An Environmentally Benign Catalytic Method for Efficient and Selective Nucleophilic Ring Opening of Oxiranes by Zirconium Tetrakis(dodecyl Sulfate)

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An operationally simple and environmentally benign protocol for a highly regio- and chemoselective preparation of β-substituted alcohols by means of ring-opening reactions of oxiranes with various aliphatic alcohols, H_2O, NaN_3, and NaCN as nucleophiles in the presence of catalytic amounts of zirconium tetrakis(dodecyl sulfate) as *Lewis* acid/surfactant-combined catalysts (LASCs) was developed. The high efficiency of the catalyst was confirmed by the high product yields obtained within desired times and, in particularly by the reusability of the Zr^{IV} complex.

Introduction. – Recently, many efforts have been devoted for employing anionic surfactants such as sodium dodecyl sulfate (SDS) in *Lewis* acid catalyzed aldol reactions [1][2] and allylation reactions [3] in H_2O to avoid the use of cosolvents, which are often required for the best efficiency. Taking this concept one step further, active metal cations carrying long anionic hydrocarbon-derived sulfate or sulfonate ligands that make them form micellar aggregates in H_2O have been developed by *Kobayashi* and co-workers as a new type of *Lewis* acids. These so-called *Lewis* acid/surfactant-combined catalysts (LASC) have been successfully employed in aqueous *Diels–Alder*, aldol, *Mannich*-type, and allylation reactions [4–14].

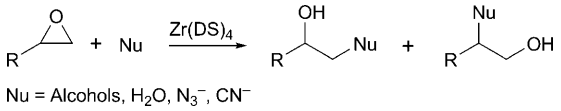
A strong coordination of Zr^{4+} (charge-to-size ratio = 22.22 e^2 m^{-10}) [15] in zirconium salts which are less costly, easily available and relatively safe materials [16] (LD_{50} [$ZrCl_4$ oral_rat] = 1688 mg/kg), (LD_{50} [$ZrOCl_2 \cdot 8\,H_2O$ oral_rat] = 2950 mg/kg), (LD_{50} [$Zr(NO_3)_4$, oral_rat] = 2290 mg/kg) [17] enable safe reactions with high to excellent yields. Thus, Zr^{IV} compounds are excellent catalysts or reagents in synthetic chemistry [18–20] as evidenced by their increasing commercial use for this purpose.

In the course of our ongoing investigations to develop new applications of zirconium salts in synthetic methods [21–26], quite recently, we described the novel catalytic activity of a zirconium/surfactant combination in catalytic *Michael* reactions of indoles and amines to enones [27] and also in the synthesis of bis- and trisindolylmethanes (= methylenebis- and methylidynetris[1*H*-indoles]) in H_2O [28]. These promising results prompted us to evaluate the potential of $Zr(DS)_4$ in nucleophilic ring opening of oxiranes which are valuable synthetic precursors in organic chemistry. A literature survey shows that only a very few reports are available dealing with the

catalytic activity of zirconium salts in nucleophilic ring opening of oxiranes [19][20][29–31].

We now present a highly selective ring-opening reaction of oxiranes with alcohols, H_2O, CN^-, or N_3^- in H_2O in the presence of a catalytic amount of $Zr(DS)_4$ under mild conditions to give β-substituted alcohols with carbon and heteroatom nucleophiles (*Scheme 1*).

Scheme 1. *Ring-Opening Reactions of Oxiranes with Alcohols, H_2O, CN^-, and N_3^- in the Presence of a Catalytic Amount of $Zr(DS)_4$*



Results and Discussion. – a) *Preliminary Experiments.* Initially, blank experiments for ring opening of styrene oxide (=2-phenyloxirane) with EtOH, H_2O, and CN^- or N_3^- in H_2O as nucleophiles were performed in the absence of any catalyst (*Table 1*). Then, the catalytic activity of different zirconium salts such as $Zr(NO_3)_4$, $ZrOCl_2 \cdot 8\,H_2O$, and $Zr(DS)_4$ in the ring opening of oxiranes with these nucleophiles were examined. It was observed that the $Zr(DS)_4$ as LASC was the best catalyst in this system in terms of yields, conversion rates, and regioselectivity (**A**/**B**) of the reactions (*Table 2*).

Table 1. *Blank Experiments for the Ring Opening of Styrene Oxide with Various Nucleophiles*

Nucleophile	Time [h]	Temperature [°]	Yield [%][a])	Nucleophile	Time [h]	Temperature [°]	Yield [%][a])
EtOH	3	70	0	N_3^- [b])	5	25	75
H_2O	3.5	90	100	CN^- [b])	7	25	45

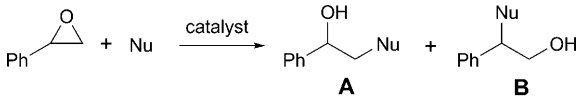
[a]) Yield determined by GC. [b]) In H_2O.

b) *Alcoholysis and Hydrolysis of Oxiranes Catalyzed by $Zr(DS)_4$.* β-Hydroxy ethers (=β-alkoxy alcohols) are important precursors for the preparation of α-alkoxy ketones and α-alkoxy acids. They are also present in some naturally occurring compounds [32][33]. A simple and straightforward method for the synthesis of β-hydroxy ethers is the ring opening of oxiranes with an appropriate alcohol [34–51].

In this study, the catalytic activity of $Zr(DS)_4$ in the cleavage of oxiranes with primary, secondary, and tertiary alcohols was examined. Initially, a series of preliminary experiments were performed with phenyl glycidyl ether (=2-(phenoxymethyl)oxirane) to determine the optimal reaction conditions. The use of phenyl glycidyl ether (1 mmol) in EtOH (4 ml) in the presence of 5 mol-% of $Zr(DS)_4$ led to complete conversion of the oxirane to the product mixture **C**/**D** (*Scheme 2*) in a 90:10 molar ratio based on the GC analysis after 20 min (*Table 3*, *Entry 4*).

To show the general applicability of the method, we applied similar reaction conditions to the alcoholysis of a variety of oxiranes with structurally different alcohols in combination with this catalyst (*Table 3*). All reactions proceeded well in good to

Table 2. *Comparison of the Catalytic Activity of $Zr(DS)_4$, with $ZrOCl_2 \cdot 8\,H_2O$ and $Zr(NO_3)_4$ for the Ring Opening of Styrene Oxide with Various Nucleophiles*[a])

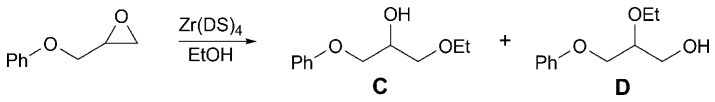


Nu = Alcohols, H_2O, N_3^-, CN^-

Catalyst	Nucleophile	Ratio **A**/**B**[b])	Time [min]	Yield [%][c])
$ZrOCl_2 \cdot 8\,H_2O$	EtOH	15 : 85	35	100
$Zr(NO_3)_4$	EtOH	15 : 85	30	100
$Zr(DS)_4$	EtOH	5 : 95	5	100
$ZrOCl_2 \cdot 8\,H_2O$	H_2O	[d])	30	100
$Zr(NO_3)_4$	H_2O	[d])	120	80
$Zr(DS)_4$	H_2O	[d])	7	100
$ZrOCl_2 \cdot 8\,H_2O$	N_3^-	15 : 85	80	100
$Zr(NO_3)_4$	N_3^-	15 : 85	150	100
$Zr(DS)_4$	N_3^-	0 : 100	60	100
$ZrOCl_2 \cdot 8\,H_2O$	CN^-	15 : 85	480	100
$Zr(NO_3)_4$	CN^-	15 : 85	480	100
$Zr(DS)_4$	CN^-	0 : 100	300	100

[a]) *i*) Ethanolysis: molar ratio oxirane/catalyst 20 : 1 in EtOH (4 ml) under reflux; *ii*) hydrolysis: molar ratio oxirane/catalyst 100 : 5 in H_2O (4 ml) under reflux; *iii*) azidolysis and cyanolysis: molar ratio oxirane/NaX/catalyst 20 : 240 : 1 in H_2O (12 ml) at r.t. [b]) Regioselectivity determined by GC and NMR. [c]) Yield determined by GC. [d]) The product was the corresponding diol (Nu = OH); thus, **A** and **B** are identical compounds.

Scheme 2. *Ring-Opening of Phenyl Glycidyl Ether in EtOH Catalyzed by $Zr(DS)_4$*

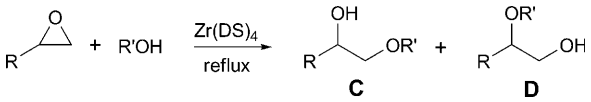


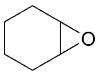
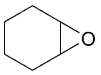
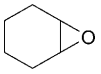
excellent yields with high regioselectivity, except in the alcoholysis of 2-hexyloxirane with sterically hindered alcohols such as ^{i}PrOH and ^{t}BuOH (*Entries 8* and *9*). Also, the results indicate that the alkoxy group was incorporated preferentially at the less hindered site of unsymmetrical oxiranes (*Entries 4–9*).

The observed trend in the ring opening of oxiranes with this catalytic system reflected well the major role of steric hindrance. The reaction of styrene oxide with structurally different alcohols proceeded well, and the oxirane ring was cleaved in appropriate times at the more hindered site with high regioselectivity. The ring opening at the more hindered site of styrene oxide suggested the formation of a carbocationic intermediate during the reaction (*Table 3*, *Entries 1–3*).

The difference in reactivity of different alcohols can be applied to achieve chemoselectivity of this new protocol. Thus, the competitive reactions of glycidyl phenyl ether with structurally different alcohols in the presence of a catalytic amount of $Zr(DS)_4$ (5 mol-%) at 50–60° resulted in good selectivities (see **E**/**F** in *Table 4*).

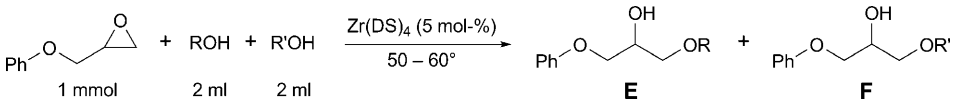
Table 3. *Alcoholysis of Oxiranes Catalyzed by Zr(DS)$_4$*[a])



Entry	Oxirane (R)	Alcohol (R′)	Ratio **C**/**D**[b])	Time [min]	Yield [%][c])[d])	Ref.
1	Ph	Et	5 : 95	3	100	[37][42][46]
2	Ph	^{i}Pr	10 : 90	15	100	[37][42][46]
3	Ph	^{t}Bu	25 : 75	30	100	[37][42][46]
4	$PhOCH_2$	Et	90 : 10	20	100	[36][42][46]
5	$PhOCH_2$	^{i}Pr	90 : 10	25	100	[37][42][46]
6	$PhOCH_2$	^{t}Bu	80 : 20	100	100	[37][42][46]
7	$Me(CH_2)_5$	Et	85 : 0	45	85	[37][42]
8	$Me(CH_2)_5$	^{i}Pr	35 : 25	60	60	[37][42]
9	$Me(CH_2)_5$	^{t}Bu	40 : 10	120	50	[37][42]
10		Et	–	90	87	[37][42][46]
11		^{i}Pr	–	100	82	[37][42][46]
12		^{t}Bu	–	150	80	[37][42][46]

[a]) Molar ratio oxirane/Zr(DS)$_4$ 20 : 1 in alcohol (4 ml) under reflux. [b]) Regioselectivity determined by GC and NMR. [c]) All products were identified by their spectral data in comparison with authentic samples [34–51]. [d]) Yield determined by GC.

Table 4. *Competitive Reaction of Glycidyl Phenyl Ether with Structurally Different Alcohols in the Presence of a Catalytic Amount of Zr(DS)$_4$*



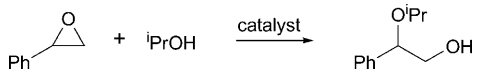
R	R′	Time [min]	Yield **E**/**F** [%][a])
Et	^{i}Pr	50	90 : 7
Et	^{t}Bu	80	90 : 10
^{i}Pr	^{t}Bu	120	75 : 20

[a]) Yield determined by GC.

To highlight the notable features of the presented protocol for the ring opening of oxiranes with alcohols, we compared the results obtained with Zr(DS)$_4$ with some other catalysts reported in the literature (*Table 5*).

Encouraged by the above results, our study was further extended to the hydrolysis of oxiranes. Having used different reaction conditions in the ring opening of styrene oxide in aqueous media, we observed that the amount of Zr(DS)$_4$ and the temperature

Table 5. *Catalytic Activity of Zr(DS)$_4$ in Comparison with Other Catalysts Used for the Ring Opening of Styrene Oxide with ^{i}PrOH*

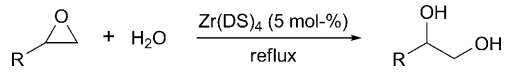


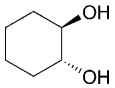
Catalyst	Mol-%	Time [h]	Yield [%]	Ref.
$Zr(DS)_4$	5	0.25	90	[a])
$Yb(OTf)_3$	0.2	12	98	[51]
Mesoporous aluminosilicate	50 mg	3.5	52	[50]
CBr_4	10	2.5	87	[49]
$(ClBu_2Sn)_2O$	100	48	65	[48]
$Cu(BF_4)_2 \cdot n\ H_2O$	1	3.5	69	[47]
$[ZrCl_2(Cp)_2]$	1.4	31	82	[44]

[a]) This work.

influenced the reaction rate. The optimum yields were obtained when the reaction mixture was stirred under reflux with 5 mol-% of $Zr(DS)_4$ in H_2O. These conditions were applied to the other oxiranes and the results are summarized in *Table 6*.

Table 6. *Hydrolysis of Oxiranes Catalyzed by Zr(DS)$_4$*[a])

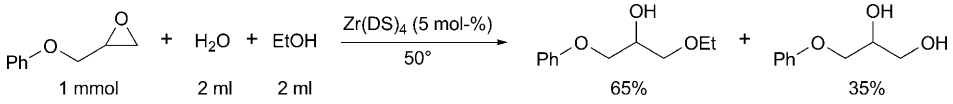


Entry	Oxirane (R)	Product (R)[b])	Time [min]	Yield [%][c])	Ref.
1	Ph	Ph	7	100	[42][64]
2	$PhOCH_2$	$PhOCH_2$	15	75	[42][64]
3	$Me(CH_2)_5$	$Me(CH_2)_5$	40 (100)	75 (90)	[42][64]
4	$CH_2{=}CHCH_2OCH_2$	$CH_2{=}CHCH_2OCH_2$	40 (70)	70 (90)	[42][64]
5			15	100	[42][64]

[a]) Molar ratio oxirane/$Zr(DS)_4$ 20 : 1 in H_2O (4 ml) under reflux. [b]) All products were identified by their spectral data in comparison with known samples. [c]) Yield determined by GC.

It must be pointed out that the competitive reactions of glycidyl phenyl ether in the presence of $Zr(DS)_4$ (5 mol-%) with EtOH and H_2O resulted in the β-ethoxy alcohol as main product, as outlined in *Scheme 3*.

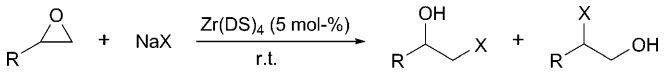
Scheme 3. *Competitive Ring Opening by Ethanolysis and Hydrolysis of Glycidyl Phenyl Ether Catalyzed by Zr(DS)$_4$*



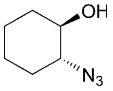
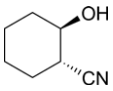
c) *Azidolysis and Cyanolysis of Oxiranes Catalyzed by Zr(DS)$_4$.* To establish the generality and the scope of the present methodology, the procedure was further extended to NaN_3 and NaCN, which are expected to produce the corresponding β-azido alcohols and β-hydroxy cyanides, respectively. β-Azido alcohols and β-hydroxy cyanides are precursors of amino alcohols [52] which are well known as versatile intermediates in a variety of organic transformations such as bioactive compounds and chiral auxiliaries [53–62]. A valuable synthetic route to β-azido alcohols [63–67] and β-hydroxy cyanides [68] consists of the ring opening of oxiranes with azide and cyanide ions, respectively. There are many methods for the synthesis of these compounds, but most of them suffer from different disadvantages, such as severe reaction conditions, commercial nonavailability of some reagents, hygroscopic nature of catalysts, refluxing temperatures, anhydrous organic solvents, expensive and hazardous reagents, non-recyclable catalysts, *etc.*

To overcome these limitations, we developed new methodologies for the synthesis of β-azido alcohols and β-hydroxy cyanides in H_2O under mild conditions in the presence of a recyclable catalyst (*Table 7*). Our study on the ring opening of glycidyl phenyl ether (1 mmol) by NaN_3 and NaCN (12 mmol) at room temperature showed that 5 mol-% of Zr(DS)$_4$ in H_2O (12 ml) was an adequate amount of the catalyst to conduct the ring-opening reaction quantitatively and yielding a single product. When similar reactions were conducted under reflux conditions, other isomers and vicinal diols were produced as by-products. The reaction at room temperature proceeded with high regioselectivity. For example, azide and cyanide ions attacked exclusively the benzylic position of styrene oxide as expected (*Entries 1* and *2*). The ring-opening reactions of other oxiranes were also found to be highly regioselective affording single

Table 7. *Azidolysis and Cyanolysis of Oxiranes Catalyzed by Zr(DS)$_4$*[a])



X= N_3, CN **G** **H**

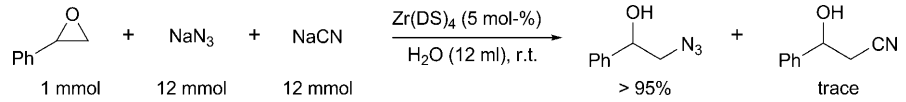
Entry	Oxirane (R)	Product (X)[b])	Time [h]	Yield [%][c])	Ref.
1	Ph	N_3	1	100 (**H**)	[63–67]
2	Ph	CN	5	100 (**H**)	[68]
3	$Me(CH_2)_5$	N_3	3	100 (**G**)	[63–67]
4	$Me(CH_2)_5$	CN	4	100 (**G**)	[68]
5	CH_2=$CHCH_2OCH_2$	N_3	2.5	100 (**G**)	[63–67]
6	CH_2=$CHCH_2OCH_2$	CN	4	100 (**G**)	[68]
7			2.5	100	[63–67]
8			6	100	[68]

[a]) Molar ratio oxirane/NaX/Zr(DS)$_4$ 20 : 240 : 1 in H_2O (12 ml) at r.t. [b]) All products were identified by their spectral data in comparison with known samples. [c]) Yield determined by GC.

products resulting from attack of the azide and cyanide ions at the terminal C-atom of the oxirane ring (*Entries 3–6*).

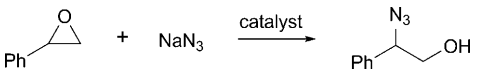
Because of the importance of chemoselectivity, a competitive reaction of styrene oxide with NaN_3, and NaCN in H_2O was performed, resulting almost exclusively in the β-azido alcohol (*Scheme 4*).

Scheme 4. *Competitive Ring Opening by Azidolysis and Cyanolysis of Styrene Oxide in H_2O Catalyzed by $Zr(DS)_4$*



To show the merit of the present protocol for the ring opening of oxiranes with NaN_3, the results obtained with $Zr(DS)_4$ were compared with some of those reported in the literature (*Table 8*).

Table 8. *Catalytic Activity of $Zr(DS)_4$ in Comparison with Other Catalysts Used for the Ring Opening of Styrene Oxide with NaN_3*



Catalyst	Mol-%	Time [h]	Yield [%][a])	Ref.
$Zr(DS)_4$	5	1	97	[b])
AMP[c])	10	3	98	[64]
Oxone®	50	0.5	91	[67]
Hot water	6 ml	3	93	[65]
[bmim](PF_6) · H_2O[d])	(2 : 1) 3 ml	3	91	[66]
[bmim](BF_4) · H_2O[d])	(2 : 1) 3 ml	5.5	84	[66]
$CeCl_3 \cdot 7\ H_2O$	50	3	86	[68]

[a]) Yield of isolated product. [b]) This work. [c]) AMP = ammonium 12-molybdophosphate. [d]) bmim = 1-butyl-3-methyl-1*H*-imidazolium ion.

It must be pointed out that in all nucleophilic ring openings of oxiranes, the catalyst $Zr(DS)_4$ can be reused several times without any loss of activity which is a salient feature of this procedure.

Conclusions. – In this study, we have introduced $Zr(DS)_4$ as a highly efficient catalyst for nucleophilic ring-opening reactions of oxiranes by various aliphatic alcohols, H_2O, NaN_3, and NaCN. This catalytic system has many advantages over currently available methodologies because of its simple reaction conditions, high regio- and chemoselectivity, commercial availability of reactants, and easy workup procedure. The reusability of the catalyst and safety of the procedure, which is expected to contribute to an ecological chemistry for the preparation of alcohols β-substituted with carbon and heteroatom nucleophiles, make this methodology more attractive for synthetic goals.

Support for this work by the *Research Council of the University of Birjand* is highly appreciated.

Experimental Part

General. $Zr(NO_3)_4$, SDS, oxiranes, alcohols, and salts were purchased from *Merck* or *Fluka Chemical Companies.* TLC: silica-gel *SIL G/UV 254* plates. GC: *Shimadzu-GC-16A* instrument, 25 m *CBPI-S25* (0.32 mm i.d., 0.5 μm coating) capillary column. NMR Spectra: *Bruker-Avance-DPX* 250 MHz and 500 MHz instruments; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. MS: *Shimadzu-GC-MS-QP-5050A* instrument; in *m/z* (rel. %).

Zirconium Tetrakis(dodecyl Sulfate) ($Zr(DS)_4$) *from $Zr(NO_3)_4$ and Sodium Dodecyl Sulfate.* As described in [69], with sodium dodecyl sulfate (20 mmol, 5.76 g), dist. H_2O (150 ml), $Zr(NO_3)_4$ (5 mmol, 1.695 g), and H_2O (50 ml): $Zr(DS)_4$ (5 g, 87%) [69]. White powder.

Alcoholysis of Oxiranes by $Zr(DS)_4$: General Procedure. The oxirane (1 mmol) was added to a suspension of $Zr(DS)_4$ (5 mol-%, 0.057 g) in dry alcohol (4 ml). The mixture was stirred under reflux for the required time (GC or TLC monitoring). After completion of the reaction, the alcohol was evaporated to give the desired product in high purity and excellent yield. Further purification was performed by prep. TLC (hexane/AcOEt 3:1).

Hydrolysis of Oxiranes by $Zr(DS)_4$: General Procedure. The oxirane (1 mmol) was added to a suspension of $Zr(DS)_4$ (5 mol-%, 0.057 g) in H_2O (4 ml), and the mixture was stirred under reflux for the appropriate time (TLC and GC monitoring). After completion of the reaction, AcOEt (5 ml) was added, and the org. phase dried ($CaCl_2$) and concentrated to give the desired product in high purity and excellent yield. Further purification was performed by prep. TLC (hexane/AcOEt 3:1).

Azidolysis and Cyanolysis of Oxiranes by $Zr(DS)_4$: General Procedure. To a soln. of NaN_3 or NaCN (12 mmol) in H_2O (12 ml) was added $Zr(DS)_4$ (5 mol-%, 0.057 g) and the oxirane (1 mmol). The mixture was stirred at r.t. for the appropriate time (TLC and GC monitoring). After completion of the reaction, AcOEt (5 ml) was added, and the org. phase dried ($CaCl_2$) and concentrated to give the desired product in high purity and excellent yield. Further purification was performed by prep. TLC (hexane/AcOEt 4:1).

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