

## Zirconyl Triflate, [ZrO(OTf)<sub>2</sub>], as a New and Highly Efficient Catalyst for Ring-Opening of Epoxides

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A highly efficient method for the ring opening of epoxides catalyzed by ZrO(OTf)<sub>2</sub> was adopted. This catalyst efficiently catalyzed alcoholysis, acetolysis and hydrolysis of epoxides and the corresponding alkoxy alcohols, acetoxy alcohols and 1,2-diols were obtained in excellent yields. Conversion of epoxides to 1,2-diacetates, thiiranes and 1,3-dioxolanes was also performed in the presence of catalytic amounts of ZrO(OTf)<sub>2</sub>, and the corresponding products were obtained in high to excellent yields. The high catalytic activity of ZrO(OTf)<sub>2</sub> is due to the replacement of Cl with OTf, which makes the ZrO(OTf)<sub>2</sub> as efficient Lewis acid.

**Keywords:** Alcoholysis, Acetolysis, 1,2-Diacetate, 1,3-Dioxolane, Zirconyl triflate

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### INTRODUCTION

Epoxides are important precursors in organic syntheses [1]. These compounds are easily prepared, and due to their ring strain, they react with different nucleophiles with high regioselectivity [2-5]. Ring opening reactions of epoxides provide various functional groups such as alcohols, diols, aldehydes, alkanes, alkenes and ketones. Under the reported conditions, these reactions have limited applicability in modern organic synthesis. In most of the epoxides, ring-opening reactions under acidic conditions, the formation of a mixture of regio isomers and polymerization is observed. Some of the reported methods suffer from drawbacks such as high acidity, the non-catalytic nature of the reagents, long reaction times and inconvenient handling [6]. Therefore, the introduction of new methods for the nucleophilic ring-opening of epoxides under mild conditions is much needed in synthetic organic chemistry. A number of methods using Lewis acids

and one-electron transfer catalysts have been also reported for the ring-opening of epoxides with different nucleophiles [7-24].

Zirconium(IV) salts have recently attracted much attention due to their low cost, high catalytic activity, easy availability and low toxicity [25]. A variety of Zr(IV) salts have been used for several organic transformations such as Friedel-Crafts reaction [26], Diels-Alder reaction [27], Michael reaction [28], acetalization of carbonyl compounds [29], conversion of nitriles to oxazolines and imidazolines [30,31] and trimethylsilylation of alcohols and phenols [32].

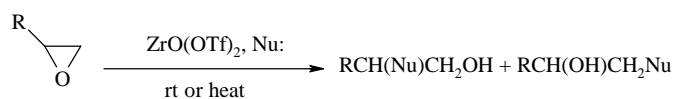
In this paper, we report zirconyl triflate, ZrO(OTf)<sub>2</sub>, as an efficient, stable and non-hygroscopic catalyst for alcoholysis, acetolysis and hydrolysis of epoxides, and for conversion of epoxides to 1,2-diacetates, thiiranes and 1,3-dioxolanes (Schemes 1-4).

### EXPERIMENTAL

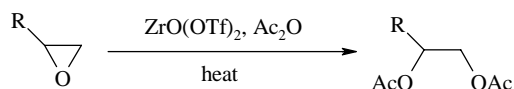
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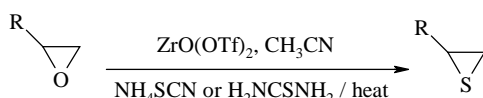
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Nu: ROH, H<sub>2</sub>O, AcOH

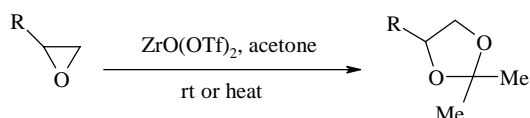
Scheme 1



Scheme 2



Scheme 3



Scheme 4

chemical companies. <sup>1</sup>H NMR spectra were recorded on a Bruker AM 80 MHz or a Bruker AC 500 MHz spectrometer in CDCl<sub>3</sub> solvent using TMS as internal standard. Infrared spectra were run on a Philips PU9716 or Shimadzu IR-435 spectrophotometer. All analyses were performed on a Shimadzu GC-16A instrument with a flame ionization detector using silicon DC-200 or Carbowax 20M columns. ZrO(OTf)<sub>2</sub> was prepared and characterized according to our previously reported procedure [32].

### General Procedure for Alcoholysis of Epoxides

To a solution of epoxide (1 mmol) in the appropriate alcohol (5 ml), ZrO(OTf)<sub>2</sub> (3 mg, 0.0075 mmol) was added and the mixture was stirred at room temperature or under reflux conditions for the appropriate time according to Table 2. The progress of the reaction was monitored by GC. After completion of the reaction, the solvent was evaporated, water was added (15 ml) and the mixture was extracted with Et<sub>2</sub>O (3 × 10 ml). The organic solution was dried (MgSO<sub>4</sub>). The filtrates were concentrated and chromatographed on a silica

gel column to give the pure product in 64-97% yields.

### General Procedure for Acetolysis of Epoxides

A mixture of epoxides (1 mmol) and ZrO(OTf)<sub>2</sub> (3 mg, 0.0075 mmol) in acetic acid (5 ml) was stirred at room temperature or under reflux conditions for appropriate time (Table 3). The progress of the reaction was monitored by GC. After completion of the reaction, the solvent was evaporated, water (15 ml) was added and the mixture was extracted with Et<sub>2</sub>O (3 × 10 ml). The filtrate was washed with 5% aqueous sodium bicarbonate and dried (MgSO<sub>4</sub>). Evaporation of the solvent, followed by column chromatography on silica-gel, gave the pure product in 83-99% yields.

### General Procedure for Hydrolysis of Epoxides

To a solution of epoxide (1 mmol) in an equal mixture of CH<sub>3</sub>CN/H<sub>2</sub>O (5 ml) was added ZrO(OTf)<sub>2</sub> (3 mg, 0.0075 mmol). The mixture was stirred under reflux conditions for the specified time (Table 3). The progress of the reaction was monitored by GC. After completion of the reaction, the solvent was evaporated. The aqueous mixture was saturated with brine and extracted with Et<sub>2</sub>O (3 × 10 ml). The resulting solution was concentrated under reduced pressure and chromatographed on a silica-gel column to afford the pure product in excellent yields.

### General Procedure for Conversion of Epoxides to 1,2-Diacetates

To a mixture of epoxide (1 mmol) in Ac<sub>2</sub>O (2 ml) was added ZrO(OTf)<sub>2</sub> (3 mg, 0.0075 mmol) and the mixture was stirred at 50 or 100 °C for the appropriate time according to Table 5. After completion of the reaction as indicated by GC, water (15 ml) was added and the mixture was extracted with Et<sub>2</sub>O (3 × 10 ml). The organic layer was concentrated and the residue was purified by column chromatography on silica gel to afford the pure 1,2-diacetate in high yield..

### General Procedure for Conversion of Epoxides to Thiiranes

To a solution of epoxide (1 mmol) in CH<sub>3</sub>CN (5 ml), ammonium thiocyanate or thiourea (2 mmol) and ZrO(OTf)<sub>2</sub> (3 mg, 0.0075 mmol) were added and the mixture was stirred under reflux conditions for 15-120 min (Table 5). After

completion of the reaction (monitored by GC), the mixture was directly passed through a short column of silica-gel (1:1 hexane-ethyl acetate) to remove the catalyst. Evaporation of the solvent, followed by distillation under reduced pressure, gave the corresponding thirane in excellent yields.

### General Procedure for Conversion of Epoxides to 1,3-Dioxolanes

Epoxide (1 mmol) and ZrO(OTf)<sub>2</sub> (3 mg, 0.0075 mmol) were dissolved in acetone (5 ml) and the mixture was stirred at room temperature or under reflux conditions for 2-60 min (Table 7). The progress of the reaction was monitored by GC. After completion of the reaction, a saturated solution of NaHCO<sub>3</sub> (10 ml) was added and the mixture was extracted with Et<sub>2</sub>O (3 × 10 ml). The etherate was dried over MgSO<sub>4</sub> and evaporated. The crude product was purified by chromatography on a short column of silica gel to give the pure product in 91-99% yields.

## RESULTS AND DISCUSSION

### Alcoholysis, Acetolysis and Hydrolysis of Epoxides Catalyzed by ZrO(OTf)<sub>2</sub>

First, we investigated the catalytic activity of different

zirconium salts in the ring opening of styrene oxide. In this manner, alcoholysis of styrene oxide was performed in the presence of ZrCl<sub>4</sub>, ZrOCl<sub>2</sub>·8H<sub>2</sub>O and ZrO(OTf)<sub>2</sub>. The results (Table 1) showed that ZrO(OTf)<sub>2</sub> is superior in terms of reaction times, yields of the products, reaction conditions and catalyst amount. Therefore, the ZrO(OTf)<sub>2</sub> was used as an efficient catalyst for ring opening of epoxides.

Alcoholysis of various epoxides such as cyclohexene and styrene oxides, (chloromethyl)oxirane, allyl oxiranylmethyl ether, isopropyl oxiranylmethyl ether, phenyl oxiranylmethyl ether and 1,2-epoxyoctane as examples of aliphatic, alicyclic, activated and deactivated epoxides in the presence of catalytic amounts of ZrO(OTf)<sub>2</sub> was performed with primary (methanol, ethanol and *n*-propanol), secondary (*iso*-propanol) and tertiary (*t*-butanol) alcohols (Scheme 1), and the corresponding β-alkoxy alcohols were obtained in high yields (Table 2). In the case of cyclohexene oxide, the reactions were stereoselective, and the only *trans* products were obtained (entries 1-5). In the alcoholysis of styrene oxide the reactions occurred on the more substituted carbon and Markovnikov type products were obtained (entries 6-10).

In the case of asymmetrical epoxides, the reactions were regioselective with the attack of the alcohols on the less substituted carbon to yield the anti Markovnikov type products

**Table 1.** Investigation of Catalytic Activity of Different Zirconium Salts in the Alcoholysis of Styrene<sup>a</sup>

R	Catalyst					
	ZrCl <sub>4</sub> (4 mol%)		ZrOCl <sub>2</sub> ·8H <sub>2</sub> O (3 mol%)		ZrO(OTf) <sub>2</sub> (0.75 mol%)	
	Time (min)	Conversion (%) <sup>b</sup>	Time (min)	Conversion (%) <sup>b</sup>	Time (min)	Conversion (%) <sup>b</sup>
Me	5/R.T.	99	5/R.T.	99	2/R.T.	99
Et	120/R.T.	80	20/R.T.	28	5/R.T.	93
<i>n</i> -Pr	60/Reflux	99	20/R.T.	14	7/R.T.	99
<i>i</i> -Pr	90/Reflux	23	20/R.T.	5	40/R.T.	99
<i>t</i> -Bu	90/Reflux	10	20/R.T.	0	45/R.T.	97

<sup>a</sup>Reaction conditions: styrene oxide (1 mmol), alcohol (5 ml). <sup>b</sup>GC yield based on the starting styrene oxide.

**Table 2.** Alcoholysis of Various Epoxides Catalyzed by  $\text{ZrO}(\text{OTf})_2^a$ 


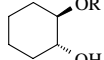
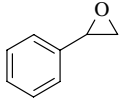
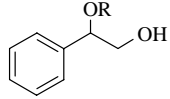
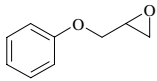
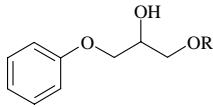
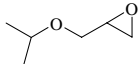
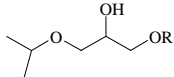
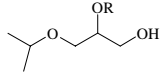
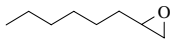
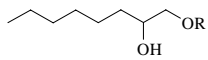
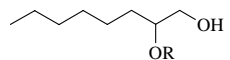
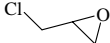
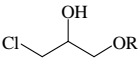
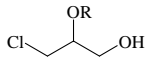
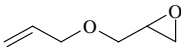
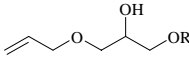
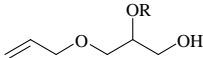
Entry	Epoxide	R-OH/Condition	Time (min)	Product/Conversion (catalyst mol%) <sup>b,c</sup>	
					
1		R = CH <sub>3</sub> /R.T.	2	99	
2		R = C <sub>2</sub> H <sub>5</sub> /R.T.	5	93	
3		R = <i>n</i> -Pr/R.T.	7	99	
4		R = <i>i</i> -Pr/R.T.	40	99	
5		R = <i>t</i> -Bu/R.T.	45	97	
					
6		R = CH <sub>3</sub> /R.T.	1	99	
7		R = C <sub>2</sub> H <sub>5</sub> /R.T.	2	99	
8		R = <i>n</i> -Pr/R.T.	5	99	
9		R = <i>i</i> -Pr/R.T.	5	97	
10		R = <i>t</i> -Bu/R.T.	30	87	
					
11		R = CH <sub>3</sub> /Reflux	20	99	
12		R = C <sub>2</sub> H <sub>5</sub> /Reflux	20	95	
13		R = <i>n</i> -Pr/Reflux	30	99	
14		R = <i>i</i> -Pr/Reflux	30	99	
15		R = <i>t</i> -Bu/Reflux	70	99	
					
16		R = CH <sub>3</sub> /R.T.	30	80	14
17		R = C <sub>2</sub> H <sub>5</sub> /Reflux	30	98	-
18		R = <i>n</i> -Pr/Reflux	40	99	-
19		R = <i>i</i> -Pr/Reflux	45	99	-
20		R = <i>t</i> -Bu/Reflux	50	99	-
					
21		R = CH <sub>3</sub> /R.T.	10	55	43
22		R = C <sub>2</sub> H <sub>5</sub> /Reflux	10	97	-
23		R = <i>n</i> -Pr/Reflux	15	99	-
24		R = <i>i</i> -Pr/Reflux	15	99	-
25		R = <i>t</i> -Bu/Reflux	25	93	-
					
26		R = CH <sub>3</sub> /Reflux	20	87	10
27		R = C <sub>2</sub> H <sub>5</sub> /Reflux	30	96	-
28		R = <i>n</i> -Pr/Reflux	40	99	-

Table 2. Continued

29	R = <i>i</i> -Pr/Reflux	75	98	-
30	R = <i>t</i> -Bu/Reflux	85	84	-
				
31	R = CH <sub>3</sub> /R.T.	30	82	12
32	R = C <sub>2</sub> H <sub>5</sub> /Reflux	35	98	-
33	R = <i>n</i> -Pr/Reflux	45	99	-
34	R = <i>i</i> -Pr/Reflux	45	99	-
35	R = <i>t</i> -Bu/Reflux	50	99	-

<sup>a</sup>Reaction conditions: epoxide (1 mmol), alcohol (5 ml), catalyst (0.0075 mmol). <sup>b</sup>All products were identified by comparison of their physical and spectral data with those of authentic samples [13,15]. <sup>c</sup>Yields refer to GC yields.

(entries 11-35). However, in the methanolysis of (chloromethyl)oxirane, allyl oxiranylmethyl ether, isopropyl oxiranylmethyl ether and 1,2-epoxyoctane small amounts of the product were obtained from the attack of the nucleophile on the more substituted carbon.

The methanolysis of styrene was also carried out under nonsolvolytic conditions to show the general applicability of the presented method. In this manner the styrene (1 mmol) was reacted with MeOH (10 mmol) in the presence of catalyst (0.0075) in acetonitrile (0.5 ml). The results were comparable to those obtained under solvolytic conditions.

Acetolysis of epoxides with acetic acid in the presence of catalytic amount of ZrO(OTf)<sub>2</sub> was carried out in the same manner as for alcoholysis, and the corresponding β-acetoxy alcohols were obtained in high yields (Table 3).

Hydrolysis of these epoxides was also performed in aqueous acetonitrile in the presence of this catalyst and the corresponding diols were obtained in high yields (Table 3).

It seems that the role of the catalyst is the activation of epoxide. The most probable interaction (according to the hard and soft concept) is coordination of the oxygen of epoxide to Zr<sup>4+</sup> to afford **1**. This makes the epoxide susceptible to nucleophilic attack by the alcohol to give **2** which in turn converts to the final product and releases the catalyst for the next catalytic cycle (Scheme 5).

In order to show the effectiveness of the presented method in the ring-opening of epoxides, we have compared the obtained results in the methanolysis of 2,3-epoxypropylphenyl ether catalyzed by ZrO(OTf)<sub>2</sub> with some others reported in the literature (Table 4). The results showed that our method was

superior in terms of catalyst amount, or reaction time, or product yield which leads to higher turnover frequency (TOF) for this catalytic system.

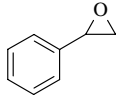
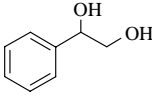
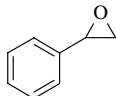
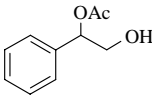

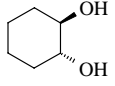

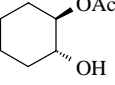
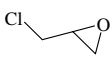
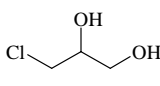

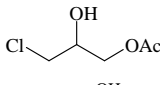
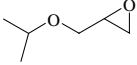
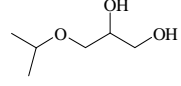
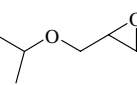
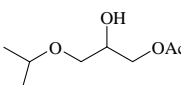
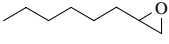
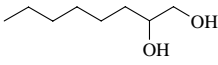
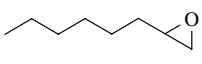
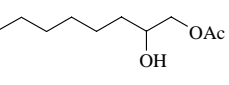
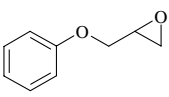
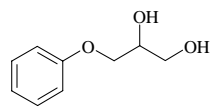
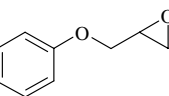
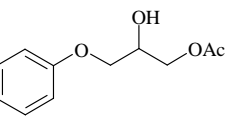
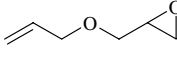
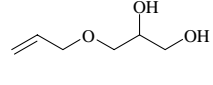
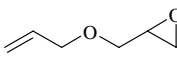
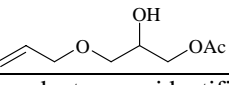
### Conversion of Epoxides to 1,2-Diacetates Catalyzed by ZrO(OTf)<sub>2</sub>

1,2-Diol esters with easily removable protecting groups are the most important intermediates in the total synthesis of natural products [33,34], and particularly for carbohydrates and steroid chemistry [35,36]. In addition, compounds with 1,2-diol ester moiety are of interest in the manufacture of pharmaceuticals and fragrances [37,38]. Therefore, the conversion of epoxides to 1,2-diacetates with acetic anhydride was investigated in the presence of catalytic amounts of ZrO(OTf)<sub>2</sub>. The results showed that all epoxides under our investigation efficiently converted to their corresponding 1,2-diacetates (Table 5). The ring opening of epoxides with Ac<sub>2</sub>O by internal or external attack of the nucleophile afforded similar products.

### Conversion of Epoxides to Thiiranes Catalyzed by ZrO(OTf)<sub>2</sub>

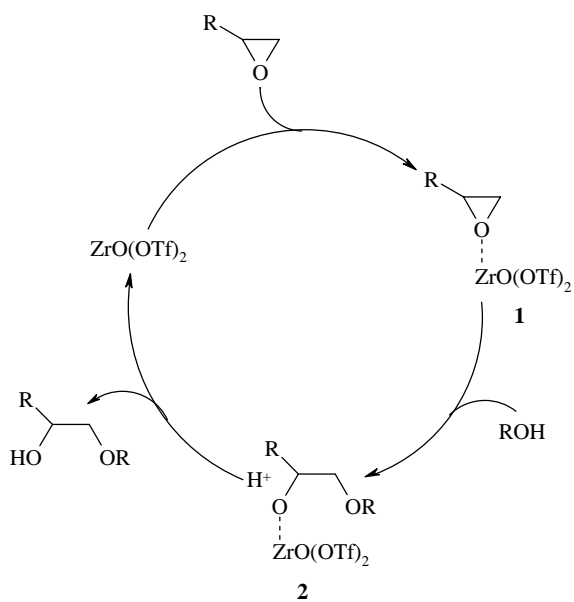
The most general method for conversion of oxiranes to thiiranes is based on an oxygen-sulfur exchange reaction. Conversion of epoxides to thiiranes with NH<sub>4</sub>SCN and thiourea in the presence of a suitable catalyst under non-aqueous conditions, different from classical methods, which are generally carried out in homogeneous or heterogeneous aqueous media, is of significance in organic chemistry [41-45]. Different aliphatic and cyclic epoxides, including the

**Table 3.** Hydrolysis and Acetolysis of Various Epoxides Catalyzed by  $\text{ZrO}(\text{OTf})_2^a$ 

Entry	Epoxide	Product <sup>b</sup>	Solvent	Time(min)/Condition	Conversion (%) <sup>c</sup>
1			$\text{H}_2\text{O}/\text{CH}_3\text{CN}$	60/Reflux	90
2			$\text{CH}_3\text{CO}_2\text{H}$	10/RT	99
3			$\text{H}_2\text{O}/\text{CH}_3\text{CN}$	25/RT	99
4			$\text{CH}_3\text{CO}_2\text{H}$	2/RT	98
5			$\text{H}_2\text{O}/\text{CH}_3\text{CN}$	110/Reflux	96
6			$\text{CH}_3\text{CO}_2\text{H}$	35/Reflux	99
7			$\text{H}_2\text{O}/\text{CH}_3\text{CN}$	120/Reflux	93
8			$\text{CH}_3\text{CO}_2\text{H}$	30/Reflux	98
9			$\text{H}_2\text{O}/\text{CH}_3\text{CN}$	150/Reflux	89
10			$\text{CH}_3\text{CO}_2\text{H}$	30/Reflux	83
11			$\text{H}_2\text{O}/\text{CH}_3\text{CN}$	100/Reflux	98
12			$\text{CH}_3\text{CO}_2\text{H}$	90/Reflux	97
13			$\text{H}_2\text{O}/\text{CH}_3\text{CN}$	120/Reflux	99
14			$\text{CH}_3\text{CO}_2\text{H}$	30/Reflux	99

<sup>a</sup>Catalyst 0.0075 molar amount. <sup>b</sup>All products were identified by comparison of their physical and spectral data with those of authentic samples [13,15]. <sup>c</sup>Yields refer to GC yields.

Zirconyl Triflate, [ZrO(OTf)<sub>2</sub>], as a New and Highly Efficient Catalyst



Scheme 5

electron-withdrawing substituents, were converted to their corresponding thiiranes with NH<sub>4</sub>SCN or thiourea in refluxing acetonitrile and in the presence of 0.0075 molar equivalent of ZrO(OTf)<sub>2</sub>. The results are summarized in Table 6.

The effects of other solvents such as acetone, dichloromethane, chloroform and carbon tetrachloride were also investigated. Compared to acetonitrile, the reaction times were longer and the yields of thiiranes were lower in all of the other solvents.

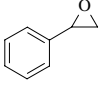
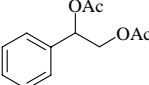

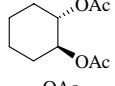
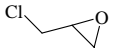
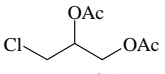
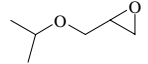
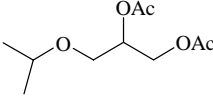
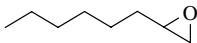
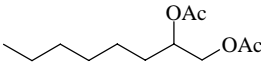
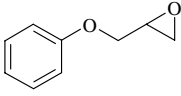
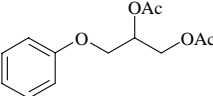
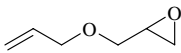
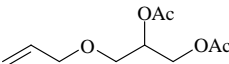
### Conversion of Epoxides to Acetonides Catalyzed by ZrO(OTf)<sub>2</sub>

1,3-Dioxolanes are widely used as protecting groups for carbonyl compounds. They are also useful intermediates, especially in carbohydrate and steroid chemistry. In addition, they are very suitable derivatives of diols for GC, GLC, and mass spectrometry [47]. Direct conversion of an epoxide into

**Table 4.** Comparison of the Obtained Results for the Methanolysis of 2,3-Epoxypropylphenyl Ether Catalyzed by ZrO(OTf)<sub>2</sub> with those Obtained by the Recently Reported Catalysts





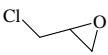
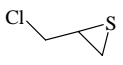
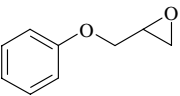
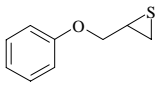
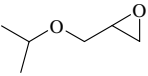
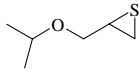
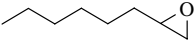
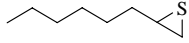
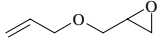
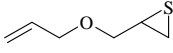
Entry	Catalyst	Catalyst (mol%)	Temperature	Time (min)	Conversion (%)	Selectivity (%)	TOF (h <sup>-1</sup> )	Ref.
1	ZrO(OTf) <sub>2</sub>	0.75	Reflux	20	99	100	400	-
2	AlPW <sub>12</sub> O <sub>40</sub>	3	r.t.	15	94	100	125.33	[3]
3	(NH <sub>4</sub> ) <sub>8</sub> [CeW <sub>12</sub> O <sub>36</sub> ]	4	Reflux	10	95	100	142.50	[4]
4	Fe(III)-Montmorillonite	0.2 g	r.t.	120	85	100	-	[5]
5	FeCl <sub>3</sub>	15	65 °C	180	95	100	2.11	[6]
6	Ce(OTf) <sub>4</sub>	5	Reflux	20	93	100	55.80	[7]
7	Fe(III)-polymer	0.01 g	r.t.	360	90	100	-	[8]
8	Cu(BF <sub>4</sub> ) <sub>2</sub> .nH <sub>2</sub> O	0.4	r.t.	120	95	100	118.6	[9]
9	K <sub>5</sub> [CoW <sub>12</sub> O <sub>40</sub> ]	5	r.t.	15	100	100	80	[11]
10	Fe(TFA) <sub>3</sub>	10	65 °C	120	94	100	4.70	[12]
11	BiCl <sub>3</sub>	10	Reflux	90	98	100	6.53	[13]
12	Sn(tpp)(OTf) <sub>2</sub>	2	Reflux	10	95	100	285	[14]
13	Sn(tpp)(BF <sub>4</sub> ) <sub>2</sub>	2	Reflux	10	95	100	285	[15]

**Table 5.** Conversion of Epoxides to 1,2-Diacetates Catalyzed by  $ZrO(OTf)_2$  in Acetic Anhydride<sup>a</sup>

Entry	Epoxide	Product <sup>b</sup>	Time (min)/Condition		Conversion (%) <sup>c</sup>
1			1/50	°C	99
2			30/50	°C	93
3			45/50	°C	88
4			7/100	°C	92
5			1/50	°C	95
6			1/100	°C	98
7			3/100	°C	99

<sup>a</sup>Reaction conditions: epoxide (1 mmol),  $Ac_2O$  (2 ml), catalyst 0.0075 molar amount. <sup>b</sup>All products were identified by comparison of their physical and spectral data with those of authentic samples [39,40]. <sup>c</sup>Yields refer to GC yields.

**Table 6.** Conversion of Epoxides to Thiiranes Catalyzed by  $ZrO(OTf)_2$  in Refluxing Acetonitrile<sup>a</sup>

Entry	Epoxide	Product <sup>b</sup>	$NH_4SCN$		$H_2NCSNH_2$	
			Time (min)	Conversion (%) <sup>c</sup>	Time (min)	Conversion (%) <sup>c</sup>
1			15	94	60	99
2			20	95	70	98
3			20	83	100	91
4			10	99	40	99
5			20	90	120	94
6			20	99	120	96
7			30	96	60	97


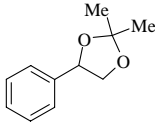

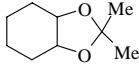

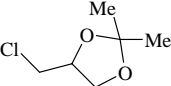

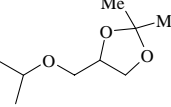
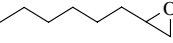
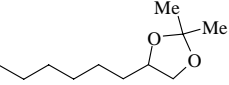
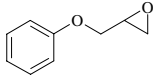
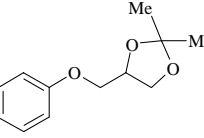
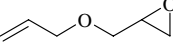
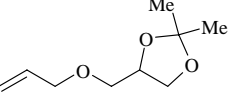
<sup>a</sup>Reaction conditions: epoxide (1 mmol),  $NH_4SCN$  or  $H_2NCSNH_2$  (2 mmol),  $CH_3CN$  (5 ml), catalyst 0.0075 molar amount.

<sup>b</sup>All products were identified by comparison of their physical and spectral data with those of authentic samples [22,42].

<sup>c</sup>Yields refer to GC yields.



**Table 7.** Conversion of Epoxides to Acetonides Catalyzed by ZrO(OTf)<sub>2</sub> in Refluxing Acetone<sup>a</sup>

Entry	Epoxide	Product <sup>c</sup>	Time (min)	Conversion (%) <sup>d</sup>
1			2 <sup>b</sup>	91
2			10 <sup>b</sup>	99
3			30	99
4			50	97
5			40	95
6			60	92
7			50	97

<sup>a</sup>Reaction conditions epoxide (1 mmol), CH<sub>3</sub>COCH<sub>3</sub> (5 ml), catalyst 0.0075 molar amount. <sup>b</sup>These reactions were carried out at room temperature. <sup>c</sup>All products were identified by comparison of their physical and spectral data with those of authentic samples [22]. <sup>d</sup>Yields refer to GC yields.

1,3-dioxolane, instead of adding water to form diol with subsequent elimination in the presence of acetone, has been studied with relatively few reagents [47-50].

Therefore, direct synthesis of acetonides from epoxides and acetone in the presence of ZrO(OTf)<sub>2</sub> was also studied. Reaction of different aliphatic and cyclic epoxides were performed in refluxing acetone (except for cyclohexene and styrene oxide which were carried out at room temperature), and in the presence of only 0.0075 molar equivalent of ZrO(OTf)<sub>2</sub>, and the corresponding 1,3-dioxolanes were obtained in excellent yields (Scheme 5, Table 7).

### Catalyst Reusability

As the catalyst is a homogenous catalyst, it is not possible

styrene oxide to the reaction mixture. At the end of each to separate it by filtration and use it in another reaction. But, the reusability of catalyst was checked by addition of fresh reaction, fresh styrene oxide and methanol were added. The obtained results showed that after five times addition, the corresponding 2-methoxy-2-phenylethanol was obtained without any decrease in its yield.

### CONCLUSIONS

In this report, we have demonstrated that zirconyl trifluoromethanesulfonate, can be considered as a mild Lewis acid for efficient and catalytic ring-opening of epoxides with different nucleophiles under both solvolytic and nonsolvolytic

reaction conditions. In addition, in the presence of this catalyst, efficient conversion of epoxides to their corresponding thiiranes and acetonides is also possible. The obtained results clearly show that replacing of Cl with OTf makes  $ZrO(OTf)_2$  to be a highly efficient Lewis acid which can catalyze the reactions that  $ZrOCl_2$  is not able to catalyze. Other application of this catalyst in organic transformation is in progress.

## ACKNOWLEDGEMENTS

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