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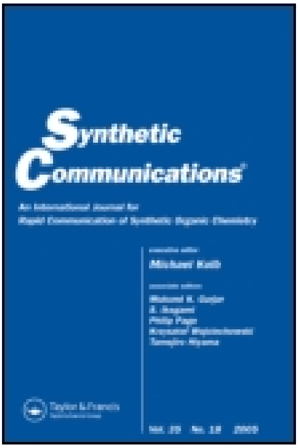

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Highly Efficient, Regio- and Stereoselective Ring Opening of Epoxides and Thiiranes with $Ce(OTf)_4$

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SYNTHETIC COMMUNICATIONS, 28(2), 347-366 (1998)

HIGHLY EFFICIENT, REGIO- AND STEREOSELECTIVE RING OPENING OF EPOXIDES AND THIIRANES WITH $Ce(OTf)_4$

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Abstract: Ceric triflate, $Ce(OTf)_4$ is used as an efficient catalyst for ring opening of epoxides in the presence of alcohols, water, and acetic acid. The reactions proceed with high regio and stereoselectivity and in excellent yields. The reaction of R(+) styrene oxide with methanol occurs with excellent optical purity. Ring opening of thiiranes in alcohols, water and acetic acid followed by dimerisation to the corresponding disulfides occur efficiently in the presence of this reagent. A mild method for the

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preparation of dithianes from thiiranes and $Ce(OTf)_4$ is also described.

Epoxides are versatile intermediates in organic synthesis and their ring opening reactions with different nucleophiles in the presence of different catalysts have been extensively studied.[1-14] In comparision with epoxides, fundamental information about ring opening of thiiranes are still scarce. The reaction of thiiranes with only primary alcohols and in the presence of highly acidic catalysts such as $BF_3.Et_2O$, HCl or H_2SO_4 has been reported to occur at high temperature and with extensive polymerisation.[15-17] Due to the increasing applications of Ce (IV) as one of the most widely used lanthanides in organic synthesis, the use of Ce(IV) both as homogenous and heterogeneous one-electron transfer catalysts and reagents were reported for nucleophilic ring opening of epoxides[8-11,18] and thiiranes[19] by our group and others.[18]

Recently lanthanides trifluoromethanesulfonates (triflates)[20] such as $Yb(OTf)_3$, $Nd(OTf)_3$, $Gd(OTf)_3$ and $Hf(OTf)_4$ have been found wide applications for different organic functional group

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transformations.[21, 22] Synthesis of Ce(OTf)$_4$ and its applications for the oxidation of benzylic alcohols and alkyl benzenes has been also reported.[23] In this study we evaluated the high potential of Ce(OTf)$_4$ for ring opening reactions of epoxides and thiiranes. We report here that Ce(OTf)$_4$ can act as a very efficient catalyst for alcoholysis, hydrolysis and acetolysis of epoxides. Ring opening of thiiranes followed by dimerisation to the corresponding disulfides or formation of dithianes can also occur in the presence of this reagent.

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Results and Discussion

Ring opening reaction of different classes of epoxides in 1°, 2°,and 3° alcohols and in the presence of 0.01-0.05 molar equivalents of ceric triflate were studied. The corresponding β-alkoxy alcohols were obtained in excellent yields and regioselectivity. The products obtained from cyclic epoxides showed the formation of trans isomer as the only product of the reaction. The results are shown in Table 1.

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Table 1. Reaction of Epoxides with Different Alcohols Catalyzed with $Ce(OTf)_4$.

Entry	Epoxide	Solvent	Mole Ratio of $Ce(OTf)_4$/Epoxide	Time/(Temp.) min. °C	%Yield^{I}	Product^{II}
1	**1a**	MeOH	0.01	2(25)	92	$PhCH(OMe)CH_2OH$
2	**1a**	EtOH	0.01	5(25)	90	$PhCH(OEt)CH_2OH$
3	**1a**	n-PrOH	0.01	5(25)	93	$PhCH(O\text{-}n.Pr)CH_2OH$
4	**1a**	i-PrOH	0.01	10(25)	95	$PhCH(O\text{-}i.Pr)CH_2OH$
5	**1a**	t.BuOH	0.01	40(25)	90	$PhCH(O\text{-}t.Bu)CH_2OH$
6	**1b**	MeOH	0.2	40(65)	90	$ClCH_2CH(OH)CH_2OMe$
7	**1b**	EtOH	0.2	10(80)	93	$ClCH_2CH(OH)CH_2OEt$
8	**1b**	n-PrOH	0.2	10(85)	99	$ClCH_2CH(OH)CH_2O\text{-}n.Pr$
9	**1b**	i-PrOH	0.2	10(85)	93	$ClCH_2CH(OH)CH_2O\text{-}i.Pr$

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10	**1b**	t-BuOH	0.2	10(80)	95	$ClCH_2CH(OH)CH_2O$-t.Bu
11	**1c**	MeOH	0.05	20(65)	90	$CH_2=CHCH_2OCH_2CH(OH)CH_2OMe$
12	**1c**	EtOH	0.05	15(80)	92	$CH_2=CHCH_2OCH_2CH(OH)CH_2OEt$
13	**1c**	n-PrOH	0.05	10(85)	93	$CH_2=CHCH_2OCH_2CH(OH)CH_2O$-n.Pr
14	**1c**	i-PrOH	0.05	10(85)	95	$CH_2=CHCH_2OCH_2CH(OH)CH_2O$-i.Pr
15	**1c**	t.BuOH	0.05	10(80)	95	$CH_2=CHCH_2OCH_2CH(OH)CH_2O$-t.Bu
16	**1d**	MeOH	0.02	15(65)	90	$C_4H_9CH(OH)CH_2OMe$
17	**1d**	EtOH	0.02	10(80)	92	$C_4H_9CH(OH)CH_2OEt$
18	**1d**	i.PrOH	0.02	10(85)	93	$C_4H_9CH(OH)CH_2O$-i.Pr
19	**1e**	MeOH	0.05	20(85)	93	$PhOCH_2CH(OH)CH_2OMe$
20	**1e**	i.PrOH	0.05	20(85)	90	$PhOCH_2CH(OH)CH_2O$-i.Pr

(continued)

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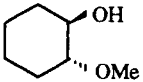
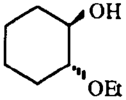
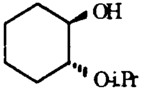
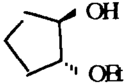
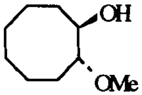
Table 1. Continued

21	**1f**	MeOH	0.02	2 (25)	93	
22	**1f**	EtOH	0.02	5(25)	95	
23	**1f**	i.PrOH	0.02	25(25)	94	
24	**1g**	MeOH	0.02	10(25)	93	
25	**1h**	MeOH	0.05	180(65°C)	83	

[I] Yield refers to isolated product.

[II] The products were compared with authentic samples.

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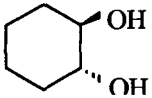
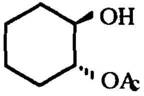
Table 2. Reaction of Epoxides with Water and Acetic acid catalysed withCe(OTf)$_4$

Entry	Epoxide	Solvent	Mole Ratio of Ce(OTf)$_4$/Epoxide	Time/(Temp.) min °C	%Yield [I]	Product [II]
1	**1a**	H_2O/CH_3CN	0.1	5(25)	98	$PhCH(OH)CH_2OH$
2	**1b**	H_2O/CH_3CN	0.3	15(80)	9	$ClCH_2CH(OH)CH_2OH$
3	**1c**	H_2O/CH_3CN	0.3	40(80)	90	$CH_2=CHCH_2OCH_2CH(OH)CH_2OH$
4	**1d**	H_2O/CH_3CN	0.1	5(80)	85	n-$C_4H_9CH(OH)CH_2OH$
5	**1e**	H_2O/CH_3CN	0.1	10(25)	92	
6	**1a**	HOAc	0.1	10(25)	95	$PhCH(OAc)CH_2OH$
7	**1b**	HOAc	0.2	5(80)	93	$ClCH_2CH(OH)CH_2OAc$
8	**1c**	HOAc	0.2	10(80)	90	$CH_2=CHCH_2OCH_2CH(OH)CH_2OAc$
9	**1d**	HOAc	0.1	10(25)	90	n-$C_4H_9CH(OH)CH_2OAc$
10	**1a**	HOAc	0.1	5(80)	90	

[I] **Yields refer to isolated Products.**

[II] **The products were compared with known samples.**

The reaction of these epoxides in water and acetic acid were also occurred efficiently in the presence of 0.1-0.3 molar equivalent of ceric triflate. The corresponding β-diols and β-acetoxy alcohols were obtained in excellent yields (Table 2).

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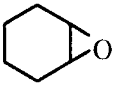
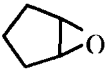
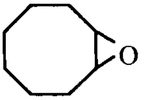
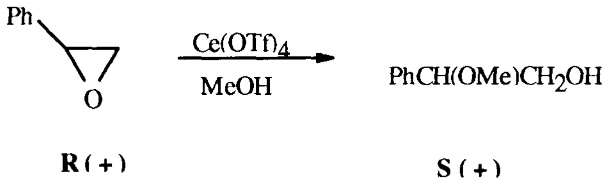
Scheme 1

1(a-h) R = Me. Et. n-Pr. i-Pr. t-Bu. H. Ac

1	R	1	Epoxide
a	Ph -	**f**	
b	$ClCH_2$ -		
c	$CH_2 = CHCH_2OCH_3$ -	**g**	
d	n - C_4H_9 -	**h**	
e	PhO -		

The stereospecificity of ring opening reaction of optical active styrene oxide was also studied. The obtained results are shown in **Scheme 2**.

Scheme 2



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The reaction is temperature dependence and maximum of optical purity was obtained at - 10 °C (Table 3).

We also studied the possibility of using ceric triflate for ring opening of thiiranes in alcohols, water, and acetic acid. The reactions of thiiranes in alcohols, water, and acetic acid were performed in the presence of equimolar amount of ceric triflate at room temperature or under reflux conditions (Scheme 3, Table 4). In these reactions, ring opening of thiiranes and dimerisation occurred together with formation of the corresponding disulfides in 75-92% yields.

The mechanism of these reactions with epoxides is not clear, but due to the formation of disulfides through a non-catalytic reaction between thiiranes , nucleophile and $Ce(OTf)_4$, a similar mechanism to that which is reported for other Ce(IV) reagents is

Table 3. Reaction of Optical Active Styrene Oxide with Methanol.

Entry	Mole Ratio of	Time/Temp.	%Yield	%ee
1	0.01	-[a] (25)	93	35
2	0.01	1 (0)	95	60
3	0.02	1.5 (-10)	93	92

[a] The reaction occurs immediately.

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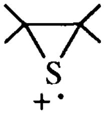
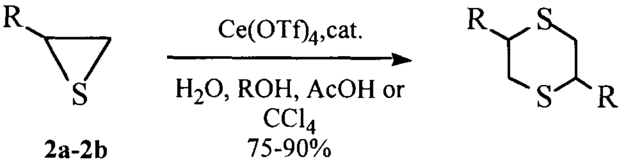
possible[8,11,19]. The occurrence of a one electron transfer reaction between Ce(IV) and thiiranes with the formation of radical cation (I) is probable. Attack of a molecule of solvent on (I) followed by dimerisation of the obtained radical could be responsible for the formation of disulfides in these reactions.



(I)

Ring opening dimerisation of thiiranes in the absence of nucleophile and formation of dithianes was also performed in CCl_4 in the presence of catalytic amounts of $Ce(OTf)_4$ (Scheme 3). In comparison with the reported methods of dithiane formation, eg, vapour phase reaction of olefin and hydrogen sulfide over alumina at above 200 °C [24] or reaction of styrene sulfide with dimethyl sulfate[25] which produce 2,5 diphenyl dithiane in 15% yield, this method is very mild and more efficient.

Scheme 3



2a-2b

R or thiirane: **2a** R=Ph, **2b** cyclohexene sulfide

In conclusion, ceric triflate can be used as an efficient catalyst for nucleophilic ring opening of epoxides and as reagent for one step ring opening dimerisation of thiiranes respectively. Ease of preparation and stability of the reagent, ease of procedure, high regio- and stereoselectivities, mild reaction conditions and high yields give a new synthetic application for Ce(OTf)$_4$ in organic synthesis.

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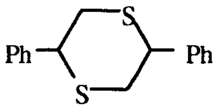
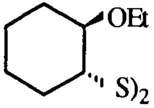
Table 4. Reaction of Thiiranes With Alcohols, Water, and Acetic Acid in the presence of $Ce(OTf)_4$

Entry	Epoxide	Solvent	Mole Ratio of $Ce(OTf)_4$/Epoxide	Time/(Temp.) h °C	%Yield [I]	Product [II]
1	**2a**	MeOH	1.5	1(25)	87	$PhCH(OMe)CH_2S]_2$
2	**2a**	EtOH	1	1(80)	90	$PhCH(OEt)CH_2S]_2$
3	**2a**	2-PrOH	1	4(85)	90	$PhCH(O\text{-}_{i}.Pr)CH_2S]_2$
4	**2a**	H_2O/CH_3CN	1	2(80)	89	$PhCH(OH)CH_2S]_2$
5	**2a**	HOAc	1	2(80)	80	$PhCH(OAc)CH_2S]_2$
6	**2a**	CCl_4	1	2(80)	80	
8	**2b**	EtOH	1	¾(80)	85	

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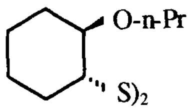
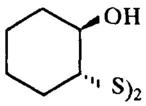
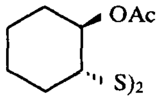
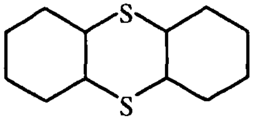
9	**2b**	n-PrOH	1	¾(80)	87	
10	**2b**	H_2O/CH_3CN		3/4(80)	90	
11	**2b**	HOAc	1	1(80)	80	
12	**2b**	CCl_4	1	1(80)	75	

[I] Yields refer to isolated products.

[II] Products were identified by comparison with authentic samples.

Experimental: Products were characterized by comparison of their physical data, IR, and NMR spectra with those of authentic samples. Ceric triflate was prepared according to the reported procedure.[23] All yields refer to isolated products. Infrared spectra were recorded on a Perkin Elmer 781 spectrometer. NMR spectra were recorded on a Bruker Avance DPX250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000EX. The purity determination of the substrate and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-14A instrument.

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General procedure for the Reaction of Epoxides with Alcohols and Water in the Presence of Ceric triflate: To a solution of epoxide (1 mmol) in the appropriate alcohol (3 ml) or in aqueous acetonitrile (1:1), $Ce(OTf)_4$ (0.01-0.2 mmol) was added and the mixture stirred at room temperature or under reflux. The reaction was monitored by gas chromatography. After completion of the reaction, solvent was evaporated under reduced pressure. Water (15 ml) was added and extracted with ether (3×15 ml). The organic

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layer was separated and dried with Na_2SO_4. Evaporation of the organic solution followed by vacuum distillation or column chromatography on a short column of silica gel afforded the pure product in 90-99% yield.

General procedure for the Reaction of Epoxides with Acetic Acid in the Presence of Ceric triflate: (0.1-0.3 mmol) of ceric triflate was added to a solution of epoxide (1 mmol) in acetic acid (3 ml). The reaction mixture was stirred for the specified time and in appropriate temperature according to **Table 2**. The progress of reaction was monitored by gas chromatography. The solvent was evaporated under reduced pressure and ether (20 ml) was added and washed with saturated $NaHCO_3$ (2×10 ml) and with water (2×10).The organic layer was separated and dried. Evaporation of the organic solution followed by vacuum distillation or column chromatography on a short column of silica gel afforded the pure product in 90-98% yield.

General procedure for the Reaction of Thiiranes with Alcohol and Water and CCl_4 in the Presence of Ceric triflate: To a

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solution of thiirane (1 mmol) in the appropriate alcohol (3 ml) or in aqueous acetonitrile (1:1) or in CCl_4 (3 ml), $Ce(OTf)_4$ (1.5-1 mmol) was added and the mixture stirred at room temperature or under reflux according to **Table 3**. The reaction was monitored by GLC. After completion of the reaction, solvent was evaporated under reduced pressure. Water (15 ml) was added and extracted with ether (3×15 ml). The organic layer was separated and dried with Na_2SO_4. Evaporation of the organic solution followed by vacuum distillation or column chromatography on a short column of silica gel afforded the pure product in 75-90% yield.

General procedure for the Reaction of Thiirane with Acetic Acid in the Presence of Ceric triflate: (1 mmol) of ceric triflate was added to a solution of thiirane (1 mmol) in acetic acid (3 ml). The reaction mixture was stirred for the specified time and in appropriate temperature according to **Table 3**. The progress of reaction was monitored by GLC. The solvent was evaporated under reduced pressure and ether (20 ml) was added and washed with saturated $NaHCO_3$ (2×10 ml) and with water (2×10 ml).The organic layer was separated and dried. Evaporation of the organic solution followed by vacuum distillation or column chromatography on a short column of silica gel afforded the pure product in 80% yield.

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