed by mineral acids<sup>2</sup> generally, new catalytic systems are being continuously explored in search for more efficiencies and lower cost. Protic acids, Lewis acids including heteropolyacid<sup>3</sup> and metal triflate<sup>4</sup> have been reported for the cleavage of cyclic ethers to diacetoxyalkanes. However, most of these methods are often involve the use of acid catalysts which always demand aqueous work-up for separation, recycling and disposal. Furthermore, some of them need expensive reagents, the procedure is lack of simplicity, the yields and selectivities are also not satisfactory due to side reactions.

Scheme 1



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Sulfamic acid ( $\text{NH}_2\text{SO}_3\text{H}$ , SA) is a dry, nonvolatile, nonhydroscopic, odorless, the white crystalline solid with an outstanding physical property and stability. It is available and cheap. 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<sup>5</sup> and deprotection of acetals<sup>6</sup>. Subsequently, we have reported sulfamic acid catalyzed tetrahydropyranylation of hydroxy compounds<sup>7</sup>, esterification of cyclic olefins with aliphatic acids under solvent-free conditions<sup>8</sup>, Beckmann rearrangement of ketoxide<sup>9</sup> in dried  $\text{CH}_3\text{CN}$  and transesterification of  $\beta$ -ketoesters in ionic liquid<sup>10</sup>. Herein, we report acetolysis of cyclic ethers catalyzed by sulfamic acid. 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 in the acetolysis of other cyclic ethers, such as methyl substituted THF and tetrahydropyran (THP). Normally inert 1,4-dioxane also can be converted to ethylene glycol diacetate effectively by this method.

### Experimental

Sulfamic acid (0.6 mmol) or other catalyst was dissolved into AcOH (5 mL) and  $\text{Ac}_2\text{O}$  (5 mL) in a round bottom flask equipped with a distillation condenser. Then THF (0.5 mL) was introduced. The reaction mixture was stirred vigorously at  $60^\circ\text{C}$ . After the reaction was completed, the reaction mixture was cooled to room temperature, and analyzed by GC (HP 1790 GC equipped with a FID detector) and GC / MS (HP 6890/5973). The pure acetolysis products could be obtained by distillation under reduced pressure.

### Results and Discussion

Initially, THF has been used as a substrate to test the feasibility of sulfamic acid as catalyst for the acetolysis reaction. As described in **Table 1**, entry 1, the acetolysis reaction was very successful over 10% of sulfamic acid, and the conversion of THF was 98% with 97% selectivity to 1, 4-diacetoxybutane after 4 hours reaction. Without sulfamic acid THF could not be acetolyzed even at prolonged reaction time (entry 2). The optimized condition is 4h and 10% of sulfamic acid. To shorten the reaction time or reduce the concentration of sulfamic acid would reduce the conversion of THF (entries 3 and 4). In the present acetolysis reaction, two ionic liquids,  $[\text{Hmim}]\text{BF}_4$  and  $[\text{Hbim}]\text{BF}_4$ , were also tested for catalyzing this acetolysis reaction, the other reaction conditions were the same. However, the yield and the selectivity were very low (**Table 1**, entries 5 and 6). Another protonated tertiary amine salt,  $\text{Me}_3\text{N}\cdot\text{HCl}$ , was also examined in this reaction, and its activity was very poor (entry 7). These results indicated that sulfamic acid is a crucial promoter for the acetolysis reaction of THF.

Having these results in hand, other cyclic ethers have been subjected to the optimized conditions, and the results are summarized in **Table 2**. All the examined tetrahydrofuran derivatives are readily reacted in equal volume of AcOH /  $\text{Ac}_2\text{O}$  mixture in the presence of 10% sulfamic acid to give corresponding 1, 4-diacetoxybutanes with


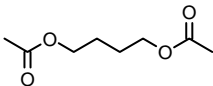

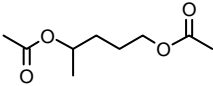

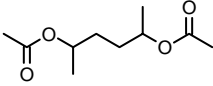

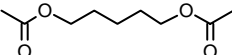

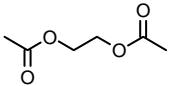
good to excellent yields (entries 1, 2 and 3). When using a six number cyclic ether, tetrahydropyran as substrate the acetolysis reaction was also successful under above-mentioned conditions and 1, 5-diacetoxypentane was obtained in more than 90% yield (entry 4). It was worthy noted, that normally inert 1,4-dioxane also can converted with this method to ethylene glycol diacetate effectively (entry 5).

**Table 1** Catalytic activities of sulfamic acid and some other zwitterionic organic acidic materials in acetolysis reaction of THF <sup>a</sup>

Entry	Catalyst	Amount of Cat. (%)	Time (hs)	Conv. (%) <sup>b</sup>	Sel. (%) <sup>c</sup>
1	H <sub>2</sub> NSO <sub>3</sub> H	10	4	98	97
2	H <sub>2</sub> NSO <sub>3</sub> H	0	8	0	0
3	H <sub>2</sub> NSO <sub>3</sub> H	5	4	80	98
4	H <sub>2</sub> NSO <sub>3</sub> H	10	2	87	98
5	[Hmim]BF <sub>4</sub>	10	4	17	71
6	[Hbim]BF <sub>4</sub>	10	4	14	68
7	[MeN <sub>3</sub> H]Cl	10	4	11	84

<sup>a</sup> Reaction conditions: THF 0.5 mL; AcOH 5 mL; Ac<sub>2</sub>O 5 mL; catalyst 0.62 mmol (10% for THF); reaction temperature 60°C; reaction time 4 hours. <sup>b</sup> conversion of THF. <sup>c</sup> selectivity to 1, 4-diacetoxypentane.

**Table 2** Sulfamic acid catalyzed acetolysis of cyclic ethers <sup>a</sup>

Entry	Cyclic ethers	Products	Boiling point (°C)	Yield (%)
1			97-99°C / 8 mmHg	97
2			109-112°C / 8 mmHg	95
3			122-125°C / 8 mmHg	91
4			110-112°C / 8 mmHg	89
5			186-189 °C	86

<sup>a</sup> Reaction conditions: sulfamic acid 0.06 g; cyclic ether 6.1 mmol; AcOH 5 mL; Ac<sub>2</sub>O 5 mL; reaction temperature 60°C; reaction time 4 h.

## Conclusions

Sulfamic acid has proved to be an efficient catalyst and green alternative for conventional acidic materials to promote the acetolysis reaction of THF to produce 1,4-diacetoxybutane. This method is also applicable in the acetolysis of other cyclic ethers, such as methyl substituted THF and tetrahydropyran. Normally, this method also can be used for acetolysis of inert 1,4-dioxane to obtain ethylene glycol diacetate. Enhanced reaction rates, improved yields and low cost are the features of this catalytic system. Another advantage of this method are simple and experimental procedure and the reaction conditions are amenable to scale-up.

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