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Investigation of the catalytic activity of an electron-deficient vanadium(IV) tetraphenylporphyrin: A new, highly efficient and reusable catalyst for ring-opening of epoxides

S. Abdolmanaf Taghavi, Majid Moghadam *, Iraj Mohammadpoor-Baltork *, Shahram Tangestaninejad, Valiollah Mirkhani, Ahmad Reza Khosropour, Venus Ahmadi

Department of Chemistry, Catalysis Division, University of Isfahan, Isfahan 81746-73441, Iran

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ABSTRACT

In this work, the catalytic activity of high-valent tetraphenylporphyrinatovanadium(IV) trifluoromethanesulfonate, [V^{IV}(TPP)(OTf)$_2$], in the nucleophilic ring-opening of epoxides is reported. This new V(IV) catalyst was used as an efficient catalyst for alcoholysis with primary (methanol, ethanol and *n*-propanol), secondary (*iso*-propanol) and tertiary alcohols (*tert*-butanol), hydrolysis and acetolysis of epoxides with acetic acid and also for the conversion of epoxides to 1,2-diacetates with acetic anhydride, conversion of epoxides to thiiranes with ammonium thiocyanate and thiourea, and for conversion of epoxides to acetonides with acetone. The catalyst was reused several times without loss of its activity.

1. Introduction

Epoxides are versatile intermediates in synthetic organic chemistry and can be opened under a variety of conditions [1]. The most practical and widely employed strategy for the synthesis of 1,2-bifunctional compounds is via nucleophilic ring-opening using a Lewis acid or a strong base [2–8].

Epoxide ring-opening reactions to give β-substituted alcohols with carbon- and heteroatomic nucleophiles, rearrangement reactions providing carbonyl compounds, and isomerization reactions leading to allylic alcohols are useful tools in organic synthesis. Recently, several reagents have been reported in the literature that can promote ring opening of epoxides [9–21]. In most of the epoxide ring-opening reactions under acidic conditions, the formation of a mixture of regioisomers and polymerization are observed. Some of the reported catalysts suffer from disadvantages such as high acidity, the non-catalytic nature of the reagents, long reaction times and inconvenient handling [22,23]. Therefore, the introduction of new methods for the nucleophilic ring-opening of epoxides, which work under mild conditions, is important in synthetic organic chemistry.

In the last decade, electron-deficient metalloporphyrins have been used as mild Lewis acid catalysts. The Suda group has reported the use of chromium and iron porphyrins in organic synthesis. They used Cr(tpp)Cl for regioselective [3,3] rearrangement of aliphatic allyl vinyl ethers and for the Claisen rearrangement of simple aliphatic allyl vinyl ethers, Fe(tpp)OTf for rearrangement of α,β-epoxy ketones into 1,2-diketones and rearrangement of monoalkyl-substituted epoxides into aldehydes, and Cr(tpp)OTf for highly regio- and stereoselective rearrangement of epoxides to aldehydes [24–30].

Recently, we have reported the use of tetraphenylporphyrinatotin(IV) perchlorate [31–33], tetraphenylporphyrinatotin(IV) trifluoromethanesulfonate [34–39] and tetraphenylporphyrinatotin(IV) tetrafluoroborate [40–42] in organic transformations.

Vanadium is required for normal health, and could act *in vivo* either as a metal cation or as a phosphate analog, depending on the oxidation state, V(IV) or V(V), respectively. Vanadium in sea squirt (tunicate), a primitive vertebrate, is concentrated in blood cells, apparently as the major cellular transition metal, but whether it participates in the transport of dioxygen (as iron and copper do) is not known. In proteins, vanadium is a cofactor in an algal bromoperoxidase and in certain prokaryotic nitrogenases. However, its oxidation state within organisms seems to be highly variable. The biochemistry of vanadium potentially involves four oxidation states that are relatively stable in aqueous solution. These are V^{2+}, V^{3+}, VO^{2+} and VO_2^+ (the oxidation states 2, 3, 4 and 5, respectively) [43]. Contrary to the oxidation states +III and +IV, the hydrolysis of vanadium(V) produces almost exclusively anionic species (the only exception is the pale yellow pervanadyl ion, VO_2^+, in very

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* Corresponding authors. Tel.: +98 311 7932712; fax: +98 311 6689732.
E-mail addresses: moghadamm@sci.ui.ac.ir, majidmoghadamz@yahoo.com (M. Moghadam), imbaltork@sci.ui.ac.ir (I. Mohammadpoor-Baltork).

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acidic solutions). The metavanadate ion, $(VO_3)_n^{n-}$, however, exists in the solid state only, and when the compound is dissolved in water, it forms a mixture of mono- and oligovanadates, depending on the pH, vanadium total concentration and the ionic strength of the medium [44,45].

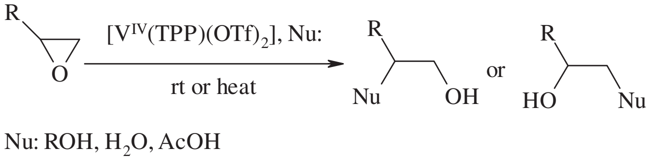
In the present work, the catalytic activity of high-valent tetraphenylporphyrinatovanadium(IV) trifluoromethanesulfonate, $[V^{IV}(TPP)(OTf)_2]$, in alcoholysis, hydrolysis, acetolysis and for the conversion of epoxides to 1,2-diacetates with acetic anhydride, for conversion of epoxides to thiiranes with ammonium thiocyanate and thiourea, and also for the preparation of 1,3-dioxolanes from epoxides and acetone is reported (Schemes 1–4).

2. Experimental

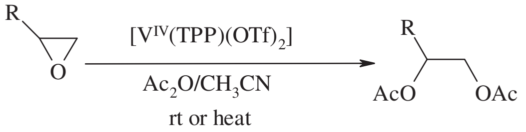
Chemicals were purchased from Fluka and Merck chemical companies. ^{1}H NMR spectra were recorded in $CDCl_3$ solvent on a Bruker-Avance 400 MHz spectrometer using TMS as an internal standard. Infrared spectra were run on a Philips PU9716 or Shimadzu IR-435 spectrophotometer. All analyses were performed on a Shimadzu GC-16A instrument with a flame ionization detector using silicon DC-200 or Carbowax 20M columns. Tetraphenylporphyrin, [VO(TPP)] and $[V(TPP)Cl_2]$ were prepared according to the literature [46–48].

2.1. Preparation of tetraphenylporphyrinatovanadium(IV) trifluoromethanesulfonate, $[V^{IV}(TPP)(OTf)_2]$

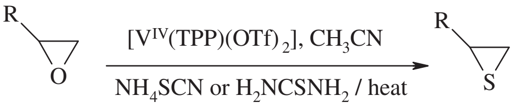
To a solution of $V(TPP)Cl_2$ (0.97 g, 1 mmol) in THF (50 mL), at 55 °C, $AgCF_3SO_3$ (0.54 g, 2 mmol) was added. The solution was stirred at 55 °C for 30 min. The AgCl precipitate was filtered through a 0.45 μM filter. The resulting solution was evaporated at room temperature. Then, the $[V^{IV}(TPP)(OTf)_2]$ was extracted with CH_2Cl_2 and crystals were obtained after evaporation of solvent at room temperature.



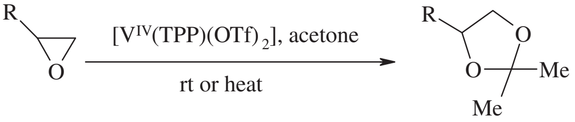
Scheme 1. Alcoholysis, acetolysis and hydrolysis of epoxides.



Scheme 2. Conversion of epoxides to 1,2-diacetates.



Scheme 3. Conversion of epoxides to thiiranes.



Scheme 4. Conversion of epoxides to 1,3-dioxolanes.

Visible spectrum: 456 (Soret), 585, 628 nm; ν (KBr): 1030, 1168, 1224, 1298 cm^{-1} (belong to SO_3 groups and porphyrin ring); *Anal.* Calc. for CHNS: C, 57.44; H, 2.93; N, 5.83; S, 6.67. Found: C, 57.35; H, 2.88; N, 5.91; S, 6.65%.

2.2. General procedure for the alcoholysis and acetolysis of epoxides catalyzed by $[V^{IV}(TPP)(OTf)_2]$

To a solution of epoxide (1 mmol) in the appropriate alcohol or acetic acid (4 mL), $[V^{IV}(TPP)(OTf)_2]$ (0.01–0.02 mmol) was added and the mixture was stirred for a specified time and at the appropriate temperature, according to Tables 1 and 2. The progress of the reaction was monitored by GC. After completion of the reaction, the solvent was evaporated, Et_2O (10 mL) was added and the catalyst was filtered. The mixture was concentrated under reduced pressure and chromatographed on a silica gel column to give the pure product in 80–100% yield.

2.3. General procedure for the hydrolysis of epoxides catalyzed by $[V^{IV}(TPP)(OTf)_2]$

To a solution of epoxide (1 mmol) in an equal mixture of CH_3CN/H_2O (v/v, 5 mL), $[V^{IV}(TPP)(OTf)_2]$ (0.02 mmol) was added and the mixture was stirred for the appropriate time under reflux conditions according to Table 3. The progress of the reaction was monitored by GC. After completion of the reaction, the solvent was evaporated, Et_2O (10 mL) was added and the catalyst was filtered. The mixture was concentrated under reduced pressure and chromatographed on a silica gel column to give the pure product in 92–99% yield.

2.4. General procedure for conversion of epoxides to 1,2-diacetates catalyzed by $[V^{IV}(TPP)(OTf)_2]$

To a mixture of epoxide (1 mmol) in CH_3CN (0.5 mL), Ac_2O (0.5 mL) and $[V^{IV}(TPP)(OTf)_2]$ (1 mol%) were added and the mixture was stirred under reflux conditions. After completion of the reaction, as indicated by GC, the solvent was evaporated; Et_2O was added (20 mL) and the catalyst was filtered. Evaporation of the solvent followed by chromatography on a short column of silica gel afforded the pure 1,2-diacetate in high yield.

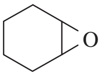
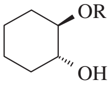
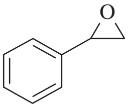
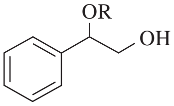
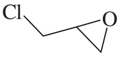
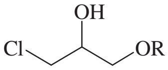
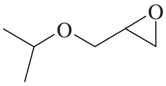
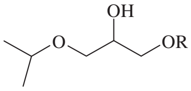
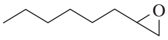
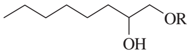
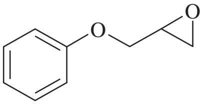
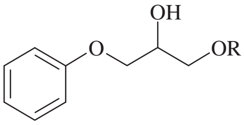
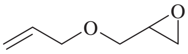
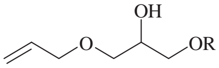
2.5. General procedure for conversion of epoxides to thiiranes with NH_4SCN or H_2NCSNH_2 in the presence of $[V^{IV}(TPP)(OTf)_2$

In a round-bottomed flask (25 mL) equipped with a condenser and a magnetic stirrer, a mixture of epoxide (1 mmol), ammonium thiocyanate or thiourea (2 mmol) in acetonitrile (4 mL) was prepared. $[V^{IV}(TPP)(OTf)_2]$ (0.01 mmol for ammonium thiocyanate and 0.01–0.02 mmol for thiourea) was added to this solution and the reaction mixture was stirred magnetically under reflux conditions. After completion of the reaction (monitored by GC), the solvent was evaporated, Et_2O (10 mL) was added and the catalyst was filtered. Evaporation of the solvent followed by chromatography on a short column of silica gel gave pure thiirane.

2.6. General procedure for conversion of epoxides to 1,3-dioxolanes catalyzed by $[V^{IV}(TPP)(OTf)_2]$

In a round-bottomed flask (25 mL) equipped with a condenser and a magnetic stirrer, a solution of epoxide (1 mmol) in acetone (5 mL) was prepared. $[V^{IV}(TPP)(OTf)_2]$ (0.015 mmol) was added to

Table 1
Alcoholysis of epoxides catalyzed by $[V^{IV}(TPP)(OTf)_2]$.[a]

Entry	Epoxide	ROH/condition	W_{cat} (g)	Time (min)	Product/yield (%)[b,c]	Selectivity (%)	TOF (h^{-1})
							
1		R = CH_3/R.T.	0.005	6	100	100	2000.0
2		R = C_2H_5/R.T.	0.005	6	100	100	2000.0
3		R = *n*-Pr/R.T.	0.005	25	96	100	460.8
4		R = *i*-Pr/R.T.	0.005	90	100	100	133.3
5		R = *t*-Bu/Ref.	0.01	4	100	100	1500.0
							
6		R = CH_3/R.T.	0.005	5	100	100	2400.0
7		R = C_2H_5/R.T.	0.005	5	99	100	2376.0
8		R = *n*-Pr/R.T.	0.005	8	99	100	1485.0
9		R = *i*-Pr/Ref.	0.005	10	96	100	1152.0
10		R = *t*-Bu/Ref.	0.005	15	90	100	720.0
							
11		R = CH_3/Ref.	0.015	90	88	100	39.1
12		R = C_2H_5/Ref.	0.015	80	92	100	46.0
13		R = *n*-Pr/Ref.	0.02	55	99	100	54.0
14		R = *i*-Pr/Ref.	0.02	70	92	100	39.4
15		R = *t*-Bu/Ref.	0.02	60	91	100	45.5
							
16		R = CH_3/Ref.	0.005	5	86	100	2064.0
17		R = C_2H_5/Ref.	0.005	10	85	100	1020.0
18		R = *n*-Pr/Ref.	0.005	15	100	100	800.0
19		R = *i*-Pr/Ref.	0.005	40	99	100	297.0
20		R = *t*-Bu/Ref.	0.005	40	90	100	270.0
							
21		R = CH_3/R.T.	0.01	15	100	100	400.0
22		R = C_2H_5/Ref.	0.01	3	99	100	1980.0
23		R = *n*-Pr/Ref.	0.01	5	99	100	1188.0
24		R = *i*-Pr/Ref.	0.01	10	95	100	570.0
25		R = *t*-Bu/Ref.	0.01	35	96	100	164.6
							
26		R = CH_3/Ref.	0.01	15	97	100	388.0
27		R = C_2H_5/Ref.	0.01	15	95	100	380.0
28		R = *n*-Pr/Ref.	0.015	15	98	100	261.3
29		R = *i*-Pr/Ref.	0.015	20	85	100	170.0
30		R = *t*-Bu/Ref.	0.01	110	97	100	52.9
							
31		R = CH_3/Ref.	0.015	15	99	100	264.0
32		R = C_2H_5/Ref.	0.015	15	97	100	258.7
33		R = *n*-Pr/Ref.	0.015	15	95	100	253.3
34		R = *i*-Pr/Ref.	0.015	30	98	100	130.7
35		R = *t*-Bu/Ref.	0.015	40	95	100	95.0

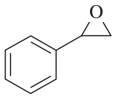
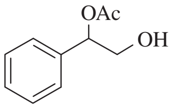
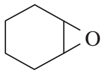
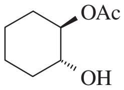
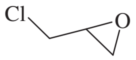
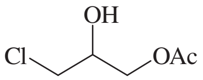
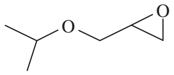
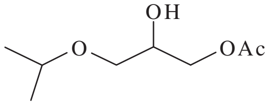
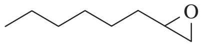
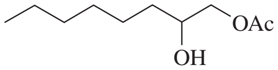
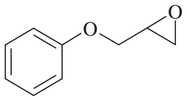
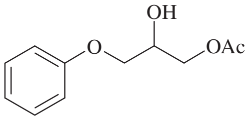
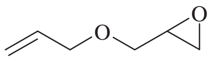
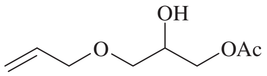
[a] Reaction conditions: epoxide (1 mmol), alcohol (4 mL), catalyst.

[b] All products were identified by comparison of their physical and spectral data with those of authentic samples [13,15].

[c] Yields refer to GC yields.

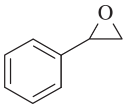
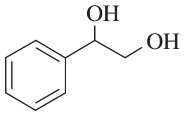
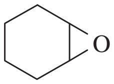
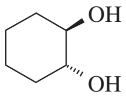
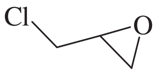
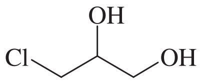
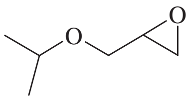
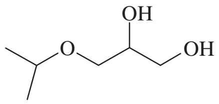
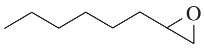
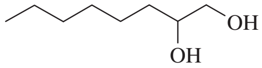
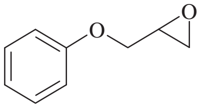
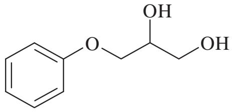
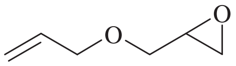
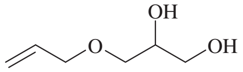
this solution and the reaction mixture was stirred magnetically under reflux conditions or at room temperature. The reaction progress was monitored by GC. After completion of the reaction, the solvent was evaporated, Et_2O (10 mL) was added and the catalyst was filtered. The solvent was evaporated under reduced pressure and the crude product was obtained in a quantitative yield. Distillation of the product under reduced pressure resulted the corresponding 1,3-dioxolane in 75–92% yield.

Table 2
Acetolysis of various epoxides catalyzed by [V^{IV}(TPP)(OTf)$_2$].[a]

Entry	Epoxide	Time (min)/condition	Product[b]	Yield (%)[c]	Selectivity (%)	TOF (h^{-1})
1		5/R.T.		86	100	688.0
2		15/R.T.		94	100	250.7
3		35/Ref.		96	100	109.7
4		15/Ref.		98	100	261.3
5		10/Ref.		98	100	392.0
6		35/Ref.		98	100	112.0
7		25/Ref.		98	100	156.8

[a] Reaction conditions: epoxide (1 mmol), acetic acid (4 mL), catalyst (1.5 mol%).
[b] All products were identified by comparison of their physical and spectral data with those of authentic samples [13,15].
[c] Yields refer to GC yields.

Table 3
Hydrolysis of epoxides catalyzed by [V^{IV}(TPP)(OTf)$_2$].[a]

Entry	Epoxide	Time (min)/condition	Product[b]	Yield (%)[c]	TOF (h^{-1})
1		5/Ref.		99	594.0
2		30/R.T.		98	98.0
3		100/Ref.		99	29.7
4		120/Ref.		90	22.5
5		35/Ref.		92	78.8
6		150/Ref.		92	18.4
7		100/Ref.		96	28.8

[a] Reaction conditions: epoxide (1 mmol), CH_3CN (2.5 mL), H_2O (2.5 mL), catalyst (2 mol%).
[b] All products were identified by comparison of their physical and spectral data with those of authentic samples [13,15].
[c] Yields refer to GC yields.

3. Results and discussion

3.1. Alcoholysis, hydrolysis and acetolysis of epoxides catalyzed by $[V^{IV}(TPP)(OTf)_2]$

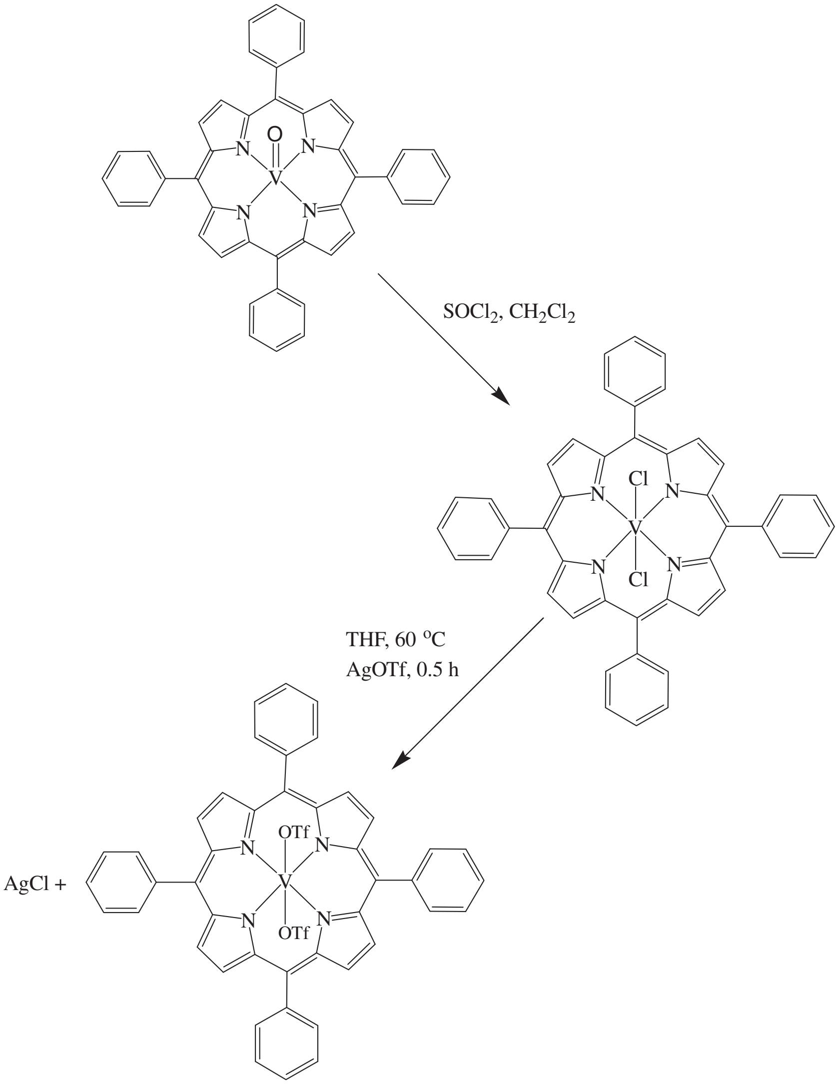
Scheme 5 shows the preparation route for $[V^{IV}(TPP)(OTf)_2]$. Fig. 1 shows the UV–Vis spectrum of this catalyst, in which three bands at 456 (Soret band), 585 and 628 nm (*Q* bands) were observed. Since V(IV) is an electron-deficient species, we decided to investigate the catalytic activity of this new catalyst for the nucleophilic ring-opening of epoxides. First, the catalytic activity of different vanadium(IV) porphyrins, such as $[V^{IV}O(TPP)]$, $[V^{IV}(TPP)Cl_2]$ and $[V^{IV}(TPP)(OTf)_2]$, were investigated in the methanolysis of styrene oxide. The results showed that the catalytic activity of the catalysts, using equal amounts of catalysts, is as following:$[V^{IV}(TPP)(OTf)_2]$ (100%) > $[V^{IV}(TPP)Cl_2]$ (43%) > $[V^{IV}O(TPP)]$ (12%). These observations show that introducing of triflate groups on the porphyrin moiety increases the electron-deficiency of V(IV) species, which in turns increases the catalytic activity of $[V^{IV}(TPP)(OTf)_2]$ toward ring-opening of epoxides.

Therefore, the $[V^{IV}(TPP)(OTf)_2]$ (0.5–2 mol%) was chosen as the catalyst for alcoholysis of epoxides. In this manner, aliphatic, alicyclic, activated and deactivated epoxides such as styrene oxide, cyclohexene oxide, (chloromethyl)oxirane, allyl oxiranylmethyl ether, isopropyl oxiranylmethyl ether and 1,2-epoxyoctane were subjected to alcoholysis with primary (methanol, ethanol and *n*-propanol), secondary (*iso*-propanol) and tertiary (*tert*-butanol) alcohols, and the corresponding β-alkoxy alcohols were obtained in high yields (80–100%). The results are summarized in Table 1. In the case of cyclohexene oxide, the reactions were stereoselective, and only *trans*-products were obtained (entries 1–5).

In the case of unsymmetrical epoxides, the reactions were regioselective, and the attack of the nucleophile (alcohol) on the less substituted oxirane carbon yielded the anti-*Markovnikov* type products (entries 11–35). The only exception is the alcoholysis of styrene oxide, in which the reactions occur on the more substituted carbon and the *Markovnikov* type products were produced (entries 6–10). In the case of active epoxides and when the alcohol has higher nucleophilicity, the reactions were carried out at room temperature.

Although the actual mechanism of these reactions is not clear at present, due to the high oxophilicity of the vanadium active site, the most probable interaction is the activation of epoxide by $[V^{IV}(TPP)(OTf)_2]$ to afford **1**. Alcohol attacks **1** to give **2**, which in turns converts to the final product and releases the catalyst for the next catalytic cycle (Scheme 6). It seems that the mechanism is similar to that of tin(IV) porphyrins [34,41].

When acetic acid was used instead of alcohols, β-acetoxy alcohols were produced in high yields (86–98%) in the presence of a



Scheme 5. The preparation route for $[V^{IV}(TPP)(OTf)_2]$.

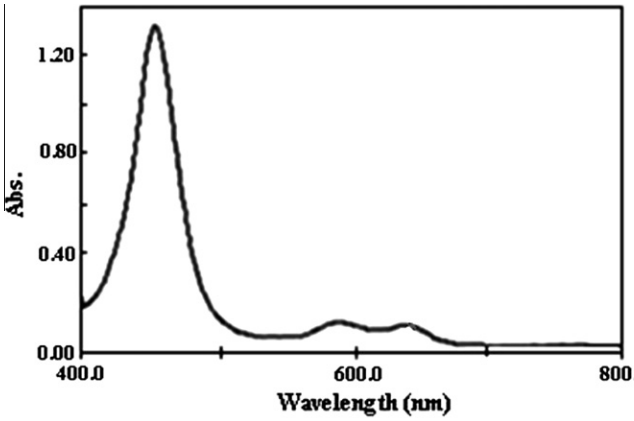
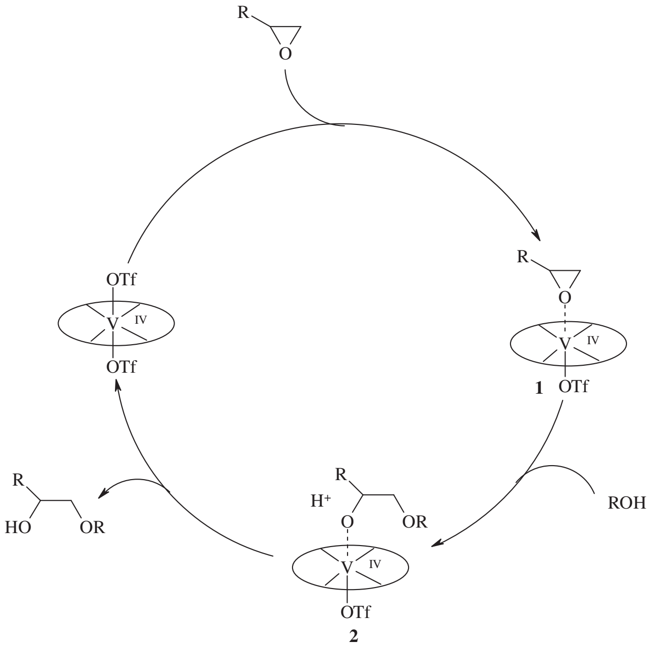


Fig. 1. UV–Vis spectrum of [V^{IV}(TPP)($OTf)_2$].

catalytic amount (1.5 mol%) of [V^{IV}(TPP)($OTf)_2$] (Table 2). Conversion of the epoxides to 1,2-diols was also performed in aqueous acetonitrile in the presence of 2 mol% of [V^{IV}(TPP)($OTf)_2$] (Table 3). In these reactions, the diols were obtained in excellent yields (90–99%).

The most important advantages of this catalyst is that in all cases the product selectivity is 100%, while by using other Lewis acids in the alcoholysis of epoxides, two products have been detected in the reaction mixture.



Scheme 6. The proposed mechanism for the ring opening of epoxides.

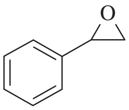
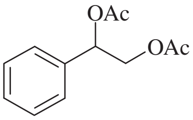
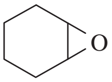
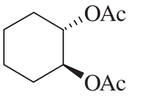
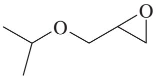
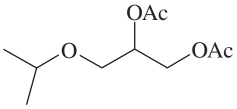
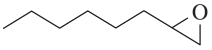
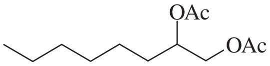
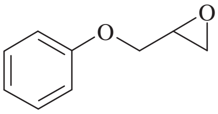
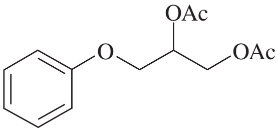
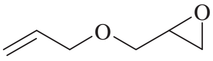
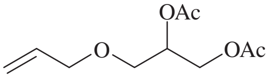
3.2. Conversion of epoxides to 1,2-diacetates with Ac_2O catalyzed by [V^{IV}(TPP)($OTf)_2$]

1,2-Diacetates bearing easily removable protecting groups are the most important intermediates in the synthesis of natural products [49,50], particularly for carbohydrates and steroid chemistry [51,52]. In addition, these compounds are of interest in the manufacturing of pharmaceuticals and fragrances [53–56]. Therefore, the conversion of epoxides to 1,2-diacetates with acetic anhydride was investigated in the presence of [V^{IV}(TPP)($OTf)_2$] (1 mol%). In this manner, different epoxides were efficiently converted to their corresponding 1,2-diacetates in good to excellent yields (Table 4). The ring opening of epoxides with Ac_2O by internal or external attack of the nucleophile afforded similar products.

3.3. Conversion of epoxides to thiiranes catalyzed by [V^{IV}(TPP)($OTf)_2$]

Conversion of epoxides to thiiranes with a sulfur-containing reagent such as NH_4SCN and thiourea in the presence of a suitable

Table 4
Conversion of epoxides to 1,2-diacetates with acetic anhydride catalyzed by [V^{IV}(TPP)($OTf)_2$] in refluxing acetonitrile.[a]

Entry	Epoxide	Product[b]	Time (h)	Conversion (%)[c]	TOF (h^{-1})
1			1.5	90	60.0
2			1.5	99	66.0
3			2	86	43.0
4			2.5	82	32.8
5			3	80	26.7
6			2	85	42.5

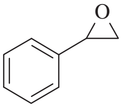
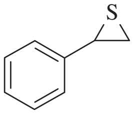
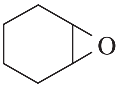
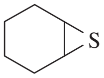
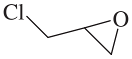
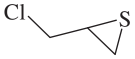
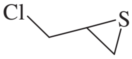
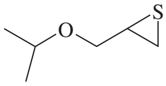
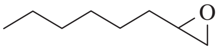
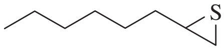
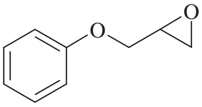
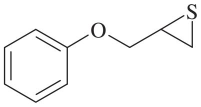
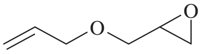
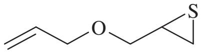
[a] Reaction conditions: epoxide (1 mmol), Ac_2O (0.5 mL), CH_3CN (0.5 mL), catalyst (1 mol%).

[b] All products were identified by comparison of their physical and spectral data with those of authentic samples [52,53].

[c] Yields refer to GC yields.

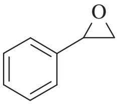
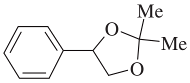
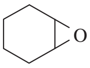
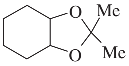
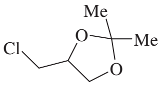
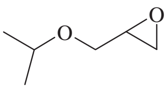
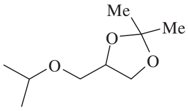
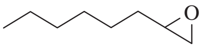
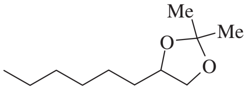
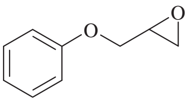
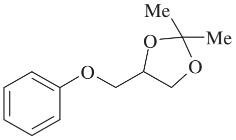
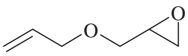
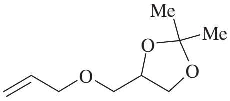
catalyst under non-aqueous conditions is important in organic chemistry [57–61]. Different aliphatic and cyclic epoxides bearing different substituents were efficiently converted to their corresponding thiiranes with NH_4SCN or thiourea in refluxing acetonitrile. The results are summarized in Table 5. The effect of other solvents such as acetone, dichloromethane, chloroform and carbon

Table 5
Conversion of epoxides to thiiranes with NH_4SCN and NH_2CSNH_2 catalyzed by $[V^{IV}(TPP)(OTf)_2]$ in refluxing acetonitrile.[a]

Entry	Epoxide	NH_4SCN			NH_2CSNH_2			Product
		W_{cat} (g)	Time (min)	Yield (%)[b]	W_{cat} (g)	Time (min)	Yield (%)[b]	
1		0.01	15	96	0.01	45	95	
2		0.01	12	99	0.01	30	95	
3		0.01	12	95	0.02	90	92	
4		0.01	15	93	0.02	30	95	
5		0.01	12	96	0.02	90	94	
6		0.01	10	99	0.01	30	95	
7		0.01	20	97	0.02	30	95	

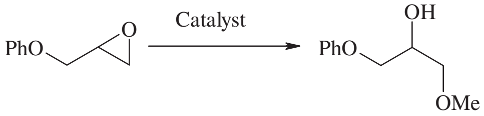
[a] Reaction conditions: epoxide (1 mmol), catalyst, NH_4SCN or NH_2CSNH_2 (2 mmol), CH_3CN (5 mL).
[b] Yields refer to GC yields.

Table 6
Conversion of epoxides to acetonides catalyzed by $[V^{IV}(TPP)(OTf)_2]$.[a]

Entry	Epoxide	Condition	Time (min)	Conversion (%)[c]	Selectivity (%)	TOF (h^{-1})	Product[b]
1		R.T. Reflux	50 5	90 92	100	72.0 736.0	
2		R.T.	45	93	100	82.7	
3		Reflux	150	75	100	20.0	
4		Reflux	190	87	100	18.3	
5		Reflux	210	90	100	17.1	
6		Reflux	240	90	100	15.0	
7		Reflux	200	92	100	18.4	

[a] Reaction conditions: epoxide (1 mmol), CH_3COCH_3 (5 mL), catalyst (1.5 mol%).
[b] All products were identified by comparison of their physical and spectral data with those of authentic samples [34].
[c] Yields refer to GC yields.

Table 7
Comparison of the results obtained for the methanolysis of epoxides catalyzed by [V^{IV}(TPP)($OTf)_2$] with those obtained by recently reported catalysts.



Entry	Catalyst	Catalyst (mol%)	Temperature	Time (min)	Yield (%)	TOF (h^{-1})	Ref.
1	[V^{IV}(TPP)($OTf)_2$]	1	Reflux	15	90	388.00	
2	$AlPW_{12}O_{40}$	3	R.T.	15	94	125.33	[9]
3	$(NH_4)_8[CeW_{12}O_{36}]$	4	Reflux	10	95	142.50	[10]
4	Fe(III)-montmorillonite	0.2 g	R.T.	120	85		[11]
5	$FeCl_3$	15	65 °C	180	95	2.11	[12]
6	$Ce(OTf)_4$	5	Reflux	20	93	55.80	[13]
7	Fe(III)-polymer	0.01 g	R.T.	360	90		[14]
8	$K_5[CoW_{12}O_{40}]$	5	R.T.	15	100	80.00	[17]
9	$Fe(TFA)_3$	10	65 °C	120	94	4.70	[18]
10	$BiCl_3$	10	Reflux	90	98	14.70	[19]
11	$ZrO(OTf)_2$	0.75	Reflux	20	99	396.00	[20]
12	[Sn^{IV}(TPP)($OTf)_2$]	2	Reflux	5	99	626.26	[34]
13	[Sn^{IV}(TPP)($BF_4)_2$]	2	Reflux	10	95	285.00	[41]

tetrachloride was also investigated. Compared to acetonitrile, the reaction times were longer and the yields of thiiranes were lower in all of the other solvents.

3.4. Conversion of epoxides to acetonides catalyzed by [V^{IV}(TPP)($OTf)_2$]

1,3-Dioxolanes are widely used as protecting groups for carbonyl compounds [62]. These compounds are useful intermediates, especially in carbohydrate and steroid chemistry. Direct conversion of an epoxide into 1,3-dioxolane, instead of adding water to form a diol, with subsequent elimination in the presence of acetone has been studied with relatively few reagents [63–66]. Therefore, direct synthesis of acetonides form epoxides and acetone in the presence of [V^{IV}(TPP)($OTf)_2$] was also performed. In this manner, different aliphatic and cyclic epoxides were reacted with refluxing acetone (except for cyclohexene and styrene oxides which were carried out at room temperature) in the presence of 1.5 mol% of [V^{IV}(TPP)($OTf)_2$], and the corresponding 1,3-dioxolanes were obtained in excellent yields (Table 6).

In order to show the effectiveness of the presented method in the ring-opening of epoxides, the obtained results in the methanolysis of 2,3-epoxypropylphenyl ether in the presence of [V^{IV}(TPP)($OTf)_2$] was compared to some of the methods reported in the literature (Table 7). Although most of the Lewis acids of these other methods are cheaper than [V^{IV}(TPP)($OTf)_2$], in most cases our reported catalyst has a higher TOF in the ring-opening reactions.

3.5. Catalyst reusability

The reusability of the catalyst was checked in the methanolysis of styrene oxide. At the end of each reaction, the solvent was evaporated, Et_2O was added and the catalyst was filtered. Then, the catalyst was used with fresh styrene oxide and methanol. The obtained results showed that after using the catalyst several times (five consecutive times were checked), the corresponding 2-methoxy-2-phenylethanol was obtained without any decrease in its yield.

4. Conclusion

In conclusion, [V^{IV}(TPP)($OTf)_2$] was used as a mild Lewis acid for the efficient ring-opening of epoxides with different nucleophiles under both solvolytic and non-solvolytic reaction conditions. In addition, in the presence of this catalyst, efficient conversion of epoxides to their corresponding thiiranes and acetonides was also performed. The obtained results clearly show that replacing Cl with OTf makes [V^{IV}(TPP)($OTf)_2$] a highly efficient Lewis acid which can catalyze reactions that [V^{IV}(TPP)Cl_2] was not able to catalyze. Finally the catalyst was reused several times without loss of its activity. It is also noteworthy that in comparison with most of the reported methods for the ring-opening of epoxides, the present method is superior in terms of yields, reaction times and the amounts of catalyst.

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